Heat and Thermodynamics

Anandamoy Manna

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Dedicated to

The almighty GOD, the creator of all…

Ahamatma Gurhakesh Sarbavutashayasthito
Ahamadishcha Madhyancha Bhutanamanta Eba Cha (GITA)

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Preface

The thought of writing a book originates from the meticulous involvement in the learning–teaching process. The opportunity of learning physics from dedicated teachers in the Ramakrishna Mission Residential College (RMRC), Narendrapur, in its excellent solitude, ashramik atmosphere devoted to magnificent educational environment stimulated our creative ability. Later, teaching physics in undergraduate and postgraduate levels in RMRC and Jadavpur University over a period of four decades enriched my perception due to the inquisitiveness of our beloved students led me to write this course-book of *Heat and Thermodynamics*.

Heat and Thermodynamics is the basic and most important branch of science involving all the working in the universe and, hence, the need and importance of its clear conception is strong. The necessary mathematical and physical conceptions are presented here in a lucid and comprehensive way with suitable examples and solved problems. It is written with the purpose of providing fundamentals of thermal physics with rigorous treatment, wherever necessary, to quench the thirst of interested minds of undergraduate and postgraduate levels of science and engineering students. I have consulted the best texts and most appropriate materials collected from the treasure of literature on thermal physics to make it comprehensive in all respects and I take the opportunity of expressing my gratitude to those authors. It would be a pleasure if the book receives attention of those for whom it is written. I welcome suggestions for the betterment of the book and will be happy to incorporate them in subsequent editions.

Anandamoy Manna

About the Author

Anandamoy Manna passed B.Sc. with honours in physics and M.Sc. in pure physics, obtaining first class in both from Calcutta University. He started his teaching career as a lecturer in physics at Ramakrishna Mission Residential College, Narendrapur, obtained Ph.D. from Calcutta University under the guidance of Professor B.N. Srivastava from the Indian Association for the Cultivation of Science. Later, he joined Jadavpur University in 1972 and retired as Professor of Physics in 2007. He has been a Visiting Research Fellow at Leeds University, UK, with Professor Peter Gray FRS under the Commonwealth Bursaries Scheme of Royal Society and Nuffield Foundation. He has published more than fifty papers in national and international journals and has authored five books. Three students were awarded Ph.D. under his supervision. He is a fellow of National Environmental Science Academy, New Delhi, and has honorary appointment to the Research Board of Advisors of the American Biographical Institute. He is still teaching physics honorarily in Ramakrishna Mission Residential College, his alma mater.

Chapter 1

MATHEMATICAL PRELIMINARIES

1.1 Partial Differentiation

Here we shall discuss differentiation of a function containg more than one independent variable. To start with, we shall consider the case of a function *u* which contains two independent variables *x* and *y*. The derivative of *u*, when *x* varies and *y* remains constant, is called *the partial derivative of u with respect to x.* Similarly, *the partial derivative of u with respect to y* is the differential coefficient of *u* with respect to *y,* when *x* remains constant.

Notation: Partial derivatives of u with respect to x and y are denoted by $\partial u/\partial x$ and $\partial u/\partial y$. Similar notations are used for higher derivatives. The formal definition of $\partial u/\partial x$, when $u = f(x, y)$, is

$$\frac{\partial u}{\partial x} = Lim_{\Delta x \to 0} \frac{f(x+\Delta x, y) - f(x, y)}{\Delta x} \tag{1.1}$$

Similarly,

$$\frac{\partial u}{\partial y} = Lim_{\Delta y \to 0} \frac{f(x, y+\Delta y) - f(x, y)}{\Delta y} \tag{1.2}$$

Example 1: Find the partial derivative of $u = ax^2 + 2bxy + cy^2$.

Solution:

$$\frac{\partial u}{\partial x} = 2ax + 2by \text{ (regarding } y \text{ as a constant)}$$

$$\frac{\partial u}{\partial y} = 2bx + 2cy \text{ (regarding } x \text{ as a constant)}$$

Example 2: Find the partial derivative of $u = \sin(ax + by + c)$

Putting $v = ax + by + c$, we have $u = \sin v$

Solution:

$$\frac{\partial u}{\partial x} = \frac{du}{dv}\frac{\partial v}{\partial x} = \cos v \times a = a\cos(ax + by + c)$$

$$\frac{\partial u}{\partial y} = \frac{du}{dv}\frac{\partial v}{\partial y} = \cos v \times b = b\cos(ax + by + c)$$

Example 3: If $u = f_1(x + ct) + f_2(x - ct)$,

prove that $$\frac{\partial^2 u}{\partial t^2} = c^2\frac{\partial^2 u}{\partial x^2}$$

Solution: Representing the first and the second derivatives by f' and f'',

$$\frac{\partial u}{\partial t} = cf_1'(x + ct) - cf_2'(x - ct) \text{ (regarding } x \text{ as a constant)}$$

$$\frac{\partial^2 u}{\partial t^2} = c^2 f_1''(x + ct) + c^2 f_2''(x - ct) \text{ (regarding } x \text{ as a constant)}$$

$$\frac{\partial u}{\partial x} = f_1'(x + ct) + f_2'(x - ct)$$

$$\frac{\partial^2 u}{\partial x^2} = f_1''(x + ct) + f_2''(x - ct)$$

Hence, $$\frac{\partial^2 u}{\partial t^2} = c^2\frac{\partial^2 u}{\partial x^2}$$

1.1.1 Total Differential of a Function

Let the function be $u = f(x, y, z)$, where x, y and z are three independent variables. The total change in u is $\Delta u = f(x + \Delta x, y + \Delta y, z + \Delta z) - f(x, y, z)$, when the variables x, y and z change by Δx, Δy and Δz respectively. This can be written as

$$\Delta u = \frac{[f(x + \Delta x, y + \Delta y, z + \Delta z) - f(x, y + \Delta y, z + \Delta z)]\Delta x}{\Delta x} + \frac{[f(x, y + \Delta y, z + \Delta z) - f(x, y, z + \Delta z)]\Delta y}{\Delta y} + \frac{[f(x, y, z + \Delta z) - f(x, y, z)]\Delta z}{\Delta z} \tag{1.3}$$

By the formal definition in Eqs 1.1 and 1.2, when in the limit Δx alone is very small, the first part of Eq. 1.3 becomes

$$\frac{\partial}{\partial x} = [f(x, y + \Delta y, z + \Delta z)]dx \tag{1.4}$$

The second part of Eq. 1.3, when Δy alone is very small in the limit, becomes

$$\frac{\partial}{\partial y} = [f(x, y, z + \Delta z)]dy \tag{1.5}$$

In the limit when Δz alone is very small, the third part of Eq. 1.3 becomes

$$\frac{\partial}{\partial z} = [f(x, y, z)]dz \tag{1.6}$$

In the limit when Δx, Δy and Δz are all infinitesimally small, each of the expressions (1.4), (1.5) and (1.6) reduce to $\partial u/\partial x$, $\partial u/\partial y$ and $\partial u/\partial z$ so that in the limit

$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy + \frac{\partial u}{\partial z}dz \tag{1.7}$$

1.1.2 Total Derivative of a Function

Let u be a function of x, y and z and let x, y and z be functions of a single variable t. We have to find an expression for du/dt. Dividing Eq. 1.3 by Δt, we get

$$\begin{aligned}\frac{\Delta u}{\Delta t} &= \frac{[f(x+\Delta x, y+\Delta y, z+\Delta z) - f(x, y+\Delta y, z+\Delta z)]}{\Delta x}\frac{\Delta x}{\Delta t}\\ &+ \frac{[f(x, y+\Delta y, z+\Delta z) - f(x, y, z+\Delta z)]}{\Delta y}\frac{\Delta y}{\Delta t}\\ &+ \frac{[f(x, y, z+\Delta z) - f(x, y, z)]}{\Delta z}\frac{\Delta z}{\Delta t}\end{aligned}$$

In the limit when Δt is infinitesimally small so that Δx, Δy and Δz are all infinitesimally small, we have

$$\frac{du}{dt} = \frac{\partial u}{\partial x}\frac{dx}{dt} + \frac{\partial u}{\partial y}\frac{dy}{dt} + \frac{\partial u}{\partial z}\frac{dz}{dt} \tag{1.8}$$

If u be a function of x and y, prove that

$$\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right) \text{ or } \frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y}$$

This means that in the case of a function of two variables, the order of differentiation may be interchanged.

We have seen that for a function $u = f(x, y), \partial u/\partial x$ represents the limiting value of

$$\frac{\Delta u}{\Delta x} = \frac{f(x+\Delta x, y) - f(x, y)}{\Delta x} \tag{1.9}$$

when Δx is very small. In this expression only x changes, so that its limiting value is a function of y.

Now, let y change to $y + \Delta y$, x remaining constant. Let us represent Eq. 1.9 as

$$\frac{\Delta u}{\Delta x} = F(x, y) = \frac{f(x+\Delta x, y) - f(x, y)}{\Delta x}$$

Then
$$\frac{\Delta F}{\Delta y} = \frac{\Delta u}{\Delta y \Delta x} = \frac{1}{\Delta y}\frac{F(x, y+\Delta y) - F(x, y)}{\Delta x}$$

or
$$\frac{\Delta F}{\Delta y} = \frac{1}{\Delta y}\frac{[f(x+\Delta x, y+\Delta y) - f(x, y+\Delta y)] - [f(x+\Delta x, y) - f(x, y)]}{\Delta x}$$

This expression can also be written as

$$\frac{\Delta F}{\Delta y} = \frac{1}{\Delta x}\frac{[f(x+\Delta x, y+\Delta y) - f(x+\Delta x, y)] - [f(x, y+\Delta y) - f(x, y)]}{\Delta y}$$

$$= \frac{1}{\Delta x}\left(\frac{\Delta u}{\Delta y}\right)$$

Thus,
$$\frac{1}{\Delta y}\left(\frac{\Delta u}{\Delta x}\right) = \frac{1}{\Delta x}\left(\frac{\Delta u}{\Delta y}\right)$$

In the limit when Δx and Δy are infinitesimally small, this becomes

$$\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right) \tag{1.10}$$

1.1.3 The Perfect or Exact Differential

Given is a differential equation of the form

$$f_1(x, y)dx + f_2(x, y)dy = 0 \tag{1.11}$$

The equation cannot be integrated unless the left-hand side of the equation is expressed as a total differential, so that

$$f_1(x, y)dx + f_2(x, y)dy = d[f(x, y)] = du \tag{1.12}$$

In that case, $u = f(x, y) +$ constant (1.13)

The total differential du is also called perfect or exact differential. In this section, we shall establish the condition under which the expression on the left-hand side of Eq. 1.11 may be a perfect differential. If u is a function of (x, y) as in Eq. 1.12,

then
$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy$$

Comparing this with Eq. 1.12, we get

$$\frac{\partial u}{\partial x} = f_1(x, y)$$

$$\frac{\partial u}{\partial y} = f_2(x, y)$$

Now, $$\frac{\partial}{\partial y}[f_1(x, y)] = \frac{\partial^2 u}{\partial y \partial x}$$

and $$\frac{\partial}{\partial x}[f_2(x, y)] = \frac{\partial^2 u}{\partial x \partial y}$$

Since u is a function of (x, y), we have from Eq. 1.10

$$\frac{\partial f_1}{\partial y} = \frac{\partial f_2}{\partial x} \tag{1.14}$$

Equation 1.14 is the condition which must be satisfied in order to make the expression on the left-hand side of Eq. 1.11 a perfect differential, so that Eq. 1.11 may be integrated.

Example 4: If $pv = RT$, where R is a constant, show that

$$\frac{\partial p}{\partial v}\frac{\partial v}{\partial T}\frac{\partial T}{\partial p} = -1$$

Solution: Keeping T constant, $$p\frac{\partial v}{\partial v} + v\frac{\partial p}{\partial v} = 0$$

or $$v\frac{\partial p}{\partial v} = -p \quad \text{or} \quad \frac{\partial p}{\partial v} = -\frac{p}{v}$$

Keeping p constant,

$$p\frac{\partial v}{\partial T} = R \quad \text{or} \quad \frac{\partial v}{\partial T} = \frac{R}{p}$$

Keeping v constant,

$$v\frac{\partial p}{\partial T} = R \quad \text{or} \quad \frac{\partial p}{\partial T} = \frac{R}{v}$$

Therefore, $$\frac{\partial p}{\partial v}\frac{\partial v}{\partial T}\frac{\partial T}{\partial p} = -\frac{p}{v}\frac{R}{p}\frac{v}{R} = -1$$

Example 5: Given $u = x^3 + y^3$, where $y = \log_e \sin x$, find du/dx

Solution: We have $$\frac{\partial u}{\partial x} = 3x^2, \frac{\partial u}{\partial y} = 3y^2$$

$$\frac{dy}{dx} = \frac{d}{d(\sin x)}[\log_e \sin x]\frac{d}{dx}(\sin x) = \frac{1}{\sin x}\cos x = \cot x$$

$$\frac{du}{dx} = \frac{\partial u}{\partial x}\frac{dx}{dx} + \frac{\partial u}{\partial y}\frac{dy}{dx} = 3x^2 + 3y^2 \cot x$$

Example 6: Find dy/dx, if $ax^2 + 2hxy + by^2 - c = 0$

Solution: Let $u = ax^2 + 2hxy + by^2 - c = 0$

$$\frac{du}{dx} = \frac{\partial u}{\partial x}\frac{dx}{dx} + \frac{\partial u}{\partial y}\frac{dy}{dx} = 0$$

$$\frac{\partial u}{\partial x} = 2ax + 2hy, \frac{\partial u}{\partial y} = 2by + 2hx$$

$$\frac{du}{dx} = (2ax + 2hy) + (2by + 2hx)\frac{dy}{dx} = 0$$

or $$\frac{dy}{dx} = -\frac{ax + hy}{hx + by}$$

Example 7: If $u = x^3 + y^3 + 3x^2y + 2xy^2$ show that $\frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y}$

Solution: $$\frac{\partial u}{\partial x} = 3x^2 + 6xy + 2y^2, \frac{\partial u}{\partial y} = 3y^2 + 3x^2 + 4xy$$

$$\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right) = 6x + 4y, \quad \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right) = 6x + 4y$$

$$\therefore \quad \frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y}$$

Example 8: Prove that the equation $(2xy - y^2 + 2x)dx + (x^2 - 2xy + 2y)dy = 0$ is exact.

Solution: Put $f_1(x, y) = 2xy - y^2 + 2x$ and $f_2(x, y) = x^2 - 2xy + 2y$

Then $$\frac{\partial f_1}{\partial y} = 2x - 2y \text{ and } \frac{\partial f_2}{\partial x} = 2x - 2y$$

so that $$\frac{\partial f_1}{\partial y} = \frac{\partial f_2}{\partial x}$$

Hence, this equation is exact.

Example 9: Examine whether the equation $x^3 - 2y^2 + 2xy\ dy/dx = 0$ is exact.

Solution: The equation can be written as

$$(x^3 - 2y^2)\ dx + 2xydy = 0$$

Put $$f_1(x, y) = x^3 - 2y^2 \quad \text{and} \quad f_2(x, y) = 2xy$$

Then $$\frac{\partial f_1}{\partial y} = -4y \quad \text{and} \quad \frac{\partial f_2}{\partial x} = 2y$$

Hence, this equation is not exact. It, however, becomes exact when multiplied by $1/x^3$.

This gives $$\frac{x^3 - 2y^2}{x^3} + \frac{2xy}{x^3}\frac{dy}{dx} = 0$$

or $$\left(1 - \frac{2y^2}{x^3}\right) dx + \frac{2y}{x^2}\ dy = 0$$

Put $$F_1(x, y) = \left(1 - \frac{2y^2}{x^3}\right) \quad \text{and} \quad F_2(x, y) = \frac{2y}{x^2}$$

Then $$\frac{\partial F_1}{\partial y} = -\frac{4y}{x^3} \quad \text{and} \quad \frac{\partial F_2}{\partial x} = -\frac{4y}{x^3}$$

Thus, the equation

$x^3 - 2y^2 + 2xy\dfrac{dy}{dx} = 0$ becomes exact when it is multiplied by $1/x^3$.

1.1.4 The Integrating Factor

The above equation shows that an equation which is not exact can be made exact by multiplying with a factor. A factor which makes an equation an exact differential is called an integrating factor.

Let μ be the integrating factor which makes the inexact differential expression ($Xdx + Ydy$) a perfect differential $d\phi$, so that

$$d\phi = \mu X dx + \mu Y dy$$

In that case,

$$\frac{\partial}{\partial y}(\mu X) = \frac{\partial}{\partial x}(\mu Y)$$

or $$\mu\frac{\partial X}{\partial y} + X\frac{\partial \mu}{\partial y} = \mu\frac{\partial Y}{\partial x} + Y\frac{\partial \mu}{\partial x}$$

or $$\mu\left(\frac{\partial X}{\partial y} - \frac{\partial Y}{\partial x}\right) = Y\frac{\partial \mu}{\partial x} - X\frac{\partial \mu}{\partial y} \tag{1.15}$$

The integrating factor μ is required to satisfy Eq. 1.15.

Thus, in Example 9, $X = f_1(x, y) = x^3 - 2y^2;\ Y = f_2(x, y) = 2xy;\ \mu = \dfrac{1}{x^3}$

This gives
$$\frac{\partial X}{\partial y} = -4y \quad \text{and} \quad \frac{\partial Y}{\partial x} = 2y$$

$$\frac{\partial \mu}{\partial x} = -\frac{3}{x^4} \qquad \frac{\partial \mu}{\partial y} = 0$$

so that
$$\mu\left(\frac{\partial X}{\partial y} - \frac{\partial Y}{\partial x}\right) = \frac{1}{x^3}(-4y - 2y) = -\frac{6y}{x^3}$$

$$Y\frac{\partial \mu}{\partial x} - X\frac{\partial \mu}{\partial y} = 2xy\left(-\frac{3}{x^4}\right) = -\frac{6y}{x^3}$$

Thus, the integrating factor $1/x^3$ satisfies the differential Eq. 1.15.

1.1.5 Geometrical Meaning of Perfect Differential

If a differential du represented by $du = Xdx + Ydy$ be exact, then it can be integrated for a definite integral

$$\int_1^2 (Xdx + Ydy) = \int_1^2 du = u_2 - u_1$$

This means that the value of the integral depends on the initial and final values of u and is independent of the path connecting the initial and final values.

1.2 DEFINITION OF MECHANICAL WORK

Let a force acting on a particle displace it over a distance dr in a direction, making an angle θ with the direction of the force (Fig. 1.1).

Then the mechanical work done by the force is

$$dw = F\,dr\cos\theta \tag{1.16}$$

The work done is a scalar quantity. If X, Y and Z are the Cartesian components of force and if dx, dy and dz are the Cartesian components of displacement dr, then

$$dW = Xdx + Ydy + Zdz \tag{1.17}$$

Equation 1.17 means that the work done by a force is equal to the work done by its components in their respective directions.

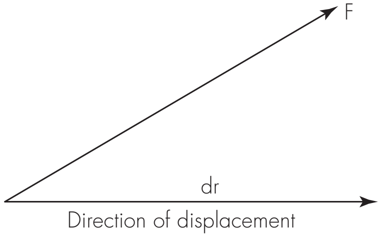

Fig. 1.1 Schematic representation of mechanical work in translational motion

1.2.1 Work Done in Rotational Motion

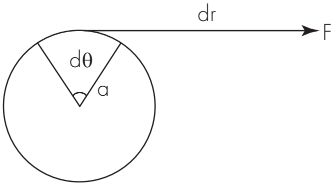

Fig. 1.2 Schematic representation of work done in rotational motion

Figure 1.2 shows a flywheel which can be rotated about its axis by pulling one end of a rope wound round its circumference with a force F. If the end of the rope moves over a distance dr, the mechanical work done by the force is Fdr. This displacement dr causes the flywheel to rotate through an angle $d\theta$ so that $dr = ad\theta$, where a is the radius of the wheel. Hence, the mechanical work in rotation through angle $d\theta$ is

$$dw = Fdr = Fad\theta$$

If G be the moment of the force F about the axis of the wheel, then $G = aF$, so that the work done in rotation is

$$dw = Gd\theta \tag{1.18}$$

Hence, the work done in rotational motion is equal to the moment of the force multiplied by the angular displacement.

1.3 ENERGY

Energy of a body is its capacity to work. The capacity of a body for doing work by virtue of its motion is called its *kinetic energy.* The capacity of a body for doing work by virtue of its position or change in configuration is called its *potential energy.*

1.3.1 Kinetic Energy

The kinetic energy of a body moving with velocity v is measured by the amount of work done by a force in generating the velocity v in the body at rest or by the amount of work required against a force to bring the body moving with velocity to rest. Thus, kinetic energy is

$$T = \int_0^x Fdx \text{ where } F \text{ is the applied force.}$$

If m be the mass of the body and f the acceleration generated,

then $$T = \int_0^x mfdx = \int_0^x m\frac{dv}{dt}dx = \int_0^x m\frac{dv}{dx}\frac{dx}{dt}dx$$

or $$T = \int_0^v mvdv = \frac{1}{2}mv^2$$

Kinetic energy of a rotating body: The kinetic energy of a body rotating with angular velocity ω is measured by the amount of work done by a moment in generating the angular velocity in the body. Thus, $T = \int_0^\theta Gd\theta$ where G is the moment of the force and $d\theta$ is the angular displacement. If I is the moment of inertia of the body about its axis of rotation, then $G = I\, d\omega/dt$, so that

$$T = \int_0^\theta I\frac{d\omega}{dt}d\theta = I\int_0^\theta \frac{d\omega}{d\theta}\frac{d\theta}{dt}d\theta \quad \text{or} \quad T = I\int_0^\omega \omega d\,\omega = \frac{1}{2}I\omega^2$$

1.3.2 Potential Energy

Potential energy due to position: When a body is raised above earth's surface, the body possesses potential energy. Let *m* be the mass of the body, *g* be the acceleration due to gravity, *h* be the vertical height through which the body is raised, the work done in raising the body = *mgh* which remains stored as the potential energy in the body. This energy is independent of the path along which it is raised to vertical height *h* because *mg* acts vertically downwards.

Potential energy due to configuration: Coiled spring in a watch or a gramophone, a bent body, compressed spring or air etc. possess potential energy for they can do work while coming back to normal configuration.

1.4 CONSERVATIVE FIELD OF FORCE

A field of force is the space throughout which force is experienced. Thus, the space surrounding the Earth is its gravitational field. Any piece of matter placed in this field is attracted towards the Earth. The field is said to be conservative if the work done in displacing a body from one position to another and back to the initial position is zero. This means that the work done in moving a body from one position A to another position B is independent of the path along which the body is carried. This can be proved as follows:

Let a particle be carried in a conservative field of force from *A* to *B* along the path *ANB* and back to *A* along the path *BQA* (Fig. 1.3). Let the same particle be carried from *A* to *B* along the path *APB* and back to *A* along the path *BQA*. Since the field is conservative, work done along the path $ANB +$ work done along the path $BQA = 0$.

Hence, work done along the path $ANB =$ work done along the path *APB*. The work done in a conservative field depends only on the initial and final positions of the body carried.

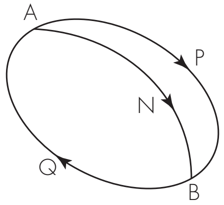

Fig. 1.3 Schematic representation of conservative field of force

1.4.1 The Work Function

The condition that a field should be conservative in the sense as mentioned in Section 1.4 can be satisfied only when the work done in displacing a particle from one standard position (*a*, *b*, *c*) to another position (*x*, *y*, *z*) is a definite single-valued function of the coordinates of position which are independent of time and velocity of the particle. Let the single-valued function called the work function be represented by *W*. This is positive if the body moves in the direction of the force. In this case, the force is said to do work. If the body is made to move against the direction of the force, the work is negative. Here the work is done against the force.

1.4.2 The Potential Function

It is convenient to introduce a single-valued function *V* of coordinates of position (*x*, *y*, *z*) independent of time (independent of velocity also) so that $(V + W)$ is constant at points of the path along which the body is carried. This function is called the *potential function* or the potential energy of the body in the conservative field.

Since $V + W = K$, where *K* is a constant,

$$\delta W = -\delta V \tag{1.19}$$

If δW is positive, that is, if work is done by a force, then the potential energy of the body diminishes and vice versa.

Let F be the intensity of the field at a point (x, y, z) and let the Cartesian components of intensity at the point be X, Y and Z.

Then
$$dW = Xdx + Ydy + Zdz \tag{1.20}$$

By Eq. 1.19
$$Xdx + Ydy + Zdz = -dV \tag{1.21}$$

Condition of existence of potential function: Since, in a conservative field, work done is independent of the path and depends only on the initial and final positions, dv must be a perfect differential so that $Xdx + Ydy + Zdz$ is integrable. The condition for integrability can be deduced as follows:

Let the integral of the equation
$$Xdx + Ydy + Zdz = 0 \tag{1.22}$$

Be
$$f(x, y, z) = a \qquad \text{where } a \text{ is constant.} \tag{1.23}$$

In that case,
$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz \tag{1.24}$$

Equations 1.22 and 1.23 are satisfied if $\partial f/\partial x$, $\partial f/\partial y$ and $\partial f/\partial z$, are proportional to X, Y and Z respectively. Let the constant of proportionality be μ.

Then
$$\mu X = \frac{\partial f}{\partial x} \tag{1.25}$$

$$\mu Y = \frac{\partial f}{\partial y} \tag{1.26}$$

$$\mu Z = \frac{\partial f}{\partial z} \tag{1.27}$$

Differentiating Eq. 1.25 by y, z, Eq. 1.26 by z, x and Eq. 1.27 by x, y, we get

$$\mu\frac{\partial X}{\partial y} + X\frac{\partial \mu}{\partial y} = \frac{\partial^2 f}{\partial y \partial x};\ \mu\frac{\partial X}{\partial z} + X\frac{\partial \mu}{\partial z} = \frac{\partial^2 f}{\partial z \partial x}$$

$$\mu\frac{\partial Y}{\partial z} + Y\frac{\partial \mu}{\partial z} = \frac{\partial^2 f}{\partial z \partial y};\ \mu\frac{\partial Y}{\partial x} + Y\frac{\partial \mu}{\partial x} = \frac{\partial^2 f}{\partial x \partial y}$$

$$\mu\frac{\partial Z}{\partial x} + Z\frac{\partial \mu}{\partial x} = \frac{\partial^2 f}{\partial x \partial z};\ \mu\frac{\partial Z}{\partial y} + Z\frac{\partial \mu}{\partial y} = \frac{\partial^2 f}{\partial y \partial z}$$

Hence,
$$\mu\frac{\partial X}{\partial y} + X\frac{\partial \mu}{\partial y} = \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} = \mu\frac{\partial Y}{\partial x} + Y\frac{\partial \mu}{\partial x}$$

$$\mu\frac{\partial Y}{\partial z} + Y\frac{\partial \mu}{\partial z} = \frac{\partial^2 f}{\partial z \partial y} = \frac{\partial^2 f}{\partial y \partial z} = \mu\frac{\partial Z}{\partial y} + Z\frac{\partial \mu}{\partial y}$$

$$\mu\frac{\partial Z}{\partial x} + Z\frac{\partial \mu}{\partial x} = \frac{\partial^2 f}{\partial x \partial z} = \frac{\partial^2 f}{\partial z \partial x} = \mu\frac{\partial X}{\partial z} + X\frac{\partial \mu}{\partial z}$$

On re-arranging, we get
$$\mu\left(\frac{\partial X}{\partial y} - \frac{\partial Y}{\partial x}\right) = Y\frac{\partial \mu}{\partial x} - X\frac{\partial \mu}{\partial y} \tag{1.28}$$

$$\mu\left(\frac{\partial Y}{\partial z}-\frac{\partial Z}{\partial y}\right)=Z\frac{\partial \mu}{\partial y}-Y\frac{\partial \mu}{\partial z} \tag{1.29}$$

$$\mu\left(\frac{\partial Z}{\partial x}-\frac{\partial X}{\partial z}\right)=X\frac{\partial \mu}{\partial z}-Z\frac{\partial \mu}{\partial x} \tag{1.30}$$

Multiplying Eq. 1.28 by *Z*, Eq. 1.29 by *X*, Eq. 1.30 by *Y*, and adding them, we get

$$X\left(\frac{\partial Y}{\partial z}-\frac{\partial Z}{\partial y}\right)+Y\left(\frac{\partial Z}{\partial x}-\frac{\partial X}{\partial z}\right)+Z\left(\frac{\partial X}{\partial y}-\frac{\partial Y}{\partial x}\right)=0 \tag{1.31}$$

Since Eq. 1.31 must be true for all values of *X*, *Y* and *Z*, the condition for existence of potential reduces to

$$\begin{aligned}\frac{\partial Y}{\partial z}-\frac{\partial Z}{\partial y}&=0\\ \frac{\partial Z}{\partial x}-\frac{\partial X}{\partial z}&=0\\ \frac{\partial X}{\partial y}-\frac{\partial Y}{\partial x}&=0\end{aligned} \tag{1.32}$$

Example 10: Prove that the field due to inverse square law of force is conservative.

Solution: Consider a point (*x*, *y* and *z*) at a distance *r* from the origin of coordinates, where the centre of force is placed.

Then $$r^2=x^2+y^2+z^2$$

The intensity at the point (*x*, *y* and *z*) is

$$F=\frac{K}{r^2},$$

where *K* is constant

The components of *F* in the directions of *x*, *y* and *z* are

$$X=\frac{K}{r^2}\frac{x}{r}\qquad Y=\frac{K}{r^2}\frac{y}{r}\qquad Z=\frac{K}{r^2}\frac{z}{r}$$

Then $$\frac{\partial Y}{\partial z}=-\frac{3Kyz}{r^4\sqrt{r}},\ \frac{\partial Z}{\partial y}=-\frac{3Kyz}{r^4\sqrt{r}}$$

∴ $$\frac{\partial Y}{\partial z}-\frac{\partial Z}{\partial y}=0$$

It can be similarly proved that

$$\frac{\partial Z}{\partial x}-\frac{\partial X}{\partial z}=0 \quad \text{and} \quad \frac{\partial X}{\partial y}-\frac{\partial Y}{\partial x}=0$$

It follows that the gravitational, magnetostatic and electrostatic fields, which vary inversely as square of distance, are conservative.

Example 11: Prove that the field, which varies directly as distance, due to the force is conservative.

Solution: This applies to elastic forces within the limit of elasticity. Consider a point (x, y and z) at a distance r from the origin of coordinates where the centre of force is placed. Then,

$$r = \sqrt{x^2 + y^2 + z^2}$$

The intensity at the point (x, y, z) is $F = Kr$ where K is constant.
The components of F in the directions of x, y and z are

$$X = Kx \quad Y = Ky \quad Z = Kz$$

Then $$\frac{\partial Y}{\partial z} = 0 \quad \frac{\partial Z}{\partial y} = 0$$

∴ $$\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} = 0$$

It can be similarly proved that

$$\frac{\partial Z}{\partial x} - \frac{\partial X}{\partial z} = 0 \quad \text{and} \quad \frac{\partial X}{\partial y} - \frac{\partial Y}{\partial x} = 0$$

From Eq. 1.21, since x, y and z are independent variables,

$$X = -\frac{\partial v}{\partial x} \quad Y = -\frac{\partial v}{\partial y} \quad Z = -\frac{\partial v}{\partial z} \tag{1.33}$$

This means that the space rate of change of potential in any direction is equal to the component of the intensity of the field in that direction.

1.4.3 The Energy Equation (for conservative system)

Let (X, Y, Z) be three Cartesian components of force acting on a particle of mass m placed at the point (x, y, z). Let $\ddot{x}$, $\ddot{y}$ and $\ddot{z}$ be the components of acceleration of the particle at time t,

then $$X = m\ddot{x}, Y = m\ddot{y}, Z = m\ddot{z}$$

or $$X\dot{x} + Y\dot{y} + Z\dot{z} = m(\dot{x}\ddot{x} + \dot{y}\ddot{y} + \dot{z}\ddot{z})$$

or $$\frac{1}{2}m\left(\frac{d}{dt}(\dot{x}^2) + \frac{d}{dt}(\dot{y}^2) + \frac{d}{dt}(\dot{z}^2)\right) = X\dot{x} + Y\dot{y} + Z\dot{z}$$

or $$\frac{1}{2}m\frac{d}{dt}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = X\dot{x} + Y\dot{y} + Z\dot{z}$$

or $$\frac{1}{2}m\frac{d}{dt}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)dt = X\frac{dx}{dt}dt + Y\frac{dy}{dt}dt + Z\frac{dz}{dt}dt$$

$$\frac{1}{2}md(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = Xdx + Ydy + Zdz \tag{1.34}$$

Equation 1.34 is called the energy equation. It can be integrated only when the right-hand side of the equation is a perfect differential of some function of (x, y, z). We have seen that the right-hand side of Eq. 1.34 is a perfect differential of the potential function when the force field is conservative. By Eq. 1.21,

$$Xdx + Ydy + Zdz = -dV$$

where V is the potential function.

Hence, $$\frac{1}{2}md(\dot{x}^2+\dot{y}^2+\dot{z}^2)=-dV$$

or $$dT=-dV \tag{1.35}$$

Equation 1.35 on integration yields

$$T+V=\text{constant} \tag{1.36}$$

This is the principle of conservation of energy for mechanical forces. This means that the sum of kinetic energy and potential energy of an isolated conservative system remains constant for all times.

1.5 NON-CONSERVATIVE SYSTEM OF FORCES

A force is said to be non-conservative when work done against it is not conserved by the body which is moved by the force. A common example of non-conservative type of force is frictional force. When a body is moved against friction, work is required to overcome friction. Friction is always an opposing force, and the work done against friction depends not only on the initial and final positions of the body but also on the length of the path traversed.

What happens to the amount of work done against friction? This work evidently is not recoverable. Work is energy and as such it cannot be lost. It is found that heat is generated when two bodies are rubbed against each other. It is a natural conclusion that heat must be a form of energy. When work is done against friction, it is converted into heat, which raises the temperature of the body. In nature, there is a tendency for equalization of temperature. This is done by three natural processes of transference of heat—conduction, convection and radiation. The heat within bodies ultimately passes into space. Once the heat passes into space it cannot be recovered and is, therefore, lost to all intents and purposes. Light is also a form of energy. Thus, a profuse quantity of sparks comes out of a grinding wheel when a hard body is rubbed against it. Electricity is also a form of energy. A dynamo converts mechanical work into electric energy and an electric motor converts electric energy into mechanical energy. Electric current flowing through a wire carries magnetic field with it. Thus, exchange of energy in nature is going on incessantly in different forms.

1.5.1 Principle of Conservation of Energy

The principle of conservation of energy states that the sum total of energy in the universe is constant. It can, however, transform into different forms.

1.6 GAMMA FUNCTIONS AND SOME INTEGRATIONS

$$\Gamma(l)=\int_0^\infty x^{l-1}e^{-x}dx$$

$$\Gamma(l)=(l-1)\Gamma(l-1)$$

$$\Gamma\left(\frac{1}{2}\right)=\int_0^\infty e^{-x}x^{\frac{1}{2}-1}dx=\sqrt{\pi}$$

1. $\int_0^\infty e^{-bu^2} u^0 du$

Putting $bu^2 = x$, where $b > 0$, differentiating $2budu = dx$,

we get
$$\int_0^\infty e^{-bu^2} u^\circ du = \int_0^\infty e^{-x} \frac{dx}{2b}\sqrt{\frac{b}{x}}$$
$$= \frac{1}{2\sqrt{b}} \int_0^\infty x^{-\frac{1}{2}} e^{-x} dx$$
$$= \frac{1}{2\sqrt{b}} \int_0^\infty x^{\frac{1}{2}-1} e^{-x} dx$$
$$= \frac{1}{2\sqrt{b}} \Gamma\left(\frac{1}{2}\right) = \frac{1}{2}\sqrt{\frac{\pi}{b}}$$

2. $\int_0^\infty e^{-bu^2} u\, du$

Putting $bu^2 = x$ and $2budu = dx$,

we get
$$\int_0^\infty e^{-bu^2} u\, du = \int_0^\infty e^{-x} \frac{dx}{2b}$$
$$= \frac{1}{2b} \int_0^\infty e^{-x} dx = \frac{1}{2b}\left(\frac{e^{-x}}{-1}\right)_0^\infty = \frac{1}{2b}$$

3. $\int_0^\infty e^{-bu^2} u^2 du$

Putting $bu^2 = x$ and $2budu = dx$
$$\int_0^\infty e^{-bu^2} u^2 du = \int_0^\infty e^{-x} \frac{x}{b} \frac{dx}{2b} \sqrt{\left(\frac{b}{x}\right)}$$
$$= \frac{1}{2b^{\frac{3}{2}}} \int_0^\infty e^{-x} x^{\frac{1}{2}} dx = \frac{1}{2b^{\frac{3}{2}}} \Gamma\left(\frac{3}{2}\right)$$
$$= \frac{1}{2b^{\frac{3}{2}}} \frac{1}{2} \Gamma\left(\frac{1}{2}\right) = \frac{1}{2b^{\frac{3}{2}}} \frac{1}{2}\sqrt{\pi} = \frac{1}{4}\sqrt{\frac{\pi}{b^3}}$$

4. $\int_0^\infty e^{-bu^2} u^3 du$

Putting $bu^2 = x$, $2budu = dx$
$$\int_0^\infty e^{-bu^2} u^3\, du = \int_0^\infty e^{-x} \frac{x}{b} \frac{dx}{2b} = \frac{1}{2b^2} \int_0^\infty e^{-x} x dx$$
$$= \frac{1}{2b^2}\left[-xe^{-x} + \int e^{-x} dx\right]_0^\infty$$
$$= \frac{1}{2b^2}\left[-x\, e^{-x} - e^{-x}\right]_0^\infty = \frac{1}{2b^2}$$

5. $\int_0^\infty e^{-bu^2} u^4 du$

Putting $bu^2 = x,\ 2budu = dx$

$$\int_0^\infty e^{-bu^2} u^4 du = \int_0^\infty e^{-x} \frac{x^2}{b^2} \frac{dx}{2b}\sqrt{\frac{b}{x}}$$

$$= \frac{1}{2b^{\frac{5}{2}}} \int_0^\infty e^{-x} x^{-\frac{3}{2}} dx$$

$$= \frac{1}{2b^{\frac{5}{2}}} \Gamma\left(\tfrac{5}{2}\right)$$

$$= \frac{1}{2b^{\frac{5}{2}}} \frac{3}{2} \frac{1}{2} \sqrt{\pi}$$

$$= \frac{3}{8}\sqrt{\frac{\pi}{b^5}}$$

Chapter 2

THERMOMETRY

2.1 INTRODUCTION

When we touch ice, we feel cold; when we stand in the sun, we feel hot. Our sense can perceive these conditions. To quantify the extent of hotness and coldness, we need to know the degree of hotness and coldness which is measured by a physical entity called temperature. The instrument by which temperature is measured is called a thermometer. A hotter body is at a higher temperature. If two bodies are at the same temperature, then they are in thermal equilibrium. If a third body is of the same temperature as the two bodies described earlier, then all the three bodies are in thermal equilibrium. This is the Zeroeth law of thermodynamics. Temperature of a body is measured based on this law.

When we heat a body, different changes are produced in it—its length, area and volume increases; if the body is a gas, its volume as well as pressure changes. Electrical as well as magnetic properties also change. The properties which change with temperature are called thermometric properties and the bodies are called thermometric bodies. An instrument utilizing any one of the thermometric properties is called a thermometer. Depending on the thermometric properties, different types of thermometers are designed and are discussed below:

Liquid thermometer: Here, expansion of liquid is chosen as the thermometric property. Common examples are mercury-in-glass thermometer and alcohol thermometer.

Gas thermometer: These thermometers use the property of expansion of gas, either at constant pressure or at constant volume, giving rise to constant pressure and constant volume gas thermometer.

Resistance thermometer: The resistance of a conductor changes with the change in temperature. Thermometers based on this principle are called resistance thermometers, such as platinum resistance thermometer.

Thermoelectric thermometer: The thermoelectric property used here is the generation of thermo-electromotive force, if the junctions of two dissimilar metals are maintained at two different temperatures; for example, copper constantan thermoelectric thermometer.

There are various other types of thermometers such as vapour pressure thermometer, radiation pyrometer and magnetic thermometer depending upon the different thermometric properties. They will be discussed at suitable places. We shall consider here the above-mentioned four types of thermometers only.

Thermometers use different scales in different countries. Generally, Centigrade (Celsius), Fahrenheit, Absolute (Kelvin) scale are in vogue. To build up a thermometric scale, we have to decide two fixed points which are taken as standards and are easily produced globally. These are ice point or lower fixed point which is 0 °C at one atmospheric pressure and the steam point or the upper fixed point which is the temperature of boiling water at one atmospheric pressure. The temperature interval between them is called the fundamental temperature interval. In Celsius scale, the ice point or lower fixed point is 0°, in Fahrenheit scale it is 32° and in Celsius scale the steam point or upper fixed point is 100°, in Fahrenheit it is 212°; if c be the temperature as recorded in Celsius scale and f be the temperature as recorded in Fahrenheit scale, then

$$\frac{c}{5} = \frac{f-32}{9}$$

If T be the temperature as recorded in absolute scale or Kelvin scale, then $T = 273 + c$.

2.2 GENERAL THEORY OF THERMOMETRY

We have seen that the thermometric property depends on the temperature, and working of all types of thermometers is based on this principle.

Specifying the thermometric property by X, its variation with temperature (t) is generally represented by

$$X_t = X_0\,(1 + \alpha t + \beta t^2 + \gamma t^3 + \dots\dots\dots) \tag{2.1}$$

where X_t = value of the thermometric property at t degree

X_0 = value of the thermometric property at zero degree

α, β and γ are constants of a thermometric substance which are of rapidly decreasing order of magnitude. So, we may take

$$X_t = X_0(1+\alpha t)$$

and

$$X_{100} = X_0(1+\alpha 100)$$

or

$$\frac{t}{100} = \frac{X_t - X_0}{X_{100} - X_0}$$

or

$$t = \frac{X_t - X_0}{X_{100} - X_0} \times 100 \tag{2.2}$$

By knowing the thermometric property at three temperatures, t can be determined. This is the fundamental equation in thermometry.

2.3 LIQUID THERMOMETER

The most common liquid thermometer is mercury-in-glass thermometer. This is very simple in construction and is widely used in laboratories. Mercury is put in a bulb of thin-walled glass tube with a graduated stem of uniform cross section. Its lower fixed point is marked zero after keeping the bulb in ice for some time when the mercury thread in the stem becomes steady. The thermometer is then introduced in a boiler where water is made to boil at one atmospheric pressure. When the position of the mercury thread becomes steady, it is marked 100 °C and the length is divided into 100 equal parts.

Mercury has been chosen as the thermometric substance for the following reasons:

1. It is obtained easily in pure state; it remains liquid over a long range of temperature from −39 °C to 356 °C. Upper range can be extended to 500 °C by putting nitrogen under pressure in the tube.
2. Expansion of mercury is uniform.
3. Its specific heat is low and conductivity is high.
4. It is a shining liquid.

Mercury has some disadvantages also; they are as follows:

1. High specific gravity lowers its sensitivity.
2. Surface tension of mercury is high, which makes its motion in the stem a bit jerky.

Alcohol thermometers are used in the low-temperature region as it remains liquid up to −112 °C. Its boiling point being 78 °C, its upper limit use is lowered. It is more sensitive as its coefficient of expansion is larger. Surface tension of alcohol is small; so, its motion in the stem is smooth.

Though mercury-in-glass thermometers were largely used at one time, they required a large number of corrections for precise measurement. So, the use of gas thermometers crept in. The main demerits of mercury-in-glass thermometers are:

1. While measuring temperature the bulb is introduced into the body whose temperature is to be measured, but the capillary tube (the stem) is more or less exposed outside the body. In order to make correction for the exposed stem, we proceed in the following way.

   Let the reading of the mercury thermometer be t' when introduced into a body whose temperature is t and n (which is nearly t') be the number of divisions of the thread being exposed outside the body where temperature is t_m. Taking the volume corresponding to one degree division as the unit of volume and γ_a as the coefficient of apparent expansion of mercury in glass, then foom the condition of measurement

   $$t - t' = t'\gamma_a(t - t_m) = t'\gamma_a(t' - t_m) \tag{2.3}$$

   as t and t' are nearly equal.
2. External pressure due to the body surrounding the bulb will compress mercury and cause mercury to rise in the capillary, thereby increasing the actual reading.
3. When the thermometer is held in the horizontal position, mercury will exert hydrostatic pressure and increase the volume of the bulb. Thus, the thermometer reading will be low in the vertical position than in the horizontal position.
4. Taking quick reading of widely varying temperature will introduce an error; because of peculiar elastic properties of glass, complete recovery to the original condition of the thermometer is not possible.
5. Because of narrow bore nature of the thermometer, great care is to be taken to make the bore uniform.
6. Eye should be placed at right angles of the thread whose reading is taken.

2.4 GAS THERMOMETER

Liquid thermometers were later replaced by gas thermometers as their expansion is larger (≈ 20 times that of mercury thermometer) and thus the measurement is more accurate. The expansion of the container is small in comparison with the gas. Permanent gases can be obtained in pure state. Their expansion is uniform for equal changes of temperature at low and high temperatures. The upper limit of temperature measurement is much greater than liquid thermometer, limited to such temperature as the container can withstand.

Gas thermometers may be of two types: constant volume and constant pressure.

2.4.1 Constant Volume Hydrogen Thermometer

The bulb C (Fig. 2.1) containing hydrogen is 1m long and 3.6 cm in diameter and contains 1litre of hydrogen. The bulb communicates with the mercury in the manometer GDEB through a connecting tube A which is also 1m long. Hydrogen gas introduced into C when surrounded by ice makes a pressure of 100 cm of mercury. When the bulb C is subjected to different higher temperatures, its volume is increased; but it is kept constant by adjusting the position of the mercury reservoir F so that mercury in D touches the pointer R. The barometer I is so placed that its stem slips in BE and stands over the tube GD. The distance between the mercury column D and I measures the pressure of hydrogen in C and is measured by a cathetometer.

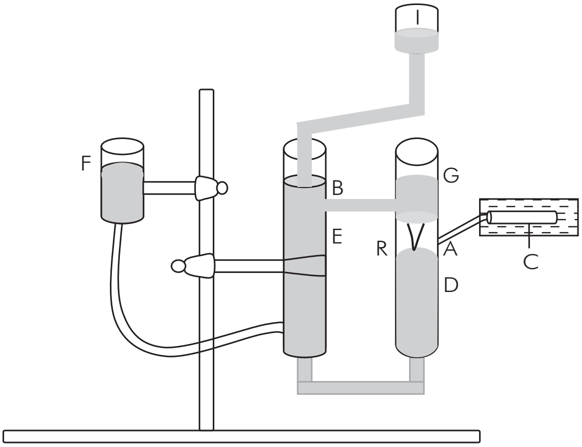

Fig. 2.1 Constant volume hydrogen themometer

The bulb C is placed in a bath to measure unknown temperature T of the bath. The pressure in C increases thereby forcing mercury in D to go down. By raising the bulb F, the level of mercury in D is made to touch the tip of the pointer R. In this adjusted position, the heights IG and GR are measured by cathetometer; IG gives the barometric pressure (say H) and GR (say h) is the excess pressure due to pressure change in C. The total pressure p at $T = H + h$. The bulb C is surrounded by ice (temperature T_0); let the pressure so measured (as in the previous way) be p. It is then surrounded by steam (temperature $T_0 + 100$); let the corresponding pressure be p_{100}. Then, we can write

$$p_0 v = nRT_0$$

where v = the volume of hydrogen in C, A and small space in DG surrounded by mercury, n = number of gm mole of hydrogen gas, R = molar gas constant.

Similarly, we can write

$$p_{100}\, v = nR\,(T_0 + 100)$$

$$pv = nRT$$

from which
$$T = \frac{100p}{p_{100} - p_0} \tag{2.4}$$

Knowing p_o, p, p_{100}, T can be determined.

2.4.2 Callendar's Compensated Constant Pressure Air Thermometer

The sketch of Callendar's compensated constant pressure air thermometer is shown in Fig. 2.2. It consists of bulbs A and B full of air, and the pressures are kept equal as indicated by the mercury meniscus in the manometer tube. The bulb A is connected to another bulb C full of mercury having the provision of introduction and withdrawal of mercury. The bulbs are connected by narrow bore tubes in such a way that their volumes are same; the connecting tubes run side by side near each other so that they are at the same temperature. The bulb C is graduated in cc's so that the volume of the gas, filling the space between mercury meniscus and the neck of the bulb, can be directly read.

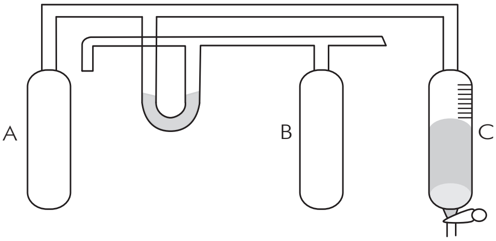

Fig. 2.2 Callendar's compensated constant pressure air themometer

To measure unknown temperature of a bath, the bulb A is immersed into it and the bulbs B and C are put in an ice bath. After a certain time when the air assumes the corresponding temperature, the equality of pressure is maintained by adjusting the mercury level in C when the two columns in the manometer are at the same level.

Let

v = volume of bulb A = volume of bulb B
u = volume of the connecting narrow bore tube
v' = volume read from the graduations in C
T = unknown temperature of the bath
t = room temperature in which the connecting tubes are placed
T_0 = ice bath temperature

We know $pv = nRT$, where p is the pressure of air, v is the volume of n gm moles of air, R is the molar gas constant, T is the absolute temperature. Then, we can write

$$p\left(\frac{v}{T}+\frac{u}{t}+\frac{v'}{T_0}\right) = nR = p\left(\frac{v}{T_0}+\frac{u}{t}\right) \tag{2.5}$$

or

$$\frac{v}{T}+\frac{v'}{T_0}=\frac{v}{T_0}$$

or

$$\frac{v}{T}=\frac{v-v'}{T_0}$$

$$T=\frac{vT_0}{v-v'} \tag{2.6}$$

T can be calculated if the quantities on the right-hand side are known. From the practical point of view, volume measurement is difficult than pressure measurement which can be done more accurately so the constant volume hydrogen thermometer is more efficient.

2.4.3 Limitations of Gas Thermometers

Gas thermometers are not handy to use; their use is tedious in nature. The thermometers are based on ideal gas equation. But, no gas is ideal. Only hydrogen and helium may be taken as perfect gases at a very low pressure and high temperature. The liquid and gas thermometers are called primary thermometers. In laboratories, the primary thermometers are replaced by secondary thermometers such as resistance thermometers and thermocouple thermometers. These are carefully standardized by comparison with a standard gas thermometer.

2.5 RESISTANCE THERMOMETER

Gas thermometers are primary thermometers; but they require many corrections. They are replaced by secondary thermometers such as resistance thermometers and thermocouple thermometers, which are standardized by standard gas thermometer.

The resistances of pure metals increase with the increase in temperature. Resistance is treated as the thermometric property.

2.5.1 Platinum Resistance Thermometer

Platinum is suitable as a thermometric substance because of its high temperature coefficient of resistance, constancy of resistance at particular temperature and reproductivity. Platinum resistance thermometer was first constructed by Sir William Siemens in 1871.

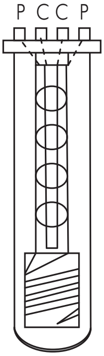

Fig. 2.3 Platinum resistance thermometer

Since then, several improvements have been made. The modern form of the platinum resistance thermometer was developed by E. H. Griffiths. Platinum—free from silicon, tin, carbon, etc.—is selected and is drawn in the form of a wire. It is then doubly wound to avoid induction effects on a thin mica frame (Fig. 2.3).

The ends of the platinum wire are joined to either copper leads or platinum leads (at high temperatures) which pass through the bores of a series of thin, circular mica plates arranged over the mica frame; whole arrangement is kept inside the hard glass or porcelain tube. These leads are connected to PP at the mouth of the tube. To compensate for these leads, a pair of similar leads starting right from the level of the end of platinum wire mounted over the mica frame passes through similar bores of thin, circular mica plates and are connected to the leads CC at the mouth of the tube. Thus, the connection between the wires inside the tube is avoided.

The tube is sealed at the top and is evacuated to avoid disposition of moisture on the mica. The compensating leads are connected to the third arm of the Wheatstone bridge (Fig. 2.4); equal resistances are given in the ratio arm and PP terminals are connected to the fourth arm.

The resistances of the compensating leads and platinum leads are same at all temperatures; then, the resistance of the platinum coil alone can be determined from the extra resistance included in the third arm for no deflection of the galvanometer.

On the basis of experimental observation of the resistance of platinum over a wide range of temperature, Callendar and Griffiths gave the relation

$$R_\theta = R_0(1 + \alpha\theta + \beta\theta^2)$$

where R_θ and R_0 are the resistances at θ°C and 0°C respectively, α and β are characteristic of platinum. The unknown temperature can be calculated by solving the above quadratic equation.

Callendar gave a simpler method to define a platinum temperature,

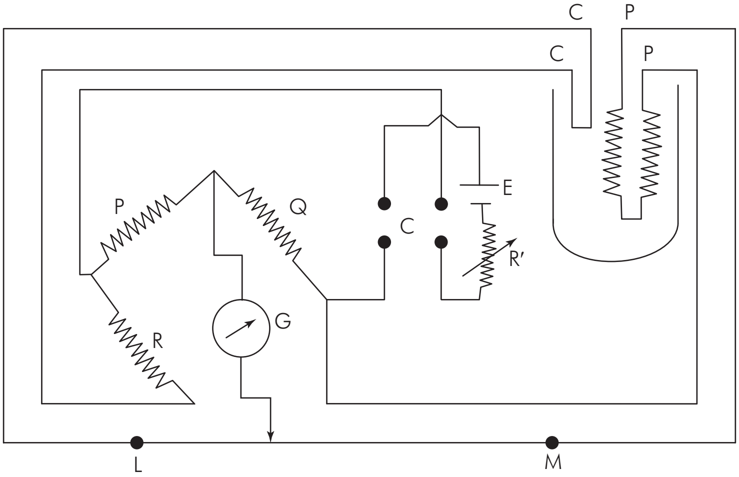

Fig. 2.4 Experimental arrangement for temperature measurement by platinum resistance thermometer

$$R_\theta = R_0(1 + C\theta_{pt}) \tag{2.7}$$

$$\theta_{pt} = \frac{R_\theta - R_0}{R_0 C} = \frac{(R_\theta - R_0)100}{R_{100} - R_0} \tag{2.8}$$

where R_0, R_{100}, R_θ are the resistances at 0 ℃, 100 °C and θ °C, respectively.

So
$$\theta_{pt} = \frac{\alpha\theta + \beta\theta^2}{100\alpha + \beta 100^2} \times 100$$

$$= \frac{\alpha\theta + \beta\theta^2}{\alpha + 100\beta}$$

The difference between the true temperature and the platinum temperature is given by

$$\theta - \theta_{pt} = \theta - \frac{\alpha\theta + \beta\theta^2}{\alpha + 100\beta}$$

$$= \frac{\alpha\theta + 100\beta\theta - \alpha\theta - \beta\theta^2}{\alpha + 100\beta}$$

$$= \frac{-\beta(\theta^2 - 100\theta)}{\alpha + 100\beta}$$

$$= \frac{-\beta 100^2}{\alpha + 100\beta}\left[\left(\frac{\theta}{100}\right)^2 - \frac{\theta}{100}\right]$$

$$= \delta\left[\left(\frac{\theta}{100}\right)^2 - \frac{\theta}{100}\right] \tag{2.9}$$

δ is a constant and for pure platinum, δ is 1.5.

In order to measure a temperature (say the boiling point of aniline), the experimental connection is as shown in Fig. 2.4. Here, P, Q and R are the arms of a post office box, C the commutator, E the battery, R' the rheostat, G the galvanometer, LM the meter bridge, CC and PP are the compensating and platinum leads, respectively.

In the arrangement shown in Fig. 2.4, if L be the balance point on the meter bridge when platinum resistance thermometer is in melting ice and the resistance in the third arm is R_1, then

$$R_1 + \sigma L + y = R_0 + \sigma(100 - L) + \delta' \tag{2.10}$$

where y and δ' are the constants of the bridge wire and denote the end resistances of the bridge wire, σ being the mean resistance per unit length of the wire and R_o is the resistance of the thermometer at 0 °C.

If $$R_1 = R_0 = 0, L = l_0$$

$Y - \delta' = 2(50 - l_0)\sigma$ where l_0 in this condition is the balance point and is known as electric midpoint.

Hence, $$R_0 = R_1 + 2\sigma(L - l_0) \tag{2.11}$$

In order to find σ, the resistance in the third arm is changed by an amount x, then null point L will be changed to L'.

So, $$R_0 = R_1 + 2\sigma(L - l_0) = R_1 + x + 2\sigma(L' - l_0)$$

or $$2\sigma L = x + 2\sigma L'$$

$$\sigma = \frac{x}{2(L - L')} \tag{2.12}$$

We get R_o putting the value of σ in Eq. 2.11. Similarly, R_{100} and R_θ are calculated by introducing the platinum resistance thermometers in steam and in boiling liquid.

θ_{pt} is calculated by putting these values in Eq. 2.8. we can find the actual boiling point θ of the aniline by putting the values of θ_{pt} in place of θ in Eq. 2.9, and by successive approximation.

The platinum resistance thermometers have certain merits; they are:

1. they are useful over a wide range of temperature;
2. they are highly accurate;
3. they are reproducibile, etc.

But it has certain limitations also, such as;

1. it cannot measure the temperature of a point as its volume is large and
2. it cannot measure the temperature of a body whose temperature varies rapidly.

2.6 THERMOCOUPLE THERMOMETERS

These are another type of secondary thermometers, the theory of which depends on the fact that when the two junctions of two metals are at different temperatures, an electromotive force (emf) is generated in the circuit. This emf is a function of the temperature difference of the junctions. Hence, it is named as thermo emf. The emf here is the thermometric property.

The choice of the metals forming the couple depends on the temperature region at which it is used. The two pure metals are taken in the form of wire and are soldered at points at their ends. The two wires must not touch each other except at the point of soldering and hence, they are insulated. One of the junctions is introduced in cold ice; it is called the cold junction and the other junction is introduced either in steam or in water at room temperature, this is called the hot junction. If the temperatures of these two junctions be 0 °C and θ°C, then the thermo emf generated is given by

(i)
$$e = a\theta + b\theta^2 \tag{2.13}$$

(ii)
$$e = a\theta^b \tag{2.14}$$

at ordinary temperatures where a and b are constants characteristic of the couple. The relation of thermo emf with temperature is different at different temperature regions, but for general case of ordinary temperature both the equations are used.

In order to measure a temperature (say the melting point of napthalene), the experimental arrangement is as shown in the Fig. 2.5.

A couple is formed, the hot junction H is alternatively placed in water at room temperature, in steam and in test tube containing the solid whose melting point is to be determined. The test tube containing the solid and hot junction of the thermocouple is introduced in a beaker of water which is heated and continually stirred. The cold junction C is placed in a funnel containing ice. ABCD is the potentiometer whose resistance is r, R is the resistance box, E is the battery, K is the key and G is the galvanometer.

With the cold junction at ice and hot junction at water at room temperature t, the emf of the couple is measured by balancing over a length l_1 of a potentiometer. If R be the resistance in the resistance box, r the resistance of the potentiometer wire and E the emf of the battery, then

$$e_1 = \frac{Erl_1}{(R+r)1000} \tag{2.15}$$

In this way if l_2 and l_3 be the balance point when the hot junction is in steam and in melting point (θ°C) of the liquid, then

$$e_2 = \frac{Erl_2}{(R+r)1000} \tag{2.16}$$

and

$$e_3 = \frac{Erl_3}{(R+r)1000} \tag{2.17}$$

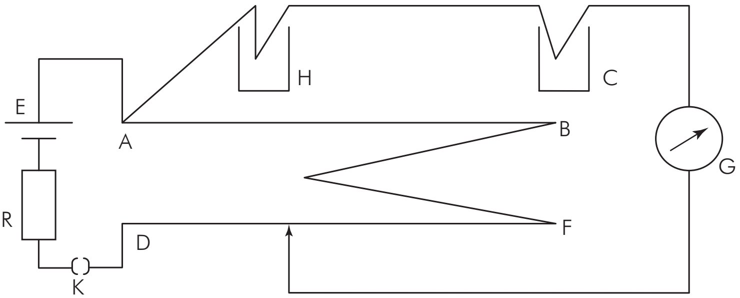

Fig. 2.5 Experimental arrangement to measure the melting point of napthalene

To find the melting point (θ °C), we may use any one of the above-mentioned two relations—2.13 and 2.14. The constants *a* and *b* are determined from e_1 and e_2 as follows:

(i) When relation 2.13 is used

$$e_1 = at_1 + bt_1^2 \tag{2.18}$$

and

$$e_2 = at_2 + bt_2^2 \tag{2.19}$$

where t_1 and t_2 are the room temperature and steam temperature, respectively.

Then, by solving

$$a = \frac{e_1 t_2^{\,2} - e_2 t_1^{\,2}}{t_1 t_2 (t_2 - t_1)} \tag{2.20}$$

$$b = \frac{e_2 t_1 - e_1 t_2}{t_1 t_2 (t_2 - t_1)} \tag{2.21}$$

Putting these value of *a* and *b* in $e_3 = a\theta + b\theta^2$, θ can be determined.

(ii) When relation 2.14 is used

$$e_1 = at_1^b \text{ and } e_2 = at_2^b$$

Solving it, we get

$$b = \frac{\log_e e_2 - \log_e e_1}{\log_e t_2 - \log_e t_1} \tag{2.22}$$

Putting the value of *b* in $e_1 = at_1^{\,b}$, the value of the constant *a* is determined. Finally, the melting point of the solid is determined from the relation $e_3 = \alpha\theta^b$ and from these values of the constants *a* and *b*.

The merits of this type of thermometers are:

1. they can measure temperature at a point;
2. they can measure changing temperature;
3. they are useful over the range −200 °C to 1500 °C;
4. they can easily be constructed and are cheap. Their main disadvantage is that the relationship between thermo emf and the temperature difference is different in different regions of temperature.

Thermometers based on other type of thermometric properties such as vapour pressure and adiabatic demagnetization are discussed in later chapters.

2.7 Low and High Temperature Thermometry

The low temperature range is bounded by a limit 0 °C, that is, 273 K and approach towards the limit of low temperature (see Fig. 2.6).

First, we take the case of mercury thermometers. The lower range of a mercury thermometer is limited by the fact that it freezes at −38.87 °C. So, temperature below −39 °C cannot be measured by mercury thermometer. With alcohol thermometers which freeze at −111.8 °C, temperature below the freezing point cannot be measured. But difficulty arises in the fact that the contractions of mercury and alcohol are not uniform towards the corresponding freezing point. A special liquid thermometer containing fractionally distilled petroleum ether can be used to measure the temperature as low as −190 °C.

The standard thermometer in the low temperature is the constant volume hydrogen and helium thermometer selected by the International Bureau Standards and Measures. Professor Dewar showed that the boiling point of hydrogen as registered by hydrogen thermometer was −253.0 °C, but by helium thermometer it was −252.7 °C. From this, Dewar concluded that a gas thermometer can measure temperature up to its boiling point. Thus, helium gas thermometer can be used to measure temperature as low as 4 K. But in the measurement of low temperature with gas thermometer, some difficulties or errors arise. The first is that the gas liquefies and even solidifies at this low temperature. Second, we assume that the real gases follow the ideal gas equation on which the principles of gas thermometers are based, but the real gases follow the ideal gas equation only at high temperature and low pressures. So when we measure low temperature, the gas does not hold ideal gas equation. Correction due to this can be done by conversion of perfect gas scale to absolute scale.

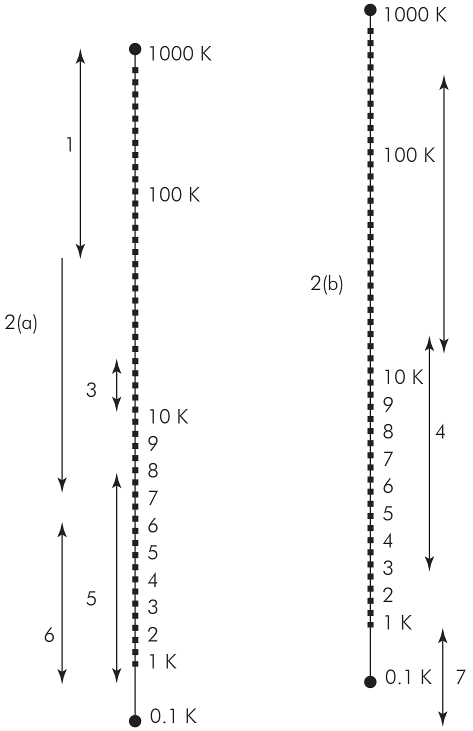

Fig. 2.6 Sketch showing low temperature measurement

Resistance thermometers are accurate in measuring low temperature to a certain extent. The substances of which the resistance thermometers are made must be absolutely pure because pure metals follow a regular decrease in resistance with decrease in temperature. It has been found that the occurrence of trace of impurity causes an appreciable increase in resistance at this region. With platinum resistance thermometer, temperature up to −190 °C can be measured. Henning and Otto used platinum resistance thermometers for measurement below −190 °C utilizing a complicated formula of variation of resistance with temperature. The formula is, however, not foolproof and cannot be used to calibrate the platinum resistance thermometer from fixed points. Onnes measured temperature as low as −259 °C by using lead resistance thermometer. With lead resistance thermometer, temperature as low as 7 K can be measured, but the alloys constantan and unannealed phosphor bronze are best suited in this region due to their large temperature coefficients. But it has the disadvantage that external magnetic field increases their resistance. Thermometers of phosphor bronze are better in this region because it has large temperature coefficient of resistance and less affected by magnetic field. Carbon resistance thermometers are used in the range of 1 K.

Copper constantan and iron constantan thermocouples are suitable in low temperature region as they develop a large emf, of about 40−60 microvolts per degree. These thermocouples can be used to measure temperature as low as −255 °C. Thermocouple thermometers made up of gold, silver and platinum silver are best suited below −200 °C. At temperatures as low as 10 K, an alloy of gold with about 2 per cent cobalt against the standard silver alloy is most sensitive.

Vapour pressure thermometers have been used for low temperature measurement because of their extreme accuracy in certain range of temperature. Oxygen vapour pressure thermometer is suitable in the range of −150 °C to −210 °C, neon in the range of −246 °C to −249 °C, hydrogen in the range of −253 °C to −262 °C and helium below about −268 °C because of moderate vapour pressure suited for measurement.

Helium vapour pressure thermometers have been used to measure as low as 0.75 K.

But for temperatures lower than this, the paramagnetic susceptibility of certain salts has been utilized. For this, it is necessary to assume that paramagnetic susceptibility varies inversely as the absolute temperature—a law which is known to fail near absolute zero.

1. Platinum resistance thermometer with a modified formula in the lower range (1000 K…….. 75 K)
2. (a) In the lower range, lead resistance thermometer (up to 7 K)
   (b) Helium gas thermometer (270 K up to below 10 K)
3. Hydrogen vapour pressure thermometer (from 20 K to 10 K)
4. Thermocouple thermometers (18 K up to 2–3 K)
5. Helium vapour pressure thermometer (8 K to below 1 K)
6. Phosphor bronze and constantan resistance thermometer (5 K up to below 1 K)
7. Paramagnetic susceptibility of certain salts below 0.1 K.

The high-temperature measurement has no limit, unlike the low temperature. The sun is at a temperature of two million degree Celsius.

We shall discuss high-temperature measurement from 100 °C. Under normal pressure mercury boils at 357 °C, so ordinary mercury thermometer can not be used for temperature higher than 357 °C (Fig. 2.7).

With hydrogen gas thermometer, temperature up to 500 °C can be measured. At higher temperatures, hydrogen diffuses through platinum. With nitrogen gas thermometer and with proper modification, the range of gas thermometers can be extended up to 1600 °C.

Then comes the resistance thermometers. The range of platinum resistance thermometer is from −200 °C to 1200 °C. If the metal is perfectly pure, the reading is accurate from 0.01 °C up to 500 °C and from 0.1 °C up to 1200 °C.

The thermocouples are important in measurement of high temperature. Up to 300 °C, couples of base metals such as iron constantan and copper constantan are satisfactory as they develop a large emf of about 40 to 60 microvolts per degree. For higher temperature, these base metals cannot be used as they oxidize and melt. Nickel iron couple may be used up to 600 °C and nickel nichrome up to 1000 °C. Above this, platinum and an alloy of platinum with iridium or rhodium must be used to measure up to 1600 °C. Above this, the thermocouple of iridium and 90 per cent iridium and 10 per cent rhodium have been used for measuring up to 2100 °C, and tungsten-molybdenum between 2000 °C and 3000 °C. Above this, temperature radiation pyrometers are used as the instrument need not be placed in contact with the hot body nor raised to the temperature of the body, so there is no upper limit of measurement of temperature.

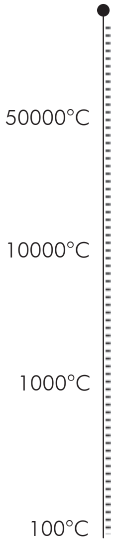

Fig. 2.7 Sketch showing high temperature measurement

The thermometers most suitable for high temperature thermometry in different ranges of temperature are summarized as follows:

1. Hydrogen gas thermometers (100 °C to 500 °C)
2. Nitrogen gas thermometers (up to 1500 °C)
3. Platinum resistance thermometers (up to 1000 °C)
4. (a) Copper constantan and iron constantan (up to 300 °C)
   (b) Nickel iron thermocouple (up to 600 °C)
   (c) Platinum and platinum iridium or platinum rhodium thermocouple (up to 1600 °C)
   (d) Couple of iridium and 10% rhodium and 90% iridium (up to 2100 °C)
   (e) Nickel nichrome thermocouple (up to 1000 °C)
   (f) Tungsten-molybdenum thermocouple (up to 3000 °C)
5. Radiation pyrometer (1600 °C to very high temperature)

SOLVED PROBLEMS

Q 1. A travelling microscope was used to note the positions of the mercury meniscus of a mercury-in-glass thermometer. The reading corresponding to melting ice was 1.23 mm. In steam at a pressure of 74.24 cm of mercury, the reading was 18.56 mm. What is the temperature in °C when the reading is 10.75 mm? What will be the reading corresponding to 50 °C? Assume that the boiling point of water changes by 1 °C for a change of pressure of 27 mm of mercury.

Ans: We know at a pressure of 76 cm of mercury, steam point is 100 °C; as boiling point changes by 1 °C for a change of pressure of 27 mm of mercury, so at a pressure of 74.24 cm of mercury, the steam point will be

$$100 - \frac{(76 - 74.24)}{2.7} = 99.35\text{°C}$$

We also know $t = \frac{l_t - l_0}{l_s - l_0}$ (steam point – melting point)

where l stands for the length of mercury meniscus

or, $$t = \frac{(10.75 - 1.23)}{(18.56 - 1.23)}(99.35 - 0) = \frac{9.52}{17.33} 99.35 = 54.58\text{°C}$$

Again if l_t be the reading corresponding to 50 °C, we have

$$50 = \frac{(l_t - 1.23)}{18.56 - 1.23} 99.35$$

$$l_t - 1.23 = \frac{(50 \times 17.33)}{99.35} = 8.72$$

$$l_t = 8.72 + 1.23 = 9.95 \text{ mm of mercury}$$

Q 2. The pressure indicated by a constant volume hydrogen thermometer are 3.5 cm, 75 cm and 102.4 cm in a certain scale when the bulb is immersed in liquid air, ice and steam, respectively. What is the temperature of the liquid air on the constant volume hydrogen scale?

Ans: We know that

$$t=\frac{p_t-p_0}{p_{100}-p_0}\times 100$$

$$=\frac{23.5-75}{102.4-75}\times 100=-187.95^\circ\text{C}$$

Q 3. If the difference of mercury level in a constant volume air thermometer is −2 cm when the temperature of the bulb is 10 °C and +22 cm when the bulb is at 100 °C, what is the height of the barometer?

Ans: Let H = height of barometer

Pressure at 10 °C = $H - 2$ cm of Hg

Pressure at 100 °C = $H + 22$ cm of Hg

Since it is a constant volume air thermometer, we can write

$$\frac{p_{10}}{273+10}=\frac{p_{100}}{273+273}$$

or,

$$\frac{H-2}{283}=\frac{H+22}{546}$$

∴

$$H=77.46\ \text{cm}$$

Q 4. A constant volume air thermometer is used to determine the temperature of a furnace and the excess pressure in the bulb is found to be equal to 152 cm of mercury. At 0 °C, the pressure in the bulb is equal to that of the atmosphere. If the barometric height throughout the experiment is 76 cm of mercury, calculate the temperature of the furnace.

Ans: At 0 °C, pressure p_0 = 76 cm of mercury. At furnace temperature,

$p_t = 76 + 152 = 228$ cm of mercury

As the volume is kept constant, we can write

$$\frac{p_0}{T_0}=\frac{p_t}{T}$$

$$\frac{76}{273}=\frac{228}{T}$$

∴

$$T=\frac{228\times 273}{76}=819\ \text{K}$$

Q 5. The resistances of a platinum thermometer at 0 °C, 100 °C and 208 °C are found to be 3.5, 5.2 and 6.9 ohms, respectively. Find the temperature of the bath in which the resistance is 9.4 ohms.

Ans: We know

$$t_{pt}=\frac{R_t-R_0}{R_{100}-R_0}\times 100$$

$$=\frac{6.9-3.5}{5.2-3.5}\times 100=\frac{3.4}{1.7}\times 100=200$$

$$t-t_{pt}=\delta\left[\left(\frac{t}{100}\right)^2-\frac{t}{100}\right]$$

$$208-200=\delta\times 2.08\times 1.08$$

$$\delta=\frac{8}{2.08\times 1.08}=3.56$$

The unknown temperature on the platinum scale is

$$t_p=\frac{9.4-3.5}{5.2-3.5}\times 100=347.06$$

So, $$t-347.06=\delta\left[\left(\frac{347.06}{100}\right)^2-\frac{347.06}{100}\right]$$

$$=3.5\times 3.4706(2.4706)=30.01$$

∴ $$=377.07°\text{C}$$

Repeating the above-mentioned process,

$$t-347.06=3.5\left[\left(\frac{377.07}{100}\right)^2-\frac{377.07}{100}\right]$$

$$=3.5\times 3.7707\times 2.7707=36.57$$

$$t=383.63\ °\text{C}$$

Repeating again,

$$t-347.06=3.5\left[\left(\frac{383.63}{100}\right)^2-\frac{383.63}{100}\right]$$

$$=3.5\times 3.8363\times 2.8363=38.08$$

$$t=385.14\,°\text{C}$$

Repeating again,

$$t-347.06=3.5\left[\left(\frac{385.14}{100}\right)^2-\frac{385.14}{100}\right]$$

$$=3.5\times 3.8514\times 2.8514=38.44$$

$$t=385.50\,°\text{C}$$

PROBLEMS

1. The pressures of a gas in a constant volume gas thermometer are 100 cm and 137 cm of mercury at 0 °C and 100 °C, respectively. On introduction in to a bath the pressure is found to be 126 cm of mercury. Calculate its temperature.

   Ans. 70 °C

2. When the bulb of a constant volume gas thermometer is placed in melting ice, the level of mercury in the upper tube is 5 cm below the level in the closed limb. When the bulb is at 273 °C, the level in the open limb is 65 cm high. Calculate the barometric pressure.

   Ans. 75 cm

3. The pressure of air in a constant volume gas thermometer is 8 cm and 109.3 cm at 0 °C and 100 °C, respectively. When the bulb is placed in some hot water, the pressure is 100 cm. Calculate the temperature of hot water.

   Ans. 68.3 °C

4. A constant mass of hydrogen maintained at constant pressure has a volume of 200 cc at 0 °C, 273.2 cc at 100 °C and 525.1 cc at the boiling point of sulphur. At these temperatures a platinum wire has resistances of 2.00, 2.778 and 5.280 ohms, respectively. What will be the values of the boiling point of sulphur obtained by the two sets of observations?

   Ans. 444.1 °C on constant pressure hydrogen gas thermometer,
   421.6 °C on platinum resistance thermometer.

5. A platinum wire has a resistance of 2 ohms at 0 °C, 2.778 ohms at 100 °C and 2.54 ohms at the boiling point of a liquid. Calculate the boiling point of the liquid in platinum scale.

   Ans. $t_{pt} = 69.38\,°\text{C}$

6. If the resistances of a platinum thermometer at 0 °C, 100 °C and at the boiling point of sulphur (444.16 °C) are 3.60, 4.60 and 7.82 ohms, respectively. Calculate the true temperature at which the resistance of the thermometer is 6.60 ohms.

   Ans. 308.7 °C

7. The resistance of a wire of platinum thermometer is 2.653 and 3.621 ohms at the lower and upper fixed points, respectively and 3.139 ohm at a temperature which is indicated by a constant volume hydrogen thermometer as 50 °C. Calculate the difference between the platinum and constant volume hydrogen scale at the last temperature.

   Ans. 0.2 °C

QUESTIONS

1. Discuss the basic principle of thermometry. How many thermometric properties are used for measuring temperature? Discuss them along with their merits and demerits.
2. What are the disadvantages of liquid thermometers? Describe constant volume hydrogen thermometer with a sketch and describe the principle of measuring temperature with this. Which is more efficient—constant volume and constant pressure gas thermometer and why?
3. Describe Callendar's compensated air thermometer with a diagram. Discuss the theory of its use to determine unknown temperature.
4. Why platinum resistance thermometers called secondary thermometers? Describe its construction, deduce its working formula.
5. Describe how thermocouples are prepared and are used to measure unknown temperature.
6. What are the various methods used for the measurement of high temperatures? State the range of temperatures over which each method is suitable.
7. Give a short account of the different methods of thermometry that may be employed for the measurement of temperatures from the ice point down to the lowest attainable temperature. Assess in your answer the merits and demerits of different methods.

Chapter 3

THE MECHANICAL EQUIVALENT OF HEAT

3.1 ON THE NATURE OF HEAT: THE CALORIC THEORY OF HEAT

According to caloric theory, heat is supposed to be an indestructible imaginary fluid called the caloric, which flows from a body at higher temperature to a body at lower temperature. The caloric can neither be created nor destroyed. Heating of a body means addition of caloric; a body is cooled by drawing out caloric from a body.

3.1.1 The Dynamical Theory of Heat

In 1798, while watching the boring of a cannon at the Munich arsenal, Count Rumford found that the supply of heat generated by friction was apparently inexhaustible. From this, he concluded that anything which an isolated system of material bodies could furnish without limitation must be of the nature of work. This idea led to the establishment of an intimate relation between mechanical work and heat, and to the recognition of heat as a form of energy.

In the investigations regarding the relation between heat and mechanical work, Rumford was followed by many scientists such as Joule, Meyer, Davy, and others.

The result of their researches can be stated as follows:

Whenever mechanical work is completely transformed into heat, the amount of heat produced is directly proportional to the amount of work spent.

Thus, if W amount of work transforms into H units of heat, then

$$W \alpha H$$

or

$$W = JH \tag{3.1}$$

This constant of proportionality J is called the Joule's equivalent or the mechanical equivalent of heat.

If the work is expressed in ergs and heat in calories, then

$$J = 4.18 \times 10^7 \text{ ergs per calorie}$$
$$= 4.8 \text{ Joules per calorie}$$

since 1 Joule is equal to 10^7 ergs.

If work is expressed in ft-lbs and heat is measured in pound degree centigrade unit, then

$J = 1{,}400$ ft-lb per pound degree centigrade

If work is expressed in ft-lbs and heat energy is expressed in B. Th. Unit., then

$$J = 778 \text{ ft-lb per B. Th. Unit.}$$

3.2 FRICTION METHODS FOR DETERMINING J. JOULE'S METHOD

A sketch of Joule's apparatus is given in Fig. 3.1.

Index of parts:

G is a wooden grating.

C, the calorimeter, is supported on *G*. A vertical section of the calorimeter is shown in Fig. 3.2. The calorimeter is divided into compartments by means of baffle plates fixed to the wall of the calorimeter. These are shown by white portions in Fig. 3.2. The baffle plates have spaces cut out in them which are

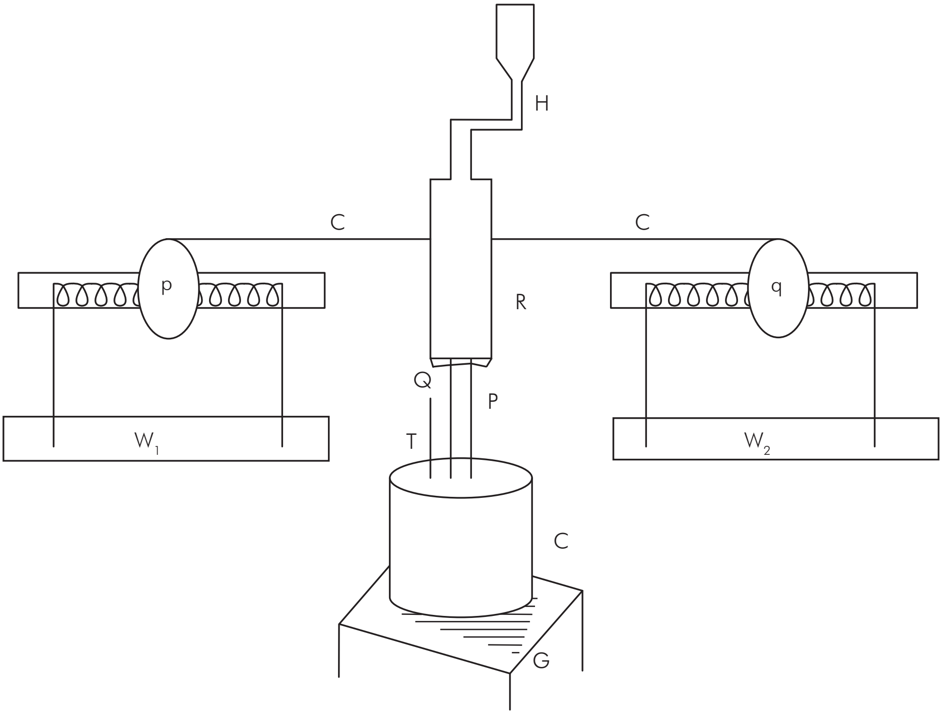

Fig. 3.1 Joule's Apparatus

just large enough to allow the rotating vanes to pass through. These vanes are shown by black portions in Fig. 3.2. *P* is the paddle to which the rotating vanes (Fig. 3.1) are attached. *R* is the roller which may be connected to the paddle by means of a pin *Q*. H is the handle by which the roller can be rotated. *p* and *q* are two pulleys over which cords c, c (bifilarly wound round the roller) pass.

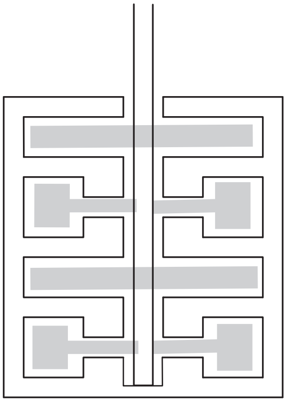

Fig. 3.2 Vertical section of calorimeter

From the axles of the wheels p and q, two loads W_1 and W_2 are suspended by cords wound on these axles. *T* is a sensitive thermometer passing through a hole in the lid of the calorimeter.

For carrying out the experiment, the calorimeter is filled with measured quantity of water. The roller R is then disconnected from the paddle P by taking out the pin *Q* and weights W_1 and W_2 are raised to the desired height by turning the handle *H*.

The roller is then connected to the paddle by means of the pin and the weights are released. As the weights descend, the vanes rotate and the liquid is set in motion. The liquid is churned every time the vanes pass through the planes of the baffle plates. This causes the kinetic energy of the liquid to be converted into heat. By this process, the potential energy of the falling weights is converted into the kinetic energy of water particles which is again transformed into heat. After the weights have descended through the desired heights, the roller is again disconnected from the paddle axle and the weights are again raised to the same height as before. The weights are again released after connecting the roller to the paddle; this process is repeated several times and the temperature of the liquid is recorded by the thermometer T at regular intervals of time. The method of calculation is as follows:

Let the water equivalent of the calorimeter and its contents be *W* gm

The rise of temperature of water in the calorimeter and its contents $= \theta$°C

Then, the heat absorbed by the calorimeter and its contents $= W\theta$ cal

Let the mass of the weights $= m$ gm and the height through which the weights descend $= h$ cm.

Let the number of the weights descended $= n$, then, the total work spent in *n* falls $= mngh$ ergs Assuming that no heat is lost by radiation and other causes, the mechanical equivalent of heat is

$$J = \frac{mngh}{W\theta} \text{ ergs per calorie} \tag{3.2}$$

The value of *J* obtained by Joule was 4.155×10^7 ergs per calorie.

Sources of error in Joule's experiment: The experiment of Joule as described earlier was subject to the following sources of error:

1. Loss of heat due to radiation.
2. Loss of energy due to friction at the wheels: This was determined by noting the amount of work required to turn the vanes when there was no liquid inside the calorimeter.
3. The kinetic energy of the falling weights: The total work done in raising the weights to the desired heights is partly spent in overcoming the frictional resistance offered by the liquid to the rotating vanes and partly in generating kinetic energy of the falling weights. This was determined by measuring the velocity of falling weights on striking the ground. If *v* is this velocity, the loss of energy due to motion of the weights is 1/2 mv^2.

3.2.1 Searle's Method of Measuring *J*

The mechanical equivalent of heat can be determined by students in the laboratory by using Searle's method. The apparatus shown in Fig. 3.3 consists of two truncated cones *C* of gunmetal which just fit into each other. The inner cone is filled with water into which the bulb of a delicate thermometer is dipped.

The outer cone is fixed to a vertical spindle *S* which can be rotated by means of a cord passing round a large rotating wheel *G*. A wooden disc *D* is attached to the top of the inner cone. As the outer cone is rotated, the inner cone also tends to rotate with it in the same direction. It is kept stationary by means of an opposing couple exerted by the weight W attached to the end of a horizontal cord passing round the rim of the wooden disc *D*.

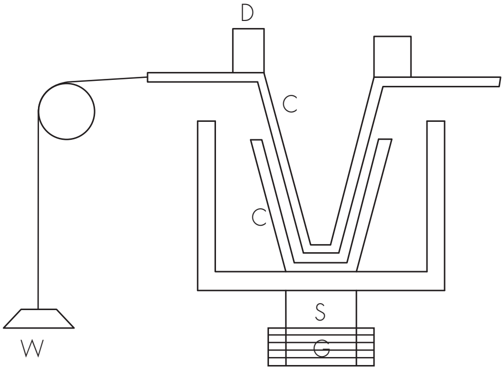

Fig. 3.3 Searle's apparatus for determining *J*

When the weight *W* is at rest while the outer cone is rotating, the moment of the couple exerted by friction between the two cones is equal to the moment applied by the weight *W*.

Let *r* be the radius of the wooden disc *D*; then the moment of the couple opposing rotation of the inner cone is *Wr*. Hence if the outer cone makes *n* revolutions, the work done is $2\pi nrW$. Let *m* be the water equivalent of the calorimeter and its contents; if θ be the rise of temperature of water, the heat absorbed by the calorimeter and its contents is $m\theta$. Hence, the mechanical equivalent of heat is

$$J = \frac{2\pi nrW}{m\theta} \tag{3.3}$$

3.3 WORK DONE DURING EXPANSION OF A GAS AT CONSTANT PRESSURE

Figure 3.4 shows some quantity of air enclosed in a cylinder under an airtight piston occupying the position A_1 B_1. Let the volume of the gas under the piston be v_1 and its pressure be *p*. Let the air expand at constant pressure forcing the piston to the position A_2 B_2. Let the mass of air now occupy the volume v_2. Let *s* be the area of the piston. Then the total force on the piston is *s p*. If *d* be the distance between the two positions of the piston, the work done in the expansion is *spd*.

But, *sd* is the volume of the cylinder between the two positions of the piston and it is equal to $(v_2 - v_1)$; hence, the work done by a gas in expanding at constant pressure from volume v_1 to volume v_2 is

$$W = p(v_2 - v_1) \tag{3.4}$$

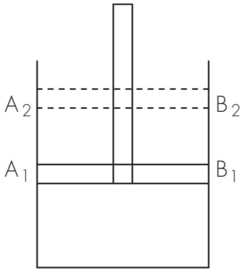

Fig. 3.4 Schematic diagram for work done during expansion at constant pressure

When the gas expands, it works against external pressure. The equivalent amount of energy must be drawn from somewhere. If all supply of energy from outside is cut off, the gas loses its own energy in the form of heat. It, therefore, cools down. The quantity of heat drawn from the gas to produce work *W* is

$$H = \frac{p(v_2 - v_1)}{J} \text{ calories} \tag{3.5}$$

where J is the mechanical equivalent of heat. Under the same condition if the gas is compressed, it develops heat.

3.3.1 Mayer's Method of Determining *J*

The equation $J = R/(C_p - C_v)$ was used by Mayer to determine the value of J.

1 cc of air at N. T. P. weighs 0.001293 gm. Therefore, the volume occupied by 1 gm of air at N. T. P. is

$$v_0 = \frac{1}{0.001293} \, cc$$

Now, normal pressure is $p_0 = 76 \times 13.6 \times 981 = 1013000$ dynes/cm^2
Hence, the specific gas constant for air is

$$R = \frac{p_0 v_0}{273} = \frac{1013000}{0.001293 \times 273}$$

From experiment, $C_p = 0.238$ and $C_v = 0.17$

Hence,
$$J = \frac{1013000}{0.001293 \times 0.068 \times 273}$$

$$= 42 \times 10^6 \text{ ergs per calorie}$$

a result which agrees fairly well with the values obtained directly from experiments.

3.4 CALLENDAR AND BARNES' STEADY FLOW METHOD

The apparatus that Callendar and Barnes used is shown in the Fig. 3.5.

AB is a glass tube whose middle portion is very narrow. Through this narrow portion, a special platinum wire is passed which is fixed to two copper tubes of negligible resistance at its two ends.

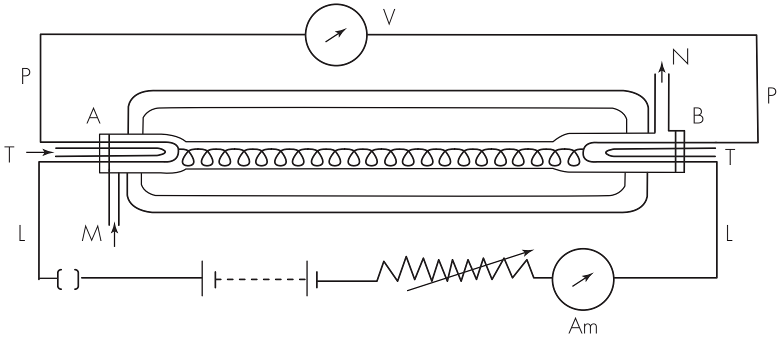

Fig. 3.5 Callendar and Barnes' apparatus of determining *J*

These copper tubes surround two platinum resistance thermometers, *T*. Due to the good conductivity of copper, the platinum resistance thermometers assume the temperature of the adjacent water very easily. These copper tubes have low resistance which prevents the generation of heat by the flow of current close to the thermometer. Water is passed through the tube by the inlet *M* and is allowed to flow outside by the outlet N. The platinum resistance thermometers (*T*, *T*) measure the temperature of the incoming and outgoing water. The tube AB is surrounded by a vacuum jacket which keeps the conduction and convection of heat minimum. This vacuum jacket is surrounded by a water jacket. The leads LL are used as the current leads and electrically connected with a series of battery and a rheostat. The current is measured by potentiometric arrangement. The leads *PP* are used as the potential leads and are connected to a voltmeter, which measures the potential difference across the wire.

Water is allowed to flow and current is passed through the coil. This raises the temperature of the outgoing water; and after some time, the steady state is reached. Let θ_1 and θ_2 be the temperature of the incoming and outgoing water, respectively, at the steady state, *E* be the potential difference across the wire and *I* be the current flowing through the wire, then the electrical energy spent per second = *E I*. If *m* be the mass of water flowing through the tube per second, then

$$EI = J[ms(\theta_2 - \theta_1) + h]$$

where *h* denotes heat lost per second due to radiation, etc. and *s* the specific heat of water. The temperature difference was maintained at about 6° − 8/°C. The loss *h* may be eliminated by adjusting the current so as to maintain the same rise of temperature for two sets of experiments, that is, for different rates of flow of water. Then for two sets, we have

$$E_1I_1 = J[m_1s(\theta_2 - \theta_1) + h]$$

$$E_2I_2 = J[m_2s(\theta_2 - \theta_1) + h]$$

Subtracting,
$$E_1I_1 - E_2I_2 = Js(\theta_2 - \theta_1)(m_1 - m_2)$$

$$J = \frac{E_1I_1 - E_2I_2}{s(\theta_2 - \theta_1)(m_1 - m_2)} \tag{3.6}$$

The specific heat *s* corresponds to the mean temperature $(\theta_2 + \theta_1)/2$. This method was also utilized to measure the specific heat of water at various temperatures. The temperature of the inflowing water is changed; hence, the mean temperature is changed. Thus, the variation of specific heat with temperature is obtained.

3.4.1 Other Methods of Determining *J*

There are other methods also for the determination of *J*. Some methods utilize the conversion of mechanical work into heat and others utilize the conversion of electrical work into heat. Works of Rowland (1880), Laby and Hercus (1927), Jaeger and Steinwehr (1921), and Osborne, Stimson and Ginning (1939) may be mentioned here.

3.5 NEWTON'S LAW OF COOLING

In article 3.1 we have discussed nature of heat. When a body is given a certain quantity of heat, its temperature rise depends on the mass of the body and nature of the body. Amount of heat is measured by a particular unit called calorie. It is defined as the amount of heat required to raise 1 gram of water through 1 °C. As this amount depends upon the initial temperature of water so a standard has been chosen, it is the amount of heat required to raise 1 gram of water from 14.5 °C to 15.5 °C. There are other units of heat such as British Thermal Unit, Centigrade heat unit or pound calorie, calorie is universally accepted and used. The nature of the body is manifested by another physical property called specific heat *c*. It is defined as the quantity of heat required to raise the temperature of unit mass of a substance through one degree. It is also defined as the ratio of the quantity of heat required to raise any mass of a substance through any range of temperature to the quantity of heat required to raise an equal mass of water through the same range of temperature. It dQ heat is required to raise 1 gm of a substance through dT then

$$dQ = 1cdT \quad \text{or} \quad c = \frac{dQ}{dT}$$

This definition is applicable to solids and liquids. But in the case of gas, application of heat changes the pressure, volume and temperature. If pressure is kept constant, volume and temperature change with application of heat. This gives rise to two specific heats, specific heat at constant volume and specific heat at constant pressure.

3.5.1 Specific Heat at Constant Volume, C_v

Specific heat at constant volume, C_v is the amount of heat required to raise the temperature of 1 gm of gas through 1 °C, volume remaining constant. When we consider 1 gram molecule (molecular weight expressed in grams) of the gas, the corresponding specific heat is known as molar specific heat (C_v) related by $C_v = M\,c_v$ where M is the molecular weight of the gas.

3.5.2 Specific Heat at Constant Pressure *Cp*

Specific heat at constant pressure c_p is the amount of heat required to raise the temperature of 1 gm of the gas through 1 °C, pressure remaining constant. If we consider 1 gram molecule of the gas, the corresponding specific heat is known as molar specific heat (C_p) related by $C_p = M\,c_p$.

3.5.3 Relation Between C_p and C_v

From the above fact, we see that when a gas is heated at constant volume, heat raises the temperature of the gas; but when a gas is heated at constant pressure a part of heat raises its temperature and another part is used to do external work to keep pressure constant, so $C_p > C_v$.

Let us suppose that 1 gm of gas at a constant pressure p, volume v and temperature T be given a certain amount of heat which raises the temperature through dT pressure remaining constant increasing the volume by dv (see Fig.3.4)

$$\text{Work done} = p \times dv$$

We know $pv = rT$ where r is the gas constant for 1 gram of the gas.

Differentiating $p\,dv + vdp = rdT$

$$dp \text{ being zero, } pdv = rdT$$

$$\text{Work done in heat units} = \frac{rdT}{J}$$

$$\text{Heat given} = 1c_p\,dT = 1c_v\,dT + \frac{rdT}{J}$$

$$\therefore \qquad C_p - C_v = \frac{r}{J}$$

If we take 1gram molecule of the gas of molecular weight M then we can write

$$MC_p - MC_v = \frac{Mr}{J}$$

$C_p - C_v = \frac{R}{J}$, R being universal gas constant.

It is found that the ratio of the specific heat of a gas at constant pressure to that at constant volume is indicated by $\left(-C = \frac{C_p}{C_v}\right)$.

For monatomic gas its value is 1.67, for diatomic gas it is 1.41, for triatomic gas it is 1.33.

3.5.4 Principle of Calorimetry

When a hot body is made to exchange its heat with a cooler body or surrounding the heat given out by the hot body is equal to the heat taken by cold body or surrounding provided heat is not lost by other means.

3.5.5 Measurement of Specific Heat of Solids

Common methods for determination of specific heats of solids are (i) method of mixture (ii) Bunsen ice calorimeter (iii) Joly's steam calorimeter (iv)Nernst and Lindermann's vacuum calorimeter, these are common and general normal methods.

3.5.6 Measurement of Specific Heat of the Liquids

Specific heat of liquids can also be determined by the above methods in addition to Calendar and Barnes steady flow method which we have discussed earlier, J being known, specific heat can be calarlated.

We shall now discuss Newton's low of cooling. It states that the rate of loss of heat by a body is proportional to the mean difference of temperature between the body and its surrounding provided the temperature difference is not too large. This rate depends on the temperature of the liquid with its container and the surrounding, nature of the liquid, area of the exposed liquid surface, the nature and extent of the surface of the containing vessel. If a liquid of mass m, specific heat c, temperature T is kept in a surrounding temperature T_o, then the amount of heat lost dQ in time dt can be written as $-dQ/dt = a(T - T_o)$ where a is a constant. Again as the body cools through dT in the same time interval then $dQ = mcdT$

$$\therefore \qquad -mc\frac{dT}{dt} = a(T - T_o)$$

$$\frac{dT}{(T - T_o)} = -\frac{a}{mc}dt = -Adt$$

Integrating $\log_e (T - To) = -At + B$

If a graph is plotted t along x axis and $\log_e (T - To)$ a long y axis, we get a straight line which verifies Newton's low of cooling.

3.6 SPECIFIC HEAT OF A GAS BY JOLY'S DIFFERENTIAL STEAM CALORIEMETER

The sketch of Joly's differential steam caloriemeter is shown in Fig. 3.6 by which specific heat of a gas can be determined. The calorimeter consists of two parts, the upper part is a balance having two scale pans A and B from which two hollow copper spheres S and R of equal thermal capacities are suspended in lower steam chamber by fine platinum wires through narrow holes as shown in the figure. *C* is the pointer of the balance. *D* and *E* are the bases placed over the lower steam chamber or which balance stands. *N* and *P* are two catch pans of same mass to collect condensed steam from *S* and *R*. *L* and *M* are two shields to save *S* and *R* from any condensed steam from above. *H* and *R* are two electrical heater arrangements meant for prevention of any condensation of steam in the holes through which the suspension wires pass. I and *O* are inlet and outlet pipes which allow steam to get in and out of the steam chamber.

With no steam in the steam chamber spheres *S* and *R* are evacuated and the balance is counterpoised. The sphere S is filled with the experimental gas at high pressure and the balance is counterpoised again. The difference in weight gives the mass *M* of the enclosed gas. The initial temperature of the steam chamber θ_1 is noted, then dry steam is allowed to enter through I. As a result steam will condense on the spheres and their temperatures will be steady and let that temperature be θ_2. More steam will condense on the sphere containing the gas than the empty sphere as heat is needed to heat up the gas also. The balance is counterpoised. The excess weight *m* gives the mass of excess steam condensed on the sphere containing the experimental gas. Then we can write.

$M c_v(\theta_2 - \theta_1) = mL$ where c_v is the specific heat at constant volume and *L* is the latent heat of steam. So C_v is calculated as other quantities are known. This method of determination is very accurate as the effect of buoyancy and thermal capacity of the container is eliminated. However more corrections are necessary for betterment of result.

(a) Corrections for any discrepancy of thermal capacities of the spheres. This can be taken into account by repeating the experiment interchanging the spheres and taking the average of the two.

(b) Corrections for the expansions of the sphere *S* owing to rise of temperature and increase of internal pressure, external work is done in such expansion.

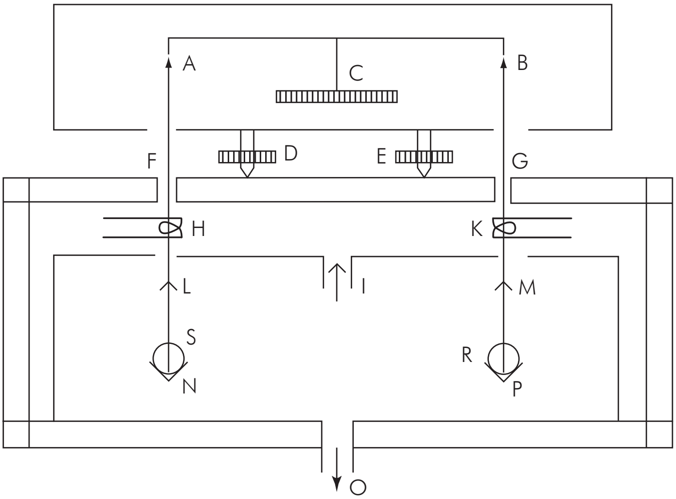

Fig. 3.6 Experimental arrangement to determine c_v by Joly's differential steam Caloriemeter

(c) Corrections for increased buoyancy due to increase in volume.

(d) Corrections for the weight of the condensed steam. This weight is taken in a moving medium as steam was flowing so this weight must be reduced to its corresponding value in vacuum.

3.7 DETERMINATION OF SPECIFIC HEAT OF A GAS AT CONSTANT PRESSURE BY REGNAULT'S METHOD

Laplace and Lavoisier used this technique first. Then it was taken up by Regnault to measure the specific heat at constant pressure of a gas. The apparatus used by him is shown in Fig.3.7.

Dry, pure, compressed experimental gas is kept in container A which is kept immersed in a constant temperatures bath B. T_1, T_2, T_3 are thermometers provided for recording the temperature of corresponding vessels. P_1, P_2, P_3, P_4 are taps to regulate the flow of experimental gas. M_1, M_2 are two manometers for recording pressures. *C* is a hot oil bath, S_1, S_2 are the stirrers, E is the condenser and *D* is the calorimeter.

During the experiment the gas under a certain pressure recorded by M_1 is allowed to flow at a constant pressure to the hot oil bath. The constancy in pressure is maintained by a constant difference of level in M_2 by opening tap P_4 more and more as the gas flows out from the container A. The oil bath is constantly stirred and the temperature is recorded by T_2. The hot gas from *C* passes through the spiral tube and connecting tube to the condenser E and then comes out through the spiral tube which is immersed in water in calorimeter *D*. The oil bath *C* and the calorimeter *D* are separated by a thermally insulated shield *Q*. The readings of the thermometer are noted at regular intervals till the temperature becomes steady. Calculating the amount of gas escaping during the experiment in terms of gram molecule we can determine the molar specific heat at constant pressure. Let *m* gram molecules gas flow out during the experiment, *M* being the mass of water in the calorimeter whose water equivalent is *W*, θ_1 be the temperature of oil bath, θ_i and θ_f be the initial and final temperature of the calorimeter, then we can write

$$mC_p\left(\theta_1 - \frac{\theta_i + \theta_f}{2}\right) = (M + W)(\theta_f - \theta_i)$$

As the gas flows for a certain time in which the temperature of the calorimeter increases from initial value θ_i to final steady value θ_f we may consider that the flow of gas has taken place at a constant temperature $\theta_i + \theta_f/2$.

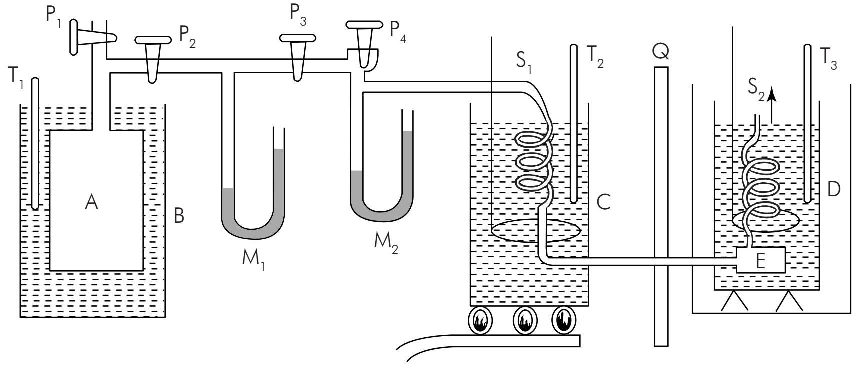

Fig. 3.7 Regnault's experimental arrangement to measure C_p

Then if m is known, C_p can be found. m is calculated using the equation of a perfect gas involving pressure, volume and temperature.

If V = volume of the container A

P_i = initial pressure of the gas in container

P_f = final pressure of the same gas at the end of the experiment

T = temperature of the gas in the container recorded by thermometer T_1

P_i, P_f are measured from M_1

Then the initial volume of the gas at NTP, V_i is given by

$$\frac{P_i V}{T} = \frac{76 V_i}{273}$$

$$V_i = \frac{273}{76}\frac{P_i V}{T}$$

After completion of the experiment the final volume of the gas at NTP, V_f is given by

$$\frac{P_f V}{T} = \frac{76 V_f}{273}$$

$$V_f = \frac{273}{76}\frac{P_f V}{T}$$

The volume of the gas that flows out is

$$V_i - V_f = \frac{273}{76}\frac{V}{T}(P_i - P_f)$$

and the mass of gas that flows out is

$$= \mathrm{e}(v_i - v_f) = \frac{273}{76}\frac{V}{T}\mathrm{e}(P_i - P_f)$$

where e = density of the gas at NTP

If the molecular weight of the gas be F, then

$$m = \frac{\mathrm{e}(V_i - v_f)}{F} = \frac{273}{76}\frac{V\mathrm{e}}{FT}(P_i - P_f)$$

This method requires some precautions. The calorimeter may lose some heat by radiation and convection and also receive heat by conduction through the connecting tube. Radiation correction should be applied.

3.8 DETERMINATION OF γ BY CLEMENT AND DESORMES' METHOD

The principle of the method of determination of γ by clement and Desormes is based on adiabatic expansion of gas. The arrangement is as shown in Fig.3.8. A is a large flask of nearly 30 liters capacity closed by a rubber cork through which a manometer M, a tube provided with a stopcock C for filling with the experimental gas and an arrangement D for adiabatic expansion of the gas are provided. A is kept inside a bowl B packed with insulating material such as cotton, wool, asbestos fiber etc, suitable for adiabatic expansion of gas in A. The manometer M is provided with sulphuric acid or suitable oil as manometer liquid.

The experiment is performed in three stages.

1. With tap C open some gas is introduced at a slightly higher pressure than the atmospheric pressure H which is manifested by the differences of level h_1 in manometer M, the initial pressure of gas p_i is $H + h_1$ let the initial temperature be T_i, tap C is now closed.

2. Then the gas is made to expand adiabatically by quickly operating *D* to atmospheric pressure, at this time the two levels in the manometer will be equal. The temperature will fall below room temperature. Let the pressure be $p_o = H$ and temperature T_o.

   then we have $\left(\dfrac{p_i}{p_o}\right)^{\gamma-1} = \left(\dfrac{T_i}{T_o}\right)^{\gamma}$

3. The traped gas in A is allowed to come to the initial temperature T_i. Volume of the gas remaining same pressure will increase to p_f there will be a difference of levels in the manometer, let that be h_2 so $p_f = H + h_2$

   so we can write $\dfrac{p_f}{p_o} = \dfrac{T_i}{T_O}$

   From the two above equations, we can write

$$\left(\frac{p_i}{p_o}\right)^{\gamma-1} = \left(\frac{p_f}{p_o}\right)^{\gamma}$$

Taking log of both sides, we get

$$(\gamma - 1)(\log_e p_i - \log_e p_o) = \gamma(\log_e p_f - \log_e p_o)$$

or $$\gamma(\log_e p_i - \log_e p_o - \log_e p_f + \log_e p_o) = \log_e p_i - \log_e p_o$$

or $$\gamma(\log_e p_i - \log_e p_f) = \log_e p_i - \log_e p_o$$

or $$\gamma = \frac{(\log_e p_i - \log_e p_o)}{(\log_e p_i - \log_e p_f)}$$

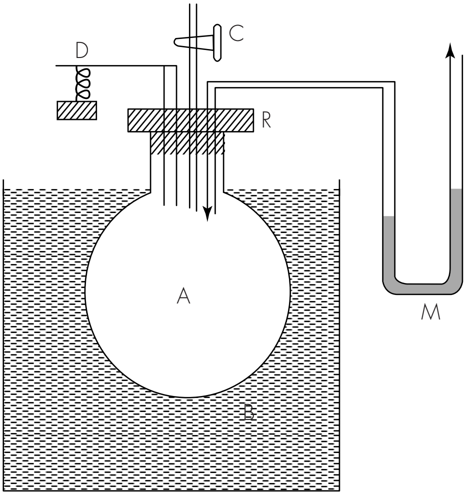

Fig. 3.8 Clement and Desormes method to measure γ

Thus knowing p_o, p_i, p_f, γ can be calculated. Here the main source of error lie in the fact that during adiabatic expansion by operating *D* the pressure does not assume atmospheric value as is evident from the oscillations of the two levels in the manometer M. It is very difficult to ascertain the exact pressure immediately on adiabatic expansion. This was taken care of by Lummer, Pringsheim and Partington's method.

Solved Problems

Q1. A calorimeter of water equivalent 20 gm contains 1030 gm of water. In it, a paddle wheel is made to rotate by means of two weights each weighing 10 kg falling a distance of 80 metres. Find the rise in temperature of the water, assuming $g = 980$ cm/sec^2.

Ans. Potential energy in the raised position for both the weights

$$= 2 \times 10{,}000 \times 980 \times 8{,}000 \text{ dyne cm}$$

If the rise in temperature be θ, then the heat gained by the calorimeter and its contents is 1,050 θ.

So, $$J = \frac{2 \times 10000 \times 980 \times 8000}{1050\ \theta}$$

$$\therefore \qquad \theta = \frac{98 \times 16 \times 10^8}{1050 \times 4.18 \times 10^7} = 3.58\ ^\circ\text{C}$$

Q2. A calorimeter of copper (specific heat 0.1) weighs 120 gm. It contains 1,400 gm of paraffin oil (specific heat 0.6). The oil is stirred by a rotating paddle which requires a couple of 10^8 dynes cm to drive it. If the temperature of the oil is raised by 16 °C after 900 revolutions, calculate the mechanical equivalent of heat.

Ans. Work done by rotating paddle per rotation $= 2\pi 10^8$

The total work done $= 2 \times 3.14 \times 900 \times 10^8$ dyne cm

Heat gained by calorimeter $= 120 \times 0.1 \times 16$ calories

Heat gained by paraffin oil $= 1{,}400 \times 0.6 \times 16$ calories

$$\therefore \qquad J = \frac{2 \times 3.14 \times 900 \times 10^8}{120 \times 0.1 \times 16 + 1400 \times 0.6 \times 16} = 4.15 \times 10^7 \text{ erg/cal}$$

Q3. The heat developed in drilling a hole in a block of iron (specific heat 0.12) of mass 25lb if 0.4 horse power is supplied for 3 minutes would suffice to raise the temperature of the block by 17 °F, calculate the mechanical equivalent of heat.

Ans. Total work done $= 0.4 \times 33{,}000 \times 3$ ft-lb,

since one horse power $= 33{,}000$ ft-lb per minute.

The amount of heat developed $= 25 \times 0.12 \times 17$ B. Th. U.

$$\text{Therefore,} \qquad J = \frac{0.4 \times 33000 \times 3 \times 10^8}{25 \times 0.12 \times 17} = 776.8 \text{ ft-lb/B. Th. U.}$$

Q4. Two blocks of lead, each of mass 210 gm moving in opposite directions with velocity relative to earth of 200 metres per second, collide with one another and are reduced to rest. The mechanical equivalent of heat being 4.2×10^7 ergs/calorie, calculate the kinetic energy of each block and the mean rise of temperature (specific heat of lead 0.03).

Ans. Kinetic energy of each block $= \frac{1}{2} mv^2$

$$= \frac{1}{2} \times 210 \times (20000)^2 \text{ ergs} = 4.2 \times 10^{10} \text{ ergs}$$

$$\text{Mean rise of temperature} = \frac{\text{Total kinetic energy}}{\text{Mechanical equivalent of heat}} \times \frac{1}{\text{Mass} \times \text{Specific heat}}$$

$$= \frac{2 \times 4.2 \times 10^{10}}{4.2 \times 10^7 \times 2 \times 210 \times 0.03} = \frac{10^2}{0.63} = 158.7\ ^\circ\text{C}$$

Q5. Calculate the rise of temperature when a lead ball strikes the ground after falling 160 feet, assuming that all the heat produced remains in the lead (specific heat of lead 0.03, mechanical equivalent of heat = 778 ft lb/B. Th. U.).

Ans. Let m lb be the mass of lead ball

Work done in falling through 160 feet $= 160\, m$ ft-lb

Heat absorbed by lead ball $= m \times 0.03 \times \theta$ where θ is the rise in temperature in °F, Then, $160\,m = 778 \times m \times 0.03 \times \theta$

$$\theta = \frac{160m}{778 \times m \times 0.03}\,°\text{F} = \frac{160m}{778 \times m \times 0.03} \times \frac{5}{9}\,°\text{C}$$

$$= 3.8\,°\text{C}\left(\text{since } 1\,°\text{F} = \frac{5}{9}\,°\text{C}\right)$$

Q6. In one of Rumford's experiments, the work done by one horse raised the temperature of 26.6 lb of water from 32 °F to 212 °F in 2.5 hours. If 25 per cent of heat generated was lost, find in ft-lb wt per min the rate at which the horse worked.

[1lb. deg. F = 778 ft-lb wt]

Ans. Let x ft-lb wt per minute be the rate at which the horse worked,
then the total work done = $x \times 150$ ft-lb wt
the amount of heat generated = $(x \times 150)/778$ lb. deg. F.

Only 75 percent of = $(x \times 150)/778$ lb. deg. F. is utilized to raise the temperature of 26.6 lb of water from 32 °F to 212 °F.

Then, $$\frac{x \times 150}{778} \times \frac{75}{100} = 26.6 \times 180$$

$$x = \frac{26.6 \times 180 \times 778 \times 100}{150 \times 75} = 33120 \text{ ft-lb wt/min}$$

Q7. A vertical glass tube 1 metre long closed at both ends contains 500 gm of mercury. Find the rise in temperature of the mercury if the tube is inverted 20 times in succession (specific heat of mercury = 0.03 cal/gm/°C and Joule's equivalent = 4.2 Joules per calorie).

Ans. Mercury falls through 100 cm each time the tube is inverted; hence, the loss in potential energy for each time = $500 \times 981 \times 100$ ergs
∴ The total loss = $500 \times 981 \times 100 \times 20$ ergs.
If θ be the rise in temperature of the mercury, then the heat developed = $500 \times 0.03 \times \theta$ cal

$$\therefore \qquad \theta = \frac{500 \times 981 \times 100 \times 20}{500 \times 0.03 \times 4.2 \times 10^7} = 1.56\,°\text{C}$$

Q8. A copper wire 0.02 cm in diameter carrying a current of 1 ampere is found to reach a steady maximum temperature of 100 °C. Assuming the specific resistance of copper at 100 °C to be 2.1 ohm cm and $J = 4.2$ Joules per calorie, find how many calories are emitted per second by 1 sq cm of the copper surface at 100 °C.

Ans. We know that if R is the resistance of a wire through which current I flows, then the electrical energy spent = I^2R (ampere)^2 ohm per sec = I^2R joules/sec

Here, we are to consider a surface of 1 sq cm area. Let l be the length corresponding to this area, then $2\pi\,(0.01)\,l = 1$ where 0.01 cm is the radius of the wire.

So, $l = (2\pi \times 0.01)^{-1}$

Resistance of the copper wire of length l, $R = \rho \dfrac{l}{A}$

where $\rho = 2.1$ ohm cm, $A = \pi(0.01)^2$

$$\therefore \qquad R = \frac{2.1}{2\pi(0.01)\pi(0.01)^2}$$

So, the work done $= 1^2 \dfrac{2.1}{2\pi^2(0.01)^3}$ joule

And the heat developed $= \dfrac{2.1}{2\pi^2(0.01)^3 \times 4.2} = 25{,}360$ calories.

Q9. A waterfall whose vertical height is 100 metres discharges 5 litres of water per second. Calculate (a) the quantity of heat produced per second, and (b) rise in temperature of water assuming that all the heat generated remains in the water. ($J = 4.18$ joules per calorie.)

Ans. (a) The mass of water = 5,000 gm

Work done in falling through 100 metres = 5,000 × 10,000 × 981 erg

The quantity of heat produced $= \dfrac{5\times10^7\times981}{4.18\times10^7}\,\text{cal} = 1132\,\text{cal}$

(b) If θ be the rise in temperature, then $1132 = 5{,}000\,\theta$

$$\therefore \qquad \theta = \frac{1132}{5000} = 0.23\,^\circ\text{C}.$$

Q10. Taking specific heat of lead as 0.03, find the rise of temperature of a lead bullet if it remains embedded in a fixed badly conducting block. The initial velocity of the bullet was 100 metres per sec and 95 per cent of its kinetic energy is converted into heat.

[$J = 4.2 \times 10^7$ ergs per calorie]

Ans. Let m be the mass of the lead bullet.

The kinetic energy of the bullet $= \dfrac{1}{2}m10000^2$

If θ be the rise in temperature, then heat produced $= m \times 0.03 \times \theta$.

Since 95 per cent of the kinetic energy is converted into heat, we have

$$m\times0.03\times\theta\times4.2\times10^7 = \frac{95}{100}\frac{1}{2}m\,10^8$$

$$\theta = \frac{95\times m\times10^8}{2\times100\times m\times0.03\times4.2\times10^7} = 37.7\,^\circ\text{C}.$$

Q11. The height of the Niagara Falls is 50 metres. Calculate the difference in temperature of the water at the top and bottom of the fall if $J = 4.2 \times 10^7$ ergs per calorie.

Ans. Let us consider m gm of water

Work done in falling through 50 metres = m × 5,000 × 981 ergs

Heat produced $= m\,\theta$ where θ is the rise of temperature, then

$$J\,m\,\theta = m \times 5{,}000 \times 981$$

$$\theta = \frac{m \times 5000 \times 981}{m \times 4.2 \times 10^7} = 0.12\ ^\circ\text{C}.$$

Q12. In an experiment using Callendar and Barnes' continuous flow method of measuring the mechanical equivalent of heat, the potential difference across the wire was 3 volts and the current 2 amperes, the rise in temperature of the water 2.7 °C and the rate of flow of water 30 gm per minute. When the rate of flow was increased to 48 gm per minute, the potential difference to 3.75 volts, and the current to 2.5 amperes, the rise in temperature of the water was the same as before. Calculate the value of *J*.

Ans. We shall use equation (3.6)

$$J = \frac{E_1 I_1 - E_2 I_2}{s(\theta_2 - \theta_1)(m_1 - m_2)}\ \text{joules/calorie}$$

$E_1 = 3.75$ volts $\qquad E_2 = 3$ volts

$I_1 = 2.5$ amperes $\qquad I_2 = 2$ amperes

$$(\theta_2 - \theta_1) = 2.7\ ^\circ\text{C} \quad m_1 = \frac{48}{60}\,\text{gm/sec}, \quad m_2 = \frac{30}{60}\,\text{gm/sec},$$

$$J = \frac{3.75 \times 2.5 - 3 \times 2}{1 \times 2.7\left(\dfrac{48}{60} - \dfrac{30}{60}\right)} = \frac{(9.375 - 6)60}{2.7 \times 18} = 4.167\,\text{joules/calorie}$$

Q13. Given that the mean radius of the earth is 6,400 km and its mean specific heat 0.15, find the rise in temperature of the earth if its energy of rotation is suddenly transformed to heat.

Ans. The rotational kinetic energy $= \frac{1}{2} I w^2$

where I = moment of inertia and w = angular velocity.

If θ is the rise in temperature of the earth and M is the mass of the earth,

then the heat produced $= M \times 0.15 \times \theta$

$$\therefore \qquad \frac{1}{2} I w^2 = J.M \times 0.15\theta$$

Now

$$I = \frac{2}{5} M r^2$$

where M = mass of the earth and r = radius of the earth

$$w = \frac{2\pi}{24 \times 60 \times 60}$$

$$\therefore \qquad \theta = \frac{I w^2}{2 \times J \times M \times 0.15} = \frac{2}{5}\,\frac{M(64 \times 10^7)^2 \times 4\pi^2}{\times 2 \times 4.2 \times 10^7 \times M \times 0.15\,(24 \times 60 \times 60)^2} = 68.7\,^\circ\text{C}$$

Q14. The specific heat of helium at constant pressure is 1.25. Assuming the gas to be monatomic, calculate the mechanical equivalent of heat. One litre of the gas at N. T. P. weighs 0.1785 gm.

Ans. Volume occupied by 1 gm of helium $= \dfrac{1000}{0.1785} cc$

Pressure of the gas $= 76 \times 13.6 \times 981$ dynes

Since $pv = rT$

$$r = \frac{pv}{T} = \frac{76\times13.6\times981\times1000}{0.1785\times273}$$

Now $\dfrac{c_p}{c_v} = \gamma = 1.66$, since the gas is monatomic

$$\therefore \qquad c_v = \frac{c_p}{\gamma} = \frac{1.25}{1.66}$$

$$\text{Now} \qquad (c_p - c_v) = \frac{r}{J} \text{ or } J = \frac{r}{c_p - c_v} = \frac{76\times13.6\times981\times1000}{0.1785\times273\left(1.25-\dfrac{1.25}{1.66}\right)}$$

$$= \frac{76\times13.6\times981\times1000\times1.66}{0.1785\times273\times1.25\times0.66} = 4.18\times10^7 \text{ ergs/calorie}$$

Q15. Assuming that for air at constant pressure the coefficient of expansion is 1/273, the density at 0 °C and atmospheric pressure is 0.001293 gm/cc, $c_p = 0.2389$ and $c_p/c_v = 1.405$, calculate the mechanical equivalent of heat.

Ans. For unit mass of the gas, $J(c_p - c_v) = pv\alpha_p$

where p = one atmospheric pressure, v = volume of unit mass,

α_p = the coefficient of expansion at constant pressure.

$$\therefore \qquad J = \frac{pv\alpha_p}{c_p - c_v} = \frac{76\times13.6\times981}{0.001293\times273\left(0.2389-\dfrac{0.2389}{1.405}\right)}$$

$$= \frac{76\times13.6\times981\times1.405}{0.001293\times273\times0.405\times0.2389} = 4.16\times10^7 \text{ ergs/calorie}$$

Q16. The following data were obtained with a continuous flow calorimeter. Rate of flow of water = 120 gm/min; temperature of incoming water = 27.30 °C; temperature of outgoing water = 33.75 °C; potential drop across the heating coil = 12.64 volts, current through the heating element = 4.35 amp. Assuming that no heat is lost, calculate the value of J in joules per calorie.

Ans. We know $EI = Jms\,(t_2 - t_1)$ where there is no loss of heat.

$$\therefore \qquad J = \frac{EI}{ms(t_2 - t_1)} \text{ joules/calorie}$$

$$= \frac{12.64 \times 4.35}{\frac{120}{60} \times (33.75 - 27.30)} = \frac{12.64 \times 4.35}{2 \times 6.45} = 4.16 \text{ joules/calorie}$$

Q17. Calculate the value of J, given that the gm molar specific heat of hydrogen at constant pressure = 6.865 calories, that at constant volume = 4.880 calories, atmospheric pressure 1.013×10^6 dynes/cm^2, gram molar volume = 22.4 litres.

Ans. We know that $$C_p - C_v = \frac{R}{J}$$

Again, $$PV = RT \quad \therefore R = \frac{PV}{T}$$

$\therefore$ $$J = \frac{R}{C_p - C_v} = \frac{PV}{T(C_p - C_v)}$$

$$= \frac{1.013 \times 10^6 \times 22.4 \times 10^3}{273(6.865 - 4.880)} = \frac{1.013 \times 22.4 \times 10^9}{273 \times 1.985} = 4.19 \times 10^7 \text{ ergs/calorie.}$$

Q18. One litre of hydrogen at 0 °C and 760 mm pressure weighs 0.0896 gm. The specific heats of hydrogen per gm at constant pressure and volume are 3.409 and 2.411, respectively. Calculate the value of J. Given: g = 981 cm/sec^2 and density of mercury = 13.6 gm/cm^3.

Ans. We know that for 1 gm of gas,

$$c_p - c_v = \frac{R}{MJ} = \frac{r}{J}$$

where c_p, c_v are specific heats per gm, r is the gas constant per gm.
Again $pv = rT$ where v is the specific volume

So, $$J = \frac{r}{c_p - c_v} = \frac{pv}{T(c_p - c_v)}$$

$$= 76 \times 13.6 \times 981 \times \frac{1000}{0.0896} \times \frac{1}{273 \times 0.998} = 4.15 \times 10^7 \text{ ergs/calorie.}$$

Q19. Calculate the specific heat at constant volume for air given that specific heat at constant pressure = 0.23. Density of air at 2.7 °C and standard atmospheric pressure = 1.18 gm per litre and $J = 4.2 \times 10^7$ ergs per calorie.

Ans. We know $$c_p - c_v = \frac{r}{J} = \frac{pv}{TJ}$$

Here, $$p = 73 \times 13.6 \times 981$$

$$v = \frac{1000}{1.18}$$

$$T = 300 \text{ K}$$

So, $$c_p - c_v = \frac{76\times13.6\times981\times1000}{300\times4.2\times10^7\times1.18} = 0.06821$$

$\therefore$ $$c_v = c_p - 0.06821 = 0.23 - 0.06821 = 0.1618\,\text{calorie}$$

Q20. A block of ice is dropped into a well of water, both ice and water at 0 °C. From what height must the ice fall in order that one-fifteenth of it may be melted?

Ans. Let *m* be the mass of the ice block and *h* be the required height.

Then, heat developed $$v = \frac{mgh}{J} = \frac{m}{15}\times L$$

$\therefore$ $$h = \frac{mLJ}{15\,mg} = \frac{L\,J}{15\,g} = \frac{80\times4.18\times10^7}{15\times981} = 2.2\times10^5\,\text{cm}$$

Q21. A lead bullet fired from a gun hits a stone and 90 per cent of the kinetic energy is converted into heat. If the temperature rise of the bullet is 80 °C on sudden stoppage, calculate the velocity of the bullet just before hitting the stone.

Assume that all the heat generated remains in the bullet (specific heat of lead = 0.03 , $J = 4.2$ Jules per calorie).

Ans. Let the velocity of the bullet be v cm/sec.

Kinetic energy of the bullet $= \frac{1}{2}mv^2$

where *m* is the mass of the bullet.

Heat required to raise the temperature through 80 °C $= m \times 0.03 \times 80$

Therefore, $$0.9\frac{1}{2}mv^2 = J\,m\times0.03\times80$$

or $$v^2 = \frac{J\times0.03\times80}{0.9}$$

or $$v = 1.5\times10^4\ \text{cm/sec}$$

Q22. A 5.0 lb lead ball of specific heat 0.032 Btu/lb °F is thrown downwards from a 50-ft building with an initial vertical speed of 20 ft/sec. If half of its energy at the instant of impact with the ground is converted to heat and absorbed by the ball, what will be its rise of temperature?

Ans. If the final velocity is *v*, then

$$v^2 = u^2 + 2fs = 400 + 2\times32.50 = 3600\ \text{sq ft.}$$

$$\text{Energy} = \frac{1}{2}mv^2 = \frac{1}{2}\times5\times3600\,\text{ft poundal}$$

$$= 9{,}000\ \text{ft poundal}$$

Heat generated from half of the energy

$$= \frac{1}{2}\frac{9000}{32\times778}\text{Btu}$$

$$\text{Rise in temperature } = \frac{1}{2}\times\frac{9000}{32\times778}\times\frac{1}{5\times0.032} = 1.1\,^\circ\text{F}$$

PROBLEMS

Q1. A mass of 10 gm moving with a speed of 300 m/sec is suddenly brought to rest. If the whole of its kinetic energy is converted into internal energy, find (a) the number of calories added, and (b) the rise in temperature of the body assuming that 70 per cent of the energy is retained by it (sp. ht. =0.03).

Ans. (a) 107.1 cal (b) 249.9 °C

Q2. From what height must a hailstone at 0 °C and at rest fall in order that 2 per cent of it may melt? Assume that 60 per cent of the energy converted is retained by it and that the temperature everywhere is 0 °C.

Ans. 1.142 km

Q3. The Victoria Falls are 343 feet in height. Calculate the difference in temperature of the waters at the foot and at the top, assuming $J = 778$ ft-lb per B. Th. U. and that 50 per cent of the energy is retained by the water.

Ans. 0.22 °F

Q4. In an experiment to determine J, 800 gm of lead shots were placed in a long cardboard tube held vertically, the length of which was such that on reversing the tube the shots fell through 100 cm. The original temperature of the shots was 25 °C and after 50 inversions of the tube the temperature was found to have risen to 28.84 °C. Find J in ergs per calorie (specific heat of lead $= 0.031$, $g = 980$ cm/sec^2).

Ans. 4.12×10^7 ergs/cal

Q5. Calculate the specific heat of air at constant volume given that the value at constant pressure is 0.2375, density of dry air at N.T.P. = 0.0807 lb per cuft. Normal atmospheric pressure = 14.7 lb per sq inch, coefficient of expansion of air = 1/273 per °C and J = 1,400 ft-lb per centigrade heat unit.

Ans. 0.1688

Q6. A lead bullet at a temperature of 47 °C strikes against an obstacle. If the heat produced by the sudden stoppage is just sufficient to melt the bullet, with what velocity does the bullet strike the obstacle? It is assumed that all the heat is produced within the bullet. Melting point of lead = 327 °C; specific heat of lead = 0.03 cal gm^{-1} °C^{-1}; latent heat of fusion of lead = 6 cal gm^{-1}; mechanical equivalent of heat = 4.2×10^7 ergs per calorie.

Ans. 3.48×10^4 cm/sec

Q7. In a continuous flow calorimeter of the Callendar and Barnes type, it is found that when the potential across the wire is 3 volts, the current passing is 2 amperes and the rate of flow of the water is 30 gm per minute and the rise in temperature of the water is 4 °C. Calculate the rate of flow necessary to show the same rise of temperature if the potential is increased to 4.5 volts and the current to 3 amperes ($J = 4.18$ joules per calorie).

Ans. 57 gm per minute

Q8. Find the value of J from the following data for air, $c_p = 0.2375$ cal per gm per °C, $c_v = 0.1688$ cal per gm per °C, density of air at N.T.P. = 0.001293 gm/cc, coefficient of expansion = 1/273 per °C, normal atmospheric pressure = 1.013×10^6 dynes/cm^2

Ans. 4.177×10^7 ergs/cal

Q9. Calculate C_v for hydrogen, given $C_p = 6.85$ cal per gm molecule, density of hydrogen at N. T. P. = 0.0899 gm per litre and $J = 4.18 \times 10^7$ ergs per calorie.

Ans. 4.87 calories per gm mol

Q10. A cylindrical tube 15 cm long made of a non-conducting material, closed at both ends, contains 500 gm of lead shots, which when the tube is held vertically occupy 6 cm of the tube length. The tube is suddenly inverted so that the end originally above is now below, and the shots fall to the other end of the tube. The tube is then again quickly inverted and the process is repeated 200 times. At the end of this process, the temperature of the shots is found by means of a thermometer to be 1.4°C higher than it was at the beginning of the experiment. Find the value of the mechanical equivalent of heat (specific heat of lead is 0.03. It is assumed that no heat is lost by radiation or conduction).

Ans. 4.2×10^7 ergs/calorie

Q11. If a lead bullet is suddenly stopped and all its energy is employed to heat it, with what velocity must the bullet be fired in order to raise the temperature through 100°C, the specific heat of lead being 0.0314?

Ans. 162×10^2 cm/sec

Q12. In an experiment by the continuous flow method for determination of *J*, when the rate of flow of water was 60 gm/min, the heating current 2 amperes and the potential difference was 5 volts, the rise of temperature of water was 2.3°C. On increasing the rate of flow to 87.6 gm per minute, the heating current to 2.4 amperes and the potential difference to 6.01 volts, the rise of temperature was still 2.3°C. Deduce the value of *J*.

Ans. 4.18×10^7 ergs/cal

Q13. Compute a value for the mechanical equivalent of heat from the following data:

Total mass allowed to fall = 2,600 gm
Distance of fall = 160 cm
Number of descents = 20
The rise in temperature was 0.30°C in the calorimeter which was thermally equivalent to 659 gm of water.

Ans. 4.13 Joules/cal

QUESTIONS

1. Define mechanical equivalent of heat. Describe Joule's method of its determination. Discuss the sources of error in Joule's experiment.
2. Describe Searle's method of measuring *J*.
3. Give an account of Meyer's method of determining *J*.
4. Describe Callendar and Barnes' steady flow method of determining *J*.

Chapter 4

KINETIC THEORY OF GASES

4.1 MACROSCOPIC AND MICROSCOPIC POINTS OF VIEW

The aim and object of science is to describe the behaviour of a system under different physical conditions. A system is a mass of matter which is isolated from its surroundings (in imagination). The system being chosen, the next step is to assign to the system certain physical quantities or parameters which suffer change when the system is interacted from outside. These parameters define the physical state of the system. By equation of state, we mean a mathematical relation which determines some parameters when others change.

In describing the physical state of a system, two points of view are generally adopted—(1) the macroscopic view and (2) the microscopic view. Under macroscopic view, we describe the gross characteristics of a quantity of matter in bulk by means of physical quantities which can be determined by our sense perception. In thermodynamics, where we consider the effect of heat on a system, the fundamental parameters are volume, pressure and temperature. There are also certain derived parameters such as entropy, enthalpy, free energy, etc. These are called the *thermodynamic coordinates* of the system. In describing the macroscopic state of a system, we make no assumption as to the internal structure of the system. Such description requires only few coordinates suggested by our sense perception and as such they may be directly measured.

From the microscopic point of view, we describe the physical behaviour of a system in terms of mechanical behaviour of the microscopic particles (such as atoms or molecules) constituting the system. To describe the behaviour of a microscopic particle, we require three coordinates of position (x, y, z) and three velocity coordinates (u, v, w). If there are N constituent particles in the system, we require $6N$ coordinates to describe the mechanical behaviour of the particles at any instant.

Thus from microscopic point of view, we require certain assumptions regarding the internal structure of the system. These may or may not be true and are, therefore, subject to change from time to time.

We also require a very large number of coordinates to describe the state of the system at an instant. These coordinates are not perceptible to our senses and are, therefore, not directly measurable.

It will be proved in this chapter that the thermodynamical coordinates mentioned earlier are only statistical averages of the change of mechanical behaviour of the constituent particles. The best test of the correctness of our assumption is the agreement of results calculated, both from microscopic and macroscopic considerations.

Whatever is the nature of assumptions regarding the internal structure of a system, the macroscopic or the thermodynamic description of a state will always remain true so long as our senses are not changed.

4.1.1 The Growth of the Kinetic Theory

The famous experiments of Joule, Rumford and others on the relation between heat and mechanical energy conclusively proved that heat is a form of energy. In the meantime, the law of so-called perfect gases $pv = RT$ was established on purely experimental basis by Boyle, Charles, Mariotte, Gay Lussac, and others. From the dimensional point of view, pressure multiplied by volume has the dimension of work. It follows that the idea of temperature is in some way connected with that of energy.

If a mass of gas enclosed in a fixed volume of space is heated, it does no external work by expansion. But there is increase of pressure and temperature of the gas. This must necessarily be due to some change in the energy content of the enclosed gas. What is the nature of this internal energy? The answer to this question led to the development of the kinetic theory of gases. The answer to the question first came from Joule who was also the first to determine the mechanical equivalent of heat.

He supposed that the molecules of a gas (or any other substance) are never at rest but are moving with all possible velocities in all possible directions. They are bombarding the walls of the containing vessel at all instants of time and thereby exerting pressure on the wall in the same way that a stream of water issuing from a hosepipe exerts pressure, when it is directed against a wall.

4.2 DERIVATION OF THE PRESSURE EXERTED BY A PERFECT GAS

In order to calculate the pressure exerted by a gas, we have to make some fundamental assumptions; they are as follows:

1. A gas consists of molecules which are identical and can be treated as small, hard elastic spheres moving at random in all directions with all possible velocities.
2. The molecules are treated as mass points, that is, their volume is negligible in comparison to the volume of the container.
3. During their motion, molecules collide with each other and with the walls of the container.
4. The collisions are considered to be perfectly elastic; there is no loss of kinetic energy when the collision occurs.
5. Though the molecules are incessantly colliding with each other, they do not affect the molecular density at the steady state.
6. The molecules are devoid of intermolecular force of attraction or repulsion, except when they actually collide.
7. The time of collision is very small in comparison with the time taken by the molecules in between the collisions.
8. Between two successive collisions, the molecules move in straight lines with uniform velocity.

4.2.1 Calculation of Pressure Exerted by a Perfect Gas

The molecules of a gas are moving in all directions with velocities ranging from zero to infinity. Let us first consider a group of molecules which move with velocity *c* in different directions. We shall designate these molecules as belonging to group *A*. Let N_c be the number of molecules per unit volume belonging to group *A*.

To find the pressure exerted by the molecules of group *A* on an element of area *ds* placed inside the mass of gas contained in unit volume, we describe a sphere of radius *c* round the centre of *ds* (Fig. 4.1).

From the centre of the sphere, we draw radii vectors in the directions of motions of molecules of group *A*. Since all directions of motion are equally probable, the end points of the radii vectors will be uniformly distributed on the surface of the sphere. The number of end points lying on unit area of the sphere is $N_c/4\pi c^2$. To find the number $N_{c\theta}$ of molecules of group *A* moving in directions lying between θ and $\theta + d\theta$ with the normal to *ds*, we describe two cones of semi-vertical angles, θ and $\theta + d\theta$, round the normal to *ds*. These cones intercept a belt of area on the surface of the sphere. The area of this belt is $2\pi c^2 \, sin\theta d\theta$. The number of end points of radii vectors lying within the range θ and $\theta + d\theta$ is

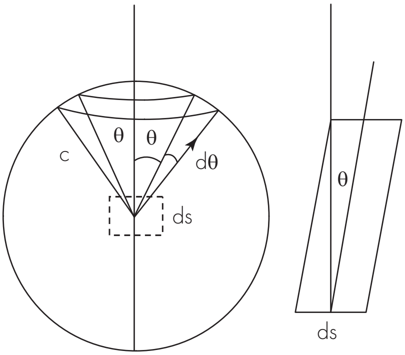

Fig. 4.1 Sketch of molecular motion

$$N_{c\theta} = N_c \frac{2\pi c^2 \sin\theta d\theta}{4\pi c^2} = \frac{1}{2} N_c \sin\theta d\theta$$

This is obviously equal to the number of molecules of group *A* in unit volume whose directions of motion lie between θ and $\theta + d\theta$ with the normal to *ds*.

To find the number of molecules of the class $N_{c\theta}$ which strike the area *ds* from one side of *ds* per second, we describe a cylinder on *ds* with its axis inclined in the direction θ and of length equal to *c*. The volume of the cylinder is *cds* cosθ. The number of molecules of class $N_{c\theta}$ contained in the cylinder is

$$dv_{c\theta} = N_{c\theta}\, cds \cos\theta = \frac{1}{2} N_c \sin\theta d\theta\, cds \cos\theta$$

These molecules evidently strike the area *ds* in 1 second. Let us now suppose that *ds* is an element of area of the containing vessel. Since the colliding surface of the molecules (supposed to be a sphere) and the wall of the containing vessel are said to be perfectly smooth and rigid, the normal component of the momentum of the molecule is reversed at each collision. If *m* be the mass of the molecule, the change of momentum at each collision is $2mc \cos\theta$. The total change of momentum in 1 second by collision with the $N_{c\theta}$ class of molecules is

$$dv_{c\theta} \times 2mc\cos\theta = N_c mc^2 \cos^2\theta \sin\theta d\theta ds$$

The total pressure exerted by molecules of group *A* striking *ds* from one side of *ds* is

$$p_c = N_c mc^2 ds \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta d\theta = -N_c mc^2 \int_0^{\frac{\pi}{2}} \cos^2\theta d(\cos\theta)$$

$$= \frac{1}{3} N_c mc^2 ds$$

Let $N_1, N_2, N_3 \ldots\ldots\ldots$ etc. molecules of the whole group of molecules have velocities $c_1, c_2, c_3 \ldots\ldots\ldots$ etc, then the total pressure exerted by all the molecules on unit area of the surface is

$$p = p_1 + p_2 + p_3 + \ldots\ldots = \frac{1}{3} m(N_1 c_1^2 + N_2 c_2^2 + N_3 c_3^2 + \ldots\ldots)$$

The mean square velocity is

$$c^2 = \frac{N_1 c_1^2 + N_2 c_2^2 + \ldots\ldots}{N_1 + N_2 + N_3 + \ldots\ldots}$$

$$\therefore \qquad N_1 c_1^2 + N_2 c_2^2 + N_3 c_3^2 + \ldots\ldots = Nc^2$$

where N is the total number of molecules per unit volume. The total pressure exerted by the gas is

$$p = \frac{1}{3} Nmc^2$$

4.3 DISTRIBUTION FUNCTION OF VELOCITIES

In the elementary kinetic theory of the so-called perfect gases discussed earlier, it was proved that the pressure and temperature of the gas depend on the mean square velocity of the molecules. There are phenomena which require for their proper description a knowledge of the distribution of velocities amongst the molecules. If we follow a particular molecule moving through the mass of the gas over a long interval of time, we shall find that both the direction of motion and the magnitude of velocity of the molecule changes from instant to instant. This is due to collision with other molecules which happen to lie in the path of the particular molecule. The molecules interact with each other only during collision.

Accordingly, the path traversed by a molecule between two successive collisions is straight, and its velocity during the interval between two collisions is uniform. This is true for every other molecule. On account of frequent collisions between the molecules, the maximum velocity of a molecule cannot acquire infinite magnitude. It follows that molecules of a gas must be moving in all directions with different possible velocities.

The problem before us is to find an expression for the distribution of velocities amongst different molecules, that is, to find the number of molecules whose velocities lie within a given small range. If the molecules are moving according to certain dynamical laws, there is every likelihood that molecules with nearly equal velocities would flock together. Accordingly, the distribution of velocities would be a function of position. This means that pressure at different points in a mass of gas would be different, so that the gas can never acquire a stable condition.

4.3.1 Assumption of Molecular Chaos

To simplify the analysis, Boltzmann made the basic assumption known as assumption of molecular chaos. It states that in the case of a large group of molecules which do not interact with each other except during collision, there is on an average no correlation between position and velocity of different molecules. This means that any velocity can occur at any point inside a mass of gas, so that the distribution of velocities in a gas is homogeneous and isotropic. This is, however, only an assumption and cannot be accepted without proof. The assumption has nevertheless stood the test of vigorous mathematical analysis.

4.3.2 The Velocity Space

The state of motion of a molecule is defined by six coordinates: (a) three coordinates of position (x, y, z), and (b) three velocity coordinates (u, v, w). To find the distribution of velocities in space at an instant we take an arbitrary point o as origin (Fig. 4.2) and draw three rectangular coordinates *ou*, *ov*, and *ow* parallel to the positional coordinates *ox*, *oy* and *oz* to represent the three component velocities (u, v, w).

From the origin, we draw radii vectors representing the velocity of each molecule at that instant. Then, the distribution of end points of these vectors gives the distribution of velocities in the velocity space. If we take a small element of volume *dudvdw* in this space, then the number of end points of the vectors lying within this volume gives the number of molecules whose velocity lies within the small range u to $u + du$, v to $v + dv$ and w to $w + dw$. If τ is the density of the end points at (u, v, w), then the number of molecules whose velocity lies within the above-mentioned range is τ *dudvdw*. It is convenient to replace τ by Nf where N is the total number of molecules and f is a function of (u, v, w) which we want to determine. When we want to specify the point, we write $f(u, v, w)$ instead of f. In this definition, τ and the element of volume *dudvdw* are not necessarily integers; but their product must be an integer, for it represents the number of end points lying within the volume. In describing an event where certain connected facts are known while others are unknown, we take recourse to the idea of probability. In the language of probability, τ *dudvdw* would mean the expectation of the number of molecules in the given volume *dudvdw* at the point (u, v, w). Since there are N molecules in the group, it follows from the theory of probability that the probability of a molecule selected at random (out of a group of N molecules) having velocity components within the range u and $u + du$, v and $v + dv$, w and $w + dw$ is $f(u, v, w)$ *dudvdw*.

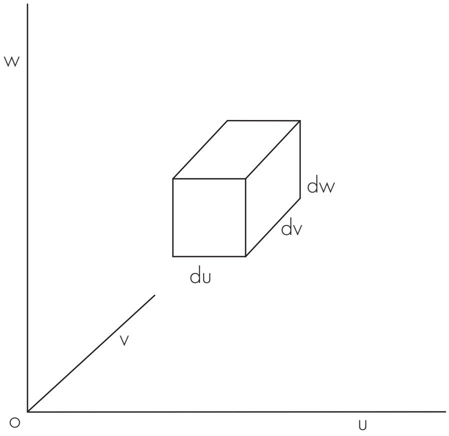

Fig. 4.2 Sketch representig distribution of molecular velocities

For the same reason the probability that a molecule selected at random out of a group of N molecules will occupy a volume element within the range x and $x + dx$, y and $y + dy$, z and $z + dz$ is $\upsilon\,(x, y, z)\,\Delta x \Delta y \Delta z$ where $\upsilon\,(x, y, z)$ is the number density of the molecules at the point (x, y, z).

The number of molecules out of the total number N whose velocity components lie within the range u to $u + du$, v to $v + dv$ and w to $w + dw$ is

$$N f\,(u, v, w) dudvdw \tag{4.1}$$

The number of molecules out of number υ per unit volume whose velocity components lie within the range u to $u + du$, υ to $v + dv$ and w to $w + dw$ is

$$\upsilon f\,(u, v, w) dudvdw \tag{4.2}$$

4.3.3 Maxwell's Law of Distribution of Velocities

At this point, Maxwell starts with the assumption that the velocity components u, v and w are independent of each other. The validity of this assumption is to be proved. Nevertheless, it leads to the correct law of distribution of velocities. This assumption stood the test of rigorous mathematical analysis by Boltzmann. For this reason, Boltzmann's name is usually associated with the Maxwellian law of distribution; and the law of distribution of velocities of molecules of a gas is known as Maxwell–Boltzmann's distribution law. Since u, v and w are quantities of the same nature obeying the same mechanical laws, the distribution function of these components cannot be different from each other; so, we shall express them by the same function f.

Let the probability of molecule having velocity component u to $u + du$ be $f(u)du$. Its probabilities of lying within the ranges v to $v + dv$ and w to $w + dw$ are, respectively, $f(v)dv$ and $f(w)dw$. Then, the joint probability of a molecule having simultaneous velocity component lying within the range u to $u + du$, v to $v + dv$ and w to $w + dw$ is

$$f(u)f(v)f(w)dudvdw$$

Then, the number of molecules (out of the total number of N molecules) whose velocity components lie within the range u to $u + du$, v to $v + dv$ and w to $w + dw$ is

$$Nf(u)f(v)f(w)dudvdw \tag{4.3}$$

Since the resultant velocity of a molecule at a given instant is

$$c^2 = u^2 + v^2 + w^2 \tag{4.4}$$

We must have

$$Nf(u)f(v)f(w)dudvdw = n\phi(c^2)dudvdw$$

so that

$$f(u)f(v)f(w) = \phi(c^2) \tag{4.5}$$

where ϕ is a function different from f. For a fixed value of c, $\phi\,(c^2)$ is constant, so that

$$d[\phi(c^2)] = 0$$

so that

$$f(v)f(w)f'(u)du + f(u)f(w)f'(v)dv + f(u)f(v)f'(w)dw = 0$$

or

$$\frac{f'(u)}{f(u)}du + \frac{f'(v)}{f(v)}dv + \frac{f'(w)}{f(w)}dw = 0 \tag{4.6}$$

Again for a constant value of c, $d(c^2) = 0$

or

$$2udu + 2vdv + 2wdw = 0 \tag{4.7}$$

Adding Eqs 4.6 and 4.7 by Laplace's method of undetermined multipliers, we get

$$\left(\frac{f'(u)}{f(u)} + 2\beta u\right)du + \left(\frac{f'(v)}{f(v)} + 2\beta v\right)dv + \left(\frac{f'(w)}{f(w)} + 2\beta w\right)dw = 0 \tag{4.8}$$

Since the velocity components are supposed to be independent, Eq. 4.8 is satisfied when each term of Eq. 4.8 is separately equal to zero so that

$$\frac{f'(u)}{f(u)} = -2\beta u$$

or $$\log_e f(u) = -\beta u^2 + \log_e \alpha = \log_e \alpha e^{-\beta u^2}$$

where $\log_e \alpha$ is the constant of integration

or $$f(u) = \alpha e^{-\beta u^2}$$

Thus, $$f(u)f(v)f(w) = \alpha^3 e^{-\beta(u^2+v^2+w^2)} \tag{4.9}$$

where α and β are constants. The number of molecules whose velocity components lie within the range u and $u + du$, v and $v + dv$, w and $w + dw$ is

$$dN = N\alpha^3 e^{-\beta(u^2+v^2+w^2)} du dv dw \tag{4.10}$$

4.3.4 Value of the Constants α and β

Since the total number of molecules is N

$$N \iiint f(u) f(v) f(w) du dv dw = N$$

or $$\iiint f(u) f(v) f(w) du dv dw = 1$$

or $$\alpha^3 \iiint e^{-\beta(u^2+v^2+w^2)} du dv dw = 1$$

This gives $$\alpha^3 \left(\frac{\pi}{\beta}\right)^{\frac{3}{2}} = 1$$

or $$\alpha = \sqrt{\frac{\beta}{\pi}} \tag{4.11}$$

Next, let us calculate the pressure exerted by the gas on a unit area perpendicular to the direction of the component u. The number of molecules striking unit area in 1 second is equal to the number of molecules lying within a cylinder of unit cross section and of length equal to u. The number of molecules having velocity within the range u to $u + du$ per unit volume is

$$\upsilon \alpha e^{-\beta u^2} du$$

where υ is the number density. The number of molecules within the cylinder is, therefore,

$$\upsilon \alpha e^{-\beta u^2} u du$$

The change of momentum suffered by a molecule at each collision is $2mu$. Hence, the pressure exerted is

$$p = 2\upsilon \alpha m \int_0^\infty e^{-\beta u^2} u^2 du$$

$$= 2\alpha \upsilon m \frac{1}{4}\left(\frac{\pi}{\beta^3}\right)^{\frac{1}{2}}$$

$$= \frac{\upsilon m}{2}\left(\frac{\beta}{\pi}\right)^{\frac{1}{2}}\left(\frac{\pi}{\beta^3}\right)^{\frac{1}{2}} = \frac{\upsilon m}{2\beta}$$

But, $$p = \upsilon kT \tag{4.12}$$

$$\therefore \qquad \beta = \frac{m}{2kT}$$

Hence, the dN of molecules out of N molecules having velocity components lying between u and $u + du$, v and $v + dv$, w and $w + dw$ is

$$dN = N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(u^2+v^2+w^2)}\, dudvdw \tag{4.13}$$

Equation 4.13 is the well-known Maxwell's law of distribution of velocities of molecules of a gas.

To find the number dN_c of molecules having velocity lying between c and $c + dc$, we have $c^2 = u^2 + v^2 + w^2$ and we have $dudvdw$ in Eq. 4.10 to be replaced by $c^2 \sin\theta\, d\theta\, d\phi\, dc$ in spherical polar coordinates and integrated for all values of θ and ϕ between two spheres of radii c and $c + dc$. Thus,

$$dN_c = N\alpha^3 e^{-\beta c^2} c^2 dc \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta$$

or $$dN_c = 4\pi N\alpha^3 e^{-\beta c^2} c^2 dc \tag{4.14}$$

Substituting the value of α and β in Eq. 4.14, we get

$$dN_c = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 dc$$

Now, the kinetic energy of a molecule moving with velocity c is $E = 1/2mc^2$ and $dE = mcdc$. Hence, the number of molecules whose energy lies between the limits E and $E + dE$ is

$$dN_E = 4\pi N\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \frac{c}{m} e^{-\frac{E}{kT}} dE$$

or $$dN_E = 4\pi N \frac{\sqrt{mc}}{(2\pi kT)^{\frac{3}{2}}} e^{-\frac{E}{kT}} dE$$

$$= 2N\sqrt{\frac{E}{\pi}} e^{-\frac{E}{kT}} (KT)^{-\frac{3}{2}} dE \tag{4.15}$$

$$\frac{dN_E}{N} = 2\sqrt{\frac{E}{\pi}} e^{-\frac{E}{kT}} (KT)^{-\frac{3}{2}} dE$$

This is the fraction of molecules having kinetic energy between E and $E + dE$.

Putting $\beta c^2 = x^2$ so that $\beta c dc = x dx$ and substituting in Eq. 4.14, we get

$$dN_c = 4N(\pi)^{-\frac{1}{2}} e^{-x^2} x^2 dx \tag{4.16}$$

Plotting the function y, where $y = 4N(\pi)^{-\frac{1}{2}} e^{-x^2} x^2$ against x, we get a curve as shown in Fig. 4.3.

Then, the number dN_c whose velocity lies between x and $x + dx$ will be given by the shaded area of the curve. The curve shows a maximum at the point P where $dy/dx = 0$

or $$\frac{d}{dx} = \left(\frac{4N}{\sqrt{\pi}} e^{-x^2} x^2\right) = 0$$

or $$\frac{4N}{\sqrt{\pi}}(e^{-x^2}.2x - x^2 e^{-x^2}.2x) = 0$$

or $$x^2 = 1$$

Since $\beta c^2 = x^2$, $\beta c^2 = 1$, the most probable velocity is $\delta = \frac{1}{\sqrt{\beta}} = \sqrt{\frac{2kT}{m}}$.

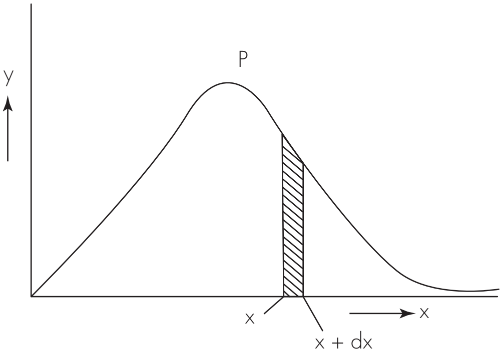

Fig. 4.3 Maxwell's velocity distribution curve

Hence, the most probable velocity is $\sqrt{\frac{2kT}{m}}$; this is the velocity which the maximum number of molecules has. In term of most probable velocity δ, the number of molecules having velocity between c and $c + dc$ is

$$dN_c = \frac{4N}{\sqrt{\pi}\delta^3} c^2 e^{-\frac{c^2}{\delta^2}} dc \tag{4.17}$$

Hence, the probability of a molecule lying between c and $c + dc$ is

$$p_c = \frac{4}{\sqrt{\pi}\delta^3} c^2 e^{-\frac{c^2}{\delta^2}} dc \tag{4.18}$$

4.3.5 Graphical Representation of the Change of the Distribution of Velocity with Temperature

The number of molecules having velocity lying between c and $c + dc$ is

$$dN_c = 4\pi N \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mc^2}{2kT}} c^2 dc$$

If we put $mN_0 = M$, $R = N_0 k$ where N_0 is the Avogadro number and M is the molecular weight,

we get $$dN_c = \frac{4N}{\sqrt{\pi}} \left(\frac{M}{2RT}\right)^{\frac{3}{2}} e^{-\frac{Mc^2}{2RT}} c^2 dc$$

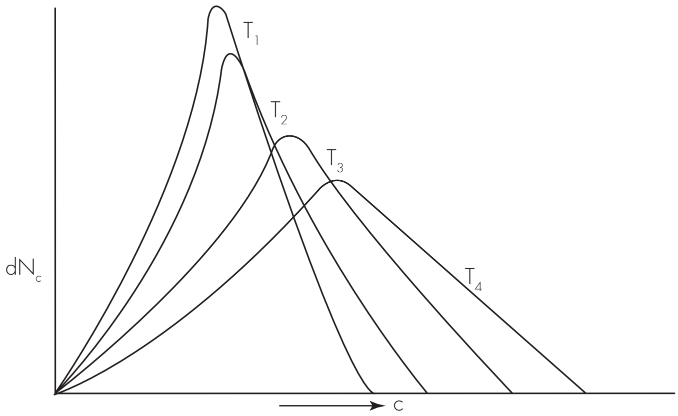

Fig. 4.4 Maxwell's velocity distribution curve for different temperatures

The Maxwell distribution curves are plotted for different temperatures T_1, T_2, T_3, T_4 such that $T_1 < T_2 < T_3 < T_4$ (Fig. 4.4). As the temperature rises, the distribution becomes more and more scattered. All the curves have the same area.

4.3.6 The Average Velocity of the Molecules

We distinguish between two types of average value: one is the root mean square (RMS) velocity and the other is the so-called mean value. The former is the squareroot of the mean square value, or

$$C^2 = \overline{c^2} = \frac{1}{N}\int_0^\infty c^2 dN_c$$

$$= \frac{1}{N}\int_0^\infty c^2\, 4\pi N\alpha^3 e^{-\beta c^2} c^2 dc$$

$$= 4\pi\alpha^3 \int_0^\infty e^{-\beta c^2} c^4 dc$$

$$= 4\pi\alpha^3 \frac{3}{8}\sqrt{\frac{\pi}{\beta^5}} \quad = \frac{3}{2\beta} = \frac{3}{2}\frac{2kT}{m} \tag{4.19}$$

$$C = \sqrt{\overline{c^2}} = \sqrt{\frac{3kT}{m}} \tag{4.20}$$

The mean or average velocity is

$$\overline{c} = \frac{1}{N}\int_0^\infty c dN_c$$

$$= \frac{1}{N}\int_0^\infty c 4\pi N\alpha^3 e^{-\beta c^2} c^2 dc$$

$$= 4\pi\alpha^3 \int_0^\infty e^{-\beta c^2} c^3 dc$$

$$= 4\pi\alpha^3 \frac{1}{2\beta^2} \quad = \frac{2}{\sqrt{\pi\beta}} = \sqrt{\frac{4.2kT}{\pi m}}$$

$$= \sqrt{\frac{8kT}{\pi m}} \tag{4.21}$$

Thus, $$\frac{\bar{c}}{C} = \sqrt{\frac{8}{3\pi}} = 0.921 \tag{4.22}$$

and $$\frac{\delta}{C} = \sqrt{\frac{2}{3}} \tag{4.23}$$

and $$\frac{\delta}{\bar{c}} = \frac{\sqrt{\pi}}{2} \tag{4.24}$$

4.3.7 Maxwell's Law

The pressure exerted by a gas on the wall of the containing vessel is

$$p = \frac{1}{3} mn\overline{c}^2$$

we have $$\frac{\overline{c}^2}{C^2} = \frac{8}{3\pi}$$

Substituting the value of $\overline{c^2}$ in the expression for p, we get

$$p = \frac{1}{8} \pi mn\overline{c}^2 = \frac{1}{8} \pi\rho\overline{c}^2 \tag{4.25}$$

where ρ is the density

Equation 4.25 is known as Maxwell's law.

4.4 ELASTIC COLLISIONS

We distinguish between two types of collisions: (a) linear (b) oblique. The collision is linear if at the moment of collision the line joining the centres of the two colliding spheres lies in the same direction as that of both the velocities before collision. The collision is oblique, if this condition is not satisfied.

4.4.1 The Mechanical Laws Obeyed by Collision

Let us consider two spheres designated 1 and 2 of equal mass m and of equal radius (Fig. 4.5). The spheres are supposed to be perfectly smooth. The mechanical laws obeyed by the colliding spheres

1. The sum total of the kinetic energies before and after collision must remain constant.
2. The sum total of the linear momentum before and after collision must remain constant.

We shall first consider the case of linear collision. Let c_1 and c_2 be their velocities of approach and C_1 and C_2 their velocities of retreat after collision.

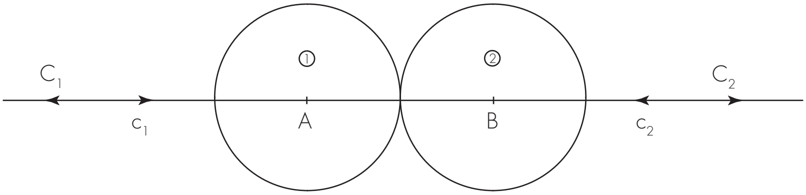

Fig. 4.5 Illustration of linear collision

The law of conservation of translational kinetic energy gives

$$c_1^2 + c_2^2 = C_1^2 + C_2^2 \tag{4.26}$$

The law of conservation of linear momentum gives

$$c_1 + c_2 = C_1 + C_2 \tag{4.27}$$

Equations 4.26 and 4.27 can also be written as

$$c_1^2 - C_1^2 = C_2^2 - c_2^2$$

and
$$c_1 - C_1 = C_2 - c_2 \tag{4.28}$$

so that
$$c_1 + C_1 = c_2 + C_2 \tag{4.29}$$

From Eqs 4.28 and 4.29

$$c_2 = C_1 \text{ and } c_1 = C_2$$

Thus by head on collision, the spheres simply interchange their velocities after collision.

We next consider the case of oblique collisions; let c_1 and c_2 be the velocities of approach of the spheres 1 and 2 in the directions shown in Fig. 4.6.

After collision, these spheres move away from each other with velocities C_1 and C_2 in the directions shown in Fig. 4.6. We resolve the velocities before collision in the direction *AB* of the line of centres. We shall represent these by subscript *n*. The components in the direction of their common tangent at the moment of collision will be represented by the subscript *t*.

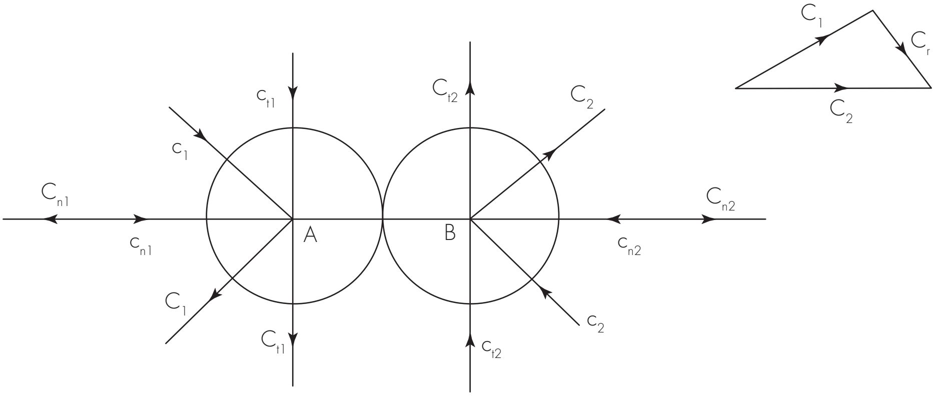

Fig. 4.6 Illustration of oblique collision

Since the spheres are supposed to be perfectly smoth, there is no change in the tangential components after collision so that

$$\left.\begin{aligned} c_{t1} &= C_{t1} \\ c_{t2} &= C_{t2} \end{aligned}\right\} \tag{4.30}$$

The tangential components remaining constant, the normal components would only exchange their velocities after collision as in the case of linear collision so that

$$\left.\begin{aligned} C_{n1} &= c_{n2} \\ C_{n2} &= \mathrm{c}_{n1} \end{aligned}\right\} \tag{4.31}$$

Writing in the vectorial way,

$$\left.\begin{aligned} \boldsymbol{c}_1 = \boldsymbol{c}_{t1} + \boldsymbol{c}_{n1} = \boldsymbol{C}_{t1} + \boldsymbol{C}_{n2} \\ \boldsymbol{c}_2 = \boldsymbol{c}_{t2} + \boldsymbol{c}_{n2} = \boldsymbol{C}_{t2} + \boldsymbol{C}_{n1} \end{aligned}\right\} \tag{4.32}$$

Introducing the relative velocity (C_r) between the retreating spheres after collision,

$$\boldsymbol{C}_r = \boldsymbol{C}_2 - \boldsymbol{C}_1 \tag{4.33}$$

Again from Fig. 4.6,

$$\boldsymbol{C}_1 = \boldsymbol{C}_{t1} + \boldsymbol{C}_{n1} \tag{4.34}$$

Substituting Eq. 4.34 in the first equation of Eq. 4.32, we get

$$\boldsymbol{c}_1 = \boldsymbol{C}_1 - \boldsymbol{C}_{n1} + \boldsymbol{C}_{n2}$$

or

$$\boldsymbol{c}_1 = \boldsymbol{C}_1 - (\boldsymbol{C}_1 - \boldsymbol{C}_2)_n \tag{4.35}$$

Using Eq. 4.33, Eq. 4.35 transforms to

$$\boldsymbol{c}_1 = \boldsymbol{C}_1 + (\boldsymbol{C}_r)_n \tag{4.36}$$

where $(\boldsymbol{C}_r)_n$ is the normal component of the relative velocity $\boldsymbol{C}_r$ that is the projection of $\boldsymbol{C}_r$ on the central line *AB*

Similarly,

$$\boldsymbol{c}_2 = \boldsymbol{c}_{t2} + \boldsymbol{c}_{n2} = \boldsymbol{C}_{t2} + \boldsymbol{C}_{n1}$$

or

$$\begin{aligned} \boldsymbol{c}_2 &= \boldsymbol{C}_{t2} + (\boldsymbol{C}_{n1} - \boldsymbol{C}_{n2}) + \boldsymbol{C}_{n2} \\ &= \boldsymbol{C}_{t2} + \boldsymbol{C}_{n2} - (\boldsymbol{C}_r)_n \end{aligned}$$

Since

$$\boldsymbol{C}_2 = \boldsymbol{C}_{t2} + \boldsymbol{C}_{n2}$$

$$\boldsymbol{c}_2 = \boldsymbol{C}_2 - (\boldsymbol{C}_r)_n \tag{4.37}$$

We shall now write the vector equations 4.36 and 4.37 in terms of their cartesian components. For this purpose, we shall represent the component velocities before collision by *u*, *v*, *w* and after collision by *U*, *V*, *W* and the direction cosines of the normal component of the relative velocity or that of the central line *AB* by (*l*, *m*, *n*). Thus, we obtain from Eq. 4.36

$$\left.\begin{aligned} u_1 &= U_1 + l(C_r)_n \\ v_1 &= V_1 + m(C_r)_n \\ w_1 &= W_1 + n(C_r)_n \end{aligned}\right\} \tag{4.38}$$

Similarly Eq. 4.37 can be written in the following form

$$\left.\begin{aligned} u_2 &= U_2 - l(C_r)_n \\ v_2 &= V_2 - m(C_r)_n \\ w_2 &= W_2 - n(C_r)_n \end{aligned}\right\} \tag{4.39}$$

By definition, the components of the relative velocity of retreat after collision are

$$\left.\begin{aligned} U_2 - U_1 &= l(C_r)_n \\ V_2 - V_1 &= m(C_r)_n \\ W_2 - W_1 &= n(C_r)_n \end{aligned}\right\} \tag{4.40}$$

Multiplying Eqs 4.38, 4.39 and 4.40 by l, m, n and adding them, we get

$$l(U_2 - U_1) + m(V_2 - V_1) + n(W_2 - W_1) = (C_r)_n \tag{4.41}$$

Substituting the value of $(C_r)_n$ from Eq. 4.41 in Eqs 4.38 and 4.39, we get

$$\left.\begin{aligned} u_1 &= U_1 + [l^2(U_2 - U_1) + lm(V_2 - V_1) + ln(W_2 - W_1)] \\ v_1 &= V_1 + [lm(U_2 - U_1) + m^2(V_2 - V_1) + mn(W_2 - W_1)] \\ w_1 &= W_1 + [ln(U_2 - U_1) + mn(V_2 - V_1) + n^2(W_2 - W_1)] \end{aligned}\right\} \tag{4.42}$$

$$\left.\begin{aligned} u_2 &= U_2 + [l^2(U_1 - U_2) + lm(V_1 - V_2) + ln(W_1 - W_2)] \\ v_2 &= V_2 + [lm(U_1 - U_2) + m^2(V_1 - V_2) + mn(W_1 - W_2)] \\ w_2 &= W_2 + [ln(U_1 - U_2) + mn(V_1 - V_2) + n^2(W_1 - W_2)] \end{aligned}\right\} \tag{4.43}$$

Equation 4.42 and 4.43 express the components (u_1, v_1, w_1) and (u_2, v_2, w_2) before collision in terms of the components (U_1, V_1, W_1) and (U_2, V_2, W_2) after collision.

4.4.2 Class-A Molecules

To avoid repetition, we shall represent the molecules whose velocity components lie within the range u_1 and $u_1 + du_1$, v_1 and $v_1 + dv_1$, w_1 and $w_1 + dw_1$, as belonging to class A.

The total number of molecules of class A out of a group of N molecules is, therefore,

$$Nf(u_1, v_1, w_1)du_1dv_1dw_1 \tag{4.44}$$

The total number of molecules of class A in 1 cubic centimetre is

$$\upsilon f(u_1, v_1, w_1)du_1dv_1dw_1 \tag{4.45}$$

The total number of molecules of class A per unit volume which occupy the element of volume $dxdydz$ is

$$\upsilon f(u_1, v_1, w_1)du_1dv_1dw_1dxdydz \tag{4.46}$$

4.4.3 Class-B Molecules

The number of molecules whose velocity components lie within the range u_2 and $u_2 + du_2$, v_2 and $v_2 + dv_2$, w_2 and $w_2 + dw_2$ will be represented as belonging to class *B*.

4.4.4 Proof of Maxwellian Law of Distribution of Velocities

The law of velocities as given by Maxwell was a guess work and was only partially established. Boltzmann proved by direct method that Maxwellian law of distribution is the only possible distribution in the stable state of equilibrium of the gas. By the steady state of equilibrium, we mean that the number of molecules whose velocity components lie within a prescribed range is the same at all times when the whole mass of the gas is examined. Further, starting from any state of distribution, the mass of the gas ultimately tends to acquire that state of stable equilibrium.

Evidently, that state of stable equilibrium of the gas is reached only by the process of collision between different molecules. For the proof, we consider two classes of collisions.

(a) Collision of class α In class α, one of the two colliding molecules belongs to class *A* and the other to class *B*. At the moment of impact, the direction cosine of the line joining the centres lies within a small solid angle *dw*. We calculate the number of molecules which have class *A* after collision in time *dt*.

(b) Collision of class β Class β is the same as class α, only their roles are interchanged. After collision, one of the colliding molecules belongs to class *A* and the other class *B*. We calculate the number of molecules which enter class *A* after collision in time *dt*.

For steady condition, the number of molecules leaving class *A* and those entering class *A* in time *dt* would be equal. From this equation, the distribution function can be calculated. This is the summary of Boltzmann method of calculation.

4.4.5 Calculation of Collisions of Class α

Figure 4.7 represents the process of impact of molecules of class *B* with a molecule *A* of class *A*. Let σ be the diameter of a molecule. With *A* as centre and radius equal to σ, we describe a sphere. At the moment of impact, the centre of the colliding molecules must be on this sphere which will be called *collision sphere*. As the molecule *A* moves through the gas, the collision sphere also moves with it but does not rotate with it. The *B* molecules approach the *A* molecule with relative velocity c_r in the line B_2B_1 with direction cosines (λ, μ, ν). In the Fig. 4.7, B_1 and B_2 are the portions of the colliding molecule at the moment of impact and just before the impact, respectively.

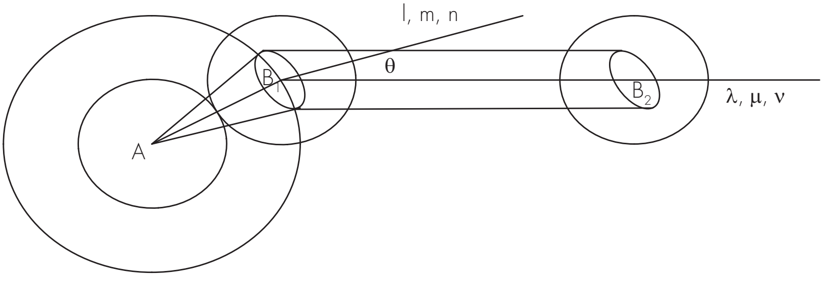

Fig. 4.7 Illustration of general collision

Let the direction cosines of the line joining the centre of the molecule *A* to the point of impact B_1 be (*l*, *m*, *n*). In the α-class of collision, the line AB_1 lies within a small solid angle *dw*. This intercepts on the collision sphere an area equal to $\sigma^2 dw$. The number of collision of class α in time *dt* is evidently equal to the number of centres of the *B* class molecules which lie within the cylinder of base area equal to $\sigma^2 dw$ and of height $c_r \cos\theta\, dt$ where θ is the angle between the line of approach and the axis of the cone of solid angle *dw* so that

$$\cos\theta = -(l\lambda + m\mu + n\nu) \tag{4.47}$$

The volume of this cylinder is

$$dk = \sigma^2 dwc_r \cos\theta dt \tag{4.48}$$

Substituting the value of *dk* from Eq. 4.48 for *dxdydz* in Eq. 4.46 and replacing u_1, v_1, w_1 by u_2, v_2, w_2, we get for the number of centres of *B* class molecules within the cylinder

$$\upsilon f(u_2, v_2, w_2) du_2 dv_2 dw_2 \sigma^2 c_r \cos\theta dwdt$$

This is true for every molecule of class *A*. The number of molecules of class *A* per unit volume is $\upsilon f(u_1, v_1, w_1) du_1 dv_1 dw_1$. Hence, the expectation of total number of collisions of class α per unit volume which occur in time *dt* is

$$\upsilon_\alpha dt = \upsilon^2 f(u_1, v_1, w_1) f(u_2 v_2 w_2) du_1 dv_1 dw_1 du_2 dv_2 dw_2 \times$$

$$\sigma^2 c_r \cos\theta dwdt \tag{4.49}$$

Representing $f(u_1, v_1, w_1)$ and $f(u_2, v_2, w_2)$ simply by f_1 and f_2 and using Eq. 4.48, Eq. 4.49 is written as

$$\upsilon_\propto dt = \upsilon^2 f_1 f_2 du_1 dv_1 dw_1 du_2 dv_2 dw_2 dk \tag{4.50}$$

This gives the number of molecules which leaves class *A* by α collisions in time *dt*.

We have yet to determine the number of molecules which enters class *A* by β collision in time *dt*. β type of collisions have the following specifications:

1. After collision, one of the two molecules belongs to class *A*, that is, its velocity point falls within the volume element $du_1 dv_1 dw_1$.
2. After collision, the second molecule belongs to class *B*, that is, its velocity point falls within the volume element $du_2 dv_2 dw_2$.
3. At the moment of collision, the central line has the direction cosine (*lmn*), that is, it passes through the area *dk* of the collision sphere.

For this purpose, we have to determine the velocities $U_1 V_1 W_1$ and $U_2 V_2 W_2$ before the collision of β class from Eqs 4.42 and 4.43 mentioned earlier. This is obtained simply by interchanging the capital letters and the small letters.

$$\left.\begin{aligned} U_1 &= u_1 - [l^2(u_1 - u_2) + lm\,(v_1 - v_2) + ln\,(w_1 - w_2)] \\ V_1 &= v_1 - [lm\,(u_1 - u_2) + m^2(v_1 - v_2) + mn\,(w_1 - w_2)] \\ W_1 &= w_1 - [ln\,(u_1 - u_2) + mn\,(v_1 - v_2) + n^2(w_1 - w_2)] \end{aligned}\right\} \tag{4.51}$$

$$\left.\begin{aligned} U_2 &= u_2 - [l^2(u_1 - u_2) + lm\,(v_1 - v_2) + ln\,(w_1 - w_2)] \\ V_2 &= v_2 - [lm\,(u_1 - u_2) + m^2(v_1 - v_2) + mn\,(w_1 - w_2)] \\ W_2 &= w_2 - [ln\,(u_1 - u_2) + mn\,(v_1 - v_2) + n^2(w_1 - w_2)] \end{aligned}\right\} \tag{4.52}$$

In complete correspondence with the collisions of the α class, we get for the total number of collisions per unit volume in time dt

$$v^2 f(U_1, V_1, W_1) f(U_2 V_2 W_2) dU_1 dV_1 dW_1 dU_2 dV_2 dW_2 dk$$

Representing $f(U_1, V_1, W_1)$ and $f(U_2, V_2, W_2)$ simply by F_1 and F_2, we get

$$v^2 F_1 F_2 dU_1 dV_1 dW_1 dU_2 dV_2 dW_2 dk \tag{4.53}$$

This, however, cannot be the number of β collisions unless dv_1 dv_1 dw_1 be so determined that $U_1 + dU_1$, $V_1 + dV_1$, $W_1 + dW_1$, $U_2 + dU_2$, $V_2 + dV_2$, $W_2 + dW_2$ transform into $u_1 + du_1$, $v_1 + dv_1$, $w_1 + dw_1$, $u_2 + du_2$, $v_2 + dv_2$ and $w_2 + dw_2$ after the collision. In order that Eq. 4.53 may represent the total number of β collisions per unit volume in time dt, the quantities dU_1 ……. dW_2 are to be determined by differentiation of Eq. 4.51 and 4.52.

To satisfy the condition of complete correspondence, we must have using Jacobi's theorem

$$dU_1 dV_1 \ldots\ldots dW_2 = \Delta du_1 dv_1 \ldots\ldots dw_2$$

where Δ is the substitution determinant given by

$$\Delta = \begin{vmatrix} \frac{\partial U_1}{\partial u_1} & \frac{\partial U_1}{\partial v_1} & \frac{\partial U_1}{\partial w_1} & \frac{\partial U_1}{\partial u_2} & \frac{\partial U_1}{\partial v_2} & \frac{\partial U_1}{\partial w_2} \\ \frac{\partial V_1}{\partial u_1} & \frac{\partial V_1}{\partial v_1} & \frac{\partial V_1}{\partial w_1} & \frac{\partial V_1}{\partial u_2} & \frac{\partial V_1}{\partial v_2} & \frac{\partial V_1}{\partial w_2} \\ \frac{\partial W_1}{\partial u_1} & \frac{\partial W_1}{\partial v_1} & \frac{\partial W_1}{\partial w_1} & \frac{\partial W_1}{\partial u_2} & \frac{\partial W_1}{\partial v_2} & \frac{\partial W_1}{\partial w_2} \\ \frac{\partial U_2}{\partial u_1} & \frac{\partial U_2}{\partial v_1} & \frac{\partial U_2}{\partial w_1} & \frac{\partial U_2}{\partial u_2} & \frac{\partial U_2}{\partial v_2} & \frac{\partial U_2}{\partial w_2} \\ \frac{\partial V_2}{\partial u_1} & \frac{\partial V_2}{\partial v_1} & \frac{\partial V_2}{\partial w_1} & \frac{\partial V_2}{\partial u_2} & \frac{\partial V_2}{\partial v_2} & \frac{\partial V_2}{\partial w_2} \\ \frac{\partial W_2}{\partial u_1} & \frac{\partial W_2}{\partial v_1} & \frac{\partial W_2}{\partial w_1} & \frac{\partial W_2}{\partial u_2} & \frac{\partial W_2}{\partial v_2} & \frac{\partial W_2}{\partial w_2} \end{vmatrix}$$

From Eqs 4.51 and 4.52, we obtain by differentiation

$$\Delta = \begin{vmatrix} 1-l^2, & -lm, & -ln, & l^2, & l\mathrm{m}, & ln \\ -lm, & 1-m^2, & -mn, & lm, & m^2, & mn \\ -ln, & -mn, & 1-n^2, & ln, & mn, & n^2 \\ l^2, & lm, & ln, & 1-l^2, & -lm, & -ln \\ lm, & m^2, & mn, & -lm, & 1-m^2, & -mn \\ ln, & mn, & n^2, & -ln, & -mn, & 1-n^2 \end{vmatrix}$$

Since we are concerned here only with the numerical value of l, we obtain after simplification $\Delta = 1$, so that

$$dU_1 dV_1 dW_1 dU_2 dV_2 dW_2 = du_1 dv_1 dw_1 du_2 dv_2 dw_2 \tag{4.54}$$

Hence, from Eq. 4.53 the number of β collisions per unit volume in time dt is

$$\upsilon_\beta dt = \upsilon^2 F_1 F_2 du_1 dv_1 dw_1 du_2 dv_2 dw_2 dk \tag{4.55}$$

This gives the increase in the number of A molecules after collision. The total increase in the number of A molecules after collision is

$$\upsilon^2 (F_1 F_2 - f_1 f_2) du_1 dv_1 dw_1 du_2 dv_2 dw_2 dk \tag{4.56}$$

By integration of all possible values of $u_2 v_2 w_2$ and overall elementary volumes in the unit volume, we get the total increase of A molecules in cubic unit metre in time dt. This is equal to

$$\upsilon^2 du_1 dv_1 dw_1 \iiint\int (F_1 F_2 - f_1 f_2)\, du_2 dv_2 dw_2 dk \tag{4.57}$$

Now, the number of A molecules in unit volume at time t is

$$\upsilon f_1 (u_1 v_1 w_1) du_1 dv_1 dw_1$$

At instant ($t + dt$), this becomes

$$\upsilon \left(f_1 + \frac{\partial f_1}{\partial t} dt \right) du_1 dv_1 dw_1$$

so that the increase in the number of A molecules in time dt is

$$\upsilon \frac{\partial f_1}{\partial t} dt\, du_1 dv_1 dw_1 \tag{4.58}$$

Equating Eqs 4.57 and 4.58, we get

$$\frac{\partial f_1}{\partial t} = \upsilon \iiint\int (F_1 F_2 - f_1 f_2) \sigma^2 c_r \cos\theta du_2 dv_2 dw_2 dw \tag{4.59}$$

substituting the value of dk from Eq. (4.48)

The necessary condition for the steady state is $\partial f/\partial t = 0$. This can be obtained by putting

$$F_1 F_2 = f_1 f_2$$

We have to prove that this is also the sufficient condition. For this purpose, we make use of the H-theorem introduced by Boltzmann.

4.4.6 Boltzmann's H–Function

This is a logarithmic function

$$H = \iiint f \log_e f\, dudvdw \tag{4.60}$$

where f is a function of u, v, w and the integration extends from $-\infty$ to $+\infty$ over all possible values of u, v, w. H is, thus, a pure number completely independent of u, v, w and dependent only on the analytical form of f or the law of distribution of velocities. It, therefore, remains unchanged so long as the law of distribution does not change. Hence, a necessary condition to be satisfied at the steady state is that

$$\frac{\partial H}{\partial t} = 0$$

To evaluate $\partial H/\partial t$, we put f_1 for f and $u_1 v_1 w_1$ for u, v, w in Eq. 4.60; this gives

$$H = \iiint f_1 \log_e f_1 du_1 dv_1 dw_1 \tag{4.61}$$

and differentiating within integration

$$\frac{\partial H}{\partial t} = \iiint \frac{\partial f_1}{\partial t}(1+\log_e f_1) du_1 dv_1 dw_1 \tag{4.62}$$

Substituting the value of $\partial f_1/\partial t$ from Eq. 4.59, we get

$$\frac{\partial H}{\partial t} = v \iiint \iiint \int (1+\log_e f_1)(F_1F_2 - f_1 f_2)\sigma^2 c_r \cos\theta dw$$
$$\times du_1 dv_1 dw_1 du_2 dv_2 dw_2 \tag{4.63}$$

Since the integration in Eq. 4.60 is to extend over all possible values of *u, v, w*, it represents a sum of contributions from each class of molecules.

In Eq. 4.60, we have considered only a particular type of molecules belonging to class *A*. If instead of class *A* the molecules chosen were of class *B*, then *H* would take the following form

$$H = \iiint f_2 \log_e f_2 du_2 dv_2 dw_2 \tag{4.64}$$

and the rate of change of *H* would be

$$\frac{\partial H}{\partial t} = \iiint (1+\log_e f_2)\frac{\partial f_2}{\partial t} du_2 dv_2 dw_2 \tag{4.65}$$

In an analogous manner, $\partial f_2/\partial t$ would be

$$\frac{\partial f_2}{\partial t} = v \iiint \int (F_1F_2 - f_1 f_2)\sigma^2 c_r \cos\theta du_1 dv_1 dw_1 dw \tag{4.66}$$

Substituting Eq. 4.66 in Eq. 4.65, we get

$$\frac{\partial H}{\partial t} = v \iiint \iiint \int (1+\log_e f_2)(F_1F_2 - f_1 f_2)$$
$$\sigma^2 c_r \cos\theta du_1 dv_1 dw_1 \times du_2 dv_2 dw_2 dw \tag{4.67}$$

Addition of Eqs 4.63 and 4.67 yields a value which takes account of collisions between *A* and *B* class of molecules. Thus,

$$\frac{\partial H}{\partial t} = \frac{v}{2} \iiint \iiint \int (2+\log_e f_1 f_2)(F_1F_2 - f_1 f_2)$$
$$\sigma^2 c_r \cos\theta \times du_1 dv_1 dw_1 \; du_2 dv_2 dw_2 dw \tag{4.68}$$

Up to this point, we have given preference to quantities with subscript 1, that is, we have considered only the α collision. We could equally well start with the β collisions. Then instead of Eqs 4.59 and 4.66 we would get two equations distinguished by interchange of quantities with subscripts 1 and 2.

Similarly, we could form another equation for H in analogy with Eqs 4.61 and 4.64 by interchange of quantities with subscripts 1 and 2. This yields

$$\frac{\partial H}{\partial t} = \frac{\upsilon}{2} \iiint \iiint \int (2 + \log_e F_1 F_2)(F_1 F_2 - f_1 f_2)$$

$$\sigma^2 c_r \cos\theta \times du_1 dv_1 dw_1 \; du_2 dv_2 dw_2 dw \tag{4.69}$$

Adding Eqs 4.68 and 4.69

$$\frac{\partial H}{\partial t} = \frac{\upsilon}{4} \iiint \iiint \int (\log_e f_1 f_2 - \log_e F_1 F_2)(F_1 F_2 - f_1 f_2)$$

$$\sigma^2 c_r \cos\theta \times du_1 dv_1 dw_1 \; du_2 dv_2 dw_2 dw \tag{4.70}$$

The integral represented by Eq. 4.70 is essentially a negative quantity since $F_1 F_2 - f_1 f_2$ and $\log_e f_1 f_2 / F_1 F_2$ are of opposite signs while all the remaining quantities are positive. Since, $\partial H/\partial t = 0$ in equilibrium state the necessary condition of equilibrium is

$$F_1 F_2 = f_1 f_2 \tag{4.71}$$

This functional relation determines the law of distribution of velocities.

Since all directions in space are equally probable, the distribution can depend only on the magnitude of c and not on its direction. It is convenient to express Eq. 4.71 as

$$\log_e F_1 + \log_e F_2 = \log_e f_1 + \log_e f_2 \tag{4.72}$$

We can, therefore, put

$$f_1 = e^{\phi(c_1^2)}, f_2 = e^{\phi(c_2^2)}, F_1 = e^{\phi(C_1^2)}, F_2 = e^{\phi(C_2^2)} \tag{4.73}$$

where c_1, c_2 and C_1, C_2 are the velocities of the two colliding molecules before and after collision.

Further $$c_1^2 + c_2^2 = C_1^2 + C_2^2$$

$$C_1^2 = c_1^2 + c_2^2 - C_2^2$$

From Eqs 4.72 and 4.73, we get

$$\phi(c_1^2) + \phi(c_2^2) = \phi(C_1^2) + \phi(C_2^2)$$

Substituting Eq. 4.73 in Eq. 4.72, we get

$$\phi(c_1^2) + \phi(c_2^2) = \phi(C_2^2) + \phi(c_1^2 + c_2^2 - C_2^2)$$

On differentiating partially with respect to c_1^2, c_2^2 and C_2^2, we obtain

$$\phi'(c_1^2) = \phi'(c_1^2 + c_2^2 - C_2^2)$$

$$\phi'(c_2^2) = \phi'(c_1^2 + c_2^2 - C_2^2)$$

$$\phi'(C_2^2) = \phi'(c_1^2 + c_2^2 - C_2^2)$$

This $\phi'(c_1^2) = \phi'(c_2^2) = \phi'(C_2^2) = -\beta^2 = \text{constant}$

$$\int \phi'(c_1^2) dc_1^2 = -\beta^2 \int dc_1^2$$

or, $$\phi'(c_1^2) = -\beta^2 c^2 + log_e \alpha^3$$

Where $\log_e \alpha^3$ is the constant of integration. On substitution in Eq. 4.73 this gives

$$f(u, v, w) = \alpha^3 e^{-\beta(u^2+v^2+w^2)} \tag{4.74}$$

This is the Maxwellian distribution which has already been deduced.

4.4.7 Experimental Verification of Maxwells' Law

Before 1920, there was no direct experimental test of the law. The indirect test of the law was provided by the finite breadth of spectral lines. The finite breadth is due to the different velocities of the radiating atoms. The examination of the variation of the intensity along the breadth of the line gives an indirect proof of the Maxwell's law. Another indirect test of the law was provided by the electrons coming from a hot filament. In the interior of a conductor, free electrons are moving in all directions and it is assumed that they behave as gas molecules. Those electrons whose velocities are large enough to overcome the barrier at the surface come out of the surface. The investigation consists in measuring the electron current from the hot body to a neighbouring electrode against various opposing potential differences. It shows that the velocity distribution among the emitted electrons is in close agreement with Maxwell's law of distribution for a gas. Different workers have done experiment using different metals.

The first direct experiment was made by Stern. The scheme of his experimental arrangement is shown in Fig. 4.8.

A is a platinum wire coated with silver so that when it is electrically heated it emits silver atoms. *B* is a cylindrical drum with slit *S* and pp_1 is another cylindrical vessel having photographic plate bent into the inner surface of the cylinder. The system *B*, pp_1 can be rotated about *A* as axis. The whole system is kept inside an enclosure which can be evacuated. At very low pressure, the silver atoms are emitted from the heated filament *A*. Some of these atoms pass through the slit *S* and form a depoit at *p*, a point in line with the slit *S* when the system is at rest. But if the whole apparatus is rotated in clockwise direction the silver atoms form deposit at points above *p*, the slow-moving atoms forming deposit at a greater distance from *p* than that formed by the fast-moving atoms. Thus, atoms of different speeds form deposit at different places and it is possible to test Maxwell's law by measuring the position and density of deposit. Unfortunately, the results are not accurate due to various reasons.

The main difficulty of Stern laid in retaining the vacuum. Later, Costa, Smyth and Compton modified the system used by Stern by electromagnetic driving of the rotating device. The principle of their method is to direct a beam of gas molecules through radial slits in two discs fixed on

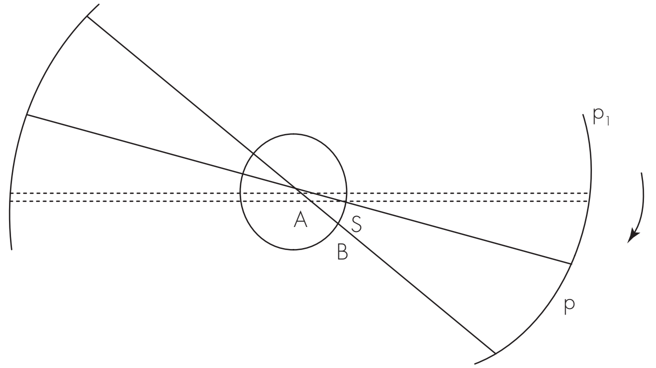

Fig. 4.8 Scheme of Stern's experimental arrangement

a common shaft. These discs are rotated in a highly evacuated enclosure. The molecules which pass through both the slits are allowed to fall on the vane of a sensitive radiometer. The variation of the radiometer deflection with the speed of the disc was in agreement with Maxwell's law.

Eldridge used induction motor for the rotation of coaxial discs with radial slits on their edge. He worked with cadmium vapour. The cadmium vapour was allowed to pass through the slits of the disc which rotated at high speed and acted as a velocity filter for the molecules. From the speed of rotation of the disc and the density of deposit of the cadmium vapour, a velocity spectrum was obtained with a micro photometer which was found to agree with that of Maxwell within experimental error.

Zartman made an attempt to have a better resolution of the velocity spectrum. The principle of his experiment is as shown in Fig. 4.9.

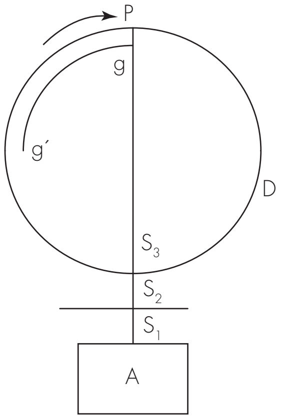

Fig. 4.9 Zartman's apparatus

A is an enclosure in which the experimental gas (bismuth vapour) was kept at a constant temperature. *A* has a small opening at S_1. Parallel to S_1, there is another slit S_2 which helps to get a sharply defined beam of bismuth vapour.

The cylinder *D*, which can be rotated, is placed in the path of the beam. It has a small opening S_3 at the periphery. The inner wall of the cylinder is provided with glass plate where the beam would be deposited. If the cylinder is at rest, the beam will form a deposit at *P* at a point diametrically opposite to S_3. If the cylinder is rotated in a clockwise direction, the molecules at the slit S_3 will require a finite time to traverse the diameter and will form a deposit on the plate *gg′* at a distance depending upon the velocity of the molecules and the speed of rotation. The molecules in the beam are moving with different velocities and, hence, a velocity spectrum will be formed at the glass plate *gg′*. The measurement of the density of deposit at different points and the speed of rotation of the cylinder agrees well with Maxwell's law of distribution of velocities.

Lammert in 1929 developed a method of sorting out groups of atoms moving with a particular velocity.

The scheme of his experiment is shown in Fig. 4.10. *O* is a source of mercury vapour having a small opening at its end from which the mercury atoms emerge.

A slit *S* on a plate and two discs W_1 and W_2 are fixed to a shaft so that they can be rotated at the desired speed with the shaft as axis. The discs W_1 and W_2 are provided with slits. The slit at W_1 is in line with *S* but the slit at W_2 is set at an angle of 2 degrees behind that in W_1. The molecules contained in a straight beam by the opening at *O* and slits *S* and at W_1 impinge on the wheel W_2 in each revolution of the system. Only those molecules whose velocity is such that they travel the distance W_1W_2 in the same

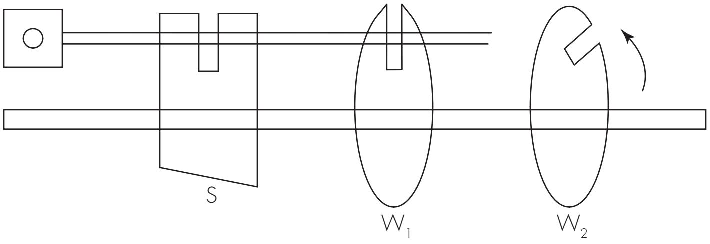

Fig. 4.10 Lammert's apparatus

time in which the disc system rotates through 2 degrees will pass through the slit in W_2 and are allowed to form a deposit on a screen placed near W_2. Other molecules will not be able to pass through the slit in W_2. By rotating the system at different speeds it is possible to sort out the molecules moving at the desired velocity. It has been found that Maxwell's law was satisfied to a considerable degree of accuracy.

4.4.8 Mixed Gases and Equipartition of Energy

Let us consider a mixture of two gases denoted by the subscript 1 and 2. Let m_1 and m_2 be the molecular masses of these gases. We have to consider here three types of collisions between

1. molecules of gas 1,
2. molecules of gas 2,
3. molecules of gases 1 and 2.

Types of collisions (1) and (2) have already been considered.

We consider here collision of type (3) (Fig. 4.11).

Since by collision the tangential components of momenta remain unchanged, we have

$$\left.\begin{aligned} m_1 c_{t1} &= m_1 C_{t1} \\ m_2 c_{t2} &= m_2 C_{t2} \end{aligned}\right\} \tag{4.75}$$

Since the normal components of momenta exchange their values,

$$\begin{aligned} m_1 C_{n1} &= m_2 c_{n2} \\ m_2 C_{n2} &= m_1 c_{n1} \end{aligned} \tag{4.76}$$

Writing in vectorial notation,

$$\left.\begin{aligned} m_1 \boldsymbol{c}_1 &= m_1 \boldsymbol{c}_{t1} + m_1 \boldsymbol{c}_{n1} = m_1 \boldsymbol{C}_{t1} + m_2 \boldsymbol{C}_{n2} \\ m_2 \boldsymbol{c}_2 &= m_2 \boldsymbol{c}_{t2} + m_2 \boldsymbol{c}_{n2} = m_2 \boldsymbol{C}_{t2} + m_1 \boldsymbol{C}_{n1} \end{aligned}\right\} \tag{4.77}$$

Also,

$$\left.\begin{aligned} m_1 \boldsymbol{C}_1 &= m_1 \boldsymbol{C}_{t1} + m_1 \boldsymbol{C}_{n1} \\ m_2 \boldsymbol{C}_2 &= m_2 \boldsymbol{C}_{t2} + m_2 \boldsymbol{C}_{n2} \end{aligned}\right\} \tag{4.78}$$

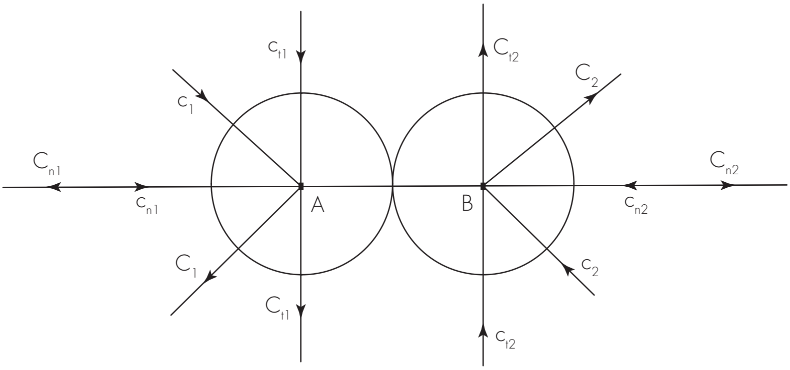

Fig. 4.11 Illustration of collision of mixed gases

Substituting first of Eq. 4.78 in the first of Eq. 4.77

$$m_1\boldsymbol{c}_1 = m_1\boldsymbol{C}_1 - m_1\boldsymbol{C}_{n1} + m_2\boldsymbol{C}_{n2}$$

$$\boldsymbol{c}_1 = \boldsymbol{C}_1 - \frac{1}{m_1}(m_1\boldsymbol{C}_{n1} - m_2\boldsymbol{C}_{n2})$$

Similarly,

$$\left.\begin{aligned} \boldsymbol{c}_1 &= \boldsymbol{C}_1 - \frac{1}{m_1}(m_1\boldsymbol{C}_1 - m_2\boldsymbol{C}_2)_n \\ \boldsymbol{c}_2 &= \boldsymbol{C}_2 - \frac{1}{m_2}(m_1\boldsymbol{C}_1 - m_2\boldsymbol{C}_2)_n \end{aligned}\right\} \tag{4.79}$$

The components of the velocities before the collision are still linear functions of the velocity components after collision.

Then, $dU_1dV_1dW_1du_1dv_1dw_1 = dU_2dV_2dW_2du_2dv_2dw_2$ forming the H function, we find that $\partial H/\partial t = 0$ when each of the following expression vanish separately

$$\left.\begin{aligned} F_{11}F_{12} - f_{11}f_{12} &= 0 \qquad \text{for the collision of type 1} \\ F_{21}F_{22} - f_{21}f_{22} &= 0 \qquad \text{for the collision of type 2} \\ F_{31}F_{32} - f_{31}f_{32} &= 0 \qquad \text{for the collision of type 3} \end{aligned}\right\} \tag{4.80}$$

In the notation used in Eq. 4.80, the first subscript (such as 1 in F_{12}) represents the type of collision (1) and the second subscript (such as 2 in F_{12}) represents the class of molecules (2) taking part in the collision. The letter f represents the distribution function before collision and the letter F represents the distribution function after collision. Thus, f_{32} represents the distribution function of the molecules of class 2 before collision of type 3 and F_{32} represents the distribution function of molecules of class 2 after collision of type 3. Referring to the last equation of 4.80, the distribution functions are

$$\begin{aligned} f_{31} &= \left(\frac{\beta_{31}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{31}(u_{31}^2 + v_{31}^2 + w_{31}^2)} = \left(\frac{\beta_{31}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{31}^2 c_{31}^2} \\ f_{32} &= \left(\frac{\beta_{32}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{32}(u_{32}^2 + v_{32}^2 + w_{32}^2)} = \left(\frac{\beta_{32}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{32}^2 c_{32}^2} \\ F_{32} &= \left(\frac{\beta_{32}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{32}(U_{32}^2 + V_{32}^2 + W_{32}^2)} = \left(\frac{\beta_{32}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{32}^2 C_{32}^2} \\ F_{31} &= \left(\frac{\beta_{31}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{31}(U_{31}^2 + V_{31}^2 + W_{31}^2)} = \left(\frac{\beta_{31}}{\pi}\right)^{\frac{3}{2}} e^{-\beta_{31}^2 C_{31}^2} \end{aligned} \tag{4.81}$$

Substituting in the last equation of 4.80, we get

$$e^{-(\beta_{31}^2 c_{31}^2 + \beta_{32}^2 c_{32}^2)} = e^{-(\beta_{31}^2 C_{31}^2 + \beta_{32}^2 C_{32}^2)}$$

so that

$$\beta_{31}^2 c_{31}^2 + \beta_{32}^2 c_{32}^2 = \beta_{31}^2 C_{31}^2 + \beta_{32}^2 C_{32}^2$$

or
$$\beta_{31}^2(c_{31}^2 - C_{31}^2) = \beta_{32}^2(C_{32}^2 - c_{32}^2) \tag{4.82}$$

By energy equation,
$$m_2 c_{32}^2 + m_1 c_{31}^2 = m_2 C_{32}^2 + m_1 C_{31}^2$$

or
$$m_1(c_{31}^2 - C_{31}^2) = m_2(C_{32}^2 - c_{32}^2) \tag{4.83}$$

From Eqs 4.82 and 4.83
$$\frac{\beta_{32}^2}{m_2} = \frac{\beta_{31}^2}{m_1} \tag{4.84}$$

By Eq. 4.19, we have
$$\left.\begin{aligned} \overline{c_{31}^2} &= \frac{3}{2\beta_{31}^2} \\ \overline{c_{32}^2} &= \frac{3}{2\beta_{32}^2} \end{aligned}\right\} \tag{4.85}$$

Substituting in Eq. 4.84, we get
$$m_1\overline{c_1^2} = m_2\overline{c_2^2}$$

This proves the equipartition theorem. It means that in the equilibrium state, the mean translational kinetic energy of all molecules is the same irrespective of their difference of mass.

4.5 ENERGY OF GAS MOLECULES

We have proved that the temperature of a mass of gas is determined by the mean kinetic energy of the molecules. We now proceed to enquire about the nature of energy possessed by a molecule. In mechanics, we are familiar with the following types of energies:

1. The kinetic energy of translational motion: This is equal to 1/2 mc^2 where m is the mass of the molecule moving with velocity c.
2. The kinetic energy of rotation: This is equal to 1/2 Iw^2 where I is the moment of inertia of the molecule rotating with angular velocity w.
3. The vibrational energy: This is partly kinetic and partly potential. The average value of vibrational kinetic energy is equal to the average value of vibrational potential energy.
4. The energy of a body placed in a conservative field of force: This energy is also partly kinetic and partly potential. The mass of a molecule being extremely small, the gravitational force on a molecule is negligible. Since the molecules react upon one another only at the moment of collision, the field of interaction of the molecules throughout their motion need not be taken into consideration in calculating the energy of the molecules. So, the molecules can only possess energy of the types 1, 2 and 3.

4.5.1 Degrees of Freedom of a Molecule

These are the number of independent parameters (or coordinates) which completely specify the configuration and motion of a molecule at an instant. The position of a complex material system is determined by the location of its centre of mass. In a space of three dimensions, this is determined by the cartesian coordinates

(x, y, z) or spherical polar coordinates (r, θ, ϕ). To know the complete configuration of the system, we must also know its orientations in space. This is determined by the three Eulerian angles θ, ϕ and ψ. Thus, the configuration of a system is determined by six independent coordinates. This gives the body six degrees of freedom in respect of its configuration. Since the energy of a molecule is not a function of the coordinates defining its configuration, these six degrees of freedom contribute nothing to the energy of the molecule.

Corresponding to each of these six coordinates of configuration, we have three velocity coordinates $\dot{x}\dot{y}\dot{z}\dot{\theta}\dot{\phi}\dot{\psi}$ which are necessarily independent of each other. The coordinates $\dot{x}\dot{y}\dot{z}$ determine the translational energy of the centre of mass of the molecule giving three translational degrees of freedom, while $\dot{\theta}\dot{\phi}$ and $\dot{\psi}$ determine rotational energy of the complex system giving three rotational degrees of freedom. The molecules in general are not rigid masses. The constituent atoms of a molecule can move relatively to each other subject to strong internal atomic forces. They can, therefore, vibrate about their mean positions. Each component vibration of an atom gives a corresponding *vibrational degree of freedom*.

An independent point mass can have only three degrees of translatory motion. The atoms of a complex molecule may be regarded as a point mass. If the number of constituent atoms of a molecule be n then *as a general rule*, the maximum number of degrees of freedom of the molecule is $3n$. Of these degrees of freedom three are due to component translatory motion of its centre of mass, three are due to rotational motion about the centre of mass, and the rest $(3n - 6)$ are the vibrational degrees of motion.

In whatever way we interpret these degrees of freedom, their total number would always be $3n$ where n is the total number of constituent atoms in the molecule. We shall illustrate this by the following examples:

1. As already explained, a monatomic molecule regarded as a point mass can have only three translatory degrees of freedom.
2. A diatomic molecule: This is a dumbbell-shaped body as shown in Fig. 4.12. Its centre of mass has three translatory degrees of freedom in the directions of the coordinate axis *CX*, *CY* and *CZ*.

   It can also rotate about these three axes. But the rotation about *CX* does not contribute anything to the energy of the molecule because the moment of inertia of the molecule about this axis is zero. It has only two rotational degrees of freedom about the axes *CY* and *CZ*. In addition, it can vibrate along the line AB joining the centre. This gives the diatomic molecule altogether six degrees of freedom.

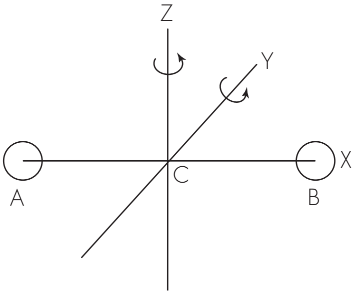

Fig. 4.12 Diatomic molecule

3. A triatomic molecule: This consists of three point masses placed at the three corners of a triangle. Let *C* be the centre of mass of the molecule (Fig. 4.13).

   This centre of mass has three degrees of freedom of translatory motion. It can have three rotational degrees of freedom about three perpendicular axes passing through its centre of gravity *C*. The atoms can also vibrate in their plane in the direction of their common centre of mass. These give the molecule altogether nine degrees of freedom.

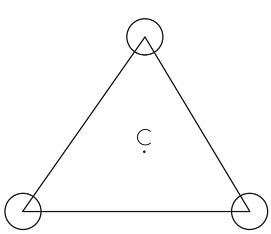

Fig. 4.13 Triatomic molecule

4. A spherical molecule is not a point mass. If the mass of the molecule is uniformly distributed over the surface of the sphere, its centre of mass will be its centre. This has three translatory degrees of freedom. If the molecule rotates about

its polar axis, it will have one degree of rotational motion. So, the maximum number of degrees of freedom of a spherical molecule is probably four.

Frozen degrees of freedom: Under certain physical conditions such as at low temperatures, some of the degrees of freedom of a molecule become frozen or inoperative in the same way that a stiff joint of a human body loses its freedom of motion. In surgery, this defect of the human body is called ankylosis. Poincare used the term ankylosed to denote frozen degrees of freedom.

4.5.2 Equipartition of Energy Amongst Different Degrees of Freedom

In 1859, Maxwell showed that in a dynamical system in thermal equilibrium energy is equally distributed among the degrees of freedom and for each degree of freedom the energy is $1/2kT$. This is called the principle of equipartition of energy. It holds not only for the translational energy but also, as was shown by Boltzmann, for the energy of rotation as well as for the energy of vibration. In the case of translation energy, it can be proved as follows:

Let u, v and w be the velocity component along the axes of x, y, z respectively of a molecule of which there are n all together. The probability that a molecule possesses a velocity component lying between u and $u + du$ is

$$\alpha e^{-\beta u^2} du \text{ where } \alpha = \sqrt{\frac{\beta}{\pi}} = \sqrt{\frac{m}{2\pi kT}} \text{ and } \beta = \frac{m}{2kT}$$

The mean energy of a molecule along the x axis is given by

$$\frac{1}{n}\int_{-\infty}^{\infty} \frac{1}{2} mu^2 dn_u \text{ where } dn_u = n\alpha e^{-\beta u^2} du$$

$$= \frac{1}{2} m\alpha \int_{-\infty}^{+\infty} u^2 e^{-\beta u^2} du$$

$$= \frac{1}{2}\frac{m\alpha}{\beta^{\frac{3}{2}}}\sqrt{\frac{\pi}{2}} = \frac{1}{2} m\sqrt{\frac{m}{2\pi kT}}\frac{2kT}{m}\sqrt{\frac{2kT}{m}}\sqrt{\frac{\pi}{2}}$$

$$= \frac{1}{2} kT$$

This is same if we consider y and z component of velocities. Therefore, the mean energy of translation per degree of freedom is $1/2\ kT$

4.5.3 Molecular Energy and Specific Heat

Each molecule of a monatomic gas possesses only three degrees of freedom. The energy of a gm-molecule of a gas is, therefore, $E = 3/2\ NkT$ where N is the Avogadro number. The molar specific heat of the monatomic gas at constant volume is

$$C_v = \frac{dE}{dT} = \frac{3}{2} Nk = \frac{3}{2} R$$

For perfect gases, we have

$$C_p - C_v = R$$

$$C_p = \frac{5}{2} R$$

Hence, the ratio of specific heats

$$\gamma = \frac{C_p}{C_v} = \frac{5R/2}{3R/2} = \frac{5}{3} = 1.66$$

For a diatomic gas whose vibrational degree of freedom is frozen or which is perfectly rigid, there can only be five degrees of freedom of which three are translational and two rotational. So, the total energy of a diatomic molecule is

$$E = \frac{5}{2}kT$$

$$c_v = \frac{dE}{dT} = \frac{5}{2}k$$

For a gm-molecule of the diatomic gas,

$$C_v = \frac{5}{2}Nk = \frac{5}{2}R$$

$$C_p = R + \frac{5}{2}R = \frac{7}{2}R$$

$$\gamma = \frac{C_p}{C_v} = \frac{7R/2}{5R/2} = \frac{7}{5} = 1.4$$

In the general case, let the molecule of a gas have n degree of freedom so that the total energy of the molecule is

$$E = \frac{1}{2}nkT$$

$$c_v = \frac{dE}{dT} = \frac{1}{2}nk$$

$$C_v = \frac{1}{2}Nnk = \frac{1}{2}Rn$$

$$C_p = C_v + R = R + \frac{Rn}{2} = R\left(1 + \frac{n}{2}\right)$$

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{n}$$

For monatomic gases, $n = 3$ so that γ per mole $= 1.66$. For monatomic gases, $n = 5$ and γ per mole is equal to 1.4. Thus knowing the value of γ from experiment, the number of degrees of freedom and therewith the structure of a molecule can be determined.

4.5.4 Dulong and Petit's Law of Specific Heat of a Monatomic Solid

The law states that the specific heat of a monatomic solid at ordinary temperature is nearly 6 calories. The kinetic theory applied to solid offers ready explanation of Dulong and Petit's law.

The molecules of a solid can have no translatory or rotational motion. It can only oscillate about its mean position. Such a molecule can have only three degrees of freedom of vibrational motion. Again, the average value of vibrational energy is equally divided between kinetic and potential forms. So vibrational energy of a solid monatomic molecule has only six degrees of freedom. The total energy of the solid per mole is

$$E = 6 \times \frac{1}{2} NkT = 3NkT = 3RT$$

$$C = \frac{dE}{dT} = 3R = 3 \times 1.99 = 5.97 \approx 6 \text{ calories}$$

4.5.5 Kinetic Theory and Variation of Specific Heat

The kinetic theory of specific heat as described earlier is unable to explain the variation of specific heat with temperature, particularly its marked decrease at extremely low temperatures. Further the decrease is gradual. So, it cannot be explained by the disappearance of any degree of freedom, because that would involve discontinuous changes by multiples of $R/2$. We cannot also assume fractional degrees of freedom. In fact in the matter of explanation of variation of specific heat with temperature, the classical or dynamical theory fails completely. The quantum theory of specific heat developed by Max Planck explains facts more satisfactorily.

4.6 FINITE VOLUME OF A MOLECULE, MEAN FREE PATH

In connection with Boltzmann's explanation of Maxwell's law of distribution of velocities, it was tacitly assumed that the molecules are not point masses. They possess finite, though small, volumes. As a result, the molecules cannot move indefinitely in a rectilinear path in an uninterrupted manner. They suffer collisions with other molecules lying in their path; and at each collision, their velocity and direction of motion are changed. If we observe a molecule for some time, its path would be found to change discontinuously in a zigzag fashion as shown in Fig. 4.14; otherwise, if the molecules were allowed to move indefinitely in a rectilinear path, a mass of gas contained in an open vessel would disappear in no time. On the contrary, the top of a cloud or smoke is found to hold together for a long time.

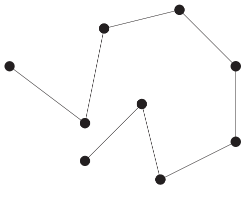

Fig. 4.14 Illustration of molecular path

4.6.1 Definition of Mean Free Path

This is equal to the total length of paths described by a molecule between successive collisions over a long interval of time divided by the number of collisions during that interval. In the case of molecules regarded as spherical bodies, the mean free path is the average distance between the molecular centres between two successive collisions.

4.6.2 Calculation of Mean Free Path

The simplest method of calculation of mean free path is to suppose all molecules in the gaseous mass except one to be at rest relatively to each other and the single molecule to be projected into the mass with the mean velocity c. If we describe round the moving molecule a sphere of radius equal to the diameter σ of the molecule (the so-called sphere of influence), then in 1 second the sphere of influence will describe a cylinder of length c and of base area equal to $\pi\sigma^2$ and then the number of collisions ω per second is equal to the number of molecular centres lying inside this cylinder. If υ is the number density of molecules, then the number of collisions per second is $\pi\sigma^2 c\upsilon$. Then, the mean free path is

$$\lambda = \frac{c}{\omega} = \frac{1}{\pi\sigma^2\upsilon} \tag{4.86}$$

This gives only an approximate value of the mean free path because of the assumption that all molecules of the gaseous mass except one are at rest.

4.6.3 Calculation of Mean Free Path on the Assumption of Uniform Molecular Velocity

Following Clausius, we shall here suppose that all the molecules are moving randomly in all possible directions with uniform average velocity c. For the purpose of calculation, we draw the velocity sphere. We take a fixed point o and from this point we draw radii vectors of the same length c representing the directions of motions of the different molecules contained in a unit volume of the gas. The sphere on which the end points of the radii vectors lie is the so-called velocity sphere. If υ be the number density, then the number of end points lying on unit area of the velocity sphere is $\upsilon/4\pi c^2$. The number of molecules out of a unit volume whose directions of motion lie between angles θ and $\theta + d\theta$ with a fixed direction (Fig. 4.15) is equal to the number of end points lying within the belt BE on the velocity sphere.

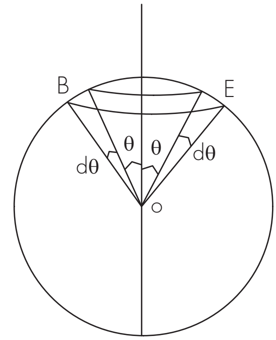

Fig. 4.15 Sketch for molecular motion

The area of this space $2\pi c^2 \sin\theta \, d\theta$. The number of end points falling on belt BE is

$$d\upsilon = \frac{2\pi c^2 \sin\theta d\theta \upsilon}{4\pi c^2} = \frac{\upsilon}{2}\sin\theta d\theta$$

To avoid repetition, we shall call the molecules whose velocity vectors lie between θ and $\theta + d\theta$ molecules of class A. The colliding molecule is also moving with velocity c.

To find the velocity of the colliding molecule relative to the molecules of class A, we add to the velocity of the colliding molecule and that of the molecule of class A a velocity equal and opposite to that of the class A molecules. The molecules of class A are then brought to rest so that the relative velocity of the colliding molecule moving originally in the direction of the X axis (say) is given by

$$\begin{aligned} c_r^2 &= c^2 + c^2 - 2c^2\cos\theta \\ &= 2c^2(1-\cos\theta) \\ &= 4c^2\sin^2\frac{\theta}{2} \\ c_r &= 2c\sin\frac{\theta}{2} \end{aligned}$$

The volume of the cylinder described by the sphere of influence of the colliding molecule in 1 second is $2\pi c\sigma^2 \sin\theta/2$. Number of molecular centres of class A lying inside this cylinder or the number of collisions with molecules of class A per second is

$$\begin{aligned} d\omega &= 2\pi c\sigma^2 \sin\frac{\theta}{2}\, dv \\ &= 2\pi c\sigma^2 \sin\frac{\theta}{2} \times \frac{1}{2} v \sin\theta d\theta \\ &= \pi c v\sigma^2 \sin\frac{\theta}{2} \sin\theta d\theta \end{aligned}$$

Hence, the number of collisions with all classes of molecules per second

$$\begin{aligned} \omega &= \pi c v\sigma^2 \int_0^{\pi} \sin\theta \sin\frac{\theta}{2}\, d\theta \\ &= 2\pi c v\sigma^2 \int_0^{\pi} \sin^2\frac{\theta}{2} \cos\frac{\theta}{2}\, d\theta \\ &= 4\pi c v\sigma^2 \int_0^{\pi} \sin^2\frac{\theta}{2}\, d\left(\sin\frac{\theta}{2}\right) \\ &= 4\pi c v\sigma^2 \left[\frac{\sin^3\frac{\theta}{2}}{3}\right]_0^{\pi} \end{aligned}$$

or

$$\omega = \frac{4}{3}\pi c v\sigma^2$$

Hence, the mean free path is

$$\lambda = \frac{c}{\omega} = \frac{1}{\frac{4}{3}\pi\sigma^2 v} = \frac{0.75}{\pi v\sigma^2} \tag{4.87}$$

In deriving this equation, we have supposed that the colliding molecule is not deviated from its path by collision. No apprehension need be felt on this account; however, the normal components of the velocities of the colliding molecules after collision are interchanged with their normal components before collision. So when one molecule is knocked out of a given course by collision, another molecule is thrown into the same course after collision. The effect is the same as if it had continued to move undeviated in its original path.

Equation 4.87 can also be deduced more simply as follows:

The average value of the relative velocity is

$$\overline{c}_r = \frac{1}{v}\int c_r dv = c\int_0^{\pi} \sin\theta \sin\frac{\theta}{2}\, d\theta = \frac{4c}{3}$$

The volume of the cylinder described by the sphere of influence of a molecule moving within velocity $\bar{c}_r$ is 4/3 $c\pi\sigma^2$. The number of molecular centres lying in this volume is 4/3 $\pi c\upsilon\sigma^2$. This is equal to the number of collisions per second. Hence, the mean free path is

$$\lambda = \frac{c}{\frac{4}{3}\pi c\upsilon\sigma^2} = \frac{3}{4\pi\upsilon\sigma^2}$$

4.6.4 Maxwell's Mean Free Path

In the Clausius' deduction of mean free path, as mentioned earlier, all molecules were supposed to be moving in all directions with the same average velocity c. Actually, however, the distribution of velocities is governed by Maxwell–Boltzmann's law. If c_1 and c_2 are the velocities of the two molecules moving relatively to each other at angle θ, then the relative velocity between them is given by

$$c_r^2 = c_1^2 + c_2^2 - 2c_1c_2\cos\theta$$

The mean value of relative velocity is

$$\bar{c}_r = \frac{1}{2}\int_0^{\pi} (c_1^2 + c_2^2 - 2c_1c_2\cos\theta)^{\frac{1}{2}} \sin\theta d\theta$$

$$= \frac{1}{6c_1c_2}\left[(c_1^2 + c_2^2 - 2c_1c_2\cos\theta)^{\frac{3}{2}}\right]_0^{\pi}$$

$$= \frac{1}{6c_1c_2}\left[(c_1^2 + c_2^2 + 2c_1c_2)^{\frac{3}{2}} - (c_1^2 + c_2^2 - 2c_1c_2)^{\frac{3}{2}}\right]$$

$$= \frac{1}{6c_1c_2}\left[(c_1 + c_2)^3 - (c_1 \sim c_2)^3\right]$$

In the integral of $\bar{c}_r$, the positive value of $(c_1^2 + c_2^2 - 2c_1c_2\cos\theta)^{1/2}$ is used. It is coming as a derivative of $(c_1^2 + c_2^2 - 2c_1c_2\cos\theta)^{3/2}$, so $(c_1^2 + c_2^2 - 2c_1c_2\cos\theta)^{3/2}$should be positive; hence, we write $(c_1 \sim c_2)^3$ for $(c_1^2 + c_2^2 - 2c_1c_2)^{3/2}$.

If $$c_1 > c_2,\ \bar{c}_r = \frac{1}{6c_1c_2}\left[(c_1 + c_2)^3 - (c_1 - c_2)^3\right]$$

$$= \frac{3c_1^2 + c_2^2}{3c_1}$$

and for $$c_1 < c_2,\ \bar{c}_r = \frac{1}{6c_1c_2}\left[(c_1 + c_2)^3 - (c_2 - c_1)^3\right]$$

$$= \frac{3c_2^2 + c_1^2}{3c_2}$$

By Eq. 4.18, the probability of velocity c_1 is

$$p_{c_1} = \frac{4}{\delta^3\sqrt{\pi}} c_1^2 e^{\frac{-c_1^2}{\delta^2}} dc_1$$

and the probability of velocity c_2 is

$$p_{c_2} = \frac{4}{\delta^3\sqrt{\pi}} c_2^2 e^{\frac{-c_2^2}{\delta^2}} dc_2$$

where δ represents the most probable velocity.

The average relative velocity of the molecule with velocity c_1 relative to all other molecules moving with velocity c_2 is

$$\begin{aligned}\bar{c}_1 &= \int_0^N \bar{c}_r \frac{4}{\delta^3\sqrt{\pi}} c_2^2 e^{\frac{-c_2^2}{\delta^2}} dc_2 \\ &= \frac{4}{\delta^3\sqrt{\pi}}\left(\int_0^{c_1} \frac{3c_1^2 + c_2^2}{3c_1} c_2^2 e^{\frac{-c_2^2}{\delta^2}} dc_2 + \int_{c_1}^{\infty} \frac{3c_2^2 + c_1^2}{3c_2} c_2^2 e^{\frac{-c_2^2}{\delta^2}} dc_2\right)\end{aligned}$$

In this equation, c_2 is the variable quantity and c_1 is kept constant. Since the first integral extends from 0 to c_1, c_2 is less than c_1. Since the second integral extends from c_1 to ∞, c_2 is greater than c_1. Accordingly, corresponding values of $\bar{c}_r$ for $c_1 > c_2$ and $c_1 < c_2$ have been used in the first and the second integral. So to obtain the average relative velocity for all values of c_1, c_2 is to be multiplied by the probability of the velocity c_1 and integrated from *0* to ∞. The integration gives for the average relative velocity

$$\begin{aligned}\bar{c}_r &= \int_0^{\infty} \bar{c}_1 \frac{4}{\delta^3\sqrt{\pi}} c_1^2 e^{-\frac{c_1^2}{\delta^2}} dc_1 \\ &= \frac{2\delta\sqrt{2}}{\sqrt{\pi}} = \bar{c}\sqrt{2}\end{aligned}$$

Thus, the average value of the relative velocity is $\sqrt{2}$ times the average velocity of molecules.

We can now suppose that all molecules except one (the colliding molecule) are at rest and the colliding molecule is moving amongst them with average velocity $c\sqrt{2}$, then the volume swept out by its sphere of influence in 1 second is $\pi\sigma^2\bar{c}\sqrt{2}$. If υ be number of molecules per cubic centimetre, then the number of collisions per second is

$$\omega = \sqrt{2}\pi\upsilon\bar{c}\sigma^2$$

so that the mean free path is

$$\lambda = \frac{\bar{c}}{\sqrt{2}\pi\upsilon\bar{c}\sigma^2} = \frac{1}{\sqrt{2}\pi\upsilon\sigma^2} = \frac{0.707}{\pi\upsilon\sigma^2} \tag{4.88}$$

4.6.5 Tait's Mean Free Path

In Maxwell's deduction described earlier, the mean free path has been obtained by dividing the average velocity by the mean number of collisions averaged over all molecules. Tait, on the other hand, follows a single molecule moving with velocity c which may have any value from 0 to ∞ and determines the number of collisions suffered by it in 1 second. From this, he determines the average mean free path appropriate to a single speed c. He then averages over all possible speed of molecules. The result obtained is

$$\lambda_T = \frac{0.677}{\pi \upsilon \sigma^2} \tag{4.89}$$

4.6.6 Jean's Mean Free Path

Taking into account the persistence of velocity after molecular impact, Jeans obtained the following relation

$$\lambda = \frac{1}{\sqrt{2}} \frac{1.319}{\pi \sigma^2 \upsilon} \tag{4.90}$$

Considering the effect of intermolecular forces during collision, he obtained the Sutherland's formula

$$\lambda = \frac{1.402}{\sqrt{2}\pi \upsilon \sigma^2 \left(1 + \dfrac{A}{T}\right)} \tag{4.91}$$

where A is a constant depending on the nature of the gas and T is the absolute temperature.

4.6.7 Mean Free Path in a Mixture of Gases

Let the mixture consist of two types of molecules A and B of dimensions σ_A and σ_B and of masses m_A and m_B. It is easily seen that during an encounter of a molecule of class A with that of class B, the centres of the two molecules cannot approach closer than $(\sigma_A + \sigma_B)/2$. Further, it has been proved that

$$m_A \overline{c_A^2} = m_B \overline{c_B^2}$$

so the average velocities of the molecules A and B would be different. It can be proved by rigorous mathematical treatment that the average relative velocity of molecule A with respect to B is

$$\bar{c}_{AB} = \sqrt{\overline{c_A^2} + \overline{c_B^2}}$$

To find the mean free path of the molecule A in the mixture, we have to find (α) the number of collisions of a molecule of class A with other molecules of class A and (β) its number of collisions with molecules of class B in 1 second. Let υ_A and υ_B be the number densities of molecules of classes A and B, respectively.

Using Maxwell's relation, $c_r = \bar{c}\sqrt{2}$

The number of collision of class (α) is

$$\pi \sigma_A^2 \bar{c}_A \sqrt{2} \upsilon_A$$

and the number of collisions of class (β) is

$$\pi \sigma_A^2 \sqrt{\overline{c_A^2} + \overline{c_B^2}}\, \upsilon_B$$

Hence, the total number of collisions in 1 second is

$$\omega_{\alpha\beta} = \sqrt{2}\pi\upsilon_A\sigma_A^2\bar{c}_A + \pi\upsilon_B\sigma_A^2\sqrt{\overline{c_A^2} + \overline{c_B^2}}$$

Therefore, the mean free path of the *A* molecules

$$\lambda_A = \frac{1}{\sqrt{2}\pi\upsilon_A\sigma_A^2 + \pi\upsilon_B\sigma_A^2\sqrt{\overline{c_A^2} + \overline{c_B^2}}/c_A} \tag{4.92}$$

Similarly, the mean free path of the *B* molecules is

$$\lambda_B = \frac{1}{\sqrt{2}\pi\upsilon_B\sigma_B^2 + \pi\upsilon_A\sigma_B^2\sqrt{\overline{c_A^2} + \overline{c_B^2}}/c_B} \tag{4.93}$$

4.6.8 Correction for Mean Free Path on Account of Finite Size of Molecules

In deducing Eq. 4.87, we have supposed that all molecules are moving with the same average velocity *c* and that number of collisions per second is equal to the number of molecular centres lying in the cylinder swept out by the sphere of influence of the colliding molecule in 1 second. We have, thus, considered the size of the colliding molecule but have neglected the size of the molecules with which it collides. We now proceed to make correction for the defect. In the following analysis, we shall again suppose that the molecules are moving with the same average velocity randomly in all possible directions. Let the diameters of the molecules be σ.

Let there be *N* molecules enclosed in a space of volume *v*. Let the area of the containing vessel be Σ. It will be seen that in the process of collision between two molecules, the centre of the colliding molecules cannot approach closer than the diameter of the molecule. In collision with the wall of the containing vessel, the centre of the colliding molecule remains at a distance of $\sigma/2$ from the wall.

Figure 4.16 represents the instantaneous picture of the molecular configuration of the mass of gas enclosed in the volume *v*. Round each molecule, we describe its sphere of influence of radius σ. Inside surface Σ of the containing vessel, we describe another surface Σ' parallel to Σ at a distance $\sigma/2$ from it.

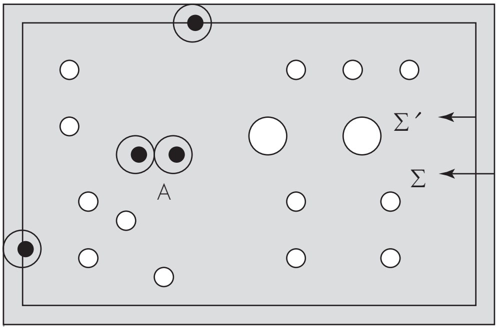

Fig. 4.16 Instantaneous picture of molecular configuration of a mass of gas

Then, the space available for the colliding molecule move freely is the space inside Σ' excluding the sum total of the spaces occupied by the spheres of influence of the $(N-1)$ molecules. We shall call this available space the exclusion space. We shall represent the volume available to the colliding molecule by *U*.

The surface for this exclusion space would, of course, be a discontinuous surface bounded by the surface Σ' and the bounding surfaces of sphere of influence of the enclosed molecule. We shall call this surface the exclusion surface. In the process of collision, the centre of the colliding molecules evidently lies on the exclusion surface. Since the molecules are moving at random relatively to each other, the exclusion surface is constantly changing its shape but the size of the exclusion space remains constant for all times. In so far as collision with other molecules is concerned, the colliding molecule may be replaced by a point mass placed at its centre.

4.6.9 The Collision Rate

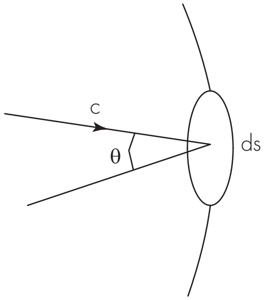

Fig. 4.17 Illustrating collision

Let *ds* be a small element of the exclusion surface and let the colliding molecule approach *ds* with velocity *c* in a direction making an angle θ with the normal to *ds* (Fig. 4.17). Since the chance of collision depends on the relative motion between *ds* and the colliding molecule, we can suppose the colliding molecule to be fixed and *ds* approaching the molecule in the opposite direction with the same velocity. Then, the chance of a collision in time *dt* is that the molecule must lie with the cylindrical space swept out by *ds* in time *dt*. The volume of this space is evidently equal to $cdtds\cos\theta$. Since all positions of the colliding molecule are equally likely, the chance of a collision with *ds* in time *dt* in the direction θ is

$$p_\theta dsdt = \frac{cdtds\cos\theta}{U} \tag{4.94}$$

To find the total number of impacts on *ds* in time *dt* by molecules moving in directions lying between θ and $\theta + d\theta$, we describe a hemisphere round the centre of *ds* of unit radius. Since all directions of motions are equally probable, the number of collisions will be proportional to the area of the belt intercepted between cones of semi-vertical angles θ and $\theta + d\theta$ round the normal to *ds* as polar axis. The area of this belt is $2\ \pi \sin\ \theta\, d\theta$. But the solid angle subtended at a point is 4π. Hence, the chance that θ lies between θ and $\theta + d\theta$ is

$$\frac{2\pi\sin\theta d\theta}{4\pi} = \frac{1}{2}\sin\theta d\theta$$

But for a collision with *ds*, θ must lie between 0 and $\pi/2$. Hence, the chance of a collision with *ds* is

$$pdtds = \frac{cdtds}{2U}\int_0^{\frac{\pi}{2}} \cos\theta\sin\theta d\theta = \frac{c}{4U}dtds$$

But *ds* is any portion of the exclusion surface. Integrating it over the whole surface,

$$p_s dt = \frac{csdt}{4U}$$

As the probability of a collision does not depend on the particular instant chosen, we can replace *dt* by a finite time Δt. Choosing Δt so that the probability is a certainty and then putting $p_s\Delta t = 1$, we get

$$\Delta t = \frac{4U}{cs}$$

If the time interval of a collision is neglected, then the number of collisions in unit time is

$$n_1 = \frac{1}{\Delta t} = \frac{cs}{4U} \tag{4.95}$$

Evaluation of s and u: The quantity *s* has been called the area of the exclusion surface. This is made of two parts: (1) the total surface area of the molecules with which the colliding one comes into contact. If *N* be the number of molecules in volume *v*, then this is equal to $4\pi(N - 1)\sigma^2$; since *N* is a very large number, the area of the molecules is equal to $4\pi N\sigma^2$; (2) The area of the surface Σ' parallel to Σ at a distance $\sigma/2$ from the latter. Since the difference between Σ and Σ' being very small in comparison with the first, it can be neglected. Thus, s can be taken to be equal to $\Sigma + 4\pi N\sigma^2$.

The quantity U has been taken to be the volume of the exclusion surface. It is necessarily less than v. Let this difference be b so that

$$U = v - b \tag{4.96}$$

Substituting the values of s and U in Eq. 4.95

$$n_1 = \frac{c}{4}\frac{\sum + 4\pi N\sigma^2}{v - b} \tag{4.97}$$

The mean free path is

$$\lambda = \frac{c}{n_1} = \frac{4(v-b)}{\sum + 4\pi N\sigma^2} \tag{4.98}$$

Neglecting Σ in comparison with $4\pi N\sigma^2$ and also neglecting b in comparison with v, we get for the mean free path the same value as obtained earlier

$$\lambda = \frac{v}{\pi N\sigma^2} = \frac{1}{\pi \upsilon\sigma^2} \tag{4.99}$$

where υ is the number density of the molecules.

4.6.10 Correction for Relative Velocity

Equation 4.98 requires further correction for relative motion between the molecules. In computing the rate of collision as described earlier, the rate of approach of the colliding molecules to the surface ds was taken to be the average velocity c. Since the molecules are supposed to be moving in all directions with the assumed average velocity c, the velocity of approach should be the relative velocity. If two molecules are moving with the same velocity c relatively to each other at an angle θ, then by vector addition the relative velocity is

$$c_r = 2c\sin\frac{\theta}{2}$$

To find the average velocity of other molecules with respect to the colliding molecule, we draw the velocity sphere with its polar axis in the direction of motion of the colliding molecule. Then, the number of velocity points on a belt intercepted between cones of semi-vertical angles θ and $\theta + d\theta$ is1/2 sin $\theta d\theta$. The average value of relative velocity is obtained by integration

$$\overline{c}_r = \int_0^{\pi} \frac{1}{2}\sin\theta \times 2c\sin\frac{\theta}{2}\,d\theta = \frac{4c}{3} \tag{4.100}$$

From Eq. 4.98

$$n_1 = \frac{c\sum}{4(v-b)} + \frac{c\pi N\sigma^2}{v-b} \tag{4.101}$$

Replacing c by $4/3c$ in the second term of Eq. 4.100, we get

$$n_1 = \frac{c}{4}\frac{\Sigma}{v-b} + \frac{4}{3}\frac{c\pi N\sigma^2}{v-b}$$

Since Σ is very small in comparison with $\pi N\sigma^2$, we can write

$$n_1 = \frac{4}{3}\frac{\pi cN\sigma^2}{v-b}$$

so that

$$\lambda = \frac{c}{n_1} = \frac{v-b}{\frac{4}{3}\pi N\sigma^2} \tag{4.102}$$

Neglecting b in Eq. 4.102, we get

$$\lambda = \frac{0.75}{\pi \upsilon\sigma^2}$$

which is the same as Eq. 4.87.

4.6.11 Pressure-Volume Relation of Clausius

Following Clausius, we shall suppose that all molecules are moving with the same root mean square velocity c and that all directions of motion are equally probable. The probability of the number of collisions per second which each molecule makes with the element ds of the exclusion surface in directions lying between θ and $\theta + d\theta$ with its normal is

$$\frac{c}{2U}\cos\theta\sin\theta d\theta ds$$

Since ds is any part of this surface, the number of collisions with the whole surface is obtained by integration over the surface. This gives

$$\frac{cs}{2U}\cos\theta\sin\theta d\theta$$

If N be the total number of molecules in the available volume $U = v - b$, then the number of collisions per second with the surface s is

$$\omega_{s\theta} = \frac{Ncs}{2(v-b)}\cos\theta\sin\theta d\theta$$

Since the surfaces of collision are supposed to be perfectly small, the tangential component of velocity remains unaltered by impact so that the normal component is reversed in direction. At each impact, the momentum transferred is $2mc\cos\theta$. The impulse communicated to the surface per second is

$$F_\theta = \frac{Nmsc^2\cos^2\theta\sin\theta d\theta}{v-b}$$

Total impulse communicated per second from all directions is

$$F = \frac{Nmsc^2}{v-b}\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta = -\frac{Nmsc^2}{v-b}\int_0^{\frac{\pi}{2}}\cos^2\theta d(\cos\theta) \tag{4.103}$$

$$= \frac{1}{3}\frac{Nmsc^2}{v-b}$$

Pressure exerted on the wall is force per unit area. Hence, the pressure is

$$p = \frac{Nmc^2}{3(v-b)}$$

or
$$p(v-b) = \frac{1}{3}Nmc^2 \tag{4.104}$$

This equation represents the volume correction by Clausius.

Evaluation of quantity b: The actual space b available to a molecule to move freely inside a mass of gas excludes (1) the thin layer inside the surface of the containing vessel of thickness equal to the radius of the molecule, and (2) the sum total of the volumes occupied by the spheres of influence of other molecules. The contribution, due to the first being negligible compared to the second, is left out of consideration. If σ be the diameter of a molecule and if N be the total number of molecules in volume v, then the volume to be excluded is

$$b' = \frac{4}{3}N\pi\sigma^3$$

Actually, however, the value of b should be only half of b'. This is because the integral in Eq. 4.103 extends from 0 to π/2, that is, it covers only the hemisphere lying on one side of the element of surface of collision. Hence, the excluded space in the volume correction is

$$b = \frac{2}{3}N\pi\sigma^3 \tag{4.105}$$

The value b can be determined experimentally. Hence knowing N, the diameter σ of a molecule can be calculated.

4.6.12 Number of Molecules Striking Unit Area of a Surface per Second

We suppose that the molecules are moving randomly in all directions with root mean square velocity c. Let ds be an element of area of the collision surface. The chance that a molecule will strike the surface ds in a direction lying between θ and $\theta + d\theta$ with the normal to the surface has already been found to be equal to 1/2 $\sin\theta d\theta$. To find the number of molecules striking the surface per second, we describe a cylinder of cross-sectional area $ds\cos\theta$ and of length c with its axis inclined at an angle θ with the normal to ds. The molecules lying inside the cylinder $\upsilon c ds\cos\theta$ where υ is the number of molecules per cc. Hence, the number striking ds per second in the direction θ is

$$N_\theta = \upsilon c ds \cos\theta \times \frac{1}{2}\sin\theta d\theta$$

Total number of molecules striking the area ds in 1 second from all possible directions is

$$\frac{1}{2}\upsilon c ds \int_0^{\frac{\pi}{2}} \sin\theta\cos\theta d\theta = \frac{\upsilon c}{4} ds$$

The number striking unit area per second

$$N_1 = \frac{\upsilon c}{4} \tag{4.106}$$

4.6.13 The Probability of a Free Path

The mean free path has been defined to be an average path described by a molecule between two successive collisions in a large number of collisions. The actual path described between any two successive collisions may be greater or less than the average path. We have to determine the probability of a free path of given length.

To determine the law of distribution of free paths, we take a small volume of the gas containing q molecules. The molecules starting out from this volume move in different direction. As they pass through the gas, they collide with other molecules. We shall calculate the probability that a molecule of the group suffer no collision in traversing a distance x from the small element of volume.

Let the number of molecules which have not suffered any collision within a distance x be p. If ω is the average number of collisions per second, then the probable number of collisions in 1 cm is ω/c. The probable number of collisions in going a further distance dx is $\omega\,(dx/c)$. This is equal to decrease in the number p, since p diminishes as x increases. We can, therefore, write

$$dp = -\frac{\omega}{c}\,pdx$$

or

$$\frac{dp}{p} = -\frac{\omega}{c}\,dx$$

Integrating, we get

$$\log_e p = -\frac{\omega}{c}x + \log_e A$$

So that

$$p = Ae^{-\frac{\omega x}{c}}$$

The limiting condition is at $x = 0$, $p = q$, so that $A = q$

Hence,

$$p = qe^{-\frac{\omega x}{c}} \tag{4.107}$$

$$dp = -q\frac{\omega}{c}e^{-\frac{\omega x}{c}}\,dx \tag{4.108}$$

Here, dp means the number of molecules which have suffered collisions in traversing a small distance between x and $x + dx$. It depends on the number of molecules q traversing the distance x, $\frac{\omega}{c}$ which is a constant called the scale factor and dx. The scale factor can be obtained in terms of the mean free path λ. By definition of mean free path,

$$\lambda = \int_0^q \frac{xdp}{q} = \int_\infty^0 \frac{-q\frac{\omega}{c}e^{-\frac{\omega x}{c}}}{q}xdx = -\frac{\omega}{c}\int_\infty^0 e^{-(\omega x/c)}xdx$$

Integrating by parts, we get

$$\lambda = -\frac{\omega}{c}\left(\left[-x\frac{c}{\omega}e^{-\frac{\omega x}{c}}\right]_\infty^0 + \frac{c}{\omega}\int_\infty^0 e^{-\frac{\omega x}{c}}dx\right)$$

$$= \frac{c}{\omega}\int_\infty^0 e^{-\frac{\omega x}{c}}d\left(-\frac{\omega x}{c}\right) = \frac{c}{\omega}\left(e^{-\frac{\omega x}{c}}\right)_\infty^0 = \frac{c}{\omega}$$

Substituting in Eq. 4.107, we get

$$p = qe^{-\frac{x}{\lambda}} \tag{4.109}$$

and

$$dp = \frac{q}{\lambda}e^{-\frac{x}{\lambda}}dx \tag{4.110}$$

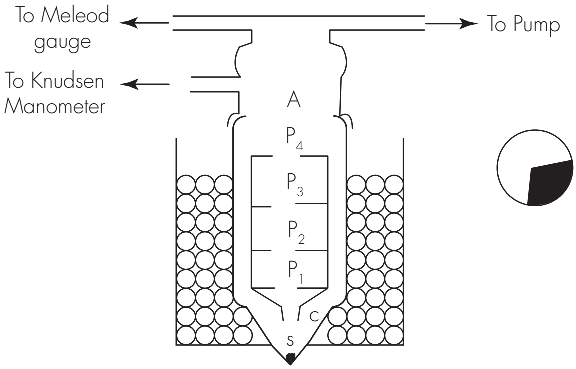

Fig. 4.18 Born's apparatus for determination of mean free path

4.6.14 Experimental Determination of Mean Free Path

The mean free path can be determined indirectly from the viscosity measurements. It can also be evaluated from the other measurements of molecular density and diameter.

The first direct experimental determination of mean free path was due to H. Born in 1920.

The experimental arrangement he used is shown in Fig. 4.18. This consists of a quartz tube A having connection to a pump for evacuation to any desired pressure and to pressure measuring instruments such as McLeod gauge and Knudsen manometer.

Silver is heated at *s* electrically. *c* is a small hole through which evaporating silver stream out in the form of a narrow beam. P_1, P_2, P_3 and P_4 are brass discs with central hole separated by 1 cm from each other. These holes are provided with glass quadrant whose apex extends to the centre of the circular hole and the quadrants are arranged in such a manner that each would receive one-fourth of the beam; that is, they are rotated through 90° relative to each other. The discs are surrounded by freezing mixture which condenses the evaporating silver atoms on to the quadrants. The relative amount of silver deposited on each quadrant is measured from photometric comparison of the density of deposit. If D and D_o be the density of deposit on a quadrant and on the next lower quadrant, respectively, x be their distance apart and λ be the mean free path, then

$$D = D_o e^{-\frac{x}{\lambda}}$$

But even at the lowest pressure, due to the geometrical spreading of the beam, the density changes on the different plates. To avoid the difficulty, a particular quadrant is chosen; if D_{10} be the density of deposit at this quadrant when the vessel is evacuated, the free path is equal to the length of the chamber; and if D_1 be the density of deposit on the same quadrant when the gas is introduced producing free path λ, x_1 being the distance of the plate from c, then

$$D_1 = D_{10} e^{-\frac{x_1}{\lambda}}$$

Similarly for another quadrant, $D_2 = D_{20} e^{-\frac{x_2}{\lambda}}$

or $$\frac{x_1}{\lambda} = \log_e \frac{D_{10}}{D_1} \text{ and } \frac{x_2}{\lambda} = \log_e \frac{D_{20}}{D_2}$$

or $$\frac{x_2 - x_1}{\lambda} = \log_e \frac{D_{20}}{D_2}\frac{D_1}{D_{10}} \text{ or } \lambda = \frac{x_2 - x_1}{\log_e \frac{D_{20}}{D_2}\frac{D_1}{D_{10}}}$$

According to actual experiment, $x_2 - x_1 = 1$, $\lambda = 1.7$ cm for $p = 5.8 \times 10^{-3}$ mm and $\lambda = 2.4$ cm for $p = 4.5 \times 10^{-3}$ mm. Hence, $p\lambda =$ constant as is predicted.

Later, Bielz repeated the experiment by improving the methods of introduction of glass quadrant and measurement of density of deposit. Similar results were obtained.

4.7 THE TRANSPORT PHENOMENA

From the standpoint of kinetic theory, we have till now considered a mass of a gas to be in a steady state of homogeneity without any mass motion or motion as a whole. A moving molecule of the gas carries with it mass, momentum and kinetic energy from one region to another. In the steady state, an equal amount of these properties are carried in the opposite direction by another molecule so that on the average, the distribution of these properties is the same at every point in the volume of the gas. Any disturbance of the state of homogeneity due to variation of temperature, pressure and concentration, etc. is always accompanied by transport of the above-mentioned physical properties in a definite direction. We shall illustrate this by the following examples:

4.7.1 Experimental Definition of Viscosity of a Gas

Let us consider a mass of a gas contained between two parallel plates of infinite extent. Let one of the plates be fixed while the other be moving in its own plane in a given direction with uniform velocity. We can suppose the moving plate to be a flat belt moving endlessly between parallel rollers as shown in Fig. 4.19. Let the plane of the belt be the plane of xy and let the normal to the plate point in the direction of z axis. As the belt moves, the layer of gas in immediate contact with it moves with the same velocity as the belt. This layer in its turn transmits a portion of its momentum to the next layer dragging it in the same direction.

By Newton's law of equality of action and reaction, the second layer exerts a retarding action on the first layer. This property of a fluid by which it tends to stop the relative motion of its parts is called viscosity.

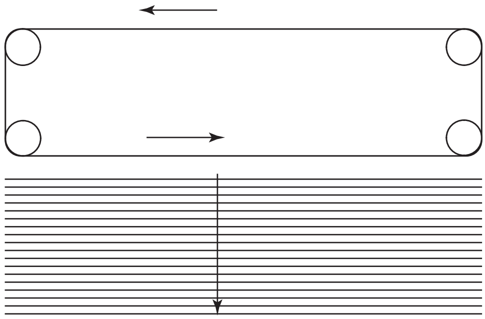

Fig. 4.19 Illustration of viscosity

It follows that on every surface of contact between two contiguous layers in relative motion, there is a tangential stress. As each moving layer transmits only a portion of its momentum to the next layer, the momentum of the successive layers would gradually diminish in the direction of the z axis so as to be of zero value at the last layer in contact with the fixed plate.

Let Δz be the thickness of two layers having a common surface of contact and moving relatively to each other with velocities u and $u + \Delta u$. Then the average velocity gradient is $\Delta u/\Delta z$ in the neighbourhood of the surface of contact at a distance z from the moving plate. Experiment shows that the tangential stress is proportional to the velocity gradient. If F be the tangential force over an area A, then the tangential stress at a distance z is

$$\frac{F}{A} \alpha \lim_{\Delta z \to 0} \frac{\Delta u}{\Delta z} \alpha \frac{du}{dz}$$

or

$$\frac{F}{A} = -\eta \frac{du}{dz} \tag{4.111}$$

where η is the constant of proportionality called coefficient of viscosity or simply viscosity of the gas. The negative sign indicates that the velocity diminishes in the direction of z axis. In this chapter, we shall try to obtain physical significance of the constant η from the standpoint of the kinetic theory.

4.7.2 Experimental Definition of Heat Conductivity of a Gas

Let us consider a mass of gas contained in a vertical cylinder of non-conducting walls. Let the gas be heated from above by hot water contained in a flat cylindrical vessel as shown in Fig. 4.20.

If the base of the gas cylinder is made of conducting material maintained at a low temperature, then there would be a gradient of temperature diminishing downwards in the direction z of the axis of the cylinder. As a result, heat energy would be conducted downwards through the gas. Experiment shows that the quantity Q of heat conducted through a layer of thickness Δz in unit time through unit area of the layer is proportional to $\Delta\theta/\Delta z$ where $\Delta\theta$ is the difference of temperature of the two faces of the layer. This gives

$$Q = -K\frac{\Delta\theta}{\Delta z}$$

where K is the constant of proportionality known as thermal conductivity of the gas. The heat conducted through unit area of a layer at a depth z in unit time is

$$Q = -K \lim_{\Delta z \to 0} \frac{\Delta\theta}{\Delta Q} = -K\frac{d\theta}{dz} \tag{4.112}$$

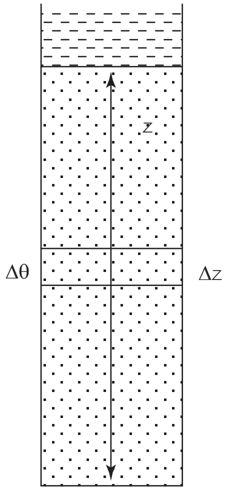

Fig. 4.20 Illustration of heat conductivity

4.7.3 Experimental Definition of Coefficient of Self-Diffusion

Diffusion is gradual passage of one gas into another by molecular movement whether there is partition or not. To fix our ideas, let us consider a mass of gas in a vertical cylinder. Let the concentration of the gas change from layer to layer diminishing downwards in the vertical z direction, the concentration remaining constant at every point in a horizontal plane. By molecular movement there would be transport of mass from the region of higher to lower concentration tending to equalize concentration at every point. By Fick's experimental law, the number of molecules crossing unit area per second in the neighbourhood of a depth z is proportional to the average rate of change of concentration so that if D is the constant of proportionality, the number crossing unit area is

$$\upsilon_1 = -D\frac{\Delta n}{\Delta z}$$

where n is the molecular concentration.

The number crossing unit area at a depth z in unit time is

$$\upsilon_1 = -D \lim_{\Delta z \to 0} \frac{\Delta n}{\Delta z} = -D\frac{dn}{dz} \tag{4.113}$$

The constant of proportionality is called the coefficient of diffusion. The negative sign indicates that the concentration diminishes as the depth increases. Here, we shall try to interpret D from the viewpoint of the kinetic theory.

4.7.4 The Transport Theorem

It will be seen that the equations for viscous resistance, conduction and diffusion of a gas are of the same form. They can, therefore, be connected by a general equation. This is known as the transport theorem.

The deduction of this theorem is based on the following assumptions:

1. The molecules of the gas are moving with the same average velocity $\bar{c}$.
2. For the purpose of calculation, we require the number of molecules crossing unit area per second in a definite direction. We take a cubical box inside the gas with sides parallel to the three rectangular axes *ox*, *oy* and *oz*.

   Since there is no preferred direction of motion of molecules, we shall, following Joule's classification, assuming that at any instant one-sixth of the total number of molecules inside the box are moving perpendicularly to each side of the box. If υ is the number of molecules in unit volume, the number υ_1 striking the surface *ds* of the box (which is parallel to the *xy* plane) in unit time is equal to the number of molecules contained in a cylinder of length $\bar{c}$ and of cross sectional area *ds*, that is

   $$\upsilon_1 = \frac{\upsilon}{6}\bar{c}\,ds \tag{4.114}$$

3. Molecules coming from a particular plane acquire the physical properties appropriate to that plane which can only be changed abruptly by collision with other molecules.
4. We shall suppose that the molecules which are crossing the plane *C* from above are coming from the plane *A* which is at a distance of mean free path λ from *C* where the molecules are supposed to have suffered their last collision. Similarly, molecules which cross the plane *ds* from below are coming from the plane *B* at distance λ from *C* (Fig. 4.21).

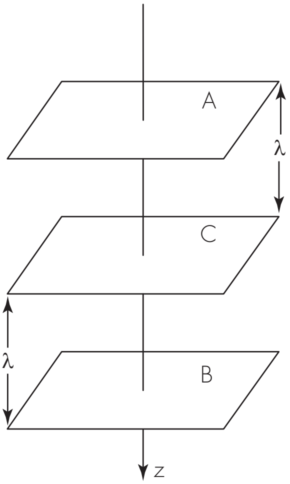

Fig. 4.21 Illustration of transport theorem

Let the magnitude of the physical property (viscosity, conductivity, diffusivity) of a molecule in the plane *C* be represented by *G*. Since the property is supposed to change uniformly in the direction of the *z* axis, its magnitude in the plane *A* is $(G + \lambda\, dG/dz)$. Its magnitude in the plane *B* is $(G - \lambda\,(dG/dz))$. Hence, the net change in magnitude of the property *G* in the plane *C* per second is

$$\Delta G = \frac{1}{6}\upsilon\bar{c}ds\left(G + \lambda\frac{dG}{dz} - G + \lambda\frac{dG}{dz}\right)$$

or

$$\Delta G = -\frac{1}{3}\upsilon\bar{c}\lambda\frac{dG}{dz}ds \tag{4.115}$$

The minus sign indicates that *G* diminishes as *z* increases. Equation 4.115 is known as the transport theorem.

4.7.5 Evaluation of Viscosity Coefficient

Equation 4.115 can be used to evaluate the coefficient of viscosity of a gas. As already explained, the viscosity of a gas is due to relative motion of different layers moving in a definite direction. Hence, the velocity and the momentum changes uniformly in the direction of the *z* axis diminishing downwards. It is evident that the momentum crossing the plane *C* from above (Fig. 4.21) is different from that carried from below in the same time. It is the net change of momentum in the plane *C* which accounts for the viscous resistance between layers separated by the surface *C*. If *m* is the mass of a molecule moving with velocity *u*, then the momentum is

$$G = mu$$

Substituting the value of *G* in Eq. 4.115, we get

$$\Delta G = -\frac{1}{3}\upsilon\bar{c}ds\lambda m\frac{du}{dz} = F \text{ (the viscous force)}$$

By Eq. 4.111, $$F = -\eta\frac{du}{dz}ds$$

So that $$\eta = \frac{1}{3}\upsilon\bar{c}m\lambda = \frac{1}{3}\rho\bar{c}\lambda \tag{4.116}$$

Substituting the value of λ from Eq. 4.87,

$$\eta = \frac{m\bar{c}}{4\pi\sigma^2} \tag{4.117}$$

4.7.6 Evaluation of Heat Conductivity of a Gas

In this case, the temperature of the gas changes from layer to layer downwards in the direction of the *z* axis. Accordingly, heat is conducted through the gas in the downward direction. In this case,

$$G = mc_vT$$

where *m* is the mass of the molecule, c_v is the specific heat at constant volume and *T* the absolute temperature of the layer *C*. Substituting the value of *G* in Eq. 4.115,

$$\Delta G = -\frac{1}{3}\upsilon\bar{c}\lambda dsmc_v\frac{dT}{dz} = \Delta Q$$

By Eq. 4.112, $$\Delta Q = -K\frac{dT}{dz}ds$$

so that $$K = \frac{1}{3}m\upsilon\bar{c}\lambda c_v = \frac{1}{3}\rho\bar{c}\lambda c_v \tag{4.118}$$

Using Eq. 4.116, the coefficient of heat conduction becomes

$$K = \eta c_v \tag{4.119}$$

4.7.7 Evaluation of Coefficient of Self-Diffusion

In this case, the property that is being transported is the number density. Let υ be the number density in the neighbourhood of the plane. Then, the number density at *A* is ($\upsilon + d\upsilon/dz\ \lambda$) and that in the plane *B* is

$(\upsilon - (d\upsilon/dz)\lambda)$. Using Joule's classification, the number crossing *ds* from above per second is $\frac{\bar{c}}{6}(\upsilon+(d\upsilon/dz)\lambda)ds$ and that crossing *ds* per second from below is $\frac{\bar{c}}{6}(\upsilon-(d\upsilon/dz)\lambda)ds$. Hence, the net number of molecules crossing *ds* per second is

$$\Delta G = -\frac{1}{3}\bar{c}\lambda\frac{d\upsilon}{dz}ds = \Delta\eta$$

By Fick's law,
$$\Delta\eta = -D\frac{d\upsilon}{dz}ds$$

so that
$$D = \frac{1}{3}\lambda\bar{c} \tag{4.120}$$

Using Eq. 4.116, the coefficient of self-diffusion becomes

$$D = \frac{\eta}{\rho} \tag{4.121}$$

4.7.8 Maxwell's Method of Evaluation of η

The method of calculation of the coefficient of velocity of a gas suffers from the following defects:

1. It assumes that all molecules are moving with the same velocity, which is its root mean square value. It takes no account of the Maxwell–Bolzmann law of distribution of velocities.
2. It assumes that one-sixth of the total number of molecules closed in a cubical box are moving perpendicularly to each side of the box. Actually, the molecules are moving in all possible directions.
3. The calculation is based on the assumption of mean free path for all molecules. It takes no account of the law of distribution of free paths.
4. The molecules have velocities appropriate to the layer in which it has suffered its last collision. It takes no account of persistence of velocities.
5. The question of intermolecular force has been totally neglected.

In the following analysis given by Maxwell, the defects due to causes mentioned above have been considered. Consider a mass of gas in which velocity gradient has been set up between different layers in the direction of the *Z*-axis, the layers parallel to the *XY* plane moving in the direction of *X* axis as shown in Fig. 4.22.

Let the velocity of the molecules corresponding to the plane at $z = 0$ (which we shall call the zero plane) be u_0. Then, the velocity at the plane *z* is $u = u_0 + (du/dz)\,z$ where du/dz is the velocity gradient, the velocity of the layers increasing in the positive direction of the *Z* axis. Consider a small element of volume *dv* of the gas at a height $Z = r\cos\theta$ from the zero plane. If $d\upsilon_c$ be the number of molecules per *cc* of the gas having velocity between *c* and $c + dc$, then the number enclosed in *dv* is $d\upsilon_c dv$. Let a molecule on an average suffer *W* collisions per second where $w = c/\lambda$, where λ is the mean free path. In time *dt*, there are $d\upsilon_c\, dv\, wdt$ new paths starting out of volume *dv* along which the molecules come out. Since all directions are equally probable, the number moving in the direction of the small area *dxdy* on the zero plane is the number in the direction of the solid angle subtended by the area *dxdy* at *dv*. The solid angle is equal to $dxdy\cos\theta/r^2$ where *r* is the distance of *dv* from the origin and θ is the angle between *r* and *z* axis. The number of

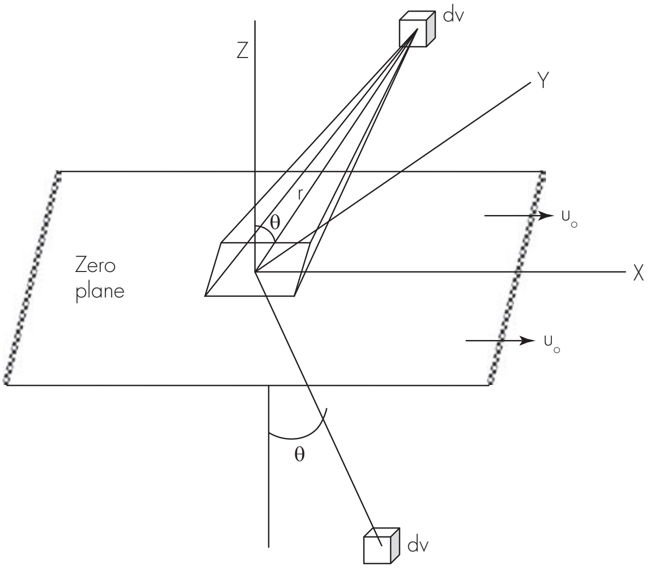

Fig. 4.22 Maxwell's analysis of evaluation of viscosity

molecules moving in the direction of unit solid angle is $dv_c dvwdt/4\pi$. Hence, the number moving in the direction of *dxdy* is

$$N'_{\theta dtdv} = dv_c dvdtw \frac{dxdy\cos\theta}{4\pi r^2} \tag{4.122}$$

Out of these $N'_{\theta dtdv}$ molecules, the number traversing the length *r* without collision is by Eq. 4.109.

$$N_{\theta dtdv} = \frac{dv_c dvdtwdxdy\cos\theta}{4\pi r^2} e^{-\frac{r}{\lambda}} \tag{4.123}$$

We assume that a molecule, on an average, has the velocity appropriate to the same of its last collision. Then, the *x* component of the momentum of a molecule coming from *dv* is

$$m\left(u_0 + r\cos\theta\frac{du}{dz}\right)$$

The momentum transferred through *dxdy* in time *dt* is

$$-N_{\theta dtdv} \times m\left(u_0 + r\cos\theta\frac{du}{dz}\right)$$

The negative sign means that the momentum is being transferred from higher to lower value of *z*. To find the total momentum transferred in this direction, we have to integrate for all values of *dv*; all values of *c* from 0 to ∞, and all values of *r* from 0 to ∞. For this purpose, we express *dv* in terms of spherical polar coordinates so that $dv = r^2 \sin\theta d\theta d\phi dr$. We then integrate ϕ from 0 to 2π and θ from 0 to $\pi/2$. So, the total momentum transferred in this direction through *dxdy* in time *dt* from the position of the gas above the zero plane is

$$M\downarrow = -\frac{mdxdydt}{4\pi}\left(u_0 \int_0^{\frac{\pi}{2}} \cos\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} c\, d\upsilon_c \int_0^{\infty} \frac{e^{-\frac{r}{\lambda}}}{\lambda} dr \right.$$

$$\left. + \frac{du}{dz} \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} c\, d\upsilon_c \int_0^{\infty} \frac{re^{-\frac{r}{\lambda}}}{\lambda} dr \right)$$

Similarly, the total momentum transferred through *dxdy* in the zero plane in time *dt* from the portion of the gas below the zero plane is

$$M\uparrow = \frac{mdxdydt}{4\pi}\left(u_0 \int_0^{\frac{\pi}{2}} \cos\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} c\, d\upsilon_c \int_0^{\infty} \frac{e^{-\frac{r}{\lambda}}}{\lambda} dr \right.$$

$$\left. - \frac{du}{dz} \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} c\, d\upsilon_c \int_0^{\infty} \frac{re^{-\frac{r}{\lambda}}}{\lambda} dr \right)$$

The net transfer of momentum through *dxdy* in time *dt* is

$$M = M\downarrow + M\uparrow = -\frac{2mdxdydt}{4\pi}\left(\frac{du}{dz} \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} cd\; \upsilon_c \int_0^{\infty} \frac{re^{-\frac{r}{\lambda}}}{\lambda} dr \right)$$

$$= -2m\frac{dxdydt}{4\pi}\frac{du}{dz}\frac{1}{3}\,2\pi\;\upsilon\bar{c}\lambda$$

$$= -\frac{1}{3}m\upsilon\bar{c}\lambda\frac{du}{dz}dxdydt$$

The viscous drag is equal to the change in momentum per unit area per second. It is equal to

$$\frac{M}{dxdydt} = -\frac{1}{3}m\upsilon\bar{c}\lambda\frac{du}{dz} = -\eta\frac{du}{dz}$$

so that

$$\eta = \frac{1}{3}m\upsilon\bar{c}\lambda \tag{4.124}$$

4.7.9 Other Expressions for the Numerical

Using Taits free path, the coefficient of viscosity becomes

$$\eta = 1.051\left(\frac{1}{3}\upsilon m\bar{c}\lambda\right) \tag{4.125}$$

Taking into account the persistence of velocities after collision in the impact of elastic spheres, Jeans obtained the following relation

$$\eta = 0.461\upsilon m\bar{c}\lambda \tag{4.126}$$

More powerful treatment of Chapman and Enskog yields the value

$$\eta = 0.499m\ \upsilon\bar{c}\lambda \tag{4.127}$$

4.7.10 Agreement of the Approximate Theory with Observation

1. Substituting Maxwell's value of mean free path

$$\lambda_M = \frac{1}{\sqrt{2}\pi\upsilon\sigma^2}$$

in the approximate value of $\eta = \frac{1}{3}\upsilon m\bar{c}\lambda_M$

one obtains

$$\eta = \frac{1}{3\sqrt{2}}\frac{m\bar{c}}{\pi\sigma^2} \tag{4.128}$$

Since $\bar{c}$ is inversely proportional to $\sqrt{m}$, η varies directly as $\sqrt{m}$. This is found to hold true for most gases.

2. In Eq. 4.128, $m, \bar{c}$ and σ are all independent of pressure. Hence, viscosity of a gas should be independent of pressure. This is actually true for pressures ranging from few millimetres of mercury to several atmospheres. At very low and very high pressures, the relation fails.
3. Substituting the value

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8R_M T}{\pi m N_0}}$$

where k is Boltzmann's constant, R_M is the universal gas constant, and N_0 is the Avogadro number in Eq. 4.128 for viscosity, we get

$$\eta = \frac{2\sqrt{mkT}}{3\pi^{\frac{3}{2}}\sigma^2} \tag{4.129}$$

According to Eq. 4.129, viscosity of a gas varies directly as the square root of the absolute temperature. But experiment shows that η varies much more rapidly than $\sqrt{T}$.

4.7.11 Sutherland's Formula for Variation of Viscosity with Temperature

The reason for the discrepancy between the calculated and observed values of η in so far as its variation with temperature is concerned, may to some extent be traced to our neglect of the intermolecular forces in the process of collision when the molecules are close together. Further, we have supposed that the molecules are elastic spheres of fixed diameter σ. If they are inelastic spheres, then their diameters would be a function of the energy and, therefore, of the temperature of the gas; for under high velocity of approach, two molecular centres of the colliding molecule can move nearer than the diameter of the sphere of influence.

The intermolecular force may either be a force of attraction or of repulsion. Sutherland based his calculation on the assumption that the molecules are rigid spheres and intermolecular force is of the nature of attractive force. The molecules were replaced by two attracting centres of force. Since nothing definite is known about the law of force, it was taken to be a function $F(r)$ of the distance r separating the molecular centres.

As the molecules are moving relatively to each other, we can suppose that one of the two colliding molecules A is fixed and the other B is moving relatively to A (Fig. 4.23). The force decreases very rapidly with distance. Accordingly at large distances compared with the diameter of the molecule, the velocity of a molecule is the same as the kinetic velocity appropriate to the temperature of the gas in a field-free space. As the molecule B approaches A, its path is curved and it describes a trajectory under a central force of attraction. Our problem is to find the distance of nearest approach of the molecular centres A and B. We take as our x axis the line Ax parallel to the original direction of motion RQS of B. The y axis is taken as the line Ay perpendicular to RQS. Let the radius AB $(= r)$ be inclined to x axis at angle ϕ at instant t. The x and y components of the force $F(r)$ acting on B at instant t are $F(r)\cos\phi = F(r)\,x/r$ and $F(r)\sin\phi = F(r)\,y/r$.

Let the mass of the molecule be taken as unity. Then by Newton's second law of motion,

$$\frac{d^2x}{dt^2} = -F(r)\frac{x}{r} \tag{4.130}$$

and

$$\frac{d^2y}{dt^2} = -F(r)\frac{y}{r} \tag{4.131}$$

Multiplying Eq. 4.130 by y and Eq. 4.131 by x and subtracting them, we get

$$\left(y\frac{d^2x}{dt^2} - x\frac{d^2y}{dt^2}\right) = 0$$

or

$$\frac{d}{dt}\left(y\frac{dx}{dt} - x\frac{dy}{dt}\right) = 0 \tag{4.132}$$

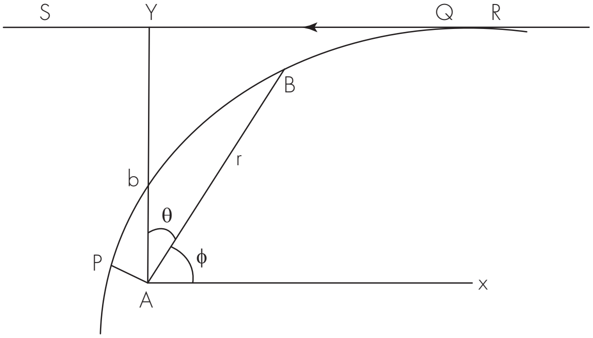

Fig. 4.23 Illustration of influence of intermolecular force on viscosity

Now, $x = r\cos\phi$ so that $\frac{dx}{dt} = -r\sin\phi\frac{d\phi}{dt} + \cos\phi\frac{dr}{dt}$

and $y = r\sin\phi$ so that $\frac{dy}{dt} = r\cos\phi\frac{d\phi}{dt} + \sin\phi\frac{dr}{dt}$

so that

$$\left.\begin{aligned} y\frac{dx}{dt} &= -r^2\sin^2\phi\frac{d\phi}{dt} + r\sin\phi\cos\phi\frac{dr}{dt} \\ x\frac{dy}{dt} &= r^2\cos^2\phi\frac{d\phi}{dt} + r\cos\phi\sin\phi\frac{dr}{dt} \end{aligned}\right\}$$

Substituting in Eq. 4.132,

$$-\frac{d}{dt}\left(r^2\frac{d\phi}{dt}\right) = 0$$

or

$$r^2\frac{d\phi}{dt} = h \quad \text{(constant)}$$

$$\frac{d\phi}{dt} = \frac{h}{r^2} \tag{4.133}$$

The constant h is the angular momentum or moment of momentum of the moving molecule B and is same for all values of r and ϕ. When $r = \infty$, the velocity of B is c, parallel to the x axis, its momentum is c (since the mass is taken as unity) and the moment of this momentum about A is cb where b is the perpendicular distance from A on the original line of motion of B. Hence,

$$h = cb \tag{4.134}$$

Multiplying Eq. 4.130 by dx/dt and Eq. 4.131 by dy/dt and adding

$$\left(\frac{dx}{dt}\frac{d^2x}{dt^2} + \frac{dy}{dt}\frac{d^2y}{dt^2}\right) = -\frac{F(r)}{r}\left(x\frac{dx}{dt} + y\frac{dy}{dt}\right)$$

or

$$\frac{1}{2}\frac{d}{dt}\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2\right] = -\frac{F(r)}{r}\frac{1}{2}\frac{d}{dt}\left(x^2 + y^2\right) \tag{4.135}$$

But

$$\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 = c^2$$

where c is the velocity of B at t

Also $x^2 + y^2 = r^2$

Substituting in Eq. 4.135, it reduces to

$$\frac{d}{dt}(c^2) = -\frac{F(r)}{r}\frac{d}{dt}(r^2) = -2F(r)\frac{dr}{dt} \tag{4.136}$$

The velocity of the moving molecule B can also be expressed in terms of its radial component (dr/dt) and its transverse component ($r\,d\theta/dt$) $= -r\,d\theta/dt$

Since in Fig.4.23, $\theta = 90° - \phi$ so that

$$c^2 = \left(\frac{dr}{dt}\right)^2 + \left(r\frac{d\phi}{dt}\right)^2$$

or $$c^2 = \left(\frac{dr}{dt}\right)^2 + \frac{h^2}{r^2} \qquad \text{by Eq. 4.133}$$

Substituting this value in Eq. 4.136, we get

$$\left(\frac{d^2r}{dt^2} - \frac{h^2}{r^3}\right) = -F(r) \tag{4.137}$$

Substituting the value of h from Eq. 4.134, this becomes

$$\left(\frac{d^2r}{dt^2} - \frac{c^2b^2}{r^3}\right) = -F(r)$$

To integrate this equation, multiply both sides by 2 $(dr/dt)dt$. This gives

$$\frac{d}{dt}\left(\frac{dr}{dt}\right)^2 dt + c^2b^2\frac{d}{dt}\left(\frac{1}{r^2}\right)dt = -2F(r)\frac{dr}{dt}dt$$

or $$d\left(\frac{dr}{dt}\right)^2 + c^2b^2 d\left(\frac{1}{r^2}\right) = -2F(r)dr$$

Integrating from $r = \infty$ to $r = r$, since at $r = \infty$, $\left(\frac{dr}{dt}\right)^2 = c^2$

$$c^2 - \left(\frac{dr}{dt}\right)^2 - \frac{c^2b^2}{r^2} = -2\int_r^\infty F(r)dr \tag{4.138}$$

At the closest point P of the orbit, the radius vector r has the smallest value so that the radial component of the velocity is the minimum $(dr/dt = 0)$. Calling this smallest value r_0, we have from Eq. 4.138

$$c^2 - \frac{c^2b^2}{r_0^2} = -2\int_r^\infty F(r)dr$$

or $$b^2 = r_0^2\left(1 + \frac{2}{c^2}\int_{r_0}^\infty F(r)dr\right) \tag{4.139}$$

The integral on the right hand side of Eq. 4.139 represents the potential energy at r_0, since at infinity the potential energy is zero. The second term inside the bracket gives the ratio of potential to the relative kinetic energy at r_0 of the moving molecule.

If the molecule moves in a forceless field, then $b = r_0$. From Eq. 4.139, we can obtain a measure of the effective collision cross section of a molecule. In order that two elastic spherical molecules may actually come in contact, the distance between their centres must be equal to σ_0 the diameter of the spherical molecules, that is, the value of r_0 in Eq. 4.139 must be equal to σ. Denoting the corresponding value of b by σ, we have

$$\sigma^2 = \sigma_0{}^2\left(1+\frac{2}{c^2}\int_{\sigma_0}^{\infty} F(r)dr\right) \tag{4.140}$$

Evidently, σ is greater than σ_0. If we draw a plane perpendicular to the direction of projection of a beam moving parallel to the x axis, then all molecules whose original directions of motion pass through the circle of radius σ_0 on this plane described round the centre of the fixed molecule would come into actual collision with the fixed molecule. The area of this circle is the collision cross section.

In the equation of mean path,

$$\lambda_M = \frac{1}{\sqrt{2}\pi\upsilon\sigma^2}$$

σ here should be replaced by its value given by Eq. 4.140, so that

$$\lambda_M = \frac{1}{\sqrt{2}\pi\upsilon\sigma_0{}^2\left(1+\frac{2}{c^2}\int_{\sigma_0}^{\infty} F(r)dr\right)} \tag{4.141}$$

The integral being definite is a constant quantity. Again, c^2 is proportional to the absolute temperature. Hence, Eq. 4.141 can be written as

$$\lambda_M = \frac{1}{\sqrt{2}\pi\upsilon\sigma_0{}^2\left(1+\frac{k}{T}\right)} \quad \text{where } k \text{ is a constant.} \tag{4.142}$$

Accordingly,

$$\eta = 0.499\upsilon m\bar{c}\lambda_M = \frac{0.499\rho\bar{c}}{\sqrt{2}\pi\upsilon\sigma_0{}^2\left(1+\frac{k}{T}\right)}$$

Now, $\bar{c}$ is proportional to $\sqrt{T}$. Let η_{T_0} and η_T be the coefficient of viscosity at temperatures T_0 and T, then

$$\eta_T = \eta_{T_0}\sqrt{\frac{T}{T_0}}\,\frac{1+\frac{k}{T_0}}{1+\frac{k}{T}} \tag{4.143}$$

Equation 4.143 is known as Sutherland's formula for viscosity at different temperatures. In the case of CO_2 this agrees very closely with experimental results within the range of temperature from 18 °C to 224 °C, the value of k for CO_2 being 277. It holds fairly for many other gases for limited range of temperature but fails hopelessly for hydrogen.

Reinganum supposed that on account of mutual attraction, the concentration of molecules in the neighbourhood of an attracting centre changes according to the following relation

$$\upsilon = \upsilon_0 \exp\left(-\int_r^{\infty} F(r)dr/kT\right)$$

This leads to the result

$$\eta = \frac{0.499\rho\bar{c}}{\sqrt{2}\pi\upsilon_0\sigma_0{}^2\exp\left(\frac{K}{T}\right)} \tag{4.144}$$

On expanding the exponential factor and retaining the first two terms, we obtain the Sutherland's formula.

A formula which fits better with the experimental results was given by Trautz and Binkele. This is

$$\eta=\frac{aT^n}{1+\dfrac{c}{T}} \tag{4.145}$$

Hasse and Cook based their calculation on the simultaneous existence of the forces of attraction and repulsion of the form

$$\phi(r)=Dr^{-m}-Gr^{-n}$$

They obtained the relation

$$\eta=\frac{5}{8}\left(\frac{\pi M}{2h}\right)^{\frac{1}{2}}(hG)^{\frac{-2/(n-1)}{D_1}} \tag{4.146}$$

where $h=(1/2)\,RT$, R is the gas constant and D_1 is a complicated function of D, G, m, n and k, with suitable values of m and n, this formula reduces to Sutherland's and Lennard–Jones formula. The equation was applied to Ar, H_2, N_2, Air, CO_2, Hg and Ne, and the results obtained were found to agree fairly well with the observed values.

Assuming the intermolecular force to be of repulsive nature $F(r)=\mu e^{-S}$, it can be proved that

$$\eta=AT^n$$

where A is a constant and $n=1/2+2/(s-1)$

It agrees fairly well with the observed values in the case of hydrogen, helium, and some other gases but fails in many cases.

4.8 VISCOSITY OF GASES AT LOW PRESSURES

The equations for the coefficient of viscosity of gases developed so far are found to be independent of pressure. This conclusion is also verified by experiments over wide ranges of pressure. Every expression for η is found to involve the mean free path λ. As the pressure of the gas is reduced, the collision between molecules becomes less frequent and the mean free path increases in length. When the value of λ is comparable with the dimensions of the containing vessel, the mathematical method of derivation of the formula necessarily fails.

The experimental methods of determination of η are generally based on Poisseuille's equation of flow of gas through a tube. In deriving this equation, it is assumed that the velocity of flow diminishes rapidly from the axis towards the inner wall of the tube, where the velocity is supposed to be zero. At very low pressures, the molecules collide directly with the wall of the tube and rebound with a definite velocity. This velocity can be resolved into a normal and a tangential component parallel to the wall of the tube. After collision the normal component is reversed, but the tangential component remains the same as before the collision (if the wall of the tube is supposed to be perfectly smooth). It follows that the velocity of flow at the inner wall is not zero and the molecules slip over the wall of the tube. This gives rise to the so-called coefficient of slip.

4.8.1 Evaluation of the Coefficient of Slip

Consider a long tube of length L and of uniform bore with internal radius R through which a gas is flowing under difference of pressures (p_1-p_2) at the two ends of the tube (Fig. 4.24). In the steady state, the lines of flow are parallel to the axis of the tube. Let us consider cylindrical layer of the gas parallel to the axis of the tube with inner and outer radii r and $r + \delta r$, respectively. The cross section of the layer is $2\pi r\delta r$. In the steady state, the driving force on the cross section is $2\pi r\ \delta r\ (p_1 - p_2)$. This is balanced by the viscous drag on the outer and the inner surfaces of the cylindrical layer. The viscous drag on the inner surface is

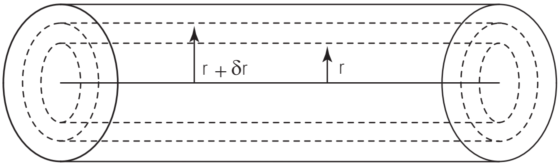

Fig. 4.24 Illustration of Poisseuille's method

$$F_r = 2\pi rL\eta\, dv/dr$$

where v is the velocity of flow at distance r from the axis. The viscous force on the outer surface of the layer is

$$F_{r+\delta r} = F_r + \frac{dF_r}{dr}\delta r = 2\pi rL\eta\frac{dv}{dr} + 2\pi L\eta\frac{d}{dr}\left(r\frac{dv}{dr}\right)\delta r \tag{4.147}$$

Hence, the resultant viscous force on the cylindrical layer is

$$2\pi L\eta\frac{d}{dr}\left(r\frac{dv}{dr}\right)\delta r$$

For steady motion of the gas,

$$2\pi r\delta r(p_1 - p_2) = -2\pi L\eta\frac{d}{dr}\left(r\frac{dv}{dr}\right)\delta r \tag{4.148}$$

or

$$-\frac{p_1 - p_2}{L\eta} = \frac{d^2v}{dr^2} + \frac{1}{r}\frac{dv}{dr} \tag{4.149}$$

The left hand side of Eq. 4.149 is constant. A particular solution of the differential equation may be taken to be

$$v = A + Br^2 \tag{4.150}$$

involving two constants A and B to be determined from the boundary conditions. From Eq. 4.150,

$$\left.\begin{aligned}&\frac{dv}{dr} = 2Br \text{ and } \frac{d^2v}{dr^2} = 2B\\ &\frac{1}{r}\frac{dv}{dr} + \frac{d^2v}{dr^2} = 4B = -\frac{p_1 - p_2}{l\eta}\end{aligned}\right\} \tag{4.151}$$

Substituting the value of B in Eq. (4.150), we get

$$v = A - \frac{p_1 - p_2}{4L\eta}r^2 \tag{4.152}$$

If $v = 0$ at $r = R$, then

$$A = \frac{p_1 - p_2}{4L\eta}R^2$$

so that

$$v = \frac{p_1 - p_2}{4L\eta}(R^2 - r^2)$$

The volume of the fluid flowing out of the tube per second is

$$V=\int_0^R 2\pi r v dr=\frac{\pi(p_1-p_2)}{2L\eta}\int_0^R r(R^2-r^2)dr$$

or
$$V=\frac{\pi(p_1-p_2)R^4}{8L\eta} \tag{4.153}$$

For a short tube, a correction term is to be added on account of turbulence at the edges of the tube.

Equation 4.153 evidently fails when the pressure difference (p_1-p_2) is either too large or too small. To take account of the slip at the inner wall of the tube, we assume that at $r=R$, $v=v_0$. This gives rise to frictional force at the wall which may be taken to be equal to $f=\in Sv_0$ where $S=2\pi RL$ and $\in$ is a numerical factor.

Thus, the total resisting force on a layer of thickness δr at the bounding wall is $-(f+2\pi RL\eta\,(dv/dr))$ and the condition for uniform motion is

$$2\pi R\delta r(p_1-p_2)=-f-2\pi RL\eta\frac{dv}{dr}$$

If δr is of infinitesimal thickness, then the left hand side is zero. So that

$$2\pi RL\eta\frac{dv}{dr}=-f=2\pi RL\in v_0$$

and
$$v_0=-\frac{\eta}{\in}\frac{dv}{dr}$$

But from Eq. 4.151
$$\frac{dv}{dr}=-\frac{r}{2}\frac{p_1-p_2}{L\eta}$$

so that
$$v_0=\frac{r}{\in}\frac{p_1-p_2}{2L} \tag{4.154}$$

Substituting the value of v_0 in Eq. 4.152

$$v_0=A-\frac{p_1-p_2}{4L\eta}R^2=\frac{R}{\in}\frac{p_1-p_2}{2L} \qquad \text{from Eq. 4.154}$$

$$\therefore \qquad A=\frac{p_1-p_2}{4L\eta}\left(R^2+\frac{2\eta R}{\in}\right)$$

Substituting the value in Eq. 4.152

$$v=\frac{p_1-p_2}{4L\eta}\left(R^2-r^2+\frac{2R\eta}{\in}\right)$$

Volume of liquid flowing through the tube per second is

$$V=\frac{\pi(p_1-p_2)R^4}{8L\eta}\left(1+\frac{4\eta}{\in R}\right) \tag{4.155}$$

The quantity $4\eta/\in$ is called the coefficient of slip. Denoting this by ζ, the volume flowing per second is

$$V=V_0\left(1+\frac{\zeta}{R}\right)$$

where V_0 is the volume flowing in the absence of slip.

4.9 COLLISIONS WITH A SOLID BOUNDARY: PRESSURE EXERTED BY A GAS INTRODUCING MEAN FREE PATH CONCEPT

In the kinetic theory of gases, it is supposed that the number density υ of the molecules is constant throughout the mass of the gas in equilibrium at constant temperature and the directions of motion of molecules are uniformly distributed in space.

To find the number of collisions per second on an element of area *ds* of the wall and there from the pressure exerted by the gas, we take a small volume *dv* of the gas at a distance *r* from the centre of the element *ds* considered on the *xy* plane, the radius vector *r* to *dv* from the centre of *ds* making an angle θ with the normal to *ds* (i.e., *z* axis) as shown in Figure 4.25.

The number of molecules within *dv* having velocity between *c* and $c + dc$ is $d\upsilon_c dv$. Let a molecule suffer ω collisions per second on an average where $\omega = c/\lambda c$, λ_c being the mean free path for these molecules.

In time *dt*, there are $d\upsilon_c dv\omega dt$ new paths starting out of volume *dv* along which the molecules come out. Since all directions are equally probable, the number moving in the direction of *ds* is the number of molecules in the direction of the solid angle subtended by the area at *dv*. The solid angle $d\Omega = ds\cos\theta/r^2$.

The number of molecules moving in the direction of unit solid angle is $d\upsilon_c dv\omega dt/4\pi$. Hence, the number moving in the direction of *ds* is

$$N'_{\theta d\Omega dt} = d\upsilon_c dv\omega dt\frac{ds\cos\theta}{4\pi r^2}$$

out of these molecules, the number which reach *ds* without suffering any further collision after leaving *dv* is

$$N_{\theta d\Omega dt} = d\upsilon_c dv\omega dt\frac{ds\cos\theta}{4\pi r^2}e^{-\frac{r}{\lambda}} \tag{4.156}$$

To find the total number of molecules striking the area *ds* in time *dt*, we have to integrate for all values of *dv*, all values of *c* from 0 to ∞, and all values of *r* from 0 to ∞. For this purpose, we express *dv* in terms of spherical polar coordinates so that $dv = r^2 \sin\theta\, d\theta\, d\phi\, dr$. We then integrate ϕ from 0 to 2π and θ from 0 to $\pi/2$. The total number of molecules striking the area *ds* in time *dt*

$$\frac{dsdt}{4\pi}\int_0^{\infty} c d\upsilon_c \int_0^{\frac{\pi}{2}} \sin\theta\cos\theta d\theta \int_0^{2\pi} d\phi \int_0^{\infty} \frac{e^{-\frac{r}{\lambda}}}{\lambda} dr$$

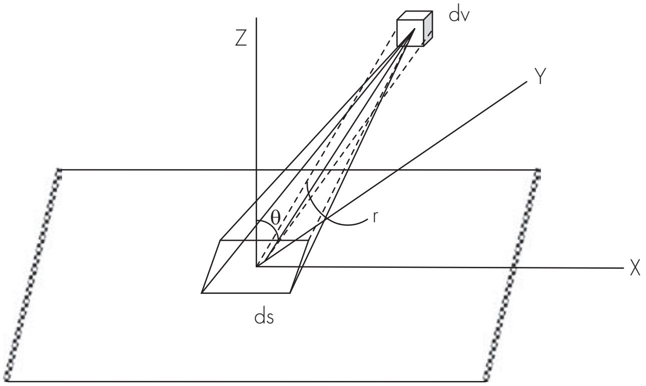

Fig. 4.25 Illustration of the theory

$$= \frac{dsdt}{4\pi}\upsilon\bar{c}\,\frac{1}{2}\,2\pi\frac{\lambda}{\lambda}$$

$$= \frac{\upsilon\bar{c}}{4}dsdt \tag{4.157}$$

The number of molecules striking unit area in unit time $= \upsilon\bar{c}/4\cdot$

In each collision, the change in momentum for the molecules having velocity c and coming from dv is $2mc\cos\theta$, so that total change in momentum imparted by all the molecules per unit area per second is

$$p = \frac{2m}{4\pi}\int_0^\infty c^2 d\upsilon_c \int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi\int_0^\infty\frac{e^{-\frac{r}{\lambda}}}{\lambda}dr$$

$$= \frac{2m}{4\pi}\upsilon c^{\bar{2}}\,\frac{1}{3}\,2\pi$$

$$= \frac{1}{3}m\upsilon c^2 \text{ where } c \text{ is the root mean square velocity.}$$

4.9.1 Knudsen's Cosine Law

The solid angle subtended by dv at the centre of ds is

$$d\Omega' = \sin\theta d\theta d\phi$$

From Eq. 4.156

$$N_{\theta d\Omega' dt} = \frac{d\upsilon_c\omega dtds(r^2\sin\theta d\theta d\phi dr)\cos\theta e^{-\frac{r}{\lambda}}}{4\pi r^2}$$

$$= \frac{d\upsilon_c\omega dtds(\sin\theta d\theta d\phi)\cos\theta}{4\pi}e^{-\frac{r}{\lambda}}dr$$

$$= d\upsilon_c\omega\frac{dtdsd\Omega'}{4\pi}\cos\theta e^{-\frac{r}{\lambda}}dr$$

The total number of molecules reaching ds in the direction of the solid angle formed by dv is

$$\frac{d\upsilon_c\omega}{4\pi}dtdsd\Omega'\cos\theta\int_0^\infty e^{-\frac{r}{\lambda}}dr$$

$$= d\upsilon_c\frac{\omega dtdsd\Omega'\lambda\cos\theta}{4\pi}$$

$$= cd\upsilon_c\frac{dtdsd\Omega'\cos\theta}{4\pi}$$

Number of molecules of all velocities reaching ds per second in the direction θ of the solid angle $d\Omega'$ is

$$\upsilon_\theta = \frac{\upsilon\bar{c}dsd\Omega'\cos\theta}{4\pi} \tag{4.158}$$

Equation 4.158 is known as Knudsen's cosine law. This is similar to the cosine law in photometry for diffuse reflection from irregular surfaces. In order that all directions of velocities of molecules in the neighbourhood of the solid boundary may be equally probable, the same number υ_θ of molecules must be leaving the same area *ds* per second in the same direction θ of approach before collision. This means that the direction of reflection of molecules is independent of the direction of incidence (as in the case of diffuse reflection of light). This led Knudsen to the hypothesis that the molecules colliding with a solid boundary are first absorbed and then re-evaporated.

Evidently, the probability of a molecule leaving a particular area *ds* in the direction θ with the normal to the area at the point of incidence is

$$p_\theta = \frac{\overline{c}}{4\pi} ds d\Omega' \cos\theta \tag{4.159}$$

Knudsen verified his hypothesis of the cosine law by the following experiment. A parallel beam of mercury vapour was let into a glass sphere through a small opening in its wall, impinging straight on a wall of area *ds* (Fig. 4.26).

This area *ds* was kept at room temperature while the rest of the surface was maintained at the temperature of the liquid air. The molecules reflected from the area *ds* were condensed on coming in contact with the cooler part of the wall of the sphere and formed a layer of uniform thickness all over the inner wall.

In the case of reflection from a crystal surface where the molecules are regularly spaced and oriented the reflection was found to be specular or regular, that is, there was no diffuse reflection.

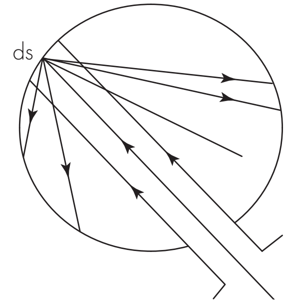

Fig. 4.26 Knudsen's experiment for verification of cosine law

Knudsen's theory of streaming: An immediate consequence of Knudsen's theory is that the molecules diffusively scattered in all directions from the solid boundary impart no momentum to the wall in the tangential direction because on an average, the tangential components of velocities of molecules leaving the surface are as often positive as negative. Therefore, the tangential momentum transferred to the wall is only due to the colliding molecules. Let *n* be the number of molecules striking the surface in a given direction. Let *m* be the mass of the molecules and *w* their tangential component of velocity. Then, the momentum transferred to the wall by these molecules is *nmw.*

Let υ be the number of molecules per cubic centimetre. Out of these molecules the number which has velocities lying between *c* and *c* + *dc* is

$$d\upsilon = \frac{4\upsilon}{\sqrt{\pi}\delta^3} c^2 e^{-\frac{c^2}{\delta^2}} dc \tag{4.160}$$

where δ is the most probable velocity. The number of molecules of this group which strike unit area of the solid wall in unit time is given by Eq. 4.157, 1/4$cd\upsilon$. The momentum transferred to the wall in unit time in the tangential direction of this group is

$$\frac{1}{4} c d\upsilon m w \tag{4.161}$$

In the case of a gas streaming through a narrow tube (whose diameter is small compared to the mean free path) under a difference of pressure applied at the two ends, the flow of gas down the tube is not due to the streaming motion combined with random thermal motion of the molecules; it is due to the thermal motion and interdiffusion on account of variation of pressure along the length of the tube. Under this condition, the numbers of molecules moving through a cross section of the tube in opposite directions are not the same so that there is net balance of flow in the direction of fall of pressure.

Knudsen assumes that w in Eq. 4.161 depends on c and is proportional to it or $w = kc$ where k is the constant of proportionality independent of c. Substituting the value of w in Eq. 4.161 the momentum transferred to the wall by collision of molecules moving with velocity c is

$$\frac{1}{4}kc^2 m d\upsilon$$

Substituting the value of $d\upsilon$ from Eq. 4.160, the momentum transferred by molecules moving with all possible velocities is

$$B = \frac{\upsilon km}{\sqrt{\pi}}\int_0^\infty \frac{c^4}{\delta^3} e^{-\frac{c^2}{\delta^2}}\, dc = \frac{3}{8}\upsilon km\,\delta^2 \tag{4.162}$$

Again, $\delta^2 = \dfrac{\pi \overline{c}^2}{4}$

where $\overline{c}$ is the arithmetical average

$$\therefore \quad B = \frac{3\pi}{32}\upsilon km\,\overline{c}^2 \tag{4.163}$$

Also, $\overline{c} = \dfrac{\Sigma c}{\upsilon}$ so that $\quad k\overline{c} = \dfrac{\Sigma kc}{\upsilon} = \dfrac{\Sigma w}{\upsilon} = v$

where v, is the velocity of mass of the gas parallel to the length of the tube. Substituting the value of $k\overline{c} = v$ in Eq. 4.163, see copy

$$B = \frac{3\pi}{32}\upsilon m v\,\overline{c} \tag{4.164}$$

Let O be the circumference of cross section of the cylindrical tube of uniform bore and dl be a small element of length of the tube. Then, the momentum transferred to the area $O.\,dl$ in time dt is

$$\frac{3\pi}{32} O\, dl \upsilon m v\,\overline{c}\, dt \tag{4.165}$$

By Maxwell's law $\overline{c} = \sqrt{\frac{8p}{\pi\rho}}$, substituting in Eq. 4.165, the momentum transferred to the element of area $O\, dl$ in time dt is

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\,\rho\,\sqrt{\frac{p}{\rho}}\, v\, O\, dldt$$

The force exerted by the element of area on the streaming gas is the rate of change of momentum and is equal to

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\,\rho\sqrt{\frac{p}{\rho}} v\, O\, dl$$

In the steady state of flow, this is balanced by pressure difference dp at the two end faces of the element dl. If A be the area of cross section of the tube, then the condition of steady flow is

$$\frac{3}{8}\sqrt{\frac{\pi}{2}}\;\rho\sqrt{\frac{p}{\rho}}v\;\;O=-A\frac{dp}{dl}$$

The quantity of gas which flows through the tube in unit time is

$$M=A\rho v=-\frac{8}{3}\sqrt{\frac{2}{\pi}}\sqrt{\frac{\rho}{p}}\frac{A^2}{O}\;\;\frac{dp}{dl}$$

Let the density of the gas per unit pressure be $\rho_1=\rho/p$, then the volume V of gas flowing per second is M/ρ_1

$$V=-\frac{8}{3}\sqrt{\frac{2}{\pi}}\;\;\frac{1}{\sqrt{\rho_1}}\frac{A^2}{O}\;\;\frac{dp}{dl} \tag{4.166}$$

For steady flow, V has the same value all over the tube. For a cylindrical tube of circular cross section of radius R,

$$\frac{A^2}{O}=\frac{(\pi R^2)^2}{2\pi R}=\frac{\pi R^3}{2}\text{ and }-\frac{dp}{dl}=\frac{p_1-p_2}{L}\qquad p_1>p_2$$

Substituting the value of A^2/O in Eq. (4.166), we get

$$V=\frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{R^3}{L}(p_1-p_2)$$

This can be written as

$$V=\frac{p_1-p_2}{\frac{4}{3}\frac{1}{\sqrt{2\pi}}\sqrt{\rho_1}\frac{L}{R^3}}=\frac{p_1-p_2}{W} \tag{4.167}$$

Representing the denominator of Eq. 4.167 by W, the equaltion is similar to the Ohm's law in current electricity. Here, W is the resistance of the tube to the flow of the gas. This equation differs materially from Eq. 4.155 involving coefficient of slip. It will be seen that at very low pressures, the volume flowing is proportional to R^3 and not to R^4. Also, V is independent of η and p.

4.9.2 Knudsen's Experiment

The apparatus used by Knudsen is shown in the Figure 4.27.

G_1 and G_2 are the two Mcleod gauges which can measure the pressure of gas in the respective reservoirs V_1 and V_2. The capillary tube under study is fixed between a_1 and a_2. u_1 and u_2 are the U tubes; u_1 is graduated and the whole apparatus is connected to a pump through one arm of u_2. g_1, g_2, g_3 and g_4 are connected to mercury reservoirs by rubber tubing. By changing the position of these reservoirs, the position of mercury column can be adjusted in each tube. Through H, the apparatus is connected to the reservoir of experimental gas.

The mercury in the tubes g_1, g_2, g_3 and g_4 are allowed to fall below the bends and the whole apparatus is evacuated by means of the pump. Then by adjusting the stop cock at H, the experimental gas is introduced in the apparatus at the desired pressure. The stop cock is closed and by raising the mercury reservoir connected to g_3, the mercury column is brought to the position a_1, a_2; the two reservoirs, V_1 and V_2, are cut off from each

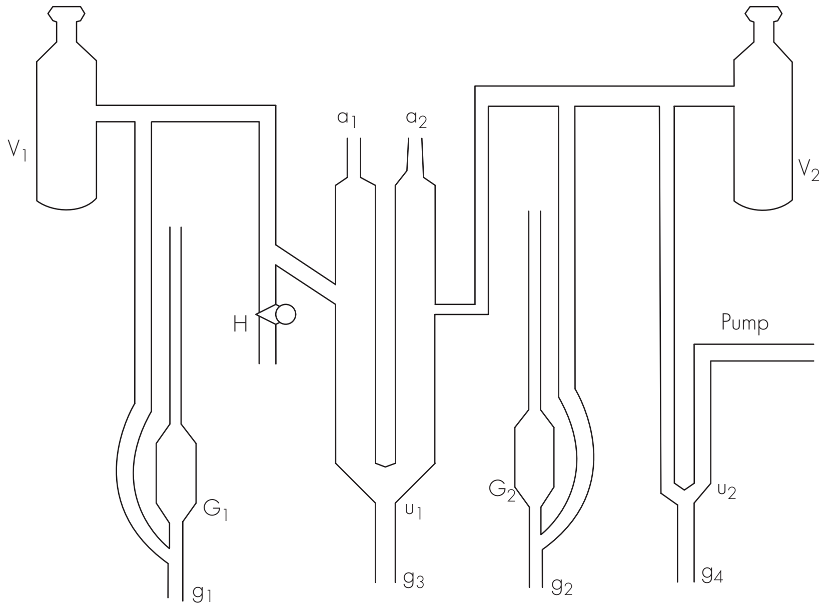

Fig. 4.27 Knudsen's apparatus

other. The pressure p_1 of the gas at reservoir V_1 is measured by G_1. The pressure of the gas in V_2 is further lowered by the pump and the corresponding pressure p_2 is measured by G_2. Then by lowering the mercury reservoir connected to g_3, the mercury column is adjusted to a position at the U tube in u_1 such that the two reservoirs V_1 and V_2 are connected to each other only through the capillary tube between a_1 and a_2. The gas is allowed to flow through the tube for a measured time and then the flow is cut off by raising the mercury column to the position a_1, a_2. The final pressures of the gas in V_1 and V_2 are measured. From the initial and final pressures and the volumes of reservoirs V_1 and V_2 together with the connecting tubes, the volume of the gas flowing from V_1 and V_2 through the capillary tube under study can be calculated.

Knudsen studied the flow of carbon dioxide through 24 capillary tubes of different dimensions. His experimental results are shown in Fig. 4.28 which gives a plot of $\log_e \lambda/r$ versus $\log_e T_0$ where

$$T_0 = \frac{4}{3}\sqrt{\frac{2\pi}{\rho_1}}\frac{R^3}{L}$$

represents the volume of the gas flowing through the capillary tube per unit difference of pressure measured at a pressure of 1 dyne. λ is inversely proportional to the pressure of the gas.

From the curve, it is found that the volume of gas flowing out at ordinary pressure decreases rapidly with the decrease of pressure according to

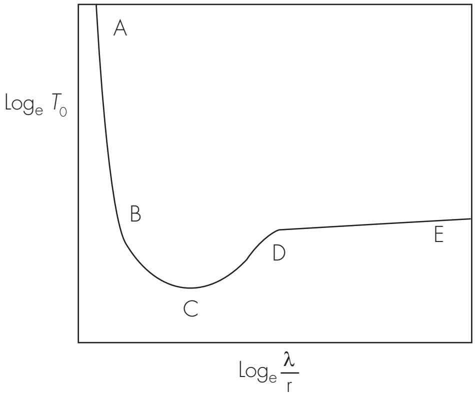

Fig. 4.28 Knudsen's experimental results

Poiseuille's law (portion *AB* of the curve). After this, the decrease is not so rapid (portion *BC* of the curve). This is in agreement with the observation of Kundt and Warburg. As the pressure is decreased further, the volume of gas flowing out increases (portion *CD* of the curve) and, ultimately, it remains constant at very low pressure (portion *DE* of the curve) which represents molecular streaming.

It has been found that the empirical relation $T_0 = ap + b(1 + c_1p/1 + c_2p)$ fits the entire experimental results where a, b, c_1 and c_2 are the constants which can be determined by least square fitting. The portion of the curve corresponding to different pressure region is considered. The expression for T_0 is modified accordingly, and it has been found that the observed values of the constant found from least square fitting are in accordance with the calculated values of the constants. This confirms Knudsen's theory.

4.10 KINETIC THEORY OF CONDUCTION OF HEAT THROUGH A GAS

In the simple calculation of heat conduction through a gas deduced from the transport theorem, it was assumed that out of the total number of molecules contained in a cubical box, one-sixth of the molecules move in a direction perpendicular to each face of the box. In the following deduction, we shall suppose that

1. the temperature of the gas increases in the direction of the z axis.
2. the mean energy of a molecule in any layer perpendicular to the z axis is that appropriate to the temperature of that layer.
3. the molecules moving in all possible directions have the same average velocity $\bar{c}$.

Let us fix our attention on the molecules which cross unit area of the plane $z_1 = z_0$. We shall call this plane the zero plane. Let molecule cross the zero plane in a direction θ after suffering its last collision at a distance equal to its mean free path λ, (Fig. 4.29). These molecules, therefore, come from a plane at a distance $z_2 = z_0 - \lambda\cos\theta$ below the zero plane. If the mean energy in the zero plane is E, then that in the plane z_2 is $E - \lambda\cos\theta\,(dE/dz)$.

Let υ_θ be the number of molecules per unit volume which move in the direction θ to $\theta + d\theta$ with the z axis. Then, the number of molecules which cross the area ds in the zero plane in the direction θ is equal to the number which lie inside a cylinder of cross section $ds\cos\theta$ and of length equal to $\bar{c}$, that is,

$$\upsilon_\theta \bar{c} ds \cos\theta$$

If υ be the total number of molecules per *cc*, then the number of molecules moving in the directions θ to $\theta + d\theta$ is

$$\upsilon_\theta = \frac{2\pi\bar{c}^2 \upsilon \sin\theta d\theta}{4\pi\bar{c}^2} = \frac{1}{2}\upsilon \sin\theta d\theta$$

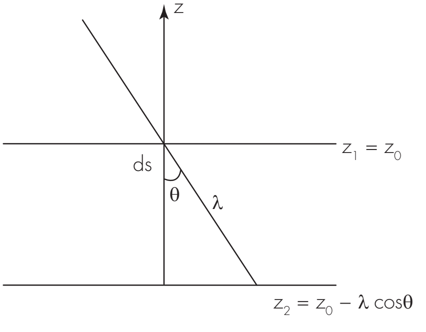

Fig. 4.29 Illustrating molecular collision

The number crossing the area *ds* in the specified direction is

$$\frac{1}{2}\upsilon \sin\theta d\,\theta \bar{c} ds \cos\theta$$

The energy transferred across unit area of the zero plane in all possible directions is

$$\frac{1}{2}\upsilon\bar{c}\int_0^{\pi}\left(E-\lambda\cos\theta\frac{dE}{dz}\right)\sin\theta\cos\theta d\theta$$

$$=\frac{1}{2}\upsilon\bar{c}E\int_0^{\pi}\sin\theta\cos\theta d\theta-\frac{1}{2}\upsilon\bar{c}\lambda\frac{dE}{dz}\int_0^{\pi}\cos^2\theta\sin\theta d\theta$$

$$=-\frac{1}{3}\upsilon\bar{c}\lambda\frac{dE}{dz}$$

$$=-\frac{1}{3}\upsilon\bar{c}\lambda\frac{dE}{dT}\frac{dT}{dz}$$

By experimental definition of conductivity, flow of energy through unit area per second is $-JK\,(dT/dz)$

so that
$$-JK\frac{dT}{dz}=-\frac{1}{3}\upsilon\bar{c}\lambda\frac{dE}{dT}\frac{dT}{dz} \tag{4.168}$$

Now,
$$c_v=\frac{1}{Jm}\frac{dE}{dT} \tag{4.169}$$

Also,
$$\eta=\frac{1}{3}\upsilon\bar{c}\lambda \tag{4.170}$$

Substituting Eqs 4.169 and 4.170 in Eq. 4.168, we get

$$K=\eta c_v \tag{4.171}$$

In this calculation, we have not considered the variation of density of the gas and the change of velocity of molecules with temperature. Instead of supposing that all molecules move with same velocity, Maxwellian distribution should be used. Further, the mean free path should be replaced by all probable values of free paths. All these modifications introduce a correction factor $\in$ whose value varies from 1 to 2.57 depending on the method of mathematical analysis.

4.10.1 Evaluation of Coefficient of Heat Conduction Considering the Distribution of Free Path and Velocities

We consider a vertical column of gas in which uniform temperature gradient has been set up in the vertical direction of the *z* axis, the layers parallel to the *xy* planes being at uniform temperatures. Let the temperature of the *xy* plane through $z = 0$ (the zero plane) be T_0. Then, the temperature of plane at height *z* is $T = T + z\,dT/dz$ (Fig. 4.30).

Let us consider a small element of volume *dv* at a height $z(= r\cos\theta)$ above the zero plane. Let υ be the number of molecules per *cc* of the gas. The number of molecules per *cc* having velocity lying between *c* and $c + dc$ is $d\upsilon_c$. Then, the number of molecules in volume *dv* having velocity lying between *c* and $c + dc$ is $d\upsilon_c dv$.

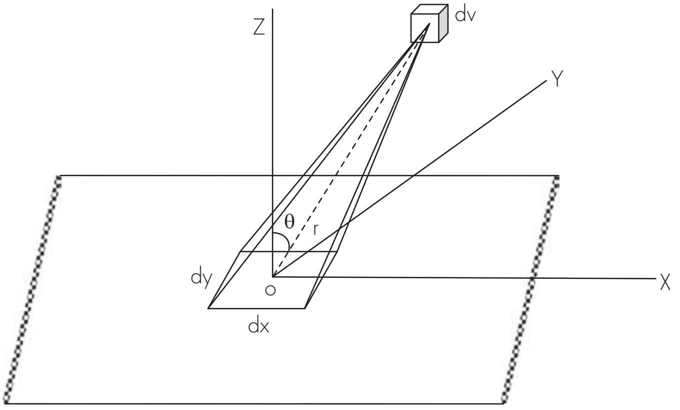

Fig. 4.30 Illustration for evaluation of coefficient of heat conduction

Let the molecules in *dv* moving with velocity *c* suffer w $= c/\lambda$ collisions per second where λ is the mean free path. In time *dt,* there are $d\upsilon_c dvwdt$ new paths starting out of volume *dv* along which the molecules come out. Since all directions are equally probable, the number of new paths for molecules moving with velocity *c* is $d\upsilon_c dvwdt/4\pi$ per unit solid angle. The number of molecules having velocity *c* and crossing the area *dxdy* at the zero plane is

$$N_1 = d\upsilon_c \frac{dvwdtdxdy\cos\theta}{4\pi r^2}$$

as the solid angle subtended by area *dxdy* at *dv* is $dxdy\ cos\ \theta/r^2\ dxdy\cos\theta/r^2$

Out of these N_1 molecules, the number traversing the distance *r* without collision is

$$N_2 = \frac{d\upsilon_c dvwdtdxdy\cos\theta}{4\pi r^2} e^{-\frac{r}{\lambda}}$$

or

$$N_2 = \frac{cd\upsilon_c dvdtdxdy\cos\theta}{4\pi r^2\lambda} e^{-\frac{r}{\lambda}}$$

We assume that the molecules on an average have the temperature appropriate to the sum of its last collision. Each molecule of mass *m* coming from the height *z* above the zero plane will carry energy of amount

$$Jmc_v\left(T_0 + r\cos\theta\frac{dt}{dz}\right)$$

Hence, energy transferred through *dxdy* from *dv* in time *dt* by the molecules having velocity between *c* and $c + dc$ is

$$Edv\ dt = -\frac{cd\upsilon_c dv\ dt\ dx\ dy\cos\theta}{4\pi r^2\lambda} e^{-\frac{r}{\lambda}}\ Jmc_v\left(T_0 + r\cos\theta\frac{dt}{dz}\right)$$

The –ve sign indicates that the energy is transferred from high temperature to low temperature region.

To find the total energy transferred through *dxdy* from all elements like *dv* above *dxdy* by molecules having all possible velocities, we express *dv* in terms of spherical polar coordinates

$$dv = r^2 \sin\theta d\theta d\phi dr$$

and integrate for all possible values of r, θ, ϕ and c. This gives

$$E_1 = -Jm\frac{dxdydt}{4\pi}c_v\left(T_0\int_0^\infty cdv_c\int_0^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_0^{2\pi}d\phi\int_0^\infty\frac{e^{-\frac{r}{\lambda}}}{\lambda}dr\right.$$

$$\left.+\frac{dT}{dz}\int_0^\infty cdv_c\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi\int_0^\infty r\frac{e^{-\frac{r}{\lambda}}}{\lambda}dr\right)$$

Similarly, the amount of energy transferred through *dxdy* from the portion of the gas below the element of area is

$$E_2 = Jm\frac{dxdydt}{4\pi}c_v\left(T_0\int_0^\infty cdv_c\int_0^{\frac{\pi}{2}}\cos\theta\sin\theta d\theta\int_0^{2\pi}d\phi\int_0^\infty\frac{e^{-\frac{r}{\lambda}}}{\lambda}dr\right.$$

$$\left.-\frac{dT}{dz}\int_0^\infty cdv_c\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi\int_0^\infty r\frac{e^{-\frac{r}{\lambda}}}{\lambda}dr\right)$$

This is because at the plane, $T = T_0 - r\cos\theta\frac{dT}{dz}$.

The net transfer of energy through *dxdy* in time *dt* is

$$E = E_1 + E_2 = -\frac{2mc_v dxdydt}{4\pi}J\frac{dT}{dz}\int_0^\infty cdv_c\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta\int_0^{2\pi}d\phi\int_0^\infty\frac{re^{-\frac{r}{\lambda}}}{\lambda}dr$$

$$= -\frac{2mc_v dxdydt}{4\pi}\bar{c}\upsilon\frac{1}{3}2\pi\lambda J\frac{dT}{dz}$$

$$= -\frac{1}{3}m\upsilon\bar{c}\lambda c_v dxdydt\, J\frac{dT}{dz} \tag{4.172}$$

Therefore, the quantity of heat transferred through the zero plane per unit area per second is

$$\frac{dQ}{dt} = -\frac{1}{3}m\upsilon\bar{c}\lambda c_v\frac{dT}{dz} \tag{4.173}$$

By definition, the coefficient of heat conduction K is given by

$$\frac{dQ}{dt} = -K\frac{dT}{dz}$$

Therefore,

$$K = -\frac{1}{3}\upsilon m\bar{c}\lambda c_v = \eta c_v \tag{4.174}$$

where η is the coefficient of viscosity.

This method of derivation of the value of K is not general for the following reasons:

Firstly, it assumes the validity of Maxwell's distribution law of velocities which is only applicable to the equilibrium state. Secondly, on account of variation of temperature, the density of the gas must change in the direction of the z axis. Rigorous treatment of the problem introduces a coefficient $\in$ such that

$$K = \in \eta c_v$$

where the value of $\in$ ranges from 1 to 2.57 depending on the method of mathematical analysis.

Chapman and Enskog following Maxwell's method discussed rigorously the transport of energy by spherically symmetric (monatomic) molecules and showed that $K/\eta c_v = 5/2$. This is in agreement with the experimental results.

Polyatomic molecules have energy due to translational motion (E_t) as well as due to internal motion (E_r). Thus, transfer of both types of energy must be taken into account. Considering this, Eucken gave an expression for $\in$. He assumed that the translational energy transfer is 5/2 times that given by Eq. 4.172, while the transfer of other forms of energy is given by Eq. 4.172. So, the total energy transfer per unit area per second is

$$-\left(\frac{5}{2}\frac{dE_t}{dz} + \frac{dE_r}{dz}\right)\frac{1}{3}\upsilon\bar{c}\lambda \tag{4.175}$$

$$\therefore \qquad -JK\frac{dT}{dz} = -\frac{1}{3}\upsilon\bar{c}\lambda\left(\frac{5}{2}\frac{dE_t}{dT} + \frac{dE_r}{dT}\right)\frac{dT}{dz}$$

$$\therefore \qquad K = \frac{\eta}{Jm}\left(\frac{5}{2}\frac{dE_t}{dT} + \frac{dE_r}{dT}\right) \tag{4.176}$$

Let the total number of degrees of freedom be $3 + 3\beta$ where 3 is due to translational motion and 3β is other than due to translational motion. So, the average energy of a molecule at temperature T is

$$E = E_t + E_r = \frac{3}{2}kT + \frac{3\beta}{2}kT$$

$$\frac{dE_t}{dT} = \frac{3}{2}k \text{ and } \frac{dE_r}{dT} = \frac{3\beta}{2}k$$

$$\therefore \qquad \frac{K}{\eta} = \frac{1}{Jm}\left(\frac{5}{2}\frac{3}{2}k + \frac{3}{2}\beta k\right) = \frac{k}{Jm}\left(\frac{15}{4} + \frac{3}{2}\beta\right) \tag{4.177}$$

Let M be the molecular weight of the gas and c_p, c_v be the specific heats at constant pressure and at constant volume, respectively, then

$$c_p - c_v = \frac{R}{JM} = \frac{R}{NJ\dfrac{M}{N}} = \frac{k}{Jm}$$

Dividing by c_v

$$\gamma - 1 = \frac{k}{Jmc_v}$$

Again,

$$c_v = \frac{1}{Jm}\frac{dE}{dT} = \frac{1}{Jm}\frac{3}{2}k(1+\beta) \tag{4.178}$$

$$\gamma - 1 = \frac{k}{Jm}\frac{2Jm}{3k(1+\beta)} = \frac{2}{3(1+\beta)}$$

or $$(1+\beta) = \frac{2}{3(\gamma-1)}$$

From Eq. 4.177

$$\frac{K}{\eta} = \frac{k}{Jm}\left(\frac{15}{4} + \frac{3}{2}\left[\frac{2}{3(\gamma-1)} - 1\right]\right)$$

$$= \frac{k}{Jm}\left(\frac{15}{4} + \frac{1}{\gamma-1} - \frac{3}{2}\right) = \frac{k}{Jm}\left(\frac{9\gamma-5}{4(\gamma-1)}\right)$$

From Eq. 4.178

$$c_v = \frac{1}{Jm}\frac{3}{2}k\frac{2}{3(\gamma-1)} = \frac{k}{Jm}\frac{1}{\gamma-1}$$

$$\therefore \quad \frac{K}{\eta} = \frac{(9\gamma-5)}{4}c_v$$

$$\therefore \quad \frac{K}{\eta c_v} = \frac{9\gamma-5}{4} = \in \tag{4.179}$$

This relation for $\in$ is in fair agreement with experimental observation.

Thus, $K = \in \eta c_v$; neglecting variation of $\in$ and c_v with pressure and temperature, it may be said that K varies with pressure and temperature in the same manner as does η. Thus, K should be independent of pressure. This was confirmed experimentally by Stefan and others. However at very high and low pressure, K is not independent of pressure. At very low pressure where the mean free path is comparable to the dimension of the vessel, the mechanism of heat transfer is different from the one considered here. Again, K should be proportional to $\sqrt{T}$, but it is found to vary much more rapidly. The reason is the same as in the case of viscosity. The nature of variation of K with temperature is, however, different in different experiments.

4.10.2 Conduction of Heat Through Rarefied Gases

In the treatment mentioned earlier, we have considered (a) conduction of heat through gases at ordinary pressure. Like viscosity of gases, we have also to consider conduction of heat (b) at intermediate pressure and (c) at very low pressures.

Conduction of Heat at Intermediate Pressure

It was suggested by Poisson that at intermediate pressure, there is a temperature discontinuity at a wall bounding a gas through which there is a temperature gradient like that of viscous slip. According to him, the discontinuity can be expressed by

$$T_k - T_w = g\frac{dT}{dn}$$

where T_w is the wall temperature, dT/dn is the temperature gradient along the outward drawn normal to the wall, T_k is the temperature of the gas at the wall had there been no discontinuity of temperature at the wall, g is the constant known as the temperature jump distance. Smoluchowski and Knudsen studied the temperature jump thoroughly and gave an expression for g in terms of the interaction of the molecule with the surface. It is mainly caused by the fact that the energy exchange between the wall and the colliding gas molecules is only partial.

Conduction of Heat at Very Low Pressure

We reproduce below Knudsen's theory of conduction of heat through a gas at very low pressures. Here, the gas is supposed to be placed between a hot plate A_1 at temperature T_1 and a cold plate A_2 at temperature T_2. At very low pressures, the mean free path becomes comparable with the thickness of the air plate so that the collision between molecules becomes rare. Such conduction of heat is called free molecule or molecular heat conduction. It is supposed that the molecules leaving the surface of a plate acquire the temperature of that plate. This requires the surfaces of the plates to be absolutely rough. The molecules striking these surfaces rebound back and forth several times between their minute projections so as to acquire velocities corresponding to temperatures of these surfaces.

Let $d\upsilon_1$ be the number of molecules with velocities lying within the range c_1 and $c_1 + dc_1$ moving from the plate A_1 in the direction of the plate A_2. If $d\upsilon$ be the number of molecules per *cc*, then the number striking unit area of the plate A_2 per second is given by Eq. 4.157 equal to 1/4 $d\upsilon c_1$. Since the molecules concerned are only those lying on one side of the plate A_1, $d\upsilon_1 = d\upsilon/2$ so that the number of molecules striking unit area of the plate A_2 in 1 second is 1/2 $d\upsilon_1 c_1$. If m be the mass of each molecule, the translational energy delivered to unit area of the plate A_2 in 1 second is

$$dE_1 = \frac{1}{2} d\upsilon_1 c_1 \left(\frac{1}{2} mc_1^2 \right) = \frac{m}{4} d\upsilon_1 c_1^3 \tag{4.180}$$

By Maxwell–Boltzmann law of distribution of velocities,

$$d\upsilon_1 = 4\pi\upsilon_1 \alpha^3 e^{-\beta c_1^2} c_1^2 dc_1$$

Total energy delivered to unit area of plate A_2 per second by molecules moving with all possible velocities is

$$\begin{aligned} E_1 &= \frac{m}{4} \int_0^\infty 4\pi\upsilon_1 \alpha^3 e^{-\beta c_1^2} c_1^5 dc_1 \\ &= \frac{m}{4} 4\pi\upsilon_1 \alpha^3 \int_0^\infty e^{-\beta c_1^2} c_1^5 dc_1 \\ &= \frac{m}{4} 4\pi\upsilon_1 \alpha^3 \frac{1}{\beta^3} = \frac{m}{4} 4\pi\upsilon_1 \left(\frac{\beta}{\pi} \right)^{\frac{3}{2}} \frac{1}{\beta} \end{aligned}$$

$$= \frac{m\upsilon_1}{\sqrt{\pi\beta}} \; \frac{1}{\beta} = \frac{m\upsilon_1}{\sqrt{\dfrac{\pi m}{2kT_1}} \; \dfrac{m}{2kT_1}} = \upsilon_1 kT_1 \sqrt{\frac{8kT_1}{\pi m}} = \upsilon_1 kT_1 \overline{c_1} \tag{4.181}$$

Similarly, the amount of translational energy falling on unit area of A_1 per second is

$$E_2 = \upsilon_2 kT_2 \overline{c}_2 \tag{4.182}$$

The amount of energy received by unit area of A_2 from A_1 per second is E_1 and that received by unit area of A_1 from A_2 is E_2. Since the mass of the plates A_1 and A_2 are equal, the net amount of energy received by unit area of A_1 in 1 second is

$$E_t = E_1 - E_2 = k(\upsilon_1 \bar{c}_1 T_1 - \upsilon_2 \bar{c}_2 T_2) \tag{4.183}$$

The number of molecules that strike unit area of A_2 per second is $1/2\upsilon_1\bar{c}_1$ where υ_1 is the number of molecules per *cc* having average velocity $\bar{c}_1$ directed towards the plate A_2. Similarly, the number striking unit area of plate A_1 per second is $1/2\upsilon_2\bar{c}_2$. In the equilibrium state the number of molecules arriving and leaving unit area of the plate A_1 or A_2 must be equal, so that

$$\upsilon_1\bar{c}_1 = \upsilon_2\bar{c}_2 \tag{4.184}$$

Again in order that the pressure in the space between the plates may remain constant, the number of molecules entering the space from outside per second must be equal to the number leaving the space in the same time. If S be the area of the edges, then the number of molecules leaving the space is $1/4(\upsilon_1\bar{c}_1 S + \upsilon_2\bar{c}_2 S)$. The number entering the space is $1/4\upsilon\bar{c}S$ where υ is the number density of molecules in the outside space having average velocity $\bar{c}$.

Then,
$$\frac{1}{4}(\upsilon_1\bar{c}_1 S + \upsilon_2\bar{c}_2 S) = \frac{1}{4}\upsilon\bar{c}S$$

or
$$\upsilon_1\bar{c}_1 + \upsilon_2\bar{c}_2 = \upsilon\bar{c}$$

By Eq. 4.184,
$$2\upsilon_1\bar{c}_1 = \upsilon\bar{c}$$

so that
$$\upsilon_1\bar{c}_1 = \upsilon_2\bar{c}_2 = \frac{1}{2}\upsilon\bar{c}$$

Substituting these values in Eq. 4.183, we get

$$E_t = E_1 - E_2 = \frac{1}{2}k\upsilon\bar{c}(T_1 - T_2) \tag{4.185}$$

If the molecule possesses energies other than translational (such as rotational and vibrational) and if E_{r1} and E_{r2} be their values at temperatures T_1 and T_2, then the loss of energy due to this is

$$E_r = \frac{1}{4}\upsilon\bar{c}(E_{r1} - E_{r2})$$

Hence, the total loss of energy due to conduction is

$$E = E_t + E_r$$

or
$$E = \frac{1}{2}\upsilon\bar{c}k(T_1 - T_2) + \frac{1}{4}\upsilon\bar{c}(E_{r1} - E_{r2}) \tag{4.186}$$

It can be proved that

$$\gamma = \frac{C_p}{C_v} = \frac{E_t + E_r + kT}{E_t + E_r}$$

Also,
$$E_t = \frac{3}{2}kT$$

Solving for E_t, we get

$$E_r = \frac{5-3\gamma}{\gamma-1}\frac{1}{2}kT$$

We have $$E_{r1}-E_{r2}=\frac{k}{2}\frac{5-3\gamma}{\gamma-1}(T_1-T_2)$$

Substituting the value of $(E_{r1}-E_{r2})$ in Eq. 4.186, we get for the total loss of heat from the plate A_1

$$E=\frac{1}{8}\upsilon\bar{c}k\frac{\gamma+1}{\gamma-1}(T_1-T_2)\text{ ergs} \tag{4.187}$$

Now, $$\bar{c}=\sqrt{\frac{8kT}{\pi m}}=\sqrt{\frac{8RT}{\pi Nm}}=\sqrt{\frac{8RT}{\pi M}}$$

where M is the molecular weight and N the Avogadro's number.

Substituting the value of $\bar{c}$ in Eq. 4.187, we get

$$E=\frac{1}{4}\upsilon k\sqrt{\frac{2kT}{\pi M}}\frac{\gamma+1}{\gamma-1}(T_1-T_2)\text{ ergs}$$

Substituting the value of υK from equation $p=\upsilon kT$

$$E=\frac{1}{4}\sqrt{\frac{2R}{\pi}}\frac{\gamma+1}{\gamma-1}\frac{T_1-T_2}{\sqrt{MT}}p\text{ ergs} \tag{4.188}$$

4.10.3 The Accommodation Coefficient

The quantity of heat transferred from the hot plate to the cold plate is thus proportional to the difference of temperature of the plates and to the pressure of the gas. Experimentally, it was found that the amount of heat transferred was less than that given by Eq. 4.188. To explain this Knudsen, following Smoluchowski, introduced what is known as accommodation coefficient represented by a. According to Smoluchowski, the surfaces of the plates are not molecularly rough, so that the molecules leaving a plate after collision do not acquire the temperature of the plate but only a fraction a of the difference of temperature of the plate and that of the molecules before collision. Let E_{inc} and E_{ref} denote the energies of the incident and reflected molecules, respectively and E_{plate} the energy corresponding to the temperature of a plate, then

$$E_{ref}-E_{inc}=a\,(E_{plate}-E_{inc})$$

Since energy E is proportional to absolute temperature, we have

$$T_{ref}-T_{inc}=a\,(T_{plate}-T_{inc}) \tag{4.189}$$

Let T_1' and T_2' be the temperatures of molecules reflected from the plates at temperatures T_1 and T_2, respectively. Referring to plate A_1 at temperature T_1, the molecules incident on A_1 are those coming from A_2 and have temperature T_2 after reflection from A_2. Hence from Eq. 4.189,

$$T_1'-T_2'=a(T_1-T_2') \tag{4.190}$$

Referring to plate A_2 at temperature T_2, the molecules incident on A_2 are coming from A_1 and have temperature T_1' after reflection from A_1. Hence from Eq. 4.189,

$$T_2'-T_1'=a(T_2-T_1') \tag{4.191}$$

From Eqs 4.190 and 4.191,

$$T_1'-T_2'=\frac{a}{2-a}(T_1-T_2) \tag{4.192}$$

Substituting $T_1' - T_2'$ for $(T_1 - T_2)$ in Eq. 4.188, we get

$$E = \frac{p}{4}\sqrt{\frac{2R}{\pi}}\frac{\gamma+1}{\gamma-1}\frac{T_1'-T_2'}{\sqrt{MT}}$$

and from Eq. 4.192, we get for the energy transferred

$$E = \frac{1}{4}\frac{ap}{2-a}\sqrt{\frac{2R}{\pi}}\frac{\gamma+1}{\gamma-1}\frac{T_1-T_2}{\sqrt{MT}} \tag{4.193}$$

For further discussion on accommodation coefficient, the student is referred to kinetic theory of gases by Leonard B. Loeb.

4.10.4 Knudsen's Absolute Manometer

We have found that at extremely low pressure the quantity of heat flowing between two plates at temperatures T_1 and T_2 is directly proportional to pressure of the gas enclosed and also to the difference of temperature $(T_1 - T_2)$. Based on this result, Knudsen developed a method of measurement of extremely low pressures. The instrument is known as Knudsen's absolute manometer. It is absolute in the sense that it gives the pressure directly in dynes without comparing the result with a standard gauge or calibration. It consists of two hot stationary plates B_1 and B_2 of platinum heated electrically to temperature T_1 (Fig. 4.31). Facing the hot plates, there are two movable plates A_1 and A_2 forming two sides of a rectangular frame suspended by a quartz fibre carrying a mirror M.

In this case, the molecules striking the surface of A_1 facing B_1 carries greater momentum than that carried by molecules striking the other face of A_1. This causes the frame A_1A_2 to rotate about the suspension. The deflection is measured with the help of lamp and scale arrangement. The controlling couple is exerted by the twist in the suspension.

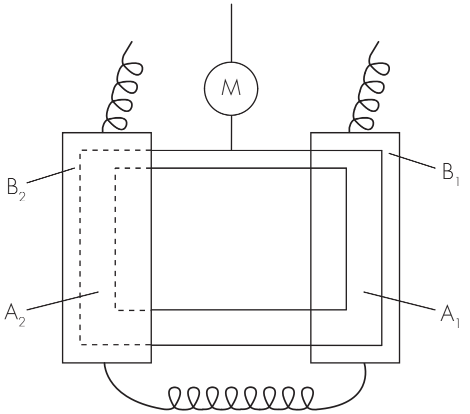

Fig. 4.31 Knudsen's absolute manometer

Theory of Knudsen absolute manometer: It is supposed that the distance between the hot and cold plates is small compared to the mean path of the molecules in the gas; further, the area of the plates is supposed to be large compared to the distance between the plates. Let υ_1 and υ_2 be the number densities of molecules leaving the plates B and A, respectively.

Then, the number densities of molecules moving towards A_1 and B are $\upsilon_1/2$ $\upsilon_2/2$. Let the average velocities of υ_1 and υ_2 molecules be $\bar{c}_1$ and $\bar{c}_2$ and let c_1^2 and c_2^2 be their mean square velocities. The momentum transferred to unit area of the plate A by molecules coming from the plate B is 1/3 $\upsilon_1 mc_1^2$ and the recoil momentum given to the plate A by molecules leaving A is1/3 $\upsilon_2 mc_2^2$. Hence, the total momentum transferred to the plate A causing it to move away from B is

$$\frac{1}{3}m(\upsilon_1 c_1^2 + \upsilon_2 c_2^2)$$

Let υ be the number density of molecules outside the plates and let $\overline{c}$ and c^2 be their average and mean square velocities. Then, the momentum given to A by outside molecules causing A to move towards B is $p = 1/3\ m\upsilon c^2$.

The resultant force acting on the plate A causing it to move towards B is

$$F = \frac{1}{3}m(\upsilon_1 c_1^2 + \upsilon_2 c_2^2) - p \tag{4.194}$$

By Eq. 4.184, we have

$$\frac{1}{2}\upsilon_1\overline{c}_1 = \frac{1}{2}\upsilon_2\overline{c}_2 = \frac{1}{4}\upsilon\overline{c}$$

or since c is proportional to $\overline{c}$

$$\upsilon_1 c_1 = \upsilon_2 c_2 = \frac{1}{2}\upsilon c$$

Substituting the value in Eq. 4.194, we get

$$F = \frac{1}{3}m\frac{1}{2}\upsilon c(c_1 + c_2) - p$$

$$= \frac{1}{2}\frac{1}{3}m\upsilon c^2\,\frac{c_1 + c_2}{c} - p$$

$$= \frac{1}{2}p\left(\frac{c_1 + c_2}{c}\right) - p$$

If the temperature of the gas be the same as the temperature T_2 of the cold plate, so that $c_2 = c$

$$\therefore \qquad F = \frac{p}{2}\left(\frac{c_1}{c_2} + 1\right) - p = \frac{p}{2}\left(\frac{c_1}{c_2} - 1\right) = \frac{p}{2}\left(\sqrt{\frac{T_1}{T_2}} - 1\right)$$

or

$$p = \frac{2F}{\sqrt{\frac{T_1}{T_2}} - 1}$$

If $T_1 = T_2 + \delta T$ where δt is very small

$$p = \frac{4FT_2}{\delta T} = \frac{4T_2 F}{T_1 - T_2}\ \text{dynes/sq cm} \tag{4.195}$$

The temperature of the hot plate can be determined by measuring the resistance of the hot plate with the help of a wheatstone's bridge. The value of F can be determined from the elastic constant of the suspension wire.

4.11 THEORY OF SELF-DIFFUSION IN A GAS

We consider a vertical column of gas in which uniform concentration gradient has been set up in the vertical direction of z axis. Let the concentration of gas in the xy plane through $z = 0$ (the zero plane) be υ_0. Then, the concentration of gas in the plane a height z is υ where

$$\upsilon = \upsilon_0 + z\frac{d\upsilon}{dz} \tag{4.196}$$

$d\upsilon/dz$ being the concentration gradient.

Let us consider a small element of volume dv at a height $z(= r\cos\theta)$ above the zero plane (Fig. 4.32). The number of molecules having velocity between c and $c + dc$ within the volume dv is B where

$$B = \left(\upsilon + r\cos\theta\frac{d\upsilon}{dz}\right)4\pi\alpha^3 e^{-\beta c^2}c^2\,dc\,dv \tag{4.197}$$

Due to collision among the molecules themselves, the number of new paths along which the molecules come out of the volume in time dt is given by $c/\lambda\ Bdt$, where λ is the mean free path. Since all directions are equally probable, the number of molecules moving in the direction of elementary area $dxdy$ is

$$\frac{c}{\lambda}Bdt\frac{dxdy\cos\theta}{4\pi r^2} \tag{4.198}$$

Of these molecules, those which strike the area $dxdy$ coming from dv without making intermediate collision are given by

$$\frac{c}{\lambda}Bdt\frac{dxdy\cos\theta}{4\pi r^2}e^{-\frac{r}{\lambda}} \tag{4.199}$$

Then, the total number of molecules crossing the area $dxdy$ in time dt downwards

$$N\downarrow = -\int\iiint\frac{c}{\lambda}Bdt\frac{dxdy\cos\theta}{4\pi r^2}e^{-\frac{r}{\lambda}}$$

$$= -\frac{dxdydt}{4\pi}\int_0^{\infty}4\pi\alpha^3 e^{-\beta c^2}c^3\,dc\left(\upsilon\int_0^{\frac{\pi}{2}}\cos\theta\sin\theta\,d\theta\int_0^{2\pi}d\phi\int_0^{\infty}\frac{e^{-\frac{r}{\lambda}}}{\lambda}dr\right.$$

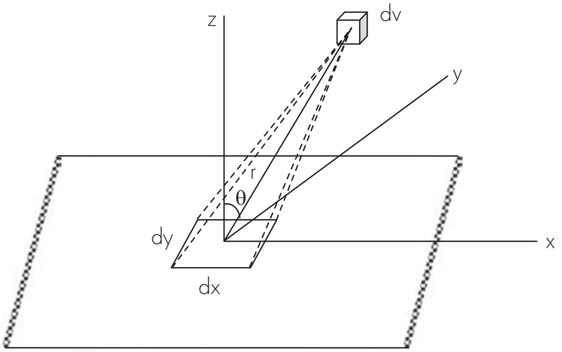

Fig. 4.32 Illustration for evaluation of diffusion coefficient

$$\left. +\frac{d\upsilon}{dz}\int_0^{\frac{\pi}{2}} \sin\theta\cos^2\theta\, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} \frac{re^{-\frac{r}{\lambda}}}{\lambda}\, dr \right) \tag{4.200}$$

The negative sign indicates that the molecules are coming from a region of higher concentration to a region of lower concentration.

Similarly, the total number of molecules crossing the area *dxdy* in time *dt* upwards

$$N\uparrow = \frac{dxdydt}{4\pi}\int_0^{\infty} 4\pi\alpha^3 e^{-\beta c^2} c^3 dc \left(\upsilon \int_0^{\frac{\pi}{2}} \cos\theta\sin\theta\, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} \frac{e^{-\frac{r}{\lambda}}}{\lambda}\, dr \right.$$

$$\left. -\frac{d\upsilon}{dz}\int_0^{\frac{\pi}{2}} \sin\theta\cos^2\theta\, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} \frac{re^{-\frac{r}{\lambda}}}{\lambda}\, dr \right) \tag{4.201}$$

The total number of molecules crossing through the area *dxdy* in time *dt* is

$$\begin{aligned} N\downarrow + N\uparrow &= -\frac{2dxdydt}{4\pi}\int_0^{\infty} 4\pi\alpha^3 e^{-\beta c^2} c^3 dc \int_0^{\frac{\pi}{2}} \sin\theta\cos^2\theta\, d\theta \times \int_0^{2\pi} d\phi \int_0^{\infty} \frac{re^{-\frac{r}{\lambda}}}{\lambda}\, dr \times \frac{d\upsilon}{dz} \\ &= -\frac{2dxdydt}{4\pi}\bar{c}\,\frac{d\upsilon}{dz}\frac{1}{3}2\pi\lambda \\ &= -\frac{1}{3}\lambda\bar{c}\,\frac{d\upsilon}{dz}\, dxdydt \end{aligned} \tag{4.202}$$

By experiment,

$$N\downarrow + N\uparrow = -D\frac{d\upsilon}{dz}\, dxdydt \tag{4.203}$$

$\therefore$

$$D = \frac{1}{3}\lambda\bar{c} = \frac{1}{3\sqrt{2}\pi\sigma^2\upsilon}\;\bar{c} \tag{4.204}$$

Thus, it is seen that $D\,\alpha\,\frac{1}{\upsilon}$ and $D\,\alpha\,\frac{T^{\frac{3}{2}}}{p}$.

Diffusion coefficient is inversely proportional to pressure and this is confirmed by experiment. However, experiment shows that diffusion coefficient varies as T^{s} where s = 1.75 to 2. This is explained by Sutherland in terms of attractive force between the molecules.

For the mutual diffusion coefficient, we have

$$D_{12} = \frac{1}{3}\frac{(\upsilon_1\lambda_2\bar{c}_2 + \upsilon_2\lambda_1\bar{c}_1)}{\upsilon_1 + \upsilon_2} \tag{4.205}$$

where suffixes 1 and 2 refer to two types of molecules involved and λ, $\bar{c}$ are their mean free path and average velocity, respectively.

4.11.1 Pressure and Thermal Diffusion

In addition to the fact that diffusion arises when there is concentration gradient, diffusion occurs when pressure as well as temperature vary from layer to layer. Diffusion occurring from the cause of pressure gradient is referred to as pressure diffusion and that arising from the cause of temperature gradient is referred to as thermal diffusion. The experimental investigation of pressure diffusion is difficult. The thermal diffusion is very important as it gives the nature of force between the molecules. The thermal diffusion experiments are also important from the point of view of separation of isotopes.

4.12 THERMAL TRANSPIRATION

Let us consider a gas enclosed in two vessels *A* and *B* at different temperatures T_1 and T_2, $T_1 > T_2$. The two vessels are separated by a heat-insulated porous plug (Fig. 4.33). Initially, the pressures are the same in both the vessels.

Let υ_1 and υ_2 be the densities of gas in the vessels. From the gas law $p = \upsilon kT$, we have $\upsilon_1/\upsilon_2 = T_2/T_1$.

The molecules from the vessel *A* moving to the vessel *B* are 1/4 $\upsilon_1\bar{c}_1$ and the molecules moving from the vessel *B* to the vessel *A* are 1/4 $\upsilon_2\bar{c}_2$.

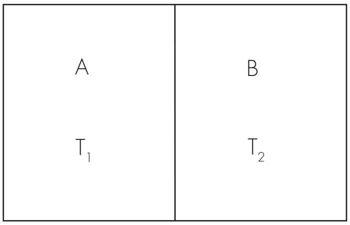

Fig. 4.33 Illustrating thermal transpiration

Now,
$$\frac{\upsilon_1\bar{c}_1}{\upsilon_2\bar{c}_2} = \frac{T_2}{T_1}\sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{T_2}{T_1}} \tag{4.206}$$

As $T_1 > T_2$, $\upsilon_2\bar{c}_2 > \upsilon_1\bar{c}_1$; so, there will be a net transfer of molecules from the vessel B to vessel A,that is, from colder to hotter vessel. This will destroy the equality of pressure in the vessels and the pressure of the hotter vessel will be increased. The phenomenon in which the difference in temperature causes transfer of molecules is known as thermal effusion or thermal transpiration. This process will go on till a steady state is reached when the transfer from both sides will be equal which gives $\upsilon_1\bar{c}_1 = \upsilon_2\bar{c}_2$. The pressure in the two vessels will be p_1 and p_2 where $p_1 = \upsilon_1 kT_1$ and $p_2 = \upsilon_2 kT_2$,so that

$$\frac{p_1}{p_2} = \frac{\upsilon_1 T_1}{\upsilon_2 T_2} = \frac{\bar{c}_2}{\bar{c}_1}\frac{T_1}{T_2} = \sqrt{\frac{T_1}{T_2}} \tag{4.207}$$

This phenomenon was experimentally investigated by Osborne Reynolds. He found that this relation holds true when the pressure is very low so that the free path is large in comparison with the dimensions of the pores. In the case of high pressure when the free path is not large compared to the dimensions of the vessel, deviation from the theory was observed.

4.12.1 Thermal Creep and the Radiometer

In 1925, Fresnel observed repulsion of a body when radiation falls on it. Later Crookes studied it thoroughly and devised an instrument by which the intensity of radiation falling on a vane can be measured

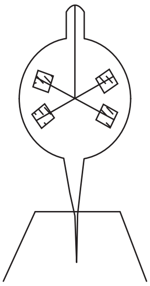

Fig. 4.34 Crookes' radiometer

from the rotation of the vane. The instrument named as Crookes' radiometer consists of thin vertical mica vanes fixed at the ends of aluminium rods (Fig. 4.34). These rods are suspended from a torsion fibre inside a partially evacuated glass vessel. The deflection of vanes can be read with mirror and telescope. The outer face of the vanes are blackened. When the radiation fall on these blackened vanes, the vanes rotate about the suspension. This is the radiometric effect.

There are different theories about the origin of radiometric force. Out of these theories, that due to Epstein is found to be most convincing.

The theories follow the ideas of Maxwell who suggested that the radiometric phenomenon is due to the thermal creep of the gas over unequally heated vane. This thermal creep is due to the following fact: Since front side of the vane is blackened, its temperature will be higher when radiation falls on it than the temperature of the back bright surface of the vane. The gas molecules striking obliquely upon the wall fall on it with higher average velocity when they come from the hotter part than when they come from the colder part and, hence, the wall will reflect them more strongly. As a result, the gas gains in tangential momentum towards the hotter side. We are giving here the results of Epstein for a thin circular disc. If a and d denote the radius and thickness of the disc respectively, then K_d and K_g denote the thermal conductivity of the disc and of the gas, I the intensity of radiation falling on the disc, then the temperature difference between the centres of the two faces of the disc Δt is given by

$$\Delta T = \frac{2}{\pi} \frac{aI}{K_g + \frac{2a}{\pi d} K_d}$$

Then, the force on the disc

$$F = -3\pi \frac{R\eta^2}{Mp} \Delta T \tag{4.208}$$

R is the molar gas constant, η the viscosity, M the molecular weight and p the pressure of the gas.

In the case of non-conducting disc, the force F is given by

$$F = -\frac{6R\eta^2 aI}{MpK_g} \text{ since } K_d = 0 \tag{4.209}$$

Thus, we see that the radiometric force F is proportional to the intensity of radiation.

Epstein's formula for non-conducting disc had been put to experimental test by Gerlach and Schutz and was found to agree with the theory in view of so many uncertainties.

4.13 EVIDENCES OF MOLECULAR MOTION

In the earlier part of this chapter we have developed the kinetic concept of matter on the basis of classical mechanics and deduced certain consequences which agree with observed facts. Untill 1908, no direct proof of the perpetual motion of molecules was available to give the kinetic theory a legitimate foundation.

In the year 1827, an English botanist Brown observed that fine colloidal suspensions in water seen under microscope were moving constantly in different directions in erratic manner apparently without any rhyme and reason. The sizes of these particles were thousands of times larger than the size of molecules of the liquid medium. On the basis of the kinetic theory, Brown ventured the assumption that the motion of the suspended particles was due to unbalanced impacts of the surrounding molecules of the liquid medium. This led to violent controversies which terminated only after the quantitative experimental verification by the French physical chemist Jean Perrin in the year 1908. Such movement of suspended particles in a fluid medium due to the molecular bombardment is known as Brownian motion.

4.13.1 Characteristic Features of Brownian Motion

1. Brownian motions are completely irregular and occur in random manner. Two suspended particles in the same locality seldom move in the same direction. Further, their motions are independent of their location in the liquid medium. Evidently, such motions are not due to eddies, convection or streaming motion of the liquid medium.
2. Brownian motions are not disturbed by jerks or jarring motions of the vessel.
3. In less viscous liquids, Brownian motion is faster.
4. The smaller the size of the particle, the greater is its velocity at the same temperature.
5. Brownian motions are continuous and eternal. Colloidal suspensions of quartz in water trapped inside specimens of quartz thousands of years old show the same Brownian motion even to day.

These facts definitely prove the validity of assumptions regarding Brownian motion. They also prove the fundamental assumptions of the kinetic theory that all molecules of a material medium are in perpetual motion.

4.13.2 Einstein and Smoluchowski's Equation for Brownian Motion

The equation was deduced independently by Einstein and Smoluchowski about the year 1905. We shall here reproduce the simplified theory by Langevin. This equation gives the average value of displacement of a Brownian particle in a given direction *ox* during a short time interval *t*.

Let X be the component of the unbalanced force of impact at an instant t on a suspended particle acting in the direction *ox*. The retarding force on the particle is the viscous drag exerted by the liquid medium. This is proportional to the velocity of the particle and is equal to $-\alpha v = -\alpha\,(dx/dt)$ where α is the constant of proportionality. Let m' be the mass of the suspended particle corrected for buoyancy.

Then,

$$m' = \frac{4}{3}\pi a^3 (D - \delta)$$

where a is the radius of the particle, D is the density of the particle and δ the density of the liquid medium. The equation of motion of the particle is

$$m'\frac{d^2x}{dt^2} = -\alpha\frac{dx}{dt} + X \tag{4.210}$$

To eliminate X, we multiply both sides of Eq. 4.210 by x so that

$$m'x\frac{d^2x}{dt^2} = -\alpha x\frac{dx}{dt} + Xx$$

or $$m'\left[x\frac{d^2x}{dt^2}+\left(\frac{dx}{dt}\right)^2\right]-m'\left(\frac{dx}{dt}\right)^2=-\frac{\alpha}{2}\frac{d}{dt}(x^2)+Xx$$

or $$m'\frac{d}{dt}\left(x\frac{dx}{dt}\right)-m'\left(\frac{dx}{dt}\right)^2=-\frac{\alpha}{2}\frac{d}{dt}(x^2)+Xx$$

or $$\frac{m'}{2}\frac{d^2}{dt^2}(x^2)-m'\left(\frac{dx}{dt}\right)^2=-\frac{\alpha}{2}\frac{d}{dt}(x^2)+Xx \tag{4.211}$$

In a large number of displacements of the particle, Xx is as often positive as negative. Hence, its average value is zero.

Applying equipartition principle to Brownian motion, the average kinetic energy of the particle is

$$\frac{1}{2}KT=\frac{1}{2}\frac{RT}{N}=\frac{1}{2}m'\left(\frac{dx}{dt}\right)^2$$

where N is the Avogadro's number.

Putting $\overline{Xx}=0$ in differential Eq. 4.211 the average value takes the form

$$\frac{m'}{2}\frac{d^2}{dt^2}(x^2)-\frac{RT}{N}=-\frac{\alpha}{2}\frac{d}{dt}(\overline{x^2}) \tag{4.212}$$

where $\overline{x^2}$ is the average value of x^2 over a long interval of time.

Putting $z=\frac{d}{dt}(\overline{x^2})$,
Eq. 4.212 becomes

$$\frac{m'}{2}\left(\frac{dz}{dt}\right)=\frac{RT}{N}-\frac{\alpha z}{2}$$

or $$\frac{m'}{\alpha}\left(\frac{dz}{dt}\right)=\frac{2RT}{N\alpha}-z$$

Putting $$\chi=z-\frac{2RT}{N\alpha},$$

we have $$\frac{d\chi}{dt}=\frac{dz}{dt}\text{ and }\frac{m'}{\alpha}\frac{d\chi}{dt}=-\chi$$

or $$\int\frac{d\chi}{\chi}=-\frac{\alpha}{m'}\int dt$$

or $$\log_e\chi=-\frac{\alpha t}{m'}+\log_e c$$

where $\log_e c$ is the constant of integration. Then,

$$\chi = ce^{\frac{-\alpha t}{m'}} \quad \text{or} \quad z = \frac{2RT}{N\alpha} + ce^{\frac{-\alpha t}{m'}}$$

or
$$\frac{d}{dt}(\overline{x^2}) = \frac{2RT}{N\alpha} + ce^{\frac{-\alpha t}{m'}} \tag{4.213}$$

By Stokes' law of terminal velocity of fall of a sphere of radius a through a liquid of viscosity η

$$\alpha = 6\pi\eta a \tag{4.214}$$

Neglecting buoyancy $m' = \frac{4}{3}\pi a^3$, putting $D = 1$

and
$$\frac{\alpha t}{m'} = 4.5\eta a^{-2} t$$

The radius of the suspended particles is of the order of 10^{-4} cm and η for water is about 0.01, then the exponential factor in Eq. 4.213 is $e^{-4.5 \times 10^{-6}}$ t which can be neglected. Restricting ourselves to finite intervals of 10^{-4} sec, represented by τ, Eq. 4.213 may be written as

$$\frac{\overline{\Delta x^2}}{\tau} = \frac{2RT}{N\alpha} \tag{4.215}$$

Substituting the value of α from Eq. 4.214 we write

$$\frac{\overline{\Delta x^2}}{\tau} = \frac{2RT}{N}\frac{1}{6\pi\eta a} \tag{4.216}$$

N can be determined if η and a are known from Eq. 4.216. Now the validity of Stokes' law in Eq. 4.214 is not unquestionable. Further there is some uncertainty in the experimentally determined value of a, the radius of the suspended particle. The radius a of the particles can be determined by the methods explained in connection with Perrin's method of determination of Avogadro number.

4.13.3 Brownian Motion in Gases

By strongly illuminating air charged with fine particles such as tobacco smoke and observing these particles through a microscope transversly to the direction of the illuminating beam, it has been possible to detect Brownian motion of the particles suspended in air. Millikan used this technique for determination of charge on the electron. For this purpose, fine drops of oil charged with electricity were suspended in air in the space between two plates of an electric condenser placed horizontally. These particles were subjected simultaneously to gravitational and electrical force in the vertical direction. If the electrical field was opposed to the gravitational field, the vertical motion of the particles was retarded; if they were in the same direction, their motion was accelerated. If the opposing electric field just neutralized the gravitational filed, there was no fall of the particle in the vertical direction. Under this condition, the Brownian motion of the suspended oil drops as the impact of the surrounding air molecules could be observed through a low power microscope when the line of sight was perpendicular to the direction of the illuminating beam and to the gravitational filed. The positions of the drops after successive equal intervals of time τ were noted on a graph paper by the camera lucida method described in the next section. From these observations, $\overline{\Delta x^2}$ could be determined. To eliminate the uncertainty about the Stokes' law and the error in the measured value of *a*, the following method was applied. In the first step, an opposing electric field was applied. Let v_1 and v_2 be the terminal velocity in these two cases. The equation of motion in the first step is

$$m'g = \alpha v_1 \tag{4.217}$$

and in the second step, it is

$$Ene - m'g = \alpha v_2 \tag{4.218}$$

where *E* is the applied electric field and *ne* is the number of units of electronic charge captured by the oil drop. Adding Eqs 4.217 and 4.218,

$$\alpha = \frac{Ene}{v_1 + v_2}$$

Substituting the value of α in Eq. 4.215, we get

$$\frac{\overline{\Delta x^2}}{\tau} = \frac{2RT}{N}\frac{v_1 + v_2}{Ene} \tag{4.219}$$

Equation 4.219 removes in one stroke the uncertainty in the assumption of validity of Stokes' law as well as the error in the experimentally determined value of the radius of the oil drop. The measurement of Avogadro's number *N* was carried out by this method with the help of Eq. 4.219 by Millikan and Fletcher in 1911.

Perrin's experimental method of observation of Brownian motion: For this purpose, a colloidal suspension was prepared by dissolving a small quantity of powdered gum gamboge or mastic in alcohol and pouring a small quantity of this solution in large volume of water. This gave spherical molecules of different sizes. Perrin separated particles of one size from this group by fractional centrifuging. A thin glass plate having a thickness of about 0.1 mm was bored with a large hole and cemented to a glass slide thereby forming a shallow cylindrical vessel. A drop of the emulsion was placed inside the hole and then covered over by microscope cover glass. The emulsion spread in the form of a fine film. This was illuminated from one side by a powerful lamp. The rays passed through a water cell to absorb the heat rays to prevent convection current within the cell. The particles were seen through a microscope transversely to the direction of the illuminating beam. Seen through the microscope, the colloidal particles appeared as fine specks of light moving hither and thither on account of unbalanced impacts of surrounding water molecules. The successive positions of a single particle after equal intervals of time τ were indicated by pencil dots on a squared paper fixed to a frame. This was viewed simultaneously with the Brownian particle by the camera lucida method illustrated in Fig. 4.35. This gave a number of zigzag paths. The successive displacements were projected on the axis *ox*. The mean square value $\overline{\Delta x^2}$ were computed from the graph.

From this value of $\overline{\Delta x^2}$, the Avogadro's number can be determined with the help of Eq. 4.219.

Perrin verified Eq. 4.216 for different values of *T*, *a*, η and τ, from the observed value of $\overline{\Delta x^2}$ at different temperatures for different values of radii of the particles, with different liquid media and for different time interval τ.

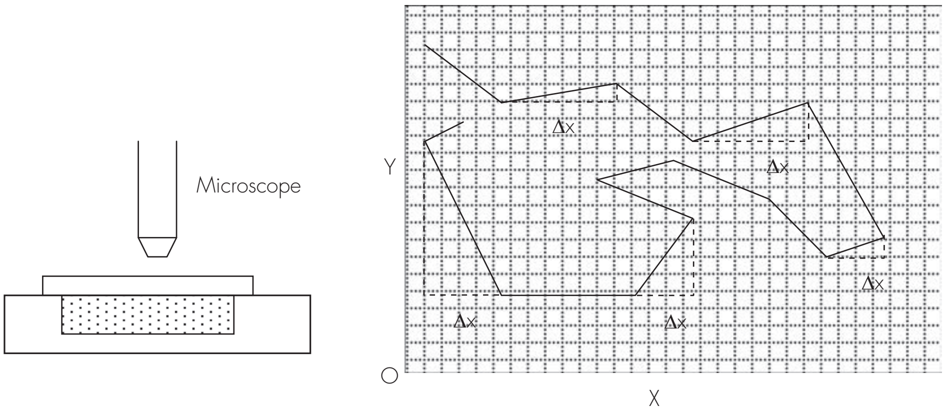

Fig. 4.35 Perrin's apparatus and his experimental observation

Distribution of particles of emulsion in the gravitational field: The law of distribution of molecules of the atmosphere under the action of gravity was first deduced by Laplace. Perrin writes, "It appeared to me almost intuitively that the granules of the emulsion should distribute themselves as a function of the height in the same manner as the molecules of a gas under the influence of gravity." This law of distribution was deduced by Perrin as follows.

Let the emulsion be contained in a cylinder of uniform cross section *S* (Fig. 4.36). Under the action of gravity, the suspended particles of the emulsion move downwards.

This is opposed by the viscous resistance of the liquid medium in which the particles are suspended. As a result, the number density of the particles increases downwards from the top towards the base of the cylinder. This gives rise to change in the osmotic pressure which also increases downwards from the top.

Let n be the number of particles per *cc* at height h from the base of the cylinder. Then, the number at height $(h + dh)$ is $(n - dn)$. The downward force on the particles due to gravity is opposed by the difference of osmotic pressure at these two heights. The law of osmosis is the same as the law of perfect gas, so that the osmotic pressure at height h is

$$P = \frac{2}{3}nW$$

where W is the mean energy of a granule. The osmotic pressure at height $(h + dh)$ is

$$P + dP = \frac{2}{3}(n - dn)W$$

Hence, the difference of osmotic force at the two heights is

$$-\frac{2}{3}dnSW$$

This must be equal to the weight of the granules between the two layers at heights h and $(h + dh)$ corrected for buoyancy of the liquid medium. Let v be the volume of a single molecule, ρ its density and

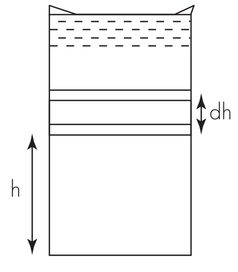

Fig. 4.36 Perrin's theory for distribution of particles of emulsion in the gravitational field

let δ be the density of the liquid medium. Then, the effective weight of the granules between the two layers is

$$nSv(\rho-\delta)gdh$$

Hence, $$-\frac{2}{3}dnSW = nSv(\rho-\delta)gdh$$

or $$-\frac{2}{3}W\frac{dn}{n} = v(\rho-\delta)gdh$$

Integrating between 0 and h where the concentrations are n_0 and n, we get

$$\frac{2}{3}W\log_e\frac{n_0}{n} = v(\rho-\delta)gh \tag{4.220}$$

or $$n = n_0\exp\left\{-\frac{3}{2W}v(\rho-\delta)gh\right\}$$

This gives the concentration n at the height h from the base of the cylinder. In deducing this equation, Perrin assumed that the mean energy of a granule of emulsion is the same as that of a molecule of a perfect gas at the same temperature. Thus, the law of perfect gas extended by Vant Hoff to solutions was extended to emulsions by Perrin. According to kinetic theory of gases,

$$W = \frac{3}{2}KT = \frac{3}{2}\frac{RT}{N}$$

Substituting the value of W in Eq. 4.220, we get

$$2.303\frac{RT}{N}\log\frac{n_0}{n} = \frac{4}{3}\pi a^3 g(\rho-\delta)h \tag{4.221}$$

where a is the radius of the granule. From Eq. 4.221, the value of the Avogadro's number N can be determined. At two different depths h_1 and h_2 measured from an arbitrary depth, Eq. 4.220 is reduced to the following form:

$$2.303\frac{RT}{N}(\log n_2 - \log n_1) = \frac{4}{3}\pi a^3 g(\rho-\delta)(h_1-h_2) \tag{4.222}$$

where n_1 and n_2 are the number of particles per *cc* at depths h_1 and h_2.

Determination of Avogadro's number by Perrin's method: This was determined from Eq. 4.222. The colloidal particles of gamboge or mastic all of the same size were obtained by centrifuging as already explained. These were placed in small cells maintained at constant temperature by water baths on the stage of a microscope of very small depth of focus. Starting from an arbitrary depth in the solution and by reducing the field of view, the numbers n_1 and n_2 of particles at different depths h_1 and h_2 were counted. The numbers n_1 and n_2 were also obtained from microscopic photographs of the particles at different depths.

To obtain the value of a, the radius of the particles, a small quantity of dilute suspension was evaporated in a glass dish. The capillary forces of the liquid caused the particles to run together more or less in rows or sheets of one particle depth. The diameter of the particles was measured by determining the length covered by a number of particles lying side by side in a line and dividing this length by the number of particles counted.

The density ρ of the suspended particles was determined by the pycnometer method. For this purpose, the pycnometer was first filled with distilled water and weighed; then, it was filled with the emulsion and reweighed. The emulsion was next evaporated to dryness and desiccated at 110°C and weighed; from these measurements, the density of the gum was determined. The density was also determined directly from the fused dry gum. The two densities should be equal unless they were changed by suspension in water.

The value of N obtained by Perrin by this method was $N = 6.5 \times 10^{23}$.

SOLVED PROBLEMS

Q1. Calculate the root mean square (RMS) velocity of an oxygen molecule at 0 °C given the gram molecular mass of the gas is 32 gm and the molar gas constant R is 8.32×10^7 ergs per mole per degree. At what temperature will the RMS velocity of the gas have the same magnitude as the velocity of sound in air, that is, 332 metres per sec?

Ans. The RMS velocity

$$= \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 8.32 \times 10^7 \times 273}{32}}$$

$$= 4.62 \times 10^4 \text{ cm/sec}$$

Let the required temperature be $T\,K$, then

$$= \sqrt{\frac{3 \times 8.32 \times 10^7 \times T}{32}} = 33200$$

$$\therefore \qquad T = \frac{33200 \times 33200 \times 32}{3 \times 8.32 \times 10^7} = 141 \text{ K}$$

Q2. At what temperature will the average speed of hydrogen molecules be the same as that of nitrogen molecules kept at 35 °C? Molecular weight of nitrogen is 28 atomic unit and that of hydrogen is 2 atomic unit.

Ans. The average speed of nitrogen molecules at 35°C is

$$= \sqrt{\frac{8 \times R \times 308}{\pi \times 28}}$$

Let the temperature of hydrogen molecules be $T\,K$, at which the average speed is

$$= \sqrt{\frac{8 \times R \times T}{\pi \times 2}}$$

$$= \sqrt{\frac{8 \times R \times T}{\pi \times 2}} = \sqrt{\frac{8 \times R \times 308}{\pi \times 28}} \quad \therefore T = 22 \text{ K}$$

Q3. The density of air at NTP is 0.00129 gm/cc. Calculate the RMS velocity at NTP.

Ans. We know, that $c = \sqrt{\dfrac{3p}{\rho}} = \sqrt{\dfrac{3 \times 76 \times 981 \times 13.6}{0.00129}}$

$$= 4.86 \times 10^4 \text{ cm/sec}$$

Q4. The normal density of hydrogen at NTP is 0.000089 gm/cc. What is the RMS velocity of oxygen at NTP?

Ans. Density of oxygen = 16 × 0.000089

$$c = \sqrt{\frac{3p}{\rho}} = \sqrt{\frac{3 \times 76 \times 981 \times 13.6}{16 \times 0.000089}}$$

$$= 4.62 \times 10^4 \text{ cm/sec}$$

Q5. Calculate the kinetic energy of a molecule of hydrogen at 0 °C.

Ans. Taking 1 mole of the hydrogen

$PV = RT = \dfrac{1}{3} mNc^2 = \dfrac{2}{3} N \dfrac{1}{2} mc^2 = \dfrac{2}{3} NE$, where E is the energy of one molecule

$$\therefore \qquad E = \frac{3RT}{2N} = \frac{3}{2} \times \frac{8.31 \times 10^7 \times 273}{6.03 \times 10^{23}}$$

$$= 5.68 \times 10^{-14} \text{ erg}$$

Q6. Find the kinetic energy of 1 gm of oxygen at 47 °C.

Ans. For 1 gm-mole of oxygen, $PV = RT = \dfrac{2}{3} E$

Where E is the energy of 1 gm-mole

$$E = \frac{3}{2} RT$$

Then for 1 gm, the kinetic energy $= \dfrac{1}{32} \dfrac{3}{2} RT$

$$= \frac{3 \times 8.31 \times 10^7 \times 320}{64} = 1.24 \times 10^9 \text{ ergs}$$

Q7. At what temperature will the RMS velocity of oxygen be one and half times its value at NTP?

Ans. We know $PV = RT = 1/3\ mNc^2$, for 1 gm-mole

$$c \,\alpha \sqrt{T} \text{ and } c_1 \,\alpha \sqrt{T_1} \quad \therefore \frac{c_1}{c} = \sqrt{\frac{T_1}{T}}$$

$$c_1 = \frac{3}{2} c \quad \text{and} \quad T = 273$$

$$\therefore \qquad T_1 = T \frac{c_1^2}{c^2} = \frac{9}{4} \times 273 = 614.3\text{K}$$

Q8. What is the kinetic energy of 2 gm-moles of an ideal gas occupying a volume of 5 litres under a pressure of 10 atmospheres?

Ans. For 1 gm-mole $PV = RT = \frac{2}{3}E$

where E is the energy of 1 gm-mole

$$E = \frac{3}{2}RT = \frac{3}{2}PV$$

For 2 gm-moles, the energy $= 3\,PV$

$$= 3 \times 10 \times 5 \times 76 \times 981 \times 13.6 \times 1000 \text{ ergs}$$

$$= 1.52 \times 10^{11} \text{ ergs}$$

Q9. Calculate the molecular energy of 1 gm of hydrogen at 50 °C, given that the molecular weight of hydrogen is 2 and the gas constant R is 8.3×10^7 ergs per degree per gm. mol.

Ans. Molecular energy per gm-mole $= \frac{3}{2}RT$

$$= \frac{3}{2} \times 8.3 \times 10^7 \times 323$$

Again molecular weight of hydrogen being 2 gm, molecular energy of 1 gm of hydrogen is

$$= \frac{1}{2} \times \frac{3}{2} \times 8.3 \times 10^7 \times 323 \text{ ergs} = 2 \times 10^{10} \text{ ergs.}$$

Q10. At what temperature, pressure remaining constant, will the RMS velocity of hydrogen be double of its value at NTP?

Ans. At NTP, RMS velocity of hydrogen $= \sqrt{\frac{3R \times 273}{M}}$

At temperature $T\,K$, the RMS velocity $= \sqrt{\frac{3R \times T}{M}}$

So, $$= \sqrt{\frac{3RT}{M}} = 2 \times \sqrt{\frac{3R \times 273}{M}}$$

$\therefore$ $$\frac{3RT}{M} = 4 \times \frac{3R \times 273}{M}$$

$$T = 1092 \text{ K}$$

Q11. Calculate the RMS velocity of the molecules of hydrogen at 0°C and 100°C from the following data:

Density of hydrogen at NTP = 0.0000896 gm/cc.

Ans. At NTP, RMS velocity $= \sqrt{\frac{3p}{\rho}} = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.0000896}} = 1.84 \times 10^5 \text{ cm/sec}$

If C_0 and C_{100} be the RMS velocity at 0°C and 100°C respectively, then

$$\frac{C_{100}}{C_0} = \sqrt{\frac{373}{273}}$$

$$\therefore \qquad C_{100} = C_0\sqrt{\frac{373}{273}} = 1.84\times10^5\sqrt{\frac{373}{273}} = 2.154\times10^5 \text{ cm/sec}$$

Q12. Calculate the root mean square velocity of molecules of a gas for which the specific heat at constant pressure is 6.84 calories per gm-mole per degree celsius, the velocity of sound in the gas being 1,300 metres per sec. $R = 8.31 \times 10^7$ ergs/gm.mole/°C

Ans. We know that $C_p - C_v = \frac{R}{J}$

or
$$C_v = C_p - \frac{R}{J} = 6.84 - \frac{8.31\times10^7}{4.2\times10^7} = 4.86$$

Again,
$$\gamma = \frac{C_p}{C_v} = \frac{6.84}{4.86} = 1.408$$

The velocity of sound in a gas is given by

$$v = \sqrt{\frac{\gamma p}{\rho}}$$

$$\therefore \qquad \sqrt{\frac{p}{\rho}} = \frac{v}{\sqrt{\gamma}} = \frac{130000}{\sqrt{1.408}} = 1.095\times10^5$$

RMS velocity
$$= \sqrt{\frac{3p}{\rho}} = \sqrt{3}\times1.095\times10^5 = 1.898\times10^5 \text{ cm/sec}$$

Q13. Calculate the average velocity of a molecule of oxygen at 27 °C in miles per hour, if Avogadro's number is 6.02×10^{23} and Boltzmann's constant k is 1.38×10^{-16} erg/degree.

Ans. Mass of each molecule of oxygen $= \frac{32}{6.02\times10^{23}}$

The average velocity $= \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8\times1.38\times10^{-16}\times300\times6.02\times10^{23}}{3.14\times32}}$

$= 44540$ cm/sec $= 997$ miles/hour.

Q14. If three particles have velocities 2.4, 2.6, and 3.7 km per second respectively, calculate the ratio of the root mean square velocity to the mean velocity.

Ans. RMS velocity of the particles $= \sqrt{\frac{2.4^2 + 2.6^2 + 3.7^2}{3}} = 2.956$ km/sec

$$\text{Mean velocity} = \frac{2.4+2.6+3.7}{3} = 2.9 \text{ km/sec}$$

$$\frac{\text{RMS velocity}}{\text{Mean velocity}} = \frac{2.956}{2.9} = 1.019$$

Q15. Calculate the mean free path in helium at 0°C and standard atmospheric pressure, being given that the number of molecules per *cc* is equal to 2.76×10^{19} and the diameter of a helium molecule is equal to 3.36×10^{-8} cm.

Ans. $$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n} = \frac{1}{1.414 \times 3.14 \times (3.36 \times 10^{-8})^2 \times 2.76 \times 10^{19}}$$

$$= 7.23 \times 10^{-6} \text{cm.}$$

Q16. Calculate the mean free path, collision rate, molecular diameter of hydrogen gas, given $\eta = 85 \times 10^{-6}$ dynes per square centimetre per unit velocity gradient, $\bar{c} = 16 \times 10^4$ cm/ sec and $\rho = 0.000089$ gm/cc.

Ans. We know that $\eta = \frac{1}{3}\rho\bar{c}\lambda$

$$\therefore \quad \lambda = \frac{3\eta}{\rho\bar{c}} = \frac{3 \times 85 \times 10^{-6}}{0.000089 \times 16 \times 10^4} = 1.79 \times 10^{-5} \text{ cm}$$

$$\text{Collision rate} = \frac{\bar{c}}{\lambda} = \frac{16 \times 10^4}{1.79 \times 10^{-5}} = 8.9 \times 10^9$$

Again, $$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

$$\therefore \quad \sigma = \left(\frac{1}{\sqrt{2}\pi n\lambda}\right)^{\frac{1}{2}} = \left(\frac{1}{1.414 \times 3.14 \times \dfrac{6.06 \times 10^{23}}{22400} \times 1.79 \times 10^{-5}}\right)^{\frac{1}{2}}$$

$$= 2.2 \times 10^{-8} \text{ cm}$$

Q17. The diameter of the molecule of a gas is 2×10^{-8}cm. Calculate the mean free path at NTP, given $k = 1.38 \times 10^{-6}$ erg per degree.

Ans. We know that $$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

Again, $$p = nkT$$

$$\therefore \quad \lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p} = \frac{1.38 \times 10^{-16} \times 273}{1.414 \times 3.14 \times 4 \times 10^{-16} \times 76 \times 13.6 \times 981} = 2.1 \times 10^{-5} \quad \text{cm.}$$

Q18. The viscosity of oxygen at a temperature of 15 °C is 196 micropoise. Calculate the diameter of a molecule of the gas. Avogadro's number is 6.02×10^{23} and molecular weight of oxygen is 32.

$k = 1.38 \times 10^{-16}$ erg per degree.

Ans. We know that the average velocity,

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}$$

where m = mass of a molecule

$$= \frac{32}{6.02\times10^{23}}\text{ gm.}$$

$$\therefore \qquad \bar{c} = \sqrt{\frac{8\times1.38\times10^{-16}\times288\times6.02\times10^{23}}{3.14\times32}}$$

$$= 4.65 \times 10^4 \text{ cm/sec}$$

Again, $\eta = \frac{1}{3}\rho\bar{c}\lambda = \frac{1}{3}\rho\bar{c}\frac{1}{\sqrt{2}\pi\sigma^2 n} = \frac{m\bar{c}}{3\sqrt{2}\pi\sigma^2}$

$$\therefore \qquad \sigma = \left(\frac{m\bar{c}}{3\sqrt{2}\pi n}\right)^{\frac{1}{2}} = \left(\frac{32\times4.65\times10^4}{6.02\times10^{23}\times3\times1.414\times3.14\times196\times10^{-6}}\right)^{\frac{1}{2}}$$

$$= 3.08\times10^{-8}\text{cm.}$$

Q19. At what pressure would an oxygen molecule have a mean free path equal to 15 cm? The temperature of the gas can be taken to be equal to 27 °C and the diameter of the molecule equal to 3×10^{-8} cm. Avogadro's number is 6.02×10^{23} and the gas constant R is 8.31×10^7 ergs per mole per degree.

Ans. We know that $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$

Again, $p = nkT$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 p} = \frac{RT}{N\sqrt{2}\pi\sigma^2 p}$$

$$\therefore \qquad p = \frac{RT}{N\sqrt{2}\pi\sigma^2\lambda}$$

$$= \frac{8.32\times10^7\times300}{6.02\times10^{23}\times1.414\times3.14\times(3\times10^{-8})^2\times15}$$

$$= 0.692 \text{ dynes/sq.cm.}$$

Q20. Calculate Avogadro's number from the following data:

Kinetic energy of a molecule of hydrogen at 0 °C is 5.64×10^{-14} ergs and molar gas constant = 8.32×10^7 ergs.

Ans. We know that $\frac{1}{3}mNc^2 = RT$

$$\therefore \qquad N = \frac{3RT}{mc^2} = \frac{3RT}{2\frac{1}{2}mc^2} = \frac{3\times8.32\times10^7\times273}{2\times5.64\times10^{-14}} = 6.08\times10^{23}$$

Q21. A shower of 5,000 molecules, each originally moving with the same velocity, traverses a gas. Calculate the number which will be travelling undeflcted even after traversing distances equal to 0.5 and 1 time the mean free path.

Ans. We know that $p = qe^{-\frac{x}{\lambda}}$

where q = total number of molecules

p = number of molecules having no collision in traversing a distance x.

Then, $p = 5000e^{-\frac{0.5\lambda}{\lambda}} = 5000/e^{0.5} = \dfrac{5000}{1.6487} = 3033$

Again, $p = 5000e^{-\frac{\lambda}{\lambda}} = \dfrac{5000}{e} = \dfrac{5000}{2.7183} = 1840$

Q22. Prove that the mean kinetic energy of a monatomic molecule corresponding to a temperature 38380 K is about 5 electron volts.

Ans. Mean kinetic energy per atom

$$= \frac{3}{2}kT$$

$$= \frac{3}{2} \times 1.38 \times 10^{-16} \times 38380 \text{ ergs}$$

$$= \frac{3 \times 1.38 \times 10^{-16} \times 38380}{2 \times 1.6 \times 10^{-12}} \text{ ev}$$

$$= 4.97\, ev$$

Q23. Determine the mean free path and collision frequency for air molecules at NTP given that the viscosity is 1.7 × 10^{-4} cgs unit and the density 1.29 gm per litre.

Ans. RMS velocity $= \sqrt{\dfrac{3p}{\rho}} = \sqrt{\dfrac{3 \times 76 \times 13.6 \times 981}{0.00129}} = 4.86 \times 10^4$ cm/sec

Mean free path $= \lambda = \dfrac{3\eta}{\rho\bar{c}} = \dfrac{3 \times 1.7 \times 10^{-4}}{0.00129 \times 4.86 \times 10^4} = 8.1 \times 10^{-5}$ cm.

Collision frequency $= \dfrac{\bar{c}}{\lambda} = \dfrac{4.86 \times 10^4}{8.1 \times 10^{-5}} = 6 \times 10^9$

Q24. In an absolute manometer the temperature of the two plates are 23.4 °C and 31.7 °C, the surrounding gas being maintained at the temperature of the cold plate. If the cold plate is repelled with a force of 1.6 × 10^{-2} dynes/cm², calculate the pressure of the gas.

Ans. Here, $T_2 = 273 + 23.4 = 296.4$ K

$T_1 = 273 + 31.7 = 304.7$ K

We know, pressure $= 4F\dfrac{T_2}{T_1 - T_2}$ dynes/cm²

$$= \frac{4 \times 1.6 \times 10^{-2} \times 296.4}{8.3} = 228.6 \text{ dynes/cm}^2$$

Q25. Estimate the size of a helium atom assuming its mean free path to be 28.5×10^{-6} cm at NTP given that the density of helium is 0.178 gm per litre at NTP and the mass of helium atom is 6×10^{-24} gm.

Ans. We know,

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

$\therefore$

$$\sigma = \left(\frac{1}{\sqrt{2}\pi n\lambda}\right)^{\frac{1}{2}}$$

$$= \left(\frac{6\times10^{-24}}{1.414\times3.14\times.000178\times28.5\times10^{-6}}\right)^{\frac{1}{2}}$$

$$= 1.69\times10^{-8}\text{ cm.}$$

Q26. Observation of the Brownian movement in water showed that the horizontal displacement of a given particle in 11 successive intervals of 30 seconds were 0, 5.6, −4.7, −10.8, 6.6, −9.8, −11.2, −4.0, 15.0, 19.1, 16.0×10^{-4} cms. The temperature was 20 °C at which viscosity of water = 0.0100 cgs unit, radius of the particle is 1.15×10^{-5} cm.

If $R = 8.32 \times 10^7$, obtain the value of N.

Ans. We know that $\overline{x^2} = \dfrac{RT}{N}\dfrac{1}{3\pi\eta a}\tau$

Now, $$\overline{x^2} = \frac{[0^2+(5.6)^2+(4.7)^2+(10.8)^2+(6.6)^2+(9.8)^2+(11.2)^2+(4)^2+(15)^2+(19.1)^2+(16)^2]\times10^{-8}}{11}$$

$$=1.18\times10^{-6}$$

$\therefore$

$$N = \frac{RT}{\overline{x^2}}\frac{\tau}{3\pi\eta a}$$

$$= \frac{8.32\times10^7\times293\times30}{1.18\times10^{-6}\times3\times3.14\times0.01\times1.15\times10^{-5}}$$

$$=5.7\times10^{23}$$

Q27. Calculate the fractional change in the number of helium atoms in the velocity range of 999.5 to 1000.5 metres per second, when a given mass of the gas is heated from 100 K to 900 K at constant volume. Assume $k = 1.38 \times 10^{-16}$ erg units and the mass of the helium atom = 6×10^{-24} gms.

Ans. Let n be the number of molecules per *cc*.

$c = 1000$ metres/sec $= 10^5$ cm/sec

$dc = 1$ metre/sec $= 100$ cm/sec

The number of molecules per *cc* at temperature 100 K

$$dn_{100} = 4\pi n\left(\frac{m}{2\pi\text{k}100}\right)^{\frac{3}{2}} e^{\frac{-m10^{10}}{2\text{k}100}}\,10^{10}10^2$$

The number of molecules per cc at temperature 900 K

$$dn_{900} = 4\pi n\left(\frac{m}{2\pi \mathrm{k}900}\right)^{\frac{3}{2}} e^{\frac{-m10^{10}}{2\mathrm{k}900}} 10^{10}10^{2}$$

$$\frac{dn_{900}}{dn_{100}} = \frac{4\pi n\left(\frac{m}{2\pi \mathrm{k}900}\right)^{\frac{3}{2}} e^{\frac{-m10^{10}}{2\mathrm{k}900}} 10^{12}}{4\pi n\left(\frac{m}{2\pi \mathrm{k}100}\right)^{\frac{3}{2}} e^{\frac{-m10^{10}}{2\mathrm{k}100}} 10^{12}}$$

$$= \left(\frac{m2\pi \mathrm{k}100}{2\pi \mathrm{k}900 m}\right)^{\frac{3}{2}} e^{\frac{m10^{8}}{\mathrm{k}}\left(\frac{1}{2}-\frac{1}{18}\right)}$$

$$= \frac{1}{27} e^{\frac{6\times 10^{-24}\times 10^{8}}{1.38\times 10^{-16}}\times\frac{8}{18}}$$

$$= \frac{1}{27} e^{\frac{8}{4.14}} = \frac{6.9109}{27} = 0.256$$

Problems

Q1. Calculate the RMS velocity of hydrogen at 300 K. The Boltzmann constant is 1.38×10^{-16} ergs per degree and mass of the hydrogen molecule is 3.34×10^{-24} gm.

Ans. 19.3×10^{4} cm/sec

Q2. Calculate the RMS velocity of nitrogen at 0 °C. The density of nitrogen at NTP is 1.25 gm/litre.

Ans. 4.93×10^{4} cm/sec

Q3. Calculate the RMS velocity of the molecules of a gas whose density is 1.4 gm/litre at a pressure of 76 cm of mercury. Density of mercury = 13.6 gm/cc and $g = 980$ cm/sec^2.

Ans. 4.66×10^{4} cm/sec

Q4. Calculate the molecular kinetic energy of 1 gm of hydrogen at 0 °C ($R = 8.32 \times 10^{7}$ ergs /mole/ degree).

Ans. 17×10^{9} ergs

Q5. One cc of oxygen weighs 0.00144 gm at NTP Find the RMS speed of an oxygen molecule at 100 °C.

Ans. 5.37×10^{4} cm/sec

Q6. The density of helium is 0.178 gm per litre at NTP. What is the RMS velocity of helium molecules under these conditions? Compare it with the velocity at 200 °C.

Ans. 1.306×10^{5} cm/sec; 1:1.316

Q7. Calculate the RMS velocity of a gas of molecular weight m at 0 °C and at 100 °C, given density of mercury = 13.6 gm/cc.

Ans. $\frac{2.6\times10^5}{\sqrt{m}}$ cm/sec, $\frac{3\times10^5}{\sqrt{m}}$ cm/sec

Q8. Find the mean free path, frequency of collision and the molecular diameter of nitrogen gas, given $\eta = 166 \times 10^{-6}$ dynes per square centimetre per unit velocity gradient, $\bar{c} = 4.5\times10^4$ cm per sec and $\rho = 1.25\times10^{-3}$ gm per cc.

Ans. 9×10^{-6} cm, 5×10^9 per sec, 3×10^{-8} cm

Q9. Express in electron volt the mean kinetic energy per atom in a gas at a temperature 3940 K.

Ans. 0.5 ev

Q10. A shower of 1,000 molecules, each originally moving with the same velocity traverses a gas. Calculate the numbers which will be traveling undeflected even after traversing distances equal to 0.2, 0.5, 1 and 2 times the mean free path.

Ans. 819, 607, 368, 135

Q11. The density of oxygen at NTP is 1.423 gm per litre. Calculate the value of RMS velocity given that $g = 981$ cm/sec.

Ans. 4.624×10^4 cm/sec

Q12. The RMS velocity of a gas enclosed in a chamber is 5×10^4 cm/sec at 27 °C and standard atmosphere pressure. Calculate the density at NTP.

Ans. 0.00127 gm/cc

Q13. In a Knudsen manometer, the two plates are maintained at 22 °C and 32 °C and the surrounding gas is at a temperature of the cold plate. Calculate the pressure of the gas if the repelling force on the cold plate is 0.02 dyne/cm^2.

Ans. 2.36 dynes/cm^2

QUESTIONS

1. State the basic assumptions of the kinetic theory of gases and prove that the pressure exerted by a perfect gas is two-thirds its kinetic energy per unit volume.
2. Outline the essential features of the kinetic theory of gases. Find an expression for the pressure of a gas on the basis of kinetic theory.
3. Outline the essential features of the kinetic theory of gases and apply it to account for the simple gas laws. What is the interpretation of temperature on this theory?
4. What are the fundamental assumptions on which the kinetic theory of gasses is based?

   Explain what is meant by root mean square velocity of a gas. Deduce the relation connecting the root mean square velocity, pressure and density of a gas.
5. Explain (a) degree of freedom, and (b) equipartition of energy. Show that the average energy of translation of the molecules of an ideal gas is $3/n$ of their total energy. Deduce the formula you would use for the purpose. (The ratio of specific heats of a gas at constant pressure and at constant volume is $(1+2/n)$ where n = number of degrees of freedom.)

6. Deduce Maxwell–Boltzmann law of distribution of velocities of molecules for an ideal gas. Give a description of the method of verification of law.
7. State and explain the Maxwell–Boltzmann distribution law for the velocities of molecules in a gas. Deduce the value of the average and the RMS velocities of the molecules from the constants of the distribution law. Describe an experiment for the verification of this law.
8. State the law of equipartition of energy. Prove that for a monatomic gas, the value of γ, the ratio between the specific heats, is 5/3 and for a diatomic gas it is 7/5.
9. Give a brief account of the law of equipartition of energy. Why is the average energy corresponding to a vibrational degree of freedom double that of a translational degree of freedom?
10. State and deduce the law of equipartition of energy. Show how you can use the law to calculate the specific heat of gases, and hence find the value of γ for diatomic and triatomic gasses.
11. What is the meaning of mean free path of a molecule of a gas? Show that it is equal to $1/\pi n\sigma^2$ where n is the number of molecules per cc and σ is the diameter of a molecule. Show that the mean free path is inversely proportional to pressure.
12. Explain what is meant by the 'mean square velocity of the molecules of a gas' and their 'mean free path'. Show how these two quantities can be found.
13. State clearly what do you understand by the principle of equipartition of energy. Explain the term 'degrees of freedom' in this connection. How is energy partitioned, when the temperature is low? Show that there is no real contradiction between this and the principle of equipartition.
14. Explain from kinetic theory the concept of temperature. Derive an expression for the pressure of a gas introducing the concept of mean free path.
15. Deduce from the law of distribution of free path $\lambda = 1/\pi\sigma^2 n$ the notations being usual. What is the value of λ according to Maxwell's law of distribution of molecular velocities?

    Describe a direct method of experimentally determining the value of λ.

    Explain the physical interpretation of temperature in the light of kinetic theory of gases.
16. Show, from the kinetic theory of gases, that $K = \eta\, c_v$ where K is the thermal conductivity, c_v is the specific heat at constant volume and η coefficient of viscosity. Is the relation sufficiently confirmed by experiment? If not, what do you think are the reasons?
17. Explain what is meant by the degrees of freedom of a mechanical system. Show that if a molecule of a gas has n degrees of freedom, the ratio γ of its principal specific heats is given by $1+2/n$.
18. Define coefficient of viscosity. Explain how kinetic theory accounts for the viscosity of a gas. Deduce and discuss the variation of viscosity with temperature.
19. Explain the term 'mean free path'; show that at constant temperature, the mean free path in a gas is inversely proportional to its density. Describe an experimental arrangement for the direct determination of the mean free path in a gaseous medium. Use the idea of free path to calculate the pressure exerted by a perfect gas.
20. How will you explain the pressure and the viscosity of a gas on the basis of kinetic theory of gases? What do you mean by the average velocity and RMS velocity of the molecules of a gas at NTP?
21. Explain clearly the origin of viscosity and thermal conductivity in a gaseous medium. Show that $K/\eta\, c_v = 1$, where K is the thermal conductivity, η the coefficient of viscosity and c_v the

specific heat at constant volume. Discuss the relation in the light of experimental results and indicate the manner in which one can obtain a better relation.

22. Explain the significance of the RMS, the mean and the most probable velocity and obtain expressions for them using Maxwell's law. Indicate how some of the concepts have been used in deducing the theory of Knudsen's absolute manometer.

23. State the importance of Brownian motion in the development of the molecular theory of heat. Give the theory of the translational Brownian motion and describe how this has been used to determine Avogadro's number. What are the possibilities of such measurements with gases?

24. **(a)** State the fundamental postulates of the kinetic theory of matter. Discuss the basic concept of temperature.

(b) Deduce an expression for the thermal conductivity of a gas from the kinetic theory. Explain why thermal conductivity of a gas becomes pressure dependent at low as well as high pressures.

25. Write down Maxwell's law of distribution of molecular velocities and explain the symbols you use. Indicate graphically how the distribution changes with rise of temperature and pressure.

26. Investigate the relation between the coefficient of thermal conductivity (K) and viscosity (η) of a gas and show that $K = \eta\, c_v$, where c_v is the specific heat at constant volume.

27. Deduce an expression for the thermal conductivity of a gas from kinetic theory. How would you actually proceed to determine the conductivity of any particular gas?

28. On the basis of kinetic theory, deduce an expression for the viscosity of a gas in terms of the mean free path of its molecules. Show that it is independent of pressure but depends upon the temperature of the gas.

29. Calculate the values of the two specific heats C_v and C_p of both monatomic and diatomic gases by applying Boltzmann's law of equipartition of energy.

30. Deduce an expression for the self-diffusion coefficient from the kinetic theory consideration. Discuss its variation with temperature and pressure.

31. What is Brownian motion? Describe a suitable arrangement for the demonstration of Brownian motion of the particles in a liquid, and give reasons for the conclusion that the motion is the result of irregular impacts on the particle by the molecules of liquid in heat motion. Give a brief survey of Perrin's work on Brownian motion and his determination of N on the basis of his results.

32. Derive Einstein's equation for Brownian motion of suspended particles assuming that the motion is due to series of impulses given by the surrounding molecules. Explain how N can be determined from it.

33. Clearly explain the meaning of the term 'mean free path'. Obtain an expression for the mean free path of a Maxwellian gas. Describe an experiment for measurement of mean free path of a gas.

34. Show with the help of the kinetic theory that the pressure of a perfect gas is directly proportional to the translational kinetic energy per unit volume. Hence, deduce (i) Avogardro's law and (ii) the law of partial pressures.

35. What is Brownian motion? Show how Avogadro's number can be determined from the observation of this motion. Describe the experiment.

Chapter 5

EQUATIONS OF STATE

5.1 EQUATION OF STATE OF PERFECT GAS

A perfect gas (or ideal gas) can be defined as a gaseous mass which obeys the following relation

$$\frac{pv}{T} = R \tag{5.1}$$

where p is the pressure (in dynes per square centimetre) exerted by a given mass of the gas occupying a volume v at absolute temperature T. R is a constant which depends on the mass of the gas and is independent of its pressure, volume and temperature. The mathematical relation connecting the three thermodynamic parameters p, v, and T of a substance is called its equation of state. The state of the gas represented by Eq. 5.1 holds approximately for the so-called permanent gases which cannot be liquefied under pressure however high the pressure is. We now know that all gases (including the so-called permanent gases) have been liquefied under the joint action of reduction of temperature and increase of pressure.

This perfect gas equation was put to experimental test by scientists working with different gases, and it was found that deviation occurs for all gases. Works of Regnault, Andrews, Amagut, Holborn, Natterer, Cailletet, K. Onnes, etc. in this field may be mentioned here. It was Regnault who showed that no gas in nature obeys Boyle's law for all temperatures and pressures. We shall describe here in detail the experiment of Andrews.

The apparatus used by him is shown in Fig. 5.1. $ABCD$ is a capillary glass tube of which portion BC is wider, the end A is closed while the end D is open. This contains pure and dry CO_2 gas trapped by a mercury pellet M, the volume of which at N.T.P. is known. $A_1B_1C_1D_1$ is a similar tube but containing pure and dry air trapped by the mercury pellet M_1. Both the tubes are calibrated; they are kept in two strong copper tubes, the ends of which are fixed by massive brass flanges and made air tight by leather washers.

Two steel screw plungers S and S_1 are filled through the lower end of the copper tubes. The copper tubes contain water; they are interconnected through E. By screwing S and S_1 into the water, pressure is produced and the applied pressure is calculated from the volume of air, the initial volume of which at N.T.P is known. For this, air is supposed to obey the law $pv = RT$. CO_2 in the tube $ABCD$ is surrounded by a bath, whose temperature can be varied at will. Starting from low temperature, CO_2 is subjected to different pressures and the corresponding volumes are noted. Such observations are repeated at different temperatures. The results of the experiment were represented graphically by Andrews as shown in Fig. 5.2.

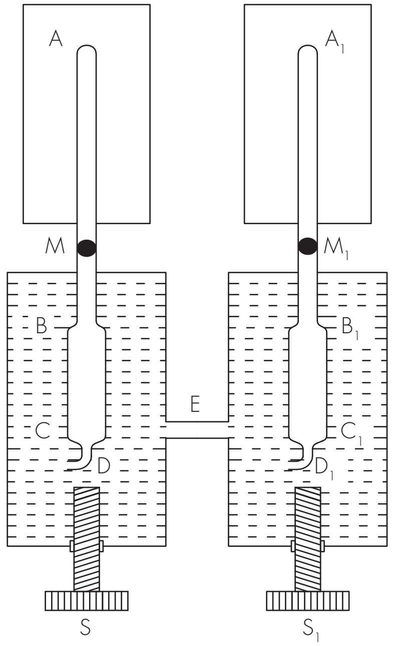

Fig. 5.1 Andrews apparatus

We see that the curves at lower temperatures are different from those at high temperatures. Considering the curve at 13.1 °C, we see that starting from low pressure if we increase the pressure of CO_2 gas, its volume diminishes untill we reach the point *B* where the gas begins to liquefy. Within the range of liquefaction from *B* to *C,* the pressure is independent of volume so that its behaviour is that of a saturated vapour. After this we see that though the pressure is increased, there is a little change in volume which indicates that the liquid is highly incompressible.

Next, we consider the isothermal corresponding to 21.5 °C. At this temperature the gas behaves in the same way as that at 13.1 °C, the only difference being the straight portion *B′C′* is shorter than that at 13.1 °C. The state of affairs continues as the temperature is increased till we reach the isothermal at 31.1 °C where the horizontal portion just disappears and the two specific volumes become identical. This isothermal is known as the critical isothermal of CO_2. At temperatures higher than this the straight portion does not appear, which means that above this temperature the gas cannot be liquefied by the increase of pressure alone however high it may be. At still higher temperature (48.1 °C) the volume decreases with the increase of pressure as in the case of isothermals of air.

Now we see that at isothermals higher than 31.1 °C, there is no formation of liquid however high the pressure is. The temperature 31.1 °C is the maximum temperature at which CO_2 may be liquefied by the application of pressure alone. This temperature is called the critical temperature (T_c) of CO_2. The critical pressure (p_c) is the pressure just necessary to liquefy the gas at the critical temperature. The critical

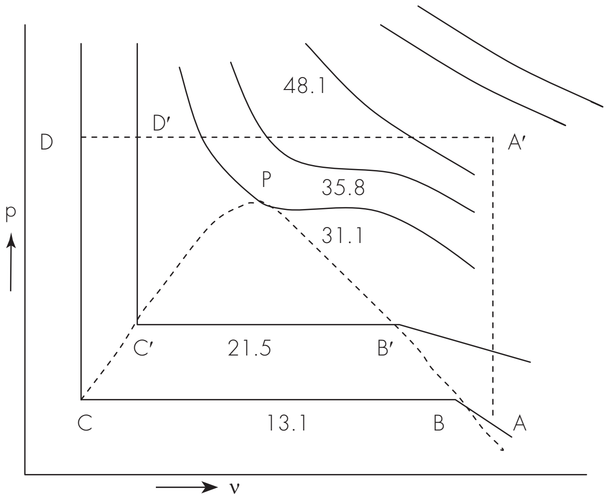

Fig. 5.2 Andrews experimental results

volume (v_c) is the volume per unit mass of the gas or of the liquid at the critical temperature and pressure. These three quantities are known as the critical constants of the gas.

It is seen from Fig. 5.2 that below the isothermal at 31.1 °C, the isothermals can be divided into three different regions depending upon the gaseous state, mixture of gaseous and liquid state, and liquid state. Within the region enclosed by the dotted curve, gaseous and liquid states coexist. The right of *PB* represents the gaseous region while the left of *PC* and below the critical isothermal represents the liquid region. When the gas liquefies during the straight horizontal portion of the isothermal lower than the critical isothermal, there are two different phases bounded by a discontinuity. If we want to go directly from the gaseous to liquid state, that is, from the point *A* to the point *D* without any discontinuity between them, we must avoid the passage through the region bounded by the dotted curve. The gas whose state is represented by this point *A* is compressed, keeping the volume constant so that the temperature increases. Let the temperature be increased above the critical temperature and the compression be stopped. This is represented by *AA′*. Now, the temperature of the gas is decreased keeping the pressure constant so that the volume is decreased to *D*. Thus, the system which was in gaseous state will be liquid at the point *D* on the same isotherm. In this operation there is no discontinuity anywhere, that is, the system does not exist in two phases simultaneously. This is known as the continuity of the liquid and gaseous state.

Experimental result of Amagut: Amagut worked with hydrogen, nitrogen, ethylene, etc. We shall consider his experimental results only. His observations are represented graphically as shown in Fig. 5.3 for hydrogen, Fig. 5.4 for nitrogen and Fig. 5.5 for ethylene where the ordinates represent the product *pv* and the abscissa the pressure.

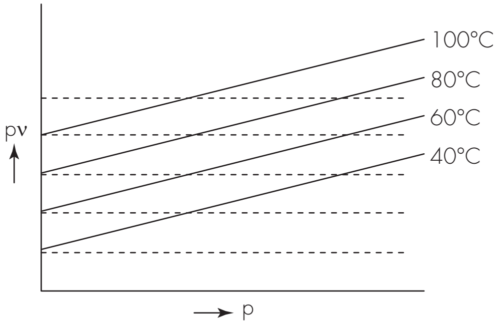

Fig. 5.3 Amagut's results for hydrogen

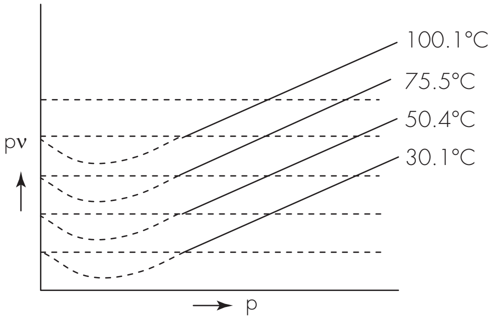

Fig. 5.4 Amagut's results for nitrogen

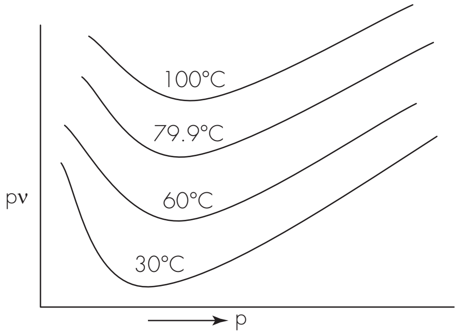

Fig. 5.5 Amagut's results for ethylene

In the case of hydrogen (Fig. 5.3), the lines are straight and are parallel to each other meaning that *pv* increases uniformly with pressure. The curve should be straight lines and parallel to the pressure axis if the gases would follow Boyle's law and Charles' law.

The behaviour of nitrogen is shown in Fig. 5.4. In low pressure region, the product *pv* decreases with pressure and then increases as in the case of hydrogen.

Figure 5.5 gives the variation of *pv* with *p* for ethylene at different temperatures. At lower temperatures the product *pv* decreases sharply with pressure, passes through a minimum, and then increases as in the case of hydrogen. As the temperature increases, the nature of the curves changes with the gradual flattening of the curves; and at high temperatures, there is always an increase of *pv* with *p*.

Gas and Vapour: A gaseous substance above the critical temperature is termed as a gas while the gaseous substance below the critical temperature is termed as vapour. Accordingly, any substance may be a gas or a vapour depending on its temperature. A vapour can be changed to its liquid state either partly or wholly by the application of pressure whereas a gas cannot be liquefied by the application of pressure alone.

5.2 VAN DER WAALS' EQUATION OF STATE

The behaviour of real gases can be explained when we consider the assumptions of the kinetic theory which are ideal, but in the real case they are to be modified. Two important assumptions of the kinetic theory— (i) the molecules are treated as mass points and (ii) there is no force between the molecules— are not valid. The molecules have finite dimensions however small they may be and the molecules are not devoid of molecular force. These two are responsible for the volume correction and pressure correction. We shall consider two methods of volume correction:

1. Simple method: Let the molecules be regarded as hard elastic spheres of diameter σ. Considering a molecule, the centre of no other molecule can come closer than σ to it. We may consider that the considered molecule has a sphere of influence $4/3\ \pi\sigma^3 = s$ within which the centre of no other molecule can come. Similar is the case with other molecules.

Let us consider a vessel of volume v containing a gas. Treating the molecules as mass points, the volume free for molecular movement is v but the free volume decreases as we consider molecules to be hard elastic spheres of diameter σ. To determine the volume inaccessible for molecules, let the molecules be introduced into the vessel one by one. When the first molecule enters, it finds volume v available to it; second molecule finds $v - s$ volume available to it where s is the sphere of influence of the first molecule; third molecule finds $v - 2s$ volume available to it and so on. Let there be N such molecules introduced, then the average free volume is given by

$$\frac{1}{N}[v+(v-s)+(v-2s)+(v-3s)+\ldots\ldots\ldots+v-(N-1)s]$$

$$=\frac{1}{N}\{Nv-[1+2+\ldots\ldots+(N-1)]s\}$$

$$=\frac{1}{N}\left[Nv-\frac{N(N-1)}{2}s\right]$$

$$=v-\frac{N-1}{2}s=v-\frac{Ns}{2}=v-b \tag{5.2}$$

As N is very large compared to unity, $(N - 1)$ can be written as N. Thus, we see that actual volume is reduced by a quantity b, where b is four times the volume of the molecules.

2. Rigorous method: Let us consider N molecules inside a vessel of volume v. Treating the molecules as rigid elastic spheres of diameter σ, we have seen that the sphere of influence is $4/3\ \pi\sigma^3$. Considering N molecules the volume inaccessible to the centre of a particular molecule is $4/3\pi\sigma^3(N-1) = 4/3\pi\sigma^3 N(\text{since N} \gg 1)$. Similar is the case with all other molecules. Hence, the space left for free motion of the molecule is $v - 4/3\pi\sigma^3 N$. Therefore, the actual molecular density is

$$n_1 = \frac{N}{v - \frac{4}{3}\pi\sigma^3 N} \tag{5.3}$$

Considering the gas confined in the vessel, molecules can approach the distance $\sigma/2$ from the wall. But a molecule at a distance σ from the wall has its sphere of influence extended upto the wall and the centre of no other molecule can lie within the hemisphere $2/3\ \pi\sigma^3$ adjacent to the wall, that is, we may consider the centre of molecules to be striking an imaginary wall at a distance σ from the real wall. Let us consider a small volume dv in the vicinity of the wall, then $n_1\ 2/3\ \pi\sigma^3$ is the fraction of volume per cc within which the centre of no other molecule can come, that is, this volume is inaccessible to the centre of other molecules. If dv_1 represents the free space in volume dv, then

$$\frac{dv - dv_1}{dv} = n_1 \frac{2}{3}\pi\sigma^3$$

or

$$1 - \frac{dv_1}{dv} = n_1 \frac{2}{3}\pi\sigma^3$$

or

$$dv_1 = dv\left(1 - n_1 \frac{2}{3}\pi\sigma^3\right)$$

$$= dv\left(1 - \frac{b}{N} n_1\right) \quad \text{where } b = \frac{2}{3}\pi\sigma^3 N$$

$$= dv\left(1 - \frac{b}{N}\frac{N}{v - 2b}\right)$$

$$= dv\left(1 - \frac{b}{v - 2b}\right) \tag{5.4}$$

Now, the actual number of molecules in volume dv is

$$n_1 dv_1 = \frac{N}{v - 2b}\ dv\left(1 - \frac{b}{v - 2b}\right)$$

$$= \frac{N}{v - 2b}\ dv\left(\frac{v - 3b}{v - 2b}\right)$$

$$= \frac{Ndv(v - 3b)}{(v - 3b)(v - b) + b^2}$$

$$= \frac{Ndv(v-3b)}{(v-3b)(v-b)} \quad \text{neglecting } b^2$$

$$= \frac{Ndv}{v-b} \tag{5.5}$$

Considering molecules as mass points, the number of molecules in $dv = Ndv/v$.

Thus, on comparing these two equations, we find that the effect of considering finite volume of the molecule is to decrease the actual volume v to $v - b$ where b is four times the volume of the molecules.

Pressure correction: The pressure correction is due to the intermolecular force. Although the actual nature of the intermolecular force is not known, yet it is well known that molecules attract strongly at very short distance which falls off rapidly with distance. Let us consider a molecule at the centre; it is attracted by all the molecules surrounding it, so the net force is zero. But a molecule near the wall will experience a net resultant inward force. Accordingly, the molecules will strike the wall with lower velocity than when there is no force of attraction. Hence, the change in momentum or the pressure is less than that for a perfect gas. The actual pressure will be sum of the observed pressure p and the correction factor due to the inward pull p'. This p' is proportional to the number of molecules attracting the striking molecules and the number of such striking molecules per unit area of the wall. Both of them are n where n is the number of molecules per cc.

$$\therefore \qquad p' \propto n^2 \propto \frac{1}{v^2} \quad \text{where } v \text{ is the volume of the gas}$$

$$\therefore \qquad p' = \frac{a}{v^2} \quad \text{where } a \text{ is a constant} \tag{5.6}$$

The total pressure is $p + p' = p + \frac{a}{v^2}$

So, the resultant equation of state is $\left(p + \frac{a}{v^2}\right)(v-b) = RT$ (5.7)

Equation 5.7 holds good in the vapour region, liquid region, near and above the critical point. Here if v is gram molar volume having mass equal to molecular weight, R is universal gas constant. The equation is valid for any mass, then b and R will be proportional to the mass taken, but a is proportional to the square of the mass.

For CO_2, the values of a and b are 0.00874 and 0.0023, respectively.

Taking $R = 1.00642/273$ Van der Waals' equation for carbon dioxide is

$$\left(p + \frac{0.00874}{v^2}\right)(v - 0.0023) = \frac{1.00642}{273}T \tag{5.8}$$

In Eq. 5.8, the unit of volume is the volume of the gas at 0 °C under the pressure of 1 atmosphere.

5.3 DETERMINATION OF THE CONSTANTS *a* AND *b*

There are different methods of determination of a and b. We shall discuss them one by one.

1. **From the coefficient of thermal expansion and compressibility of the liquid:**

   Let v_1 be the volume of 1 gm of a liquid at pressure p_1 and temperature T_1. Let v_2 be volume of the some mass of the liquid at the same pressure p_1 and at different temperature T_2, then

$$\left(p_1+\frac{a}{v_1^2}\right)(v_1-b)=\frac{T_1}{T_2}\left(p_1+\frac{a}{v_2^2}\right)(v_2-b) \tag{5.9}$$

The volume v_1 of the same mass of liquid could be changed to v_2 by changing the pressure from p_1 to p_2 at constant temperature T_1. Then

$$\left(p_1+\frac{a}{v_1^2}\right)(v_1-b)=\left(p_2+\frac{a}{v_2^2}\right)(v_2-b) \tag{5.10}$$

From Eqs 5.9 and 5.10, we get

$$\left[\left(p_2+\frac{a}{v_2^2}\right)-\frac{T_1}{T_2}\left(p_1+\frac{a}{v_2^2}\right)\right](v_2-b)=0$$

or

$$p_2+\frac{a}{v_2^2}=\frac{T_1}{T_2}\left(p_1+\frac{a}{v_2^2}\right) \tag{5.11}$$

Knowing the values of p_1, p_2, T_1, T_2 and v_2 'a' can be calculated. From the value of 'a' thus obtained, the value of 'b' can be calculated from any of the Eqs. 5.9 or 5.10.

Very accurate value of density of water at 20 °C was obtained by Chappuis. Under pressure of 1 atmosphere the density of water is 0.9982328 gm/cc, so that the volume of 1 gm of water at 293 K and under 1 atmosphere pressure is 1/0.9991285 = 1.001770 cc. The density of water at 15 °C is 0.9991285 gm/cc under pressure of 1 atmosphere. Hence, the volume of 1 gm of water at 15 °C and under pressure of 1 atmosphere is 1/0.9991285 = 1.000873 cc. By reducing the temperature from 20 °C to 15 °C, the volume of water changes by 0.000897 cc.

According to Pagliani and Vincentini, an increase of pressure by 1 atmosphere on 1 gm of water at 20 °C produces a volume strain (change in volume per unit volume) of 4.44×10^{-5}. The bulk modulus E of water is given by

$$\delta p=-E\frac{\delta v}{v}$$

$$1\text{ atm}=-E\times 4.44\times 10^{-5}$$

$$\text{giving } E=-1/4.44\times 10^{-5}$$

The change in pressure required to produce a change in volume by 0.000897 cc in a volume 1.001770 cc is

$$\delta p=\frac{0.000897}{1.001770}\times\frac{1}{4.44\times 10^{-5}}=20.16\text{ atmos}$$

It follows that 1 gm of water at 20 °C occupies the volume 1.000873 cc under a pressure of 1 + 20.16 = 21.16 atmosphere.

Substituting the volumes p_1 = 1 atmos, p_2 = 21.16 atmos, v_1 = 1.001770 cc, v_2 = 1.000873, T_1 = 293 K and T_2 = 288 K in Eq. 5.11, the value of 'a' obtained is 1164.1 atmos.

Substituting the value of 'a' in Eq. 5.10, the value of 'b' obtained is 0.954.

2. **Constant volume method:**

This method is simple and accurate. From the Van der Waals' equation,

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

we have
$$p=\frac{RT}{v-b}-\frac{a}{v^2} \tag{5.12}$$

Differentiating with respect to T and keeping v constant,

$$\left(\frac{\partial p}{\partial T}\right)_v=\frac{R}{v-b} \quad \text{or} \quad v-b=\frac{R}{\left(\frac{\partial p}{\partial T}\right)_v}$$

$$\therefore \qquad p=\frac{RT}{\frac{R}{\left(\frac{\partial p}{\partial T}\right)_v}}-\frac{a}{v^2}=T\left(\frac{\partial p}{\partial T}\right)_v-\frac{a}{v^2}$$

$$\therefore \qquad a=v^2\left[T\left(\frac{\partial p}{\partial T}\right)_v-p\right] \quad \text{and} \quad b=v-\frac{R}{\left(\frac{\partial p}{\partial T}\right)_v} \tag{5.13}$$

From the observation of variation of pressure with temperature from a constant volume gas thermometer, a and b can be calculated.

3. **Isothermal method:**

A study of the isothermals of a gas serves to supply a method for the determination of a and b. We have from Van der Waals' equation

$$p=\frac{RT}{v-b}-\frac{a}{v^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_T=-\frac{RT}{(v-b)^2}+\frac{2a}{v^3} \tag{5.14}$$

If we find the value of the slope $(\partial p/\partial T)_T$ of an isothermal at any temperature T and if we know the pressure and volume of a gas at the same temperature, we can substitute these quantities in the Eq. 5.14 and on solving it, we get the values of a and b.

4. **From critical constants:**

We know that critical volume $v_c = 3b$, critical pressure $p_C = a/27b^2$ and critical temperature $T_C = 8a/27bR$. Hence knowing the values of the critical constants, a and b can be determined. This method is, however, not very accurate because Van der Waals' equation cannot be expected to hold good in the critical region.

5. **From inversion temperature:**

The temperature of inversion for the Joule Thomson effect is given by

$$T_i = 2a/bR \tag{5.15}$$

Knowing the value of either a or b previously and the inversion temperature, the other can be calculated.

5.4 DISCUSSIONS ON VAN DER WAALS' EQUATION

Van der Waals' equation is given by

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

or $$(pv^2+a)(v-b)=RTv^2$$

or $$pv^3-bpv^2+av-ab=RTv^2$$

or $$v^3-\left(b+\frac{RT}{p}\right)v^2+\frac{av}{p}-\frac{ab}{p}=0 \tag{5.16}$$

This is a cubic equation in v for a particular isotherm; and for a particular p, we get three roots of v which are

1. All real and different;
2. All real and identical;
3. One real and two imaginary.

Again, from $$p=\frac{RT}{v-b}-\frac{a}{v^2}$$

in the limit v tending to infinity, p tends to zero and v tending to b, p tends to infinity, Van der Waals' equation when plotted for CO_2 in terms of p vs v curves as shown in Fig. 5.6 are obtained. To have an idea of the intermediate regions of an isotherm, let us investigate the slope from

$$p=\frac{RT}{v-b}-\frac{a}{v^2}$$

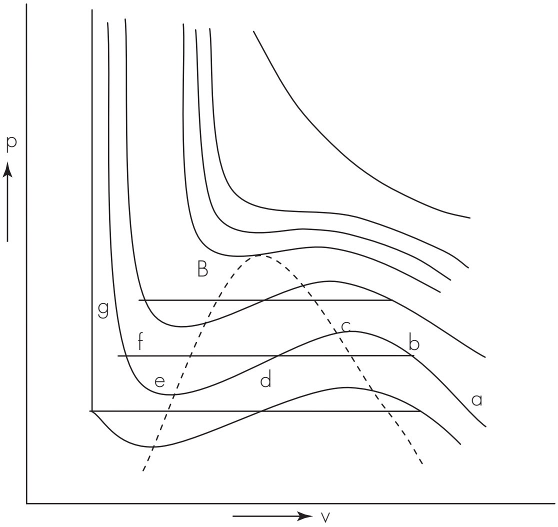

Fig. 5.6 Van der Waals' curves for CO_2

We get
$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} \tag{5.17}$$

So, the rate of change of the slope
$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} \tag{5.18}$$

For large values of T, $(\partial^2 p/\partial v^2)_T$ is positive; so, the equation $p = (RT/v - b) - a/v^2$ must have a minimum in this region. When the temperature is not high, the nature of the isothermal will be governed by values of v. When v approaches b, the first term of Eq. 5.18 predominates; so, $\partial^2 p/\partial v^2$ is positive and hence the isotherm has a minimum. Again as v increases slowly above b, the first term in Eq. 5.18 decreases till it becomes equal to the second term giving
$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 \tag{5.19}$$

For very large values of v, the first term of Eq. 5.18 again becomes predominant and $(\partial^2 p/\partial v^2)_T$ is positive. In the lower isotherms, there is one maxima and one minima. These maxima and minima come closer as the temperature increases (for isothermals below the critical isothermal) and finally at critical isothermal, the two points meet at which there is only one tangent parallel to v – axis instead of two tangents (one at maxima and the other the minima) at lower isothermals.

At maxima and minima,
$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \tag{5.20}$$

So, from Eq. 5.17
$$\frac{RT}{(v-b)^2} = \frac{2a}{v^3}$$

or
$$\frac{RT}{v-b} = \frac{2a}{v^3}(v-b)$$

Putting the value of $\frac{RT}{v-b}$ in Van der Waals' equation, we get
$$p = \frac{2a}{v^3}(v-b) - \frac{a}{v^2} = \frac{2a}{v^2} - \frac{2ab}{v^3} - \frac{a}{v^2} = \frac{a}{v^2} - \frac{2ab}{v^3} \tag{5.21}$$

Eq. 5.21 represents a curve passing through the maxima and minima of the isothermals. The maxima of this curve touches the critical isothermal at B. The value of the critical pressure and volume can be obtained by differentiating p with respect to v and at maxima putting $\partial p/\partial v = 0$.

So, from
$$p = \frac{a}{v^2} - \frac{2ab}{v^3}$$
$$\frac{\partial p}{\partial v} = -\frac{2a}{v^3} + \frac{6ab}{v^4} = 0$$

Representing the critical volume by v_c, critical pressure p_c and critical temperature T_c, we get
$$\frac{6ab}{v_c^4} = \frac{2a}{v_c^3} \quad \therefore v_c = 3b \tag{5.22}$$

Again from Eq. 5.21, the critical pressure p_c is given by

$$p_c = \frac{a}{v_c^2} - \frac{2ab}{v_c^3} = \frac{a}{9b^2} - \frac{2ab}{27b^3} = \frac{a}{9b^2} - \frac{2a}{27b^2} = \frac{a}{27b^2} \tag{5.23}$$

The critical temperature T_c is obtained by putting the values of p_c and v_c in Van der Waals' equation

$$\left(p_c + \frac{a}{v_c^2}\right)(v_c - b) = RT_c$$

or

$$\left(\frac{a}{27b^2} + \frac{a}{9b^2}\right)(3b - b) = RT_c$$

or

$$\frac{4a}{27b^2} \times 2b = RT_c \quad \therefore T_c = \frac{4a}{27b^2} \times \frac{2b}{R} = \frac{8a}{27bR} \tag{5.24}$$

The ratio

$$\frac{RT_c}{p_c v_c} = \frac{\dfrac{R\,8a}{27bR}}{\dfrac{a}{27b^2}3b} = \frac{R8a\,27b^2}{27bR\,3ab} = \frac{8}{3} = 2.67$$

The values of the critical constants can also be found out in another way. The critical isothermal has only one point of inflexion; for such a point on the $p - v$ curve,

$$\left(\frac{\partial p}{\partial v}\right) = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial v^2}\right) = 0$$

that is,

$$-\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \quad \text{and} \quad \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \tag{5.25}$$

Solving these two equations and from equation

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

we get the same values of p_c, v_c and T_c.

5.5 COMPARISON OF VAN DER WAALS' EQUATION WITH ANDREWS' EXPERIMENTAL CURVES

The $p - v$ curves for CO_2 obtained from Van der Waals' equation are similar to the experimental $p - v$ curves of Andrews for CO_2 only at and above the critical temperature. Below the critical temperature, the curves due to Van der Waals' equations are different from Andrews' experimental curves. If the isothermals of Andrews' experimental curves are made to overlap the theoretical curves for the same temperatures, it is found that above the critical temperature the two sets of curves coincide whereas below the critical temperature the two sets of curves are coincident only at the purely gaseous and liquid region, and there is a prominent difference in the central region (Fig. 5.6). Instead of maxima and minima as in the theoretical curves, there is a flat horizontal portion in Andrews' experimental curves. Let us consider such a set of curves below the critical temperature. Curve *a b c d e f g* is the theoretical curve, whereas curve *a b d f g* is the Andrews' experimental curve. The two portions *a b* and *f g* are same, and they represent gaseous and liquid state of the substance. Instead of the straight horizontal portion of the experimental curves, where condensation occurs, theory gives an s-shaped curve *b c d e f*.

The discrepancy between the two curves in the region *b f* may be considered in the following: the part *c d e* of the theoretical curve shows that the volume increases with the increase in pressure. This represents an unrealizable condition and cannot be realized in practice. Hence, the part *c d e* is not obtained in Andrews' experimental curves. The part *b c* and *e f* of the theoretical curves represent supercooled vapour and superheated liquid, both of which are metastable states and may be realized only under certain conditions. But this metastable state is easily disturbed by mechanical shocks, the presence of slightest trace of impurity, etc. Hence, these portions are not present in Andrews' experimental curves.

Van der Waals' theory cannot indicate the point *b* where the condensation begins. From thermodynamic reasoning, Maxwell and Clausius both reached the conclusion that if the line *a b c d e f g* is to represent the actual isothermal path from *a* to *g*, it must be so chosen that the areas *b c d* and *d e f* are equal. For example, let us consider that the substance is taken through the cycle *b c d e f b,* the temperature remaining constant throughout the cyclic process; the net work done in carrying out the process is according to the second law of thermodynamics nil, that is, the area of the closed curve representing the cycle must vanish. Hence, the area *b c d* and *d e f* must be equal being described in opposite senses.

5.6 EXPERIMENTAL DETERMINATION OF CRITICAL CONSTANTS

The three critical constants—critical pressure, critical volume and critical temperature—are very much important in the study of gases, especially in liquefaction.

Of the three constants, measurement of critical temperature and critical pressure is very easy. The measurement of critical volume is very difficult because it varies considerably for slightest variation of temperature and pressure near the critical region; hence for the measurement of critical volume, the substance must be kept in perfectly critical temperature and pressure.

The experimental arrangement of the determination of critical pressure and critical temperature is shown in Fig. 5.7. *A* is a hard glass tube containing the experimental liquid. *A* is connected to a pump

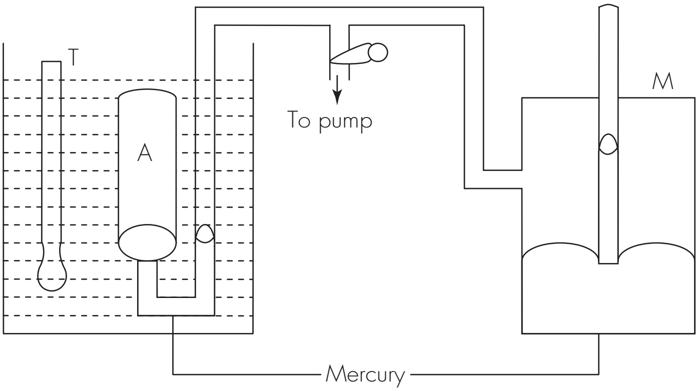

Fig. 5.7 Experimental arrangement of the determination of critical constants

and a manometer *M*, for measurement of pressure. *A* is surrounded by a liquid bath the temperature of which can be varied. *T* is a thermometer for the measurement of temperature. By means of the pump, different pressures are applied. The temperature of the bath is also increased in small steps from a very low value. At a particular temperature and pressure, the liquid disappears suddenly. The corresponding temperature and pressure are noted.

Now the temperature of the bath is decreased in small steps, and the pressure is also recorded until the liquid appears again all of a sudden. The corresponding temperature and pressure are again noted. The mean of these two pressures gives the critical pressure and the mean of these two temperatures gives the critical temperature.

This method is applicable for those liquids which do not wet glass. The hard glass tube is replaced by a platinized steel tube for liquid which wets glass such as water.

The simple method of measurement of critical volume consists of two glass tubes containing different amount of the same liquid. These tubes are graduated in volume and are surrounded by a bath, the temperature of which can be varied. At any particular temperature, the volume occupied by the liquid and the corresponding vopours are noted in both the tubes. If ρ_l, ρ_v be the densities of liquid and the vapour, v_l, v'_l be the volume of the liquid in the two tubes, v_v, v'_v be the volume of the vapour in the two tubes, *m* and *m*′ be the mass of the contents of the two tubes, then

$$\rho_l v_l + \rho_v v_v = m \tag{5.26}$$

and

$$\rho_l v'_l + \rho_v\ v'_v = m' \tag{5.27}$$

Solving these two equations, ρ_l, ρ_v can be found for this particular temperature. Similar observations are made at different temperature till the two densities become identical at critical temperature. When these densities are plotted against temperature, a parabolic curve as shown in Fig. 5.8 is obtained.

The mean of these densities at different temperatures lie on a straight line which meets the curve at the critical point where ρ_v and ρ_l are same. This is the law of rectilinear diameter. The coordinates of the point of intersection gives T_c and ρ_c. The reciprocal of ρ_c gives v_c.

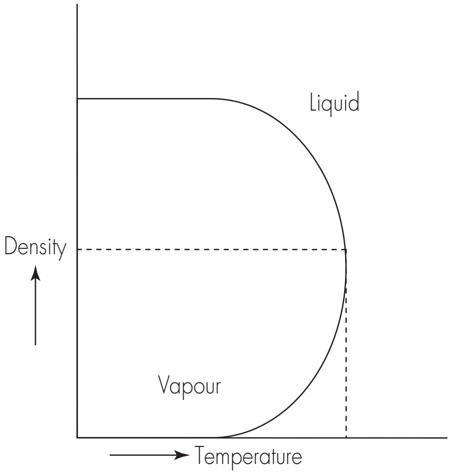

Fig. 5.8 Plotting of densities of liquid and vapour against temperature

5.7 REDUCED EQUATION OF STATE AND LAW OF CORRESPONDING STATES

Van der Waals' equation of state contains a, b and R, the first two of which are the characteristic constants of a gas and the third one is universal gas constant. The presence of a and b makes the nature of the isothermals different for different gases hence, the equation of state is not universal. The attempt of building up an equation of state which is of universal use succeeded in developing reduced equation of state. If the three variables are measured in units of their corresponding critical values, then the resulting equation is called the reduced equation of state. Let us define three reduced quantities p_r, v_r, T_r as

$$p_r = \frac{p}{p_c} \tag{5.28}$$

$$v_r = \frac{v}{v_c} \tag{5.29}$$

$$T_r = \frac{T}{T_c} \tag{5.30}$$

Then from Van der Waals' equation of state,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

we get

$$\left(p_r p_c + \frac{a}{v_r^2 v_c^2}\right)(v_r v_c - b) = RT_r T_c$$

$$\left(p_r \frac{a}{27b^2} + \frac{a}{v_r^2 9b^2}\right)(3bv_r - b) = RT_r \frac{8a}{27bR}$$

or

$$\left(p_r + \frac{3}{v_r^2}\right)\left(v_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{5.31}$$

This is known as reduced equation of state. It is independent of the nature of the gas because it does not contain characteristic constants of the gas hence, it is universal. Since the reduced equation of state is derived from Van der Waals' equation, it is not free from the intrinsic defects of Van der Waals' equation.

It is apparent from Eq. 5.31 that if any two of the quantities p_r, v_r, T_r of two substances are identical, the third quantity will also be identical. This is called the law of corresponding states. This means that if pressure and temperature of two substances bear the same ratio to their corresponding critical values, volume will also bear the same ratio to its critical value.

5.8 MERITS AND DEMERITS OF VAN DER WAALS' EQUATION

In spite of the fact that Van der Waals' equation has been very helpful in understanding many of the properties of real gases, the evaluation of critical constants, the derivation of the equation of corresponding states, the continuity of the gaseous to the liquid state, when it is subjected to experimental verification, we find considerable discrepancies. These are:

1. We have seen that for CO_2, the curves drawn from Van der Waals' equation do not coincide with the experimental curves of Andrews. Marked discrepancy is observed for isothermals below the critical one where Van der Waals' equation gives one maxima and one minima.
2. Van der Waals' equation supposes a and b to be constants, but these are different for different substances and even vary with temperature for a particular substance.
3. It predicts that $v_c = 3b$, but experimental observation shows that $v_c = 2b$.
4. According to Van der Waals' equation b is equal to 4 times the volume occupied by all gas molecules, but b is found to be $4\sqrt{2}$ times the volume occupied by all the gas modules.
5. Van der Waals' equation shows that the ratio RT_c/p_cv_c is constant and its value is 2.67, but actually its value is 3.7 and it varies from gas to gas.
6. Boyle temperature derived from Van der Waals' equation does not tally with the experimental facts.
7. Van der Waals' reduced equation of state is said to be of universal application, but it is not so because the intrinsic defects of Van der Waals' equation are inherent in the reduced equation of state.

5.9 BOYLE TEMPERATURE FROM VAN DER WAALS' EQUATION

Van der Waals' equation is

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

or

$$p=\frac{RT}{v-b}-\frac{a}{v^2}$$

or

$$pv=\frac{RTv}{v-b}-\frac{a}{v} \tag{5.32}$$

At Boyle Temperature, T becomes T_B; our perfect gas equation becomes

$$pv=RT_B \tag{5.33}$$

From Eqs 5.32 and 5.33, we get

$$RT_B=\frac{RT_Bv}{v-b}-\frac{a}{v}$$

or

$$\frac{RT_Bv}{v-b}-RT_B=\frac{a}{v}$$

or

$$RT_B\left(\frac{v}{v-b}-1\right)=\frac{a}{v}$$

or

$$RT_B\left(\frac{v-v+b}{v-b}\right)=\frac{a}{v}$$

or

$$RT_B\frac{b}{v-b}=\frac{a}{v}$$

∴ $$T_B = \frac{a}{v}\frac{(v-b)}{bR} = \frac{a}{bR}, \text{ as } b \text{ is small} \tag{5.34}$$

Again, $$T_c = \frac{8a}{27bR} \therefore T_B = \frac{27}{8}T_c \tag{5.35}$$

5.10 OTHER EQUATIONS OF STATE

We have discussed the merits and demerits of Van der Waals' equation. In order to overcome the defect of Van der Waals' equation, different equations of states have been proposed. The main object of such equations of state is to fit the experimental results of the real gases. Some of the equations of state are derived from rigorous theoretical considerations while others have been derived empirically. We shall mention a few of them.

1. **Clausius equation**

   According to Clausius, the equation of state is

$$\left(p + \frac{a'}{T(v+c)^2}\right)(v-b) = RT \tag{5.36}$$

The constant a of Van der Waals' equation has been changed to $\frac{a'}{T}$ in order to incorporate the variation of a with temperature. This equation fits Andrews' curve better than Van der Waals' equation but fails in the case of other gases.

2. **Berthelot equation**

   Berthelot proposed an equation of state of the form

$$\left(p + \frac{a'}{Tv^2}\right)(v-b) = RT \tag{5.37}$$

This equation shows better agreement with experiment at moderate pressure. It may also be written in terms of the critical constants as

$$pv = RT\left[1 + \frac{9}{128}\frac{T_c}{p_c}\frac{p}{T}\left(1 - \frac{6T_c^2}{T^2}\right)\right] \tag{5.38}$$

3. **Dieterici equation**

   According to Dieterici, the equation of state is

$$p = \frac{RT}{v-b}e^{\frac{-a}{RTv}} \tag{5.39}$$

This equation agrees with experimental observation well up to a pressure of 12 atmospheres but fails at high pressures.

To a first approximation it yields Van der Waals' equation, so it has the advantage of Van der Waals' equation; it is better than Van der Waals' equation in the sense that it gives $v_c = 2b$ and the ratio

$$\frac{RT_c}{p_c v_c} = 3.667 \tag{5.40}$$

From Eq. 5.39,

$$pe^{\frac{a}{RTv}} = \frac{RT}{v-b} \tag{5.41}$$

or
$$p\left[1+\frac{a}{RTv}+\frac{1}{2}\left(\frac{a}{RTv}\right)^2+\ldots\ldots\ldots\right] = \frac{RT}{v-b} \tag{5.42}$$

To a first approximation, we may write

$$p\left(1+\frac{a}{RTv}\right) = \frac{RT}{v-b}$$

or
$$p\left(1+\frac{a}{pv^2}\right) = \frac{RT}{v-b}$$

or
$$\left(p+\frac{a}{v^2}\right)(v-b) = RT \tag{5.43}$$

Thus, Van der Waals' equation can be derived from Dieterici equation.

To find the values of critical constants, we apply the condition $dp/dv = 0$ and $d^2p/dv^2 = 0$ at the point of inflexion.

From Eq. 5.39,

$$\frac{dp}{dv} = -\frac{RT}{(v-b)^2}e^{\frac{-a}{RTv}} + \frac{RT}{(v-b)}e^{\frac{-a}{RTv}}\left(\frac{a}{RTv^2}\right) = 0$$

or
$$\frac{RT}{v-b}e^{\frac{-a}{RTv}}\left(\frac{a}{RTv^2}-\frac{1}{v-b}\right) = 0$$

or
$$\frac{a}{RTv^2}-\frac{1}{v-b} = 0 \tag{5.44}$$

or
$$\frac{a}{RT} = \frac{v^2}{v-b} \tag{5.45}$$

Again,
$$\frac{d^2p}{dv^2} = \frac{2RT}{(v-b)^3}e^{\frac{-a}{RTv}} - \frac{RT}{(v-b)^2}\left(\frac{a}{RTv^2}\right)e^{\frac{-a}{RTv}}$$

$$-\frac{RT}{(v-b)^2}e^{\frac{-a}{RTv}}\frac{a}{RTv^2} + \frac{RT}{(v-b)}e^{\frac{-a}{RTv}}\left(\frac{a}{RTv^2}\right)^2 + \frac{RT}{(v-b)}e^{\frac{-a}{RTv}}\left(-\frac{2a}{RTv^3}\right) = 0$$

or
$$\frac{RT}{v-b}e^{\frac{-a}{RTv}}\left[\frac{2}{(v-b)^2}-\frac{1}{(v-b)}\frac{a}{RTv^2}-\frac{a}{RTv^2(v-b)}+\left(\frac{a}{RTv^2}\right)^2-\frac{2a}{RTv^3}\right] = 0$$

Substituting the value of a/RT from Eq. 5.45, we get

$$\frac{2}{(v-b)^2}-\frac{2}{(v-b)^2}+\frac{1}{(v-b)^2}-\frac{2}{v(v-b)} = 0$$

or
$$\frac{1}{(v-b)^2}=\frac{2}{v(v-b)}$$

or
$$\frac{1}{v-b}=\frac{2}{v}$$

or
$$2v-2b=v \quad \therefore v=2b$$

This v is the critical volume, so we write $\therefore v_c=2b$ (5.46)
From Eq. 5.45,

$$\frac{a}{RT_c}=\frac{v_c^2}{v_c-b}=\frac{4b^2}{b}=4b$$

$$T_c=\frac{a}{4bR} \tag{5.47}$$

Putting the values of v_c and T_c in Eq. 5.39,

$$p_c=\frac{RT_c}{v_c-b}e^{\frac{-a}{RT_cv_c}}=\frac{\frac{Ra}{4bR}}{2b-b}e^{\frac{-a4bR}{Ra\,2b}}=\frac{Ra}{4bR\,b}e^{-2}=\frac{a}{4b^2e^2} \tag{5.48}$$

The ratio
$$\frac{RT_c}{p_cv_c}=\frac{\frac{Ra}{4bR}}{\frac{a\,2b}{4b^2e^2}}=\frac{Ra4b^2e^2}{4bR\,2ab}=\frac{e^2}{2}=3.667 \tag{5.49}$$

4. **Saha and Bose equation**

   Saha and Bose derived an equation of state from thermodynamic consideration and theory of probability which gives

$$p=\frac{RT}{v-b}e^{\frac{-a}{RTv}}\log_e\left(\frac{v-2b}{v}\right) \tag{5.50}$$

This gives $RT_c/p_cv_c = 3.53$ and is suitable for simple gases. Van der Waals' equation of state can be deduced from this as a special case.

5. **Beattie and Bridgemann equation**

   Beattie and Bridgemann suggested the following equation of state:

$$p=\frac{RT}{v^2}\left(1-\frac{c}{vT^3}\right)\left(v+B_o-\frac{bB_o}{v}\right)-\frac{A_o}{v^2}\left(1-\frac{a}{v}\right) \tag{5.51}$$

where a, b, c, A_o, B_o are constants. Suitable adjustment of the parameters makes the equation widely applicable and fits the experimental data well.

6. **Kamerlingh Onnes equation**

   Kamerlingh Onnes investigated the experimental data of a number of gases and proposed an equation of state containing as many as 26 constants. According to him,

$$pv=A+Bp+Cp^2+Dp^3+\ldots\ldots\ldots\ldots\ldots \tag{5.52}$$

where A, B, C, D, ……… are constants called virial coefficients, the values of which decrease successively. These constants are functions of temperature and are independent of pressure. At very low pressure, this equation reduces to

$$pv = A$$

which gives the ideal gas equation $pv = RT$. For all gases, the second virial coefficient B is negative at low temperature; it increases to zero with rise of temperature and then becomes positive. The temperature corresponding to $B = 0$ is called the Boyle temperature. At this temperature Boyle's Law holds true.

7. **F. G. Keyes equations**

Based on nuclear atom model and the influence of surrounding molecules on Van der Waals' volume correction constant b, F. G. Keyes proposed the equation

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v+\ell)^2} \tag{5.53}$$

where A, β, α, ℓ are constants.

8. **Callendar equation**

While studying the behavior of steam, Callendar proposed the equation

$$v - b = \frac{RT}{p} - \frac{a}{T^n} \tag{5.54}$$

For steam, b = volume of 1 gm of condensed steam, $n = 3.33$.

This equation may also be applied to gases and vapours at moderate pressure.

SOLVED PROBLEMS

Q1. If the critical temperature of a gas is 31 °C and the critical pressure 73 atmospheres, calculate the value of the constants a and b in Van der Waals' equation ($R = 0.00366$ taking unit pressure as standard barometric pressure and unit volume as the volume at N.T.P).

Ans. According to the problem,

$$\frac{8a}{27bR} = 304 \quad \text{and} \quad \frac{a}{27b^2} = 73$$

or

$$\frac{\dfrac{8a}{27bR}}{\dfrac{a}{27b^2}} = \frac{304}{73} \quad \text{or} \quad \frac{8a27b^2}{27bRa} = \frac{304}{73}$$

or

$$b = \frac{304 \times 0.00366}{8 \times 73} = 0.00191$$

$\therefore$

$$a = 73 \times 27b^2 = 73 \times 27 \times (0.00191)^2 = 0.00719$$

Q2. Show that the Boyle temperature of a Dieterici gas is the same as that obtained for a Van der Waals' gas.

Ans. The Dieterici equation of state is

$$p=\frac{RT}{v-b}e^{\frac{-a}{RTv}} \quad \text{or} \quad pe^{\frac{a}{RTv}}=\frac{RT}{v-b}$$

or
$$p\left[1+\frac{a}{RTv}+\frac{1}{2}\left(\frac{a}{RTv}\right)^2+\ldots\ldots\ldots\right]=\frac{RT}{v-b}$$

To a first approximation, we may write (as v >> a)

$$p\left(1+\frac{a}{RTv}\right)=\frac{RT}{v-b} \quad \text{or} \quad p\left(1+\frac{a}{pvv}\right)=\frac{RT}{v-b}$$

or
$$p\left(1+\frac{a}{pv^2}\right)=\frac{RT}{v-b} \quad \text{or} \quad \left(p+\frac{a}{v^2}\right)=\frac{RT}{v-b}$$

or
$$p=\frac{RT}{v-b}-\frac{a}{v^2} \quad \text{or} \quad pv=\frac{RTv}{v-b}-\frac{a}{v}$$

At Boyle temperature T becomes T_B and our perfect gas equation becomes $pv = RT_B$; so, we can write

$$RT_B=\frac{RT_Bv}{v-b}-\frac{a}{v} \quad \text{or} \quad \frac{RT_Bv}{v-b}-RT_B=\frac{a}{v}$$

or
$$RT_B\left(\frac{v}{v-b}-1\right)=\frac{a}{v} \quad \text{or} \quad RT_B\left(\frac{v-v+b}{v-b}\right)=\frac{a}{v}$$

or
$$T_B=\frac{a}{v}\frac{(v-b)}{bR}=\frac{a}{bR} \text{ as } b \text{ is small}$$

For a gas obeying Van der Waals' equation,

$$T_B=\frac{a}{bR}$$

So, the Boyle temperature for a gas obeying Dieterici equation is the same for a gas obeying Van der Waals' equation.

Q3. Show that for a gas obeying Berthelot equation the Boyle temperature is given by $\sqrt{\frac{a'}{Rb}}$.

Ans. Berthelot equation of state is given by

$$\left(p+\frac{a'}{Tv^2}\right)(v-b)=RT$$

or
$$p+\frac{a'}{Tv^2}=\frac{RT}{v-b} \quad \text{or} \quad p=\frac{RT}{v-b}-\frac{a'}{Tv^2}$$

or
$$pv = \frac{RTv}{v-b} - \frac{a'}{Tv}$$

At Boyle temperature, T becomes T_B and our perfect gas equation becomes $pv = RT_B$; so, we can write

$$RT_B = \frac{RT_B v}{v-b} - \frac{a'}{T_B v}$$

or
$$\frac{a'}{T_B v} = \frac{RT_B v}{v-b} - RT_B = RT_B\left(\frac{v}{v-b} - 1\right) = \frac{RT_B b}{v-b}$$

or
$$T_B^2 = \frac{a'(v-b)}{Rbv} = \frac{a'v}{Rbv} \qquad \therefore T_B = \sqrt{\frac{a'}{Rb}}$$

Q4. Calculate the Van der Waals' constants for a gas for which $T_c = 132$ K, $p_c = 37.2$ atm, R per mole = 82.07 cm^3 atm K^{-1}.

Ans. We know

$$p_c = \frac{a}{27b^2} \text{ and } T_c = \frac{8a}{27bR} \quad \text{or} \quad T_c^2 = \frac{64a^2}{(27)^2 b^2 R^2}$$

$$\therefore \qquad \frac{T_c^2}{p_c} = \frac{\dfrac{64a^2}{(27)^2 b^2 R^2}}{\dfrac{a}{27b^2}} = \frac{64a^2\, 27b^2}{(27)^2 b^2 R^2 a} = \frac{64}{27}\frac{a}{R^2}$$

$$a = \frac{27R^2T_c^2}{64p_c} = \frac{27(82.07)^2(132)^2}{64(37.2)^2} = 13.3 \times 10^5 \text{atm cm}^{-6}\text{mol}^{-2}$$

and
$$\frac{T_c}{p_c} = \frac{\dfrac{8a}{27bR}}{\dfrac{a}{27b^2}} = \frac{8a27b^2}{27bRa} = \frac{64}{27}\frac{a}{R^2}$$

$$\therefore \qquad b = \frac{RT_c}{8p_c} = \frac{82.07 \times 132}{8 \times 37.2} = 36.4 \text{ cm}^3\text{mol}^{-1}$$

Q5. Calculate the critical temperature of a gas from the following data:

$$\text{Critical pressure} = 2.26 \times 1.013 \times 10^5 \, \frac{\text{N}}{\text{m}^2}$$

$$\text{Critical volume} = \frac{4}{69}\frac{\text{m}^3}{\text{k mole}}$$

$$R = 8.31 \times 10^3 \, \frac{\text{J}}{\text{k mol.K}}$$

Ans. We know that

$$\frac{RT_c}{p_c v_c} = \frac{8}{3} \quad \text{or} \quad T_c = \frac{8}{3}\frac{p_c v_c}{R}$$

$$T_c = \frac{8 \times 2.26 \times 1.013 \times 10^5 \times 4}{3 \times 8.31 \times 10^3 \times 69} = 4.26 \text{K}$$

PROBLEMS

Q1. Calculate the value of critical temperature for CO_2 given that $a = 0.00874$ atm, $b = 0.0023$ cc assuming $p = 1$ atm, $v = 1$ cc and $T = 273$ K.

Ans. 307.4 K

Q2. Using the values of $T_c = 5.3$, $p_c = 2.25$ atm, calculate a and b for gm-molecule of He gas.

Ans. $a = 7.1 \times 10^{-5}$, $b = 107.8 \times 10^{-5}$

Q3. Calculate the critical temperature and critical pressure from the following data: $a = 6.15 \times 10^{-5}$, $b = 9.95 \times 10^{-4}$ per gm-molecule where unit of pressure is the atmosphere and the unit of volume is the volume of the gas at N.T.P.

Ans. $T_c = 5$ K, p_c 2.3 atm

Q4. Show at the critical temperature the departure of the Van der Waals' gas laws from that of the ideal gas $p_c v_c / T_c = R$ measures 62.5 per cent.

Q5. Show that from the Dieterici equation of state you can derive $p_c = \dfrac{a}{4e^2b^2}, v_c = 2b, T_c = \dfrac{a}{4bR}$.

Q6. Using Berthelot equation of state $\left(p + \dfrac{a'}{Tv^2}\right)(v - b) = RT$, calculate the values of the critical constants.

Ans. $p_c = \dfrac{1}{12b}\sqrt{\dfrac{2a'R}{3b}}, v_c = 3b, T_c = \sqrt{\dfrac{8a'}{27bR}}$

Q7. The critical temperature and pressure of argon are 151 K and 48 atmospheres, respectively. Calculate the radius of an argon atom.

Ans. 3.37Å

QUESTIONS

1. Describe the experimental study of CO_2 gas by Andrews. Discuss critical pressure, critical volume, and critical temperature.
2. Deduce Van der Waals' equation of state of real gas. Describe how far the Van der Waals' equation explains the experimental results of Andrews.
3. What are the critical constants of a gas? Deduce their values in terms of the constants of Van der Waals' equation. Deduce the law of corresponding states.
4. Discuss how pressure correction and volume correction creeps into the Van der Waals' equation of state and deduce the equation of state after considering them.
5. Describe how the constants a and b can be determined by different methods.
6. Describe how the critical constants are determined experimentally.
7. Describe the merits and demerits of Van der Waals' equation of state of real gases.
8. Discuss other equations of state and their advantages and disadvantages.
9. Define Boyle temperature and show that its expression is the same whether it is derived from Van der Waals' equation or Dieterici equation.

Chapter 6

CHANGE OF STATE

6.1. DEDUCTION OF CLAUSIUS–CLAPEYRON'S EQUATIONS

Let AD and BC be two isothermal lines corresponding to two temperatures T and $T + dT$ (Fig. 6.1). Let AB and CD be the liquid line and vapour line, respectively, of the Amagat's curves. Along the border line AB, the substance is wholly in liquid state and along the line CD it is wholly in the state of saturated vapour. Let 1 gm of the substance be taken round the cycle ABCD reversibly.

The quantity of heat absorbed during the cycle transformation is equal to mechanical work done. We proceed to calculate the quantities of heat absorbed during the cycle process.

Heat absorbed in the path AB: From A to B along the border line, the substance is in the liquid state. If c_1 is the specific heat of the liquid, the heat absorbed in the path AB is $c_1\, dT$.

Heat absorbed in the path BC: At B the substance is wholly liquid, and at C it is wholly in the state of vapour. The temperature remaining constant, the substance absorbs latent heat of evaporation from B to C. If L be the latent heat per gram at temperature T, that at temperature $(T + dt)$ is $(L + dL/dT\, dT)$. The heat absorbed in the path BC is $(L + dL/dT\, dT)$.

Heat given out in the path CD: The substance is wholly in the state of saturated vapour along the border line from C to D. Let c_2 be the specific heat of saturated vapour; then, the heat given out in the path CD is $c_2\, dT$.

Heat given out in the path DA: At D the substance is in the state of vapour, and at A it is in the state of liquid. The temperature remaining constant, the substance gives out its latent heat from D to A. If L be the latent heat at temperature T, the heat given out in the path DA is L. Hence, the total heat absorbed is

$$c_1 dT + \left(L + \frac{dL}{dT} dT\right) - c_2 dT - L = \left(c_1 - c_2\right) dT + \frac{dL}{dT} dT \tag{6.1}$$

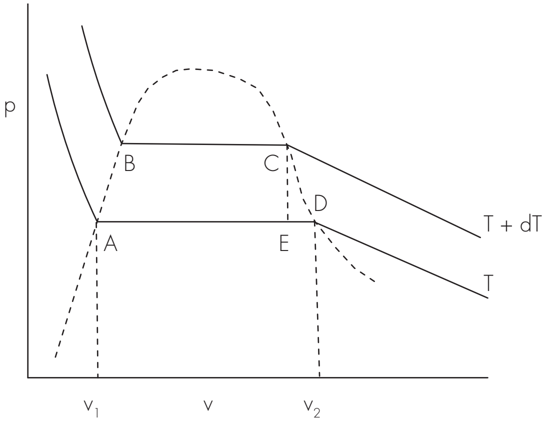

Fig. 6.1 Amagut's curves

Work done in the cycle: The area of the cycle is AD × CE. Now AD = $v_2 - v_1$ where v_1 and v_2 are the specific volumes in the liquid and vapour phases, respectively. CE is the perpendicular distance between AD and BC. It is equal to $\left(p + \frac{dp}{dT}dT\right)$ where p is the saturation pressure at temperature T. Hence,

$$\text{Area ABCD} = (v_2 - v_1)\frac{dp}{dT}dT \tag{6.2}$$

Equating Eqs 6.1 and 6.2, we get

$$(c_1 - c_2) + \frac{dL}{dT} = (v_2 - v_1)\frac{dp}{dT} \tag{6.3}$$

Since the cycle ABCD is reversible, the total change of entropy in the cycle is zero. This gives

$$\frac{c_1 dT}{T + \frac{dT}{2}} + \frac{L + \frac{dL}{dT}dT}{T + dT} - \frac{c_2 dT}{T + \frac{dT}{2}} - \frac{L}{T} = 0 \tag{6.4}$$

$$\frac{c_1 dT}{1 + \frac{dT}{2T}} + \frac{L + \frac{dL}{dT}dT}{1 + \frac{dT}{T}} - \frac{c_2 dT}{1 + \frac{dT}{2T}} - L = 0$$

or

$$c_1 dT\left(1 - \frac{dT}{2T}\right) + \left(L + \frac{dL}{dT}dT\right)\left(1 - \frac{dT}{T}\right) - c_2 dT\left(1 - \frac{dT}{2T}\right) - L = 0$$

Neglecting squares of small terms, this gives

$$c_1 dT + L - L\frac{dT}{T} + \frac{dL}{dT}dT - c_2 dT - L = 0$$

or
$$(c_1 - c_2) + \frac{dL}{dT} = \frac{L}{T} \tag{6.5}$$

Equating Eqs 6.3 and 6.5, we get

$$(v_2 - v_1)\frac{dp}{dT} = \frac{L}{T} \tag{6.6}$$

Eq. 6.6 is known as Clapeyron's equation and Eq. 6.5 is known as the equation of Clausius. It is convenient to express Eq. 6.5 as

$$(c_{vap} - c_{liq}) = \frac{dL}{dT} - \frac{L}{T} \tag{6.7}$$

Again,
$$\frac{dL}{dT} - \frac{L}{T} = T\frac{d}{dT}\left(\frac{L}{T}\right)$$

Hence, Eq. 6.7 can be written in the following form

$$c_{vap} - c_{liq} = T\frac{d}{dT}\left(\frac{L}{T}\right) \tag{6.8}$$

Similarly, Eq. 6.6 can be written in the following form

$$(v_{vap} - v_{liq})\frac{dp}{dT} = \frac{L}{T} \tag{6.9}$$

Since v_{vap} is always greater than v_{liq}, dp/dT is always a positive quantity. This means that the boiling point of a liquid is raised by increasing the superincumbent pressure.

Equation 6.6 also holds for the case of change of state from solid to liquid. In this case, the equation can be written in the following form

$$(v_{liq} - v_{sol})\frac{dp}{dT} = \frac{L}{T} \tag{6.10}$$

where v_{liq} and v_{sol} are the specific volumes in the liquid and the solid states, respectively.

If v_{sol} is greater than v_{liq}, as in the case of water, dp/dT is necessarily negative. This means that if a substance diminishes in volume on melting, then its melting point is lowered on increasing the superincumbent pressure.

If v_{sol} is less than v_{liq}, as in the case of paraffin, then dp/dT is positive. This means that if a substance increases in volume on melting, then its melting point is increased by increase of the superincumbent pressure.

At the critical temperature, $v_{liq} = v_{vap}$. Hence at the critical temperature, latent of heat of evaporation is zero.

Clapeyron's equation can also be put in another useful form as follows:

Since $v_{vap} >> v_{liquid}$, we can write Eqn. 6.9 in the follwoing form

$$v_{vap}\frac{dp}{dT} = \frac{L}{T}$$

where v_{vap} is the specific volume of saturated vapour.

Assuming that saturated vapour obeys the perfect gas law,

$$v_{vap} = \frac{RT}{pM}$$

so that
$$\frac{dp}{dT} = \frac{L}{T}\frac{pM}{RT} = \frac{LpM}{RT^2}$$

where R is the universal gas constant and M the is molecular weight

or
$$\frac{1}{p}\frac{dp}{dT} = \frac{ML}{RT^2}$$

or
$$\frac{d}{dT}(\log_e p) = \frac{LM}{RT^2} = \frac{\lambda}{RT^2} \tag{6.11}$$

where $\lambda = LM$ is the molar latent heat and R is the universal gas constant.

Equation 6.11 gives the change of pressure of saturated vapour with change of temperature.

Integration of Clapeyron's equation. Eq. 6.11, thus, can be easily integrated

$$\int_1^2 d(\log_e p) = \frac{\lambda}{R}\int_1^2 \frac{dT}{T^2}$$

or
$$\log_e \frac{p_2}{p_1} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or
$$\log_e \frac{p_2}{p_1} = \frac{\lambda}{R}\frac{(T_2 - T_1)}{T_1 T_2} \tag{6.12}$$

In Eq. 6.12, λ is the molecular heat of evaporation and p_1 and p_2 are the pressures of saturated vapour at temperature T_1 and T_2, respectively. This formula has, however, been deduced on two assumptions which are not valid. These are:

1. The saturated vapour obeys perfect gas laws.
2. Latent heat of a liquid is independent of temperature.

λ in Eq. 6.12 is not constant, but it depends on temperature. Expressing λ as a function of T such as

$$\lambda = \lambda_0 + aT + bT^2$$

$$\int d(\log_e p) = \int \frac{\lambda_0}{RT^2} dT + \frac{a}{R}\int \frac{dT}{T} + \frac{b}{R}\int dT$$

or
$$\log_e p = -\frac{\lambda_0}{RT} + \frac{a}{R}\log_e T + \frac{b}{R}T + K$$

where K is the integration constant

or
$$\log_e p = -\frac{A}{T} + B\log_e T - CT + \mathrm{K} \tag{6.13}$$

Equation 6.13 forms the basis of the so-called vapour pressure thermometers.

6.2 SPECIFIC HEAT OF SATURATED VAPOURS

The latent heat of evaporation of water at temperature T is given by

$$L = 800 - 0.705\,T$$

$$\frac{L}{T} = \frac{800}{T} - 0.705$$

$$\frac{dL}{dT} = -0.705$$

Substituting these values in Eq. 6.7,

$$c_{vap} - c_{liq} = \frac{dL}{dT} - \frac{L}{T}$$

we get

$$c_{vap} - c_{liq} = -0.705 - \frac{800}{T} + 0.705$$

or

$$c_{vap} - c_{liq} = -\frac{800}{T}$$

Since for water $\quad c_{liq} = 1, \quad c_{vap} = 1 - \dfrac{800}{T}$

at 0 °C, $c_{vap} = 1 - 2.9304 = -1.9304$

at 100 °C, $c_{vap} = 1 - 2.144 = -1.144$

Thus, specific heat of saturated vapour is a negative quantity. The meaning of "saturated vapour at 100 °C is −1.144" is as follows:

If a gram of water vapour at 100 °C and 760 mm pressure has its pressure increased to the vapour pressure corresponding to 101 °C and if at the same time 1.144 calories are withdrawn, then the water vapour will remain saturated at 101 °C.

Table 6.1 gives the specific heat of saturated vapour of some liquids deduced by Clausius from Regnault's experiment.

Table 6.1 Specific heat of saturated vapour of some liquids

Substance	0 °C	50 °C	100 °C	150 °C
Water vapour	−1.916	−1.465	−1.133	−0.674
Ether	+0.1057	+0.1222	+0.1309	+0.1344
Carbon disulphide	−0.1837	−0.1600	−0.1406	−0.1325
Chloroform	−0.1079	−0.0549	−0.0153	+0.0155
Acetone	−0.1482	−0.0883	−0.0515	−0.0223

Equilibrium of vapour and liquid: Suppose a cylinder filled with 1 gm of substance partly in the state of vapour and partly in the state of liquid at temperature T. Let a fraction m of this substance be in the state of vapour and the remainder $(1 - m)$ in the liquid state. Let a small quantity of heat dQ be supplied to the mass. This will produce a rise of temperature dT and will evaporate a small quantity dm of the liquid.

$$dQ = [(1-m)c_{liq} + mc_{vap}]dT + Ldm$$

The small amount of external work done in this process is neglected. If the process be adiabatic, that is, if no heat is supplied to the mass of liquid and vapour, $dQ = 0$

$$dT[(1-m)c_{liq} + mc_{vap}] + Ldm = 0$$

or

$$\left(\frac{dm}{dT}\right)_S = -\frac{1}{L}[(1-m)c_{liq} + mc_{vap}] \tag{6.14}$$

There will be neither evaporation nor condensation, that is, the vapour will be in equilibrium with the liquid, if

$$(1-m)c_{liq} + mc_{vap} = 0$$

For water at 100 °C $c_{vap} = -1.144$ and $c_{liq} = 1$
so that $(1 - m) = 1.144\, m$

or

$$m = \frac{1}{2.144} \text{ gm}$$

Hence, water vapour remains in equilibrium with water at 100 °C if only a fraction 1/2.144 of the total mass is in the state of vapour.

Adiabatic expansion of saturated vapours: By Eq. 6.8, we have

$$c_{vap} - c_{liq} = T\frac{d}{dT}\left(\frac{L}{T}\right)$$

$$(1-m)c_{liq} + mc_{vap} = c_{liq} + m(c_{vap} - c_{liq}) = c_{liq} + mT\frac{d}{dT}\left(\frac{L}{T}\right)$$

For water, $L = 800 - 0.705\, T$

$$\frac{L}{T} = \frac{800}{T} - 0.0705$$

$$\frac{d}{dT}\left(\frac{L}{T}\right) = -\frac{800}{T^2}$$

Also, for water $c_{liq} = 1$

Hence, $(1-m)c_{liq} + mc_{vap} = 1 - \dfrac{800\, m}{T}$

Substituting the value in Eq. 6.14, we get

$$\left(\frac{dm}{dT}\right)_S = -\frac{1}{L}\left(1 - \frac{800\, m}{T}\right) \tag{6.15}$$

Evidently, $(dm/dT)_s$ is positive or negative depending on whether the right hand side is positive or negative. This will depend on the relative values of m and T. Thus, if $m = 1/2$ and $T = 150 + 273 = 423$, then

$$\left(\frac{dm}{dT}\right)_s = -\frac{1}{L}\left(1-\frac{400}{423}\right) = -\frac{0.054}{L} \tag{6.16}$$

Now, adiabatic expansion is always accompanied by reduction of temperature. Under the circumstance given in the Eq. 6.16, dm must be positive. Hence, adiabatic expansion would cause some quantity of liquid to evaporate. If, however, m is a large fraction—nearly equal to unity—then at moderately high temperature, the right hand side of Eq. 6.15 must be positive. Adiabatic expansion under this circumstance would make dm negative; so that, some quantity of vapour would condense.

This result was verified by Cazin in the following way. The end of a long cylinder was closed by a parallel plate of glass. This was connected to another cylinder in which a piston worked. It was placed in an oil bath whose temperature could be raised. Steam was allowed to enter the cylinder from a boiler at a pressure of 5 atmospheres. By means of the piston, the saturated steam could be suddenly expanded or compressed. A cloud was always formed in the case of saturated steam never by compression. The same result was obtained with disulphide of carbon. The ether vapour condensed during compression but never during expansion. In the case of steam engine, steam expands adiabatically in the cylinder. This causes some of the steam to condense and settle on the cylinder wall and thereby give some of its heat to the cylinder. This heat is lost as far as mechanical work is concerned.

6.3 INTERNAL AND EXTERNAL LATENT HEATS

The heat that is supplied to a liquid to change it into vapour is spent in two ways: a portion is used up to change it to vapour or to change the internal energy of the liquid and the remainder is spent in doing external work against the superincumbent pressure in changing the volume. The former is called the true latent heat or internal latent heat L_i and the latter is called the external latent heat. If v_{vap} and v_{liq} are the specific volume of the vapour and of the liquid, respectively, then the external latent heat is

$$L_e = p(v_{vap} - v_{liq})$$

where p is the superincumbent pressure. The total latent heat is

$$L = L_e + L_i$$

so that

$$L_i = L - L_e = L - p(v_{vap} - v_{liq}) \tag{6.17}$$

Now, by Eq. 6.9

$$(v_{vap} - v_{liq})\frac{dp}{dT} = \frac{L}{T}$$

or

$$L = T(v_{vap} - v_{liq})\frac{dp}{dT}$$

Substituting the value of L in Eq. 6.17, we get

$$L_i = T(v_{vap} - v_{liq})\frac{dp}{dT} - p(v_{vap} - v_{liq})$$

$$= T(v_{vap} - v_{liq})\left(\frac{dp}{dT} - \frac{p}{T}\right)$$

$$L_i = T^2\left(v_{vap} - v_{liq}\right)\frac{d}{dT}\left(\frac{p}{T}\right) \tag{6.18}$$

For water at 100 °C, $v_{vap} - v_{liq} = 1673$

Hence, $$L_e = \frac{1673 \times 76 \times 13.6 \times 981}{4.2 \times 10^7} = 40.21\ \text{Cal}$$

Therefore, $L_i = 496.29$

Change of state occurs at a constant temperature, pressure remaining constant. Hence in change of state, thermodynamic potential remains constant. It is specially suited for investigation relating to change of state.

6.4 DEDUCTION OF CLAPEYRON'S EQUATIONS FROM THERMODYNAMIC POTENTIAL

Let a certain quantity of liquid and vapour of a substance be enclosed in a cylinder. Let the masses of vapour and liquid be m_v and m_l, respectively and let their specific volumes be v_v and v_l, respectively. Let the internal energy, entropy and thermodynamic potential of the vapour and the liquid per unit mass be represented by U_v, S_v and G_v and U_l, S_l and G_l, respectively. From the properties of saturated vapours, the quantities U, S and G are functions of temperatures only.

The thermodynamic potential of the whole mass composed of liquid and vapour is

$$G = m_l G_l + m_v G_v \tag{6.19}$$

The system composed of vapour and liquid is supposed to remain in the equilibrium state. Let us then perform an isothermal operation in which a mass dm of vapour condenses to the liquid state. Then, the altered value of the thermodynamic potential would be

$$G + dG = (m_l + dm)G_l + (m_v - dm)G_v \tag{6.20}$$

From Eqs 6.19 and 6.20,

$$dG = dm(G_l - G_v)$$

or $$\frac{dG}{dm} = (G_l - G_v) \tag{6.21}$$

Since the system is supposed to be in equilibrium, G must be a minimum so that

$$\frac{dG}{dm} = 0$$

or $$G_l = G_v$$

or $$U_l - TS_l + pv_l = U_v - TS_v + pv_v$$

This gives $$(U_v - U_l) - T(S_v - S_l) + p(v_v - v_l) = 0 \tag{6.22}$$

Differentiating Eq. 6.22 with respect to *T*, we get

$$\frac{d}{dT}(U_v - U_l) - T\frac{d}{dT}(S_v - S_l) - (S_v - S_l) + (v_v - v_l)\frac{dp}{dT} + p\frac{d}{dT}(v_v - v_l) = 0 \tag{6.23}$$

But $$T\frac{dS_l}{dT} = \frac{dU_l}{dT} + p\frac{dv_l}{dT}$$

and $$T\frac{dS_v}{dT} = \frac{dU_v}{dT} + p\frac{dv_v}{dT}$$

$$T\frac{d}{dT}(S_v - S_l) = \frac{d}{dT}(U_v - U_l) + p\frac{d}{dT}(v_v - v_l) \tag{6.24}$$

Substituting these values in Eq. 6.23, we get

$$(S_v - S_l) = (v_v - v_l)\frac{dp}{dT} \tag{6.25}$$

But $(S_v - S_l)$ is the change of entropy when 1 gm of liquid is vapourized at constant temperature. Hence, it is equal to *L*/*T*. Hence, Eq. 6.25 transforms into

$$(v_v - v_l)\frac{dp}{dT} = \frac{L}{T}$$

which is Clapeyron's equation. We shall write Eqs 6.24 and 6.25 in the form

$$(S_v - S_l) = \mu_{vl}\left(\frac{dp}{dT}\right)_{vl} \tag{6.26}$$

$$= \frac{L_{vl}}{T} \tag{6.27}$$

where $\mu_{vl} = v_v - v_l$ = the difference of specific volumes.

6.5 THE STEAM LINE, THE HOAR FROST LINE AND THE ICE LINE

Any possibility of a spontaneous change in an isothermal isobaric process is conditioned by the corresponding negative change in the thermodynamic potential. This means that for such transformation

$$dG < 0$$

Or, by Eq. 6.21 $$dm\,(G_l - G_v) < 0$$

If $G_l > G_v$, then *dm* must be negative, that is, a quantity of liquid must evaporate. Conversely if $G_l < G_v$, *dm* must be positive, that is, a quantity of vapour must condense to the liquid state. There will evidently be no evaporation or condensation if $G_l = G_v$. This is, therefore, the condition of equilibrium

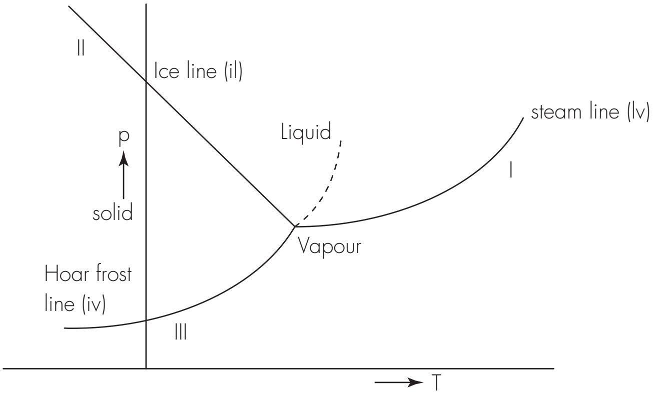

Fig. 6.2 Temperature-pressure curve in change of state

between the liquid and the vapour phases. The line I in the $(p - T)$ space over which the functional relation $G_l = G_v$ holds is called the steam line (Fig. 6.2).

Let G_i be the thermodynamic potential of ice per gram. It can be proved in the same way as that ice and water can remain in equilibrium when $G_i - G_l = 0$. The line II in the $(p - T)$ space where the functional relation $G_i = G_l$ holds good is called the ice line.

For a similar reason, the curve over which the functional relation $G_i = G_v$ holds good in the curve of equilibrium is between a solid and its vapour. This line (III) is called the hoar frost line. These lines give the pressure corresponding to any temperature at which all the phases can remain in equilibrium. The steam line, the ice line and the hoar frost line divide the $(p - T)$ space into three distinct regions. In the space bounded by the steam line and the ice line, the substance can only exist in the liquid state. The region bounded by steam line and the hoar frost line is the vapour region. The ice line and the hoar frost line enclose the region where the substance can exist only in the solid state.

The triple point: Regnault concluded from his experimental results that the steam line and hoar frost line are continuous. It was proved later by Prof. James Thomson that three curves meet at a point called the triple point. Physical meaning of this is that there is a particular temperature (the triple point) at which ice, water and water vapour can remain in equilibrium.

At this temperature, the pressure of saturated vapour of the liquid is equal to the pressure of sublimed vapour of the solid.

That these curves must meet at a point can be proved as follows:

$$\left.\begin{array}{ll}\text{The equation of the steam line is} & G_l - G_v = 0 \\ \text{The equation of the hoar frost line is} & G_v - G_l = 0 \\ \text{Adding these two equations, we get} & G_l - G_v = 0\end{array}\right\} \qquad (6.28)$$

This is again the equation of the ice line. Thus, every point of intersection of any two curves lies on the third curve. Evidently, the thermodynamic potentials for ice, water and vapour at the triple point must satisfy the equation

$$G_i = G_l = G_v$$

That the three curves meet at the triple point at different angles can be proved as follows:

For this purpose, we shall use the following notations

$$\mu_{vl} = v_v - v_l,\ \mu_{li} = v_l - v_i,\ \mu_{iv} = v_i - v_v$$

where v_i, v_l and v_v are the specific volumes of ice, water and vapour, respectively, at the triple point. Then,

$$\mu_{vl} + \mu_{li} + \mu_{iv} = 0 \tag{6.29}$$

or
$$\mu_{iv} = -\left(\mu_{vl} + \mu_{li}\right) \text{ or } \mu_{iv} = \mu_{il} + \mu_{lv}$$

Let T_o be the temperature at the triple point. Then applying Eq. 6.25 to the cases of fusion, evaporation and sublimation, we get

$$\left.\begin{aligned} \frac{L_{vl}}{T_0} &= S_v - S_l = \mu_{vl}\left(\frac{dp}{dT}\right)_{vl} \text{ for steam line} \\ \frac{L_{li}}{T_0} &= S_l - S_i = \mu_{li}\left(\frac{dp}{dT}\right)_{li} \text{ for ice line} \\ \frac{L_{iv}}{T_0} &= S_i - S_v = \mu_{iv}\left(\frac{dp}{dT}\right)_{iv} \text{ for hoar frost line} \end{aligned}\right\} \tag{6.30}$$

From Eq. 6.30, we get by addition

$$\frac{1}{T_0}(L_{vl} + L_{li} + L_{iv}) = (S_v - S_l) + (S_l - S_i) + (S_i - S_v) = 0$$

or
$$L_{vl} + L_{li} + L_{iv} = 0 \tag{6.31}$$

or
$$L_{iv} = -\left(L_{vl} + L_{li}\right) = L_{lv} + L_{il}$$

Equation 6.31 holds good only at the triple point T_o.

In Eq. 6.30, (dp/dT) gives the tangent of slope of the respective curves at the triple point. Difference of these tangents for the hoar frost line and the steam line is

$$\left(\frac{dp}{dT}\right)_{iv} - \left(\frac{dp}{dT}\right)_{vl} = \frac{1}{T_0}\left(\frac{L_{iv}}{\mu_{iv}} - \frac{L_{vl}}{\mu_{vl}}\right)$$

$$= \frac{1}{T_0}\left(\frac{L_{il} + L_{lv}}{\mu_{il} + \mu_{lv}} - \frac{L_{vl}}{\mu_{vl}}\right)$$

$$= \frac{1}{T_0}\left(\frac{L_{il} + L_{lv}}{\mu_{il} + \mu_{lv}} - \frac{L_{lv}}{\mu_{lv}}\right)$$

Since μ_{il} is very small compared to μ_{lv}, it can be neglected. Hence,

$$\left(\frac{dp}{dT}\right)_{iv} - \left(\frac{dp}{dT}\right)_{vl} = \frac{1}{T_0}\frac{L_{il}}{\mu_{lv}}$$

Example

Calculate, approximately, the triple point constants for water from the following data:

Latent heat of ice at 0 °C and 760 mm press = 80 cal
Specific volume of ice at 0 °C = 1.091 cc
Specific volume of water at 0 °C = 1.002 cc
Vapour pressure of water at 0 °C = 4.58 mm of Hg

Answer

Using $$L_{li} = T_0 \mu_{li} \left(\frac{dp}{dT} \right)_{li}$$

$$\mu_{li} = v_l - v_i = -0.0908,\ dp = 760 - 0.458 = 75.542 \text{ cm of Hg},\ T_0 = 273$$

$$dT = \frac{0.0908 \times 75.542 \times 13.6 \times 981 \times 273}{80 \times 4.2 \times 10^7} = 0.007437 \text{ deg}$$

6.6 THE PHASE RULE

In order to understand the implications of the phase rule, we must understand the meaning of terms involved. These terms are as follows:

Homogeneous system: A material medium is said to be homogeneous when its properties (both physical and chemical) are the same in all parts of the medium. It is a system in which there are no surfaces of discontinuity in physical and chemical properties. A medium with such discontinuities is said to be heterogeneous. These surfaces of discontinuity are not surfaces in mathematical sense. They are regions of very small thickness which are of great importance in the study of surface phenomena like surface tension, absorption, contact potential and the like.

Phase: This is measured by the sum of those portions of a material system which are identical in chemical composition and physical state. Thus if there are several pieces of ice floating on a mass of water, then the system composed of ice and water is heterogeneous because there are surfaces of discontinuity of physical states, though not of chemical composition. The system is composed of two phases: the solid phase and the liquid phase.

Components and constituents: Constituents of a system are the discrete elemental parts or molecular species (elements, radicals, chemical compounds, dissociated ions, etc.) which build up the system. Thus, water has two constituents: hydrogen and oxygen. When sodium chloride is dissolved in water, we may have the following molecular species present:

$-H_2O$, $(H_2O)_2$, $(H_2O)_3$, NaCL, Na^+, Cl_2 and hydrated ions. All these are constituents of the system.

Components are the independent variables which determine the constitution (the number of constituents and their proportions) of the system. Thus in the case of water, there is one component but two constituents. Here, the proportion of oxygen and hydrogen is invariable. In the case of NaCl solution, there are two components: water and sodium chloride. The quantities of water and NaCl can be altered independently of each other. The quantities of the constituents of the solution will depend on the proportion of common salt in water.

Both water and the solution are homogeneous systems and each of them has got only one phase.

Number of degrees of freedom or degrees of variability: This is determined by the number of variables which may be altered arbitrarily (with certain limits) without causing the disappearance of any phase or appearance of a new phase.

By variables we mean pressure, temperature and concentration in the several mixtures.

The Phase rule: This rule states that the number of degrees of freedom (F) of a system of N independent components in P phases in any equilibrium state

$$F = N + 2 - P \tag{6.32}$$

This is the famous phase rule, first enumerated by Willard Gibbs. In applying this rule, the chemical reactions between the ingredients are not ruled out. The only restriction is that there must be full opportunity of communication and interchange between various parts of the system.

Example 1: In the case of a homogenous fluid (such as water), there is only one phase and only one component. Hence, $P = 1$ and $N = 1$ so that $F = 2$. Thus, water remains as water if its pressure and temperature are changed and there is no other method of changing its thermodynamic state. Such a system is said to be divariant.

Example 2: In the case of water in contact with its vapour, we have two phases but only one component. Here $P = 2$ and $N = 1$ so that $F = 1$. Thus water can remain in equilibrium with its vapour, if the temperature is changed. But, in that case, the pressure must be allowed to adjust itself according to pressure–temperature functional relation.

Example 3: In the case of ice, water and vapour in equilibrium, we have three phases, but only one component. Here, $P = 3$ and $N = 1$ so that $F = 0$. In this case, none of the variables can be changed. This means that three phases can remain in equilibrium only under one definite pressure and one definite temperature. If any of these variables is changed, some of the phases would disappear. Such a system is said to be non-variant.

6.7 THERMODYNAMICS OF SOLUTIONS

The following terminologies are used in describing properties of solutions. We shall describe the properties of binary solutions.

Molar concentration: It is measured by number of moles of solute in 1 litre of solution. We shall represent molar concentration by C_R.

Molal concentration: It is measured by number of moles of solute in 1,000 gm of solvent. We shall represent molal concentration by C_L.

Molar fraction: Molar fraction or mole fraction of a particular component in a solution is the ratio of the number of moles of this component to the total number of moles present in the solution. We shall represent this by C_F.

Mass fraction: Mass fraction of a particular component in the solution is the ratio of mass of the component to the mass of the whole solution. We shall represent this by μ_F.

Density concentration: It is the mass of a component per unit volume of solution. We shall represent this by C_D.

Prove that if ρ be the density of solution,

1. $C_{DA} = \rho\mu_{FA}$
2. $C_{DA} = M_A C_{RA}$
3. $C_{FA} = \dfrac{M_B m_A}{M_A m_B + M_B m_A}$
4. $\rho = C_{DA} + C_{DB} = M_A C_{RA} + M_B C_{RB}$

Let A and B be the two components of the solution of molecular weights M_A and M_B. Let the masses of A and B in the solution be m_A and m_B, respectively. Then, the number of moles of A and B in the solution are

$$n_A = \frac{m_A}{M_A} \quad \text{and} \quad n_B = \frac{m_B}{M_B}$$

The molar fraction of A is $$C_{FA} = \frac{n_A}{n_A + n_B}$$

The molar fraction of B is $$C_{FB} = \frac{n_B}{n_A + n_B}$$

Osmosis: Figure 6.3 shows a cylindrical vessel separated into two compartments by a semi-permeable membrane. The lower half of the vessel is filled with a solution (say of cane sugar in water); the upper half of the vessel is filled with solvent.

The semi-permeable membrane allows only the water molecules to pass through it but stops diffusion of the sugar molecules. The pressure of the solution increases as a result of diffusion of water molecules into the solution.

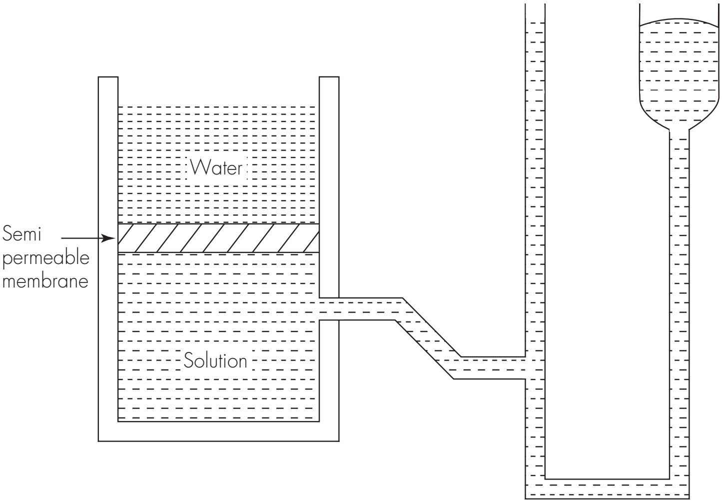

Fig. 6.3 Osmosis

To maintain the volume of water constant, a pressure must be exerted on the solution. The pressure required to stop diffusion of water into the solution is called osmotic pressure.

Laws of osmotic pressure: The following laws apply to the case of dilute solutions of non-electrolytes:

1. The osmotic pressure of a solution is proportional to the mass of the solute per unit volume of solution or density concentration and is independent of nature of the solvent.
2. Equal numbers of molecules of different solutes per unit volume exert equal pressure.
3. For a given concentration, the osmotic pressure is proportional to the absolute temperature of the solution.

Combining the first law and the third law, we get osmotic pressure

$$p \,\alpha\, C_D T$$

where C_D is the density concentration and T is absolute temperature

Or $$p = KC_D T$$

Now if m_u is the mass of solute of molecular weight M_u and v is the volume of the solution, then

$$C_D = \frac{m_u}{v} = M_u \frac{m_u/M_u}{v} = M_u \frac{n_u}{v} = M_u C_{Ru}$$

Hence, $$p = KM_u C_{Ru} T = K' C_{Ru} T \tag{6.33}$$

The value KM_u determined experimentally is equal to that of the gas constant per gm-molecule. Thus, the equation for osmotic pressure is

$$\frac{p}{C_{Ru} T} = R \tag{6.34}$$

where R is the gas constant per mole.

Since osmotic pressure is independent of the solvent's nature, we may conclude that the pressure exerted by non-electrolytic solute molecules dissolved in a solvent is the same as it would be if the molecules of the solute were in the gaseous state occupying the same volumes as that of the solution and at the same temperature.

6.7.1 Raoult's Law

The vapour pressure of a solution is lower than that of the pure solvent. The law of lowering of vapour pressure of dilute solutions of non-electrolytic solutes was given by Raoult. It is as follows:

The ratio of decrease in vapour pressure of a solution to the vapour pressure of the pure solvent at the same temperature is equal to the molar fraction of the solute.

Deduction of Raoult's law from thermodynamical considerations: Raoult's law can be deduced from thermodynamical consideration as given below. For this purpose, we shall represent the number of moles of the solvent and solute forming the solution by n_v and n_u, respectively. We shall also represent the pressure of solvent and of solution by p_v and p_n, respectively. With these notations, Raoult's law can be expressed mathematically as

$$\frac{p_v - p_n}{p_v} = \frac{n_u}{n_u + n_v} \tag{6.35}$$

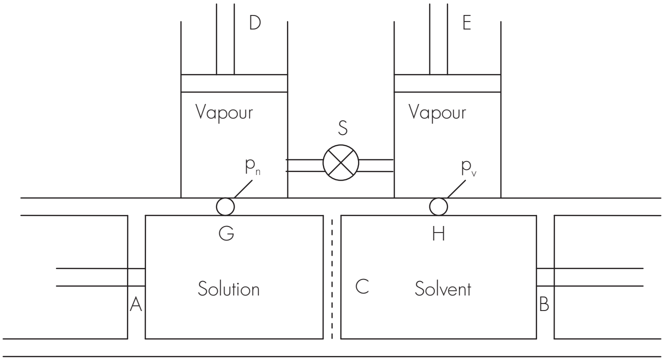

Fig. 6.4 Vant Hoff's equilibrium box

To prove Raoult's law, we perform an imaginary experiment using the so-called Vant Hoff's equilibrium box. It consists of a cylindrical box closed at its two ends by two pistons *A* and *B* as shown in Fig. 6.4. The cylinder is divided into two compartments by a semi-permeable membrane *C* which is impervious to the solute but not to the solvent.

Each compartment is provided with two side chambers which in turn are provided with two valves, *G* and *H*.

The side chambers are closed by two pistons *D* and *E*. The two side chambers are connected by a pipe which can be closed by a stop cock *S*. The two side chambers are supposed to be filled with saturated vapour from the solvent and the solutions.

Let these vapour pressures be p_v and p_n

We now perform the following cycle of operations:

Operation I: Close the stop cock *S* and open the valve *H*. Pull the piston *E* upwards so as to evaporate *dn* moles of the solvent at constant temperature *T* and pressure p_v. Since the pressure is that of saturated vapour, $dp = 0$ so that $\int vdp = 0$, in this operation.

Operation 2: Close the valve on *E* further upwards isothermally till the pressure of the vapour falls to p_n, the vapour pressure of the solution. In this case,

$$\int vdp = dnRT\int_{p_n}^{p_v}\frac{dp}{p} = dnRT\log_e\frac{p_v}{p_n}$$

where *R* is the universal gas constant, assuming that the vapour obeys the perfect gas laws.

Operation 3: Close the valve *H*, open the stop cock *S* and transfer the *dn* moles of vapour at pressure p_n to the side chamber on the left by slowly pushing down the piston *E*. In this operation, pressure remains constant so that the vapour evidently condenses to the liquid state. By operation, the valve *G* transfers the condensed vapour to the chamber containing the solution.

Work done in certain operation in the $p - v$ space is integrating this by parts

$$\int_1^2 pdv = [pv]_1^2 - \int_1^2 vdp$$

$$= p_2v_2 - p_1v_1 - \int_1^2 vdp$$

In a cyclic process, the total amount of external work done is

$$\sum\int_1^2 pdv = \sum(p_2v_2 - p_1v_1) - \sum\int_1^2 vdp$$

where the summation extends over the whole cycle. But in a cyclic process, the end values of p, v are the same so that

$$\sum(p_2v_2 - p_1v_1) = 0$$

$$\sum\int_1^2 pdv = -\sum\int_1^2 vdp = \sum\int_2^1 vdp$$

Operation 4: Close the valve G. Push the piston A inwards so as to transfer dn moles of solvent isothermally and reversibly into the solvent through the semi-permeable membrane C. The cycle is now complete and the system has now returned to its initial state. In this operation, dv volume of solvent of mass dn mol has passed from the pressure region p_n to pressure region p_v so that

$$\int vdp = dv\int_{p_v}^{p_n} dp = dv(p_n - p_v) = -p\ dv$$

where p is the osmotic pressure.

The entire operation has been conducted under isothermal conditions. Hence, the amount of work done must be equal to zero. From the thermodynamic relation

$$\frac{W}{Q} = \frac{T_1 - T_2}{T_1}$$

If $T_1 = T_2$, then $W = 0$.

Hence,

$$\sum\int vdp = -pdv + dnRT\log_e\frac{p_v}{p_n} = 0$$

or

$$dnRT\log_e\frac{p_v}{p_n} = pdv$$

or

$$p\frac{dv}{dn} = RT\log_e\frac{p_v}{p_n}$$

or

$$RT\log_e\left(1 + \frac{p_v - p_n}{p_n}\right) = p\frac{dv}{dn}$$

or

$$RT\left(\frac{p_v - p_n}{p_n}\right) = p\frac{dv}{dn} \tag{6.36}$$

neglecting higher terms. In Eq. 6.36, dv and dn are the small volume and molar mass of the solvent, respectively.

Let the solution contain m_v *gm* of solvent of molecular weight M_v and let the volume of the solvent be v. Then,

$$dn = \frac{m_v}{M_v} \text{ and } dv = v$$

Substituting these values in Eq. 6.36, we get

$$RT\left(\frac{p_v - p_n}{p_n}\right) = p\frac{M_v v}{m_v} \tag{6.37}$$

Let m_u be the mass of the solute of molecular weight M_u, then the gram-molecular weight of the solute is m_u/M_u and its molar concentration is

$$C_{Ru} = \frac{m_u/M_u}{v}$$

By Eq. 6.34,
$$p = RTC_{Ru} = \frac{RTm_u}{v\,M_u}$$

where R is gas constant per mole.

Substituting these values in Eq. 6.37, we get

$$RT\left(\frac{p_v - p_n}{p_n}\right) = \frac{RT}{v}\frac{m_u}{M_u}\frac{M_v v}{m_v}$$

or
$$\frac{p_v - p_n}{p_n} = \frac{m_u}{M_u}\frac{M_v}{m_v} = \frac{n_u}{n_v}$$

or
$$\frac{p_v}{p_n} - 1 = \frac{n_u}{n_v}$$

or
$$\frac{p_v}{p_n} = \frac{n_u + n_v}{n_v}$$

or
$$\frac{p_n}{p_v} = \frac{n_v}{n_u + n_v}$$

or
$$\frac{p_v - p_n}{p_v} = \frac{n_u}{n_u + n_v} \tag{6.38}$$

Eq. 6.38 represents Raoult's law.

Elevation of the boiling point by an involatile solute: Figure 6.5 shows the vapour pressure curves of a solvent and that of solution of an involatile solute in the same solvent. Let p_v be the vapour pressure of the pure solvent at its boiling point at temperature T.

At the same temperature, the vapour pressure of the solution is p_n. Evidently p_v must be the value of the superincumbent pressure, to make the vapour pressure of the solution equal to the superincumbent pressure, the temperature of the solution must be raised.

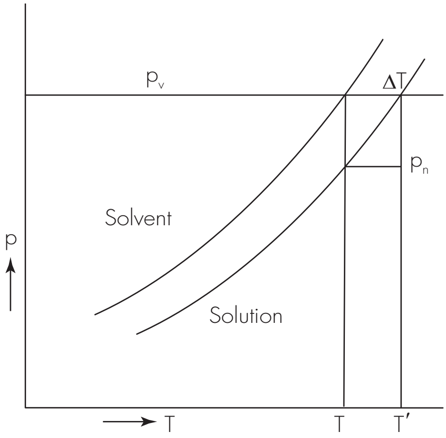

Fig. 6.5 Vapour pressure curves of a solvent and that of a solution of an involatile solute in the same solvent

By Eq. 6.11, the relation between vapour pressure and temperature is

$$\frac{d}{dT}(\log_e p) = \frac{\lambda}{RT^2}$$

where λ is the latent heat per gm-molecule and R is gas constant per gm-molecule.

Integrating this equation between p_n and p_v, we get

$$\log_e \frac{p_v}{p_n} = \frac{\lambda}{R}\int_T^{T'} \frac{dT}{T^2}$$

where T' is the temperature of the solution at which its vapour pressure becomes p_v. On integration, the last equation becomes

$$\log_e \frac{p_v}{p_n} = \frac{\lambda}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) = \frac{\lambda}{R}\left(\frac{T'-T}{TT'}\right)$$

If p_v and p_n differ by a small quantity, then

$$\log_e \frac{p_v}{p_n} = \frac{\Delta T}{T^2}\frac{\lambda}{R}$$

or $$-\log_e\left(\frac{p_n}{p_v}\right) = -\log_e\left(1 - \frac{p_v - p_n}{p_v}\right) = \frac{\Delta T}{T^2}\frac{\lambda}{R}$$

or $$\frac{p_v - p_n}{p_v} = \frac{\Delta T}{T^2}\frac{\lambda}{R}$$

By Raoult's law, $$\frac{p_v - p_n}{p_v} = \frac{n_u}{n_u + n_v}$$

$$\therefore \qquad \frac{\Delta T}{T^2}\frac{\lambda}{R} = \frac{n_u}{n_u + n_v}$$

or

$$\Delta T = \frac{RT^2}{\lambda}\frac{n_u}{n_u + n_v} \tag{6.39}$$

In the case of very dilute solutions, $n_u << n_v$

so that

$$\frac{n_u}{n_u + n_v} = \frac{n_u}{n_v}$$

$$\Delta T = \frac{RT^2}{\lambda}\frac{n_u/v}{n_v/v} = \frac{RT^2}{\lambda}\frac{C_{Ru}}{n_v/v} = \frac{RT^2}{\lambda}\frac{C_{Ru}}{\frac{m_v}{M_v}/v}$$

or

$$\Delta T = \frac{RT^2}{\lambda/M_v}\ \frac{C_{Ru}}{m_v/v} = \frac{RT^2}{\lambda/M_v}\ \frac{C_{Ru}}{\rho}$$

or

$$\Delta T = \frac{RT^2}{L}\frac{C_{Ru}}{\rho} \tag{6.40}$$

where L is the latent heat per gram.

The above result can be deduced directly from elementary principles of thermodynamics. For this purpose, we work an engine on the Carnot's principle as follows:

Figure 6.6 represents two cylinders, one containing pure solvent in equilibrium with its vapour at atmospheric pressure p and at temperature T, the boiling point of the solvent. The other cylinder contains solution of an involalite solute in equilibrium with its vapour also at temperature $T + \Delta T$, the boiling point of the solution and at atmospheric pressure p. The solvent in chamber 1 is connected to the solution through a semi-permeable membrane which can be moved as a piston.

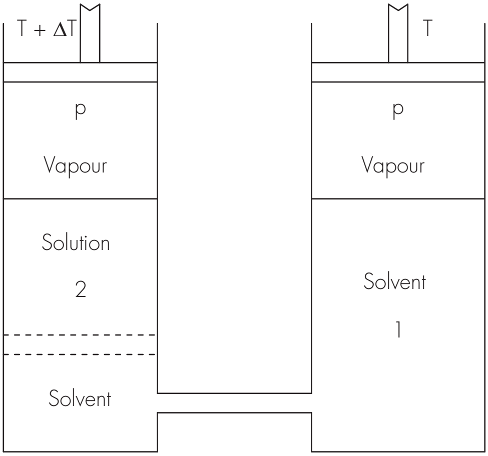

Fig. 6.6 Arrangement for working an engine on Carnot's principle

In addition, there are two sources at temperatures $T + \Delta T$ and T. We perform the following cycle of operation:

Operation I: Evaporate *dm gm* of the solvent from the solution chamber by pulling the piston outwards at temperature $T + \Delta T$ and at pressure p. If $L + \Delta L$ be the latent heat of vapourization per gram at temperature $(T + \Delta T)$, the quantity of heat absorbed by the mass dm is $dm\ (L + \Delta L)$. If dv be the additional volume which *dm gm* of the vapour occupies, the amount of work done by the vapour is $p\ dv$.

Operation 2: Cool the vapour to temperature T. Heat given out by the mass of vapour in this operation is dm $c_1 dT$ where c_1 is the specific heat of vapour at constant pressure.

Operation 3: Transfer the vapour to the solvent chamber and condense it to liquid. If L be the latent heat at temperature T, the quantity of heat given out by the vapour is $L\ dm$. The amount of work done upon the vapour is $p\ dv$.

Operation 4: Isolate the mass of condensed vapour. Raise its temperature to $(T + \Delta T)$ and transfer it to the solution in cylinder 2 by moving the semi-permeable membrane outwards. Let c_2 be the specific heat of the solvent at temperature T. Then, heat given out in the operation is $c_2\ dm\ \Delta T$. Let p be the osmotic pressure. Then, work done by the osmotic pressure is $p\ dv$ where dv is the volume of mass dm of the solvent.

The system has now returned to its initial state. By the first law of thermodynamics, the total heat absorbed in the cycle is equal to the amount of external work done.

Hence,

$$(\mathrm{L} + \Delta L)dm - c_1\ dm\Delta T - Ldm + c_2\ dm\Delta T = p\ dv$$

$$\Delta L - (c_1 - c_2)\Delta T = \frac{pdv}{dm} \tag{6.41}$$

Since the cycle is reversible, the total change of entropy must be equal to zero. Thus,

$$\frac{(L+\Delta L)dm}{T+\Delta T} - \frac{c_1 dm\Delta T}{T+\dfrac{\Delta T}{2}} - \frac{Ldm}{T} + c_2\frac{dm\Delta T}{T+\dfrac{\Delta T}{2}} = 0$$

$$(L+\Delta L)\left(1-\frac{\Delta T}{T}\right) - (c_1 - c_2)\left(1-\frac{\Delta T}{2T}\right)\Delta T - L = 0$$

or

$$\Delta L - L\frac{\Delta T}{T} - (c_1 - c_2)\Delta T = 0 \tag{6.42}$$

Combining Eqs 6.41 and 6.42, we get

$$L\frac{\Delta T}{T} = p\frac{dv}{dm} \tag{6.43}$$

$$\frac{dv}{dm} = \frac{1}{\rho_\upsilon}$$

where ρ_υ = the density of the solvent

By Eq. 6.34.

$$p = RC_{Ru}T$$

Substituting the value in Eq. 6.43 it reduces to

$$L\frac{\Delta T}{T} = RC_{Ru}T/\rho_{\upsilon}$$

or
$$\Delta T = \frac{RT^2}{L\rho_{\upsilon}}C_{Ru} \tag{6.44}$$

Let m_u be the mass of the solute and let M_u be its molecular weight. Let this mass be dissolved in m_v gm of solvent.

Let v be the volume of the solution. Then, v is the volume of the solvent and also of the solute.

Then,

$$C_{Ru} = \frac{m_u/M_u}{v}$$

The density of the solvent is
$$\rho = \frac{m_v}{v}$$

Substituting the values of C_{Ru} and ρ in Eq. 6.44, we get

$$\Delta T = \frac{RT^2}{L}\frac{m_u}{M_u v}\frac{v}{m_v}$$

or
$$\Delta T = \frac{RT^2}{LM_u}\frac{m_u}{m_v} \tag{6.45}$$

From Eq. 6.45, the molecular weight of the solute can be determined from a known value of ΔT. In this equation, R is the universal gas constant and L is the latent heat per gm.

Example

An elevation of the boiling point of 1.09 °C is produced by dissolving 0.674 gm of camphor in 6.81 gm of acetone. What is the molecular weight of camphor?

Given: Boiling point of acetone = 56.1 °C
Latent heat of vapourization = 124.5 cal per gm
$R = 1.985$ cal per gm

Substituting these values in Eq. 6.45,

$$M_u = \frac{1.985 \times (329.1)^2 \times 0.674}{124.5 \times 1.09 \times 6.81} = 156.8$$

The formula for camphor is $C_{10}H_{16}O$. Its molecular weight is 152.

Depression of freezing point by an involatile solute: The presence of a non-volatile solute lowers the freezing point of a solution. The amount of lowering of freezing point can be calculated from simple thermodynamic considerations.

For this purpose, we perform a cyclic operation on Carnot's principle as follows:

Figure 6.7 shows two cylinders, one containing pure solvent in contact with frozen solvent at temperature *T*, the freezing point of the solvent; the second cylinder containing solution in contact with frozen solvent at temperature $T - \Delta T$, the freezing point of the solution. At the top of the vessel 2, there is a semi-permeable membrane which also acts as a piston. We now perform the following operations:

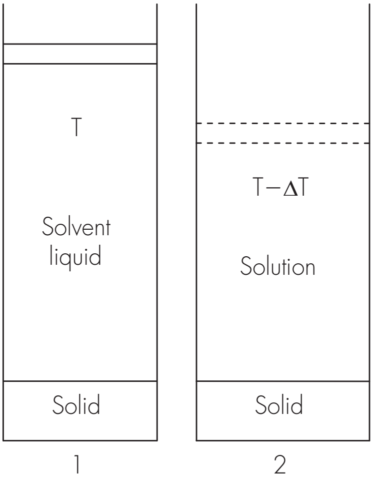

Fig. 6.7 Arrangement representing cyclic operation on Carnot's principle

Operation 1: Melt *dm* gm of frozen solvent in cylinder 1 to obtain a volume *dv* of the liquid solvent. Let *L* be the latent heat of fusion at temperature *T*. The quantity of heat absorbed in this operation is *L dm*. A certain amount of work *dw* is also done on the substance.

Operation 2: Cool the liquid formed in operation 1 to the temperature $T - \Delta T$ and reversibly transfer it to the solution in vessel 2 by moving the semi-permeable membrane. Let c_1 be the specific heat of the liquid at temperature *T* and pressure *p*, the osmotic pressure of the solution, then the heat given out by the liquid is $c_l\, dm$ and the work done by the osmotic pressure is *p dv*.

Operation 3: The mass *dm* of the solvent is frozen up at temperature $T - \Delta T$. The quantity of heat given out is $(L - \Delta L)\, dm$ where $(L - \Delta L)$ is the latent heat at temperature $(T - \Delta T)$. Also, certain amount of work *dw* is done by the solid which is equal and opposite to that done in operation 1.

Operation 4: The mass *dm* of the solid at temperature $(T - \Delta T)$is then heated to temperature *T* and transferred to vessel 1.

The quantity of heat absorbed is $c_2\, dm\, \Delta T$.

The whole system has now been restored to its initial state. Hence by the first law of thermodynamics, the quantity of heat absorbed is equal to the external work done.

Thus,

$$Ldm - c_1 dm\Delta T - (L - \Delta L)dm + c_2 dm\Delta T = pdv$$

or
$$\Delta L - (c_1 - c_2)\Delta T = p\frac{dv}{dm} \tag{6.46}$$

Since the cycle is supposed to be reversible, the total change of entropy must be equal to zero. This gives

$$\frac{Ldm}{T} - \frac{c_1\Delta Tdm}{T - \dfrac{\Delta T}{2}} - \frac{(L - \Delta L)dm}{T - \Delta T} + \frac{c_2\Delta Tdm}{T - \dfrac{\Delta T}{2}} = 0$$

or
$$(L - c_1\Delta T)\left(1 + \frac{\Delta T}{2T}\right) - (L - \Delta L)\left(1 + \frac{\Delta T}{T}\right) + c_2\Delta T\left(1 + \frac{\Delta T}{2T}\right) = 0$$

or
$$\Delta L - (c_1 - c_2)\Delta T - L\frac{\Delta T}{T} = 0 \tag{6.47}$$

Combining Eqs 6.46 and 6.47, we get

$$L\frac{\Delta T}{T} = p\frac{dv}{dm} \tag{6.48}$$

But, $$\frac{dv}{dm} = \frac{1}{\rho_v} \text{ and } p = RC_RT$$

where C_R is molar concentration, that is, the number of moles of solute in 1 litre of solution.

Substituting the values in Eq. 6.48, we get

$$\Delta T = \frac{RT^2}{L\rho}C_R \tag{6.49}$$

SOLVED PROBLEMS

Q 1. Volume of 1 gm of water at 0 °C and at 760 mm pressure is 1cc and volume of 1 gm of ice at 0 °C and at 760 mm pressure is 1.0908 cc. Calculate the change in melting point of ice by 1 atmosphere increase of pressure.

Given L = 80 calories at N.T.P.

Ans. From the given data, $(v_{liq} - v_{sol}) = -0.0908$

$$T = 273$$

$$dp = 1 \text{ atmosphere}$$

$$= 76 \times 13.6 \times 981 \text{ dynes/sq. cm}$$

Putting the values in Eq. 6.10, we get

$$-0.0908 \times \frac{76 \times 13.6 \times 981}{dT} = \frac{80 \times 4.2 \times 10^7}{273}$$

or $$dT = -\frac{0.0908 \times 273 \times 76 \times 13.6 \times 981}{80 \times 4.2 \times 10^7}$$

2^nd method

From the given data, $(v_{liq} - v_{sol}) = -0.0908$

$$T = 273$$

$$dp = 1 \text{ atmosphere}$$

$$L = 80 \text{ calories}$$

$$= \frac{80}{0.024208} \text{ atoms. cc}$$

Putting these values in Eq. 6.10, we get

$$-0.0908 \times \frac{1}{dT} = \frac{80}{0.0242 \times 273}$$

$$dT = -0.0908 \times \frac{0.0242 \times 273}{80}$$

$$1\,\text{atmosphere} \times \text{litre} = \frac{76 \times 13.6 \times 981(\text{dynes})}{(\text{cm})^2} \times (\text{cm})^3$$

$$= 76 \times 13.6 \times 981\,\text{dynes cm}$$

$$= 76 \times 13.6 \times 981\,\text{ergs}$$

$$= \frac{76 \times 13.6 \times 981}{4.2 \times 10^7}\,\text{cal}$$

$$= 24.205\ \text{cal}$$

$$1.\ \text{atm.} \times \text{cc} = 0.024205\ \text{cal.}$$

Q 2. Volume of 1 gm of steam at 100 °C and 760 mm pressure is 1674 cc and volume of 1 gm of water at the same temperature and pressure is 1 cc. On increasing the superincumbent pressure by 27.12 mm, the boiling point of water is raised by 1 degree. Calculate the latent heat of vaporization of water.

Ans. From the given data,

$$(v_{vap} - v_{liq}) = 1673\,\text{cc.}$$

$$\frac{dp}{dT} = 27.12 \frac{\text{mm}}{\text{deg.}} = \frac{27.12}{760} \frac{\text{atm}}{\text{degree}}$$

Putting these values in Eq. 6.9, we get

$$(1673\ \text{cc}) \frac{27.12}{760} \frac{\text{atm}}{\text{degree}} = \frac{L}{(273 + 100)} \frac{1}{\text{degree}}$$

or, $$L = \frac{1673 \times 27.12 \times 373}{760}\,\text{atm. cc.}$$

$$L = \frac{1673 \times 27.12 \times 373 \times 0.024203}{760}\,\text{calories.}$$

or $$L = 538.9\ \text{calories.}$$

Q 3. One gm of cane sugar dissolved in 100 c.c. water at 16 °C gives an osmotic pressure of 535 mm of Hg. Find the value of K'.

Ans. Molecular composition of cane sugar is $C_{12}H_{22}O_{11}$ and its molecular weight is 342.

1 gm of cane sugar =1/342 mole of cane sugar

Hence, molar concentration of cane sugar $= \frac{1}{342 \times 100}$

$$= 2.924 \times 10^{-5}\ \text{mole/cm}^3$$

Putting these values in Eq. 6.33, we get

$$K' = \frac{53.5\times13.6\times981\times10^5}{289\times2.924} = 8.4\times10^7\ \frac{\text{ergs}}{\text{mole deg.}}$$

Q 4. Calculate the temperature for the triple point of water in absence of air. Given that the vapour pressure at 0 °C and 1 °C are 4.60 and 4.94 mm, respectively and the lowering of melting point per atmosphere is 0.0072 °C.

Ans: Let the temperature of the triple be t°C above 0 °C. The vapour pressure at 0 °C = 4.60 mm and the vapour pressure at 1 °C = 4.94 mm.

The rate of increase of vapour pressure = 4.94 − 4.6 = 0.34 mm per °C. The vapour pressure at the triple point = $(4.60 + 0.34 \times t)$ mm

Hence, change in pressure = $760 - (4.60 + .34t)$ mm

The lowering of melting point per atmosphere = 0.0072 °C

Therefore, the rise in melting point t due to decrease in $760 - (4.6 + 0.34t)$ mm pressure is

$$\frac{0.0072}{760}(755.4 - 0.34t)$$

$$\therefore \qquad t = 0.00716°\text{C}$$

Q 5. Calculate the slopes of the vapourization and sublimation curves for water at 0 °C from the given data. Show that these are two different lines.

Latent heat of sublimation = 687 calories.

Latent heat of vapourization = 607 calories.

And $\quad v_v - v_l \approx v_0 - v_s = 21\times10^4\,\text{cc}$

Ans: From Clapeyron's equation

$$\frac{dp}{dt} = \frac{L}{T(v_2 - v_1)}$$

slopes of vapourisation curve at 0 °C,

$$\frac{dp}{dt} = \frac{607\times4.2\times10^7}{273\times21\times10^4} = 4.45\times10^2\,\text{dyne/cm}^2/°\text{C}$$

slopes of sublimation curve at 0 °C

$$\frac{dp}{dt} = \frac{687\times4.2\times10^7}{273\times21\times10^4} = 5.03\times10^2\,\text{dyne/cm}^2/°\text{C}$$

They are two different lines since the slopes being different.

PROBLEMS

1. Calculate the variation of latent heat of fusion of ice with temperature from the following data:
   Specific heat of water at 0 °C = 1
   Specific heat of ice at 0 °C = 0.505
   $L = 80$, $v_2 = 1$, $v_1 = 1.09$, $\left(\frac{dv_2}{dT}\right)_p = -0.00006$, $\left(\frac{dv_1}{dT}\right)_p = 0.00011$
   Ans. $\frac{dL}{dT} = 0.79$
2. At normal pressure, melting point of mercury is −39 °C. Its density in solid state is 14.19 gm/cc and at liquid state 13.59 gm/cc and the latent heat of fusion is 2.33 cal/gm. Calculate the melting point of mercury at 1,000 atm.
   Ans. 241.6 K
3. The excess pressure inside a pressure cooker is maintained by a mass of 130 gm placed on the vapour exit tube having cross sectional area 0.13 sq. cm. If latent heat of vaporization of water is 540 calories and specific volume of water vapour is 1674 cc, calculate the boiling point of water inside the cooker.
   Ans. 400 K
4. Iodine boils at 185.3 °C when its density is 3.71 gm/cc and its latent heat of vaporization is 40.9 calories/gm. A change of pressure 17 mm of Hg pressure changes its boiling point by 1 °C. Calculate the specific volume of iodine vapour.
   Ans. 164.7 cc
5. Ether boils at 35 °C and the specific heat of liquid ether at boiling point is 0.55 calories. Latent heat of vaporization at 35 °C and at 40 °C is 90.2 calories and 80.5 calories, respectively. Calculate the specific heat of saturated ether vapour.
   Ans. 2.197 calorie

QUESTIONS

1. Deduce Clausius–Clapeyron equation. If a substance increases in volume on melting, how is its melting point changed by increase of pressure?
2. Derive the equation which gives the change of pressure of saturated vapour with change of temperature.
3. Deduce the equation which is the basis of vapour pressure thermometers.
4. Show that specific heat of saturated vapour is a negative quantity.
5. At the boiling point of water, some fraction of the total mass of water and its vapour is in vapour state which is in equilibrium with water; what is that fraction?
6. What do you mean by internal and external latent heat? Formulate them.
7. What are steam line, hoar frost line, ice line and triple point? Can the triple point of water serve as a fixed point of a temperature scale?
8. Define the terms: phase, component, degree of freedom. State phase rule giving examples.
9. What is osmosis? State the laws of osmotic pressure.
10. Deduce Raoult's law from thermodynamical considerations.

Chapter 7

THE JOULE–THOMSON COOLING EFFECT

7.1. INTRODUCTION

In Joule's experiment, a quantity of compressed gas was allowed to expand into a vacuous space without doing external work. No change of temperature of the gas was detected after expansion. The consequence of this was

$$\left(\frac{du}{dv}\right)_T = 0 \text{ and } \left(\frac{du}{dp}\right)_T = 0$$

Thus at constant temperature, u is not a function of p and v. It must, therefore, be a function of T only.

The thermal capacity of the apparatus employed was very large in comparison with that of the gas experimented upon. To detect any thermal effect that might reasonably have been expected, a more delicate arrangement was necessary. Joule in collaboration with Thomson carried out extensive series of researches lasting over the period from 1852 to 1862.

In their experiments, the gas instead of flowing suddenly into vacuum was allowed to flow continuously from a region of high to a region of low pressure. To maintain this difference of pressure in the flowing mass of gas, it was forced through the porous plug of cotton wool inside the tube through which the gas was flowing.

The actual apparatus is shown in Fig. 7.1. The gas is pumped through a coil of copper pipe immersed in a bath of water whose temperature was measured by the thermometer *a*, *bb* was the upper end of the copper vessel, *cc* were two perforated plates between which an India rubber ring *ee* containing a silk plug *s* was placed. The plug could be compressed to any desired extent by pressing the plates *cc* together. To prevent conduction from bath, a ring of cork *ff* with loosely packed cotton wool is placed inside the copper vessel. A delicate thermometer *h* was placed inside the cotton wool plug to record any change of temperature of the gas issuing from the plug. The pressure of the inflowing gas was recorded by a gauge. The pressure of the gas issuing from the plug was that of the atmosphere.

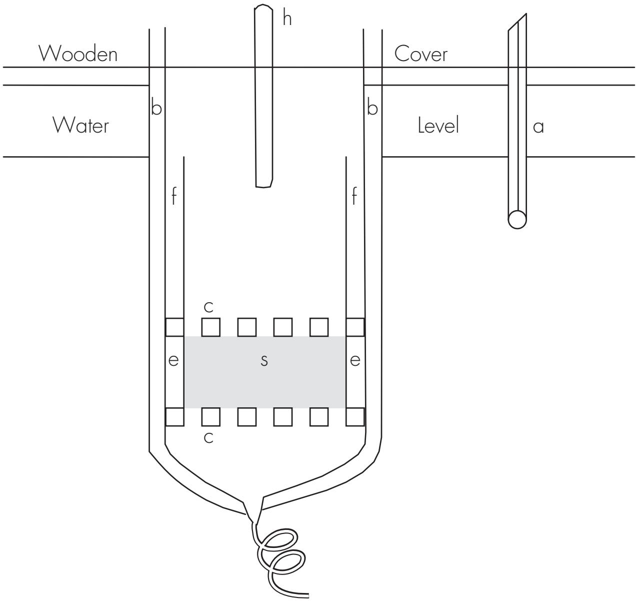

Fig. 7.1 Joule and Thomson's porous plug experiment

7.2 THE THEORY OF THE EXPERIMENT

Figure 7.2 shows a cylinder separated into two chambers *A* and *B* by a partition wall perforated with a very fine hole. Let p_A and T_A, p_B and T_B be pressures and temperatures of the gas in the chambers *A* and *B*, respectively and let $p_A > p_B$. Let v_A and v_B be the specific volumes of the gas in the two chambers *A* and *B*. When the gas is forced through the orifice, the issuing jet possesses certain amount of kinetic energy which gradually subsides at some distance from the orifice and is converted into heat by fluid friction. Near the orifice there would be a lowering of temperature due to kinetic energy produced. At a distance from the orifice where the turbulence has subsided, the temperature of the chamber *B* will be higher or lower than in the chamber *A* depending on the nature of the gas.

Let us follow the changes produced in the unit mass of the gas as it is forced from the chamber *A* to chamber *B*. We may suppose the transference to be effected by pushing the piston *M* exposed to pressure p_A in the forward direction so as to sweep out a volume v_A in the chamber *A*. The work done by the piston is $p_A v_A$. The mass of gas thus transferred pushes another piston *N* in the chamber *B* exposed to pressure

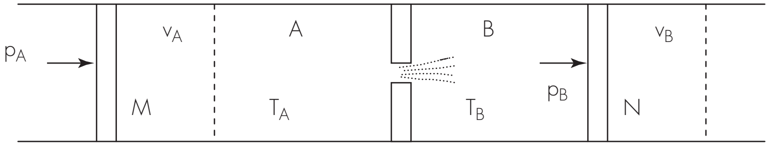

Fig. 7.2 Schematic representation of porous plug experiment

p_B in the outward direction so as to sweep out a volume v_B. The work done by the unit mass of the gas on the piston *N* is $p_B v_B$. Let u_A and u_B be the internal energies of unit mass of the gas in the chambers *A* and *B*. If *dQ* be the quantity of heat absorbed from outside by the unit mass of the gas in the process of transference, then

$$dQ = du + dW$$

$$= (u_A - u_B) + (p_A v_A - p_B v_B) \tag{7.1}$$

or

$$dQ = (u_A + p_A v_A) - (u_B + p_B v_B)$$

or

$$dQ = H_A - H_B$$

where H_A and H_B are the specific enthalpies of the gas in the chambers *A* and *B*, respectively. If the process is adiabatic,

$$dQ = 0$$

so that

$$H_A = H_B \tag{7,2}$$

Such a process is called throttling process. Thus in a throttling process, enthalpy remains constant. The imaginary pistons were introduced only to make the argument clear, the result is of general application to all cases of throttling, or frictional drop of pressure and to any fluid. Let c_v be the specific heat of the gas at constant volume. Then Eq. 7.1 can be written as follows:

$$Jc_v(T_A - T_B) = p_B v_B - p_A v_A \quad \text{for } dQ = 0\ldots \tag{7.3}$$

From Eq. 7.3, we draw the following conclusions:

(1) If $T_A = T_B$, then $p_A v_A = p_B v_B$

This is the same result as that obtained by Joule in his original experiment. It holds only for the case of perfect gases.

(2) If $T_A > T_B$, then $p_B v_B > p_A v_A$

This means that the gas does greater amount of work than what was done upon it in the chamber *A*.

(3) If $T_A < T_B$, then $p_B v_B < p_A v_A$

In this case, the gas yields only a part of the work done upon it in the chamber *A*.

How to account for this excess amount of work or loss of work? The explanation is that two molecules of a gas may either attract or repel each other. If the molecules attract, work will have to be done on the gas to make it expand. On the other hand, if the molecules repel each other, work will be done by the gas on expansion. These works are added to or subtracted from the internal energy. Hence, Joule–Thomson cooling effect is produced by internal work done on or done by the gas molecules in the process of expansion. In an adiabatic expansion, ($K_1 E_1 + pv$) remains constant while in a throttling process ($u + pv$) is constant.

7.3 CALCULATION OF AMOUNT OF COOLING

In a throttling process,

$$dH = 0$$

$$TdS = du + p\,dv$$

or
$$du = T\,dS - p\,dv$$

Now
$$du + d\,(pv) = T\,dS - p\,dv + d\,(p\,v)$$

$$= T\,dS - p\,dv + p\,dv + v\,dp$$

$$d(u + pv) = T\,dS + v\,dp$$

or
$$dH = T\,dS + v\,dp$$

or
$$T\,dS + v\,dp = 0 \tag{7.4}$$

Expressing S as a function of p and T,

$$dS = \left(\frac{dS}{dT}\right)_p dT + \left(\frac{dS}{dp}\right)_T dp$$

Substituting the value of dS in Eq. 7.4, we get

$$T\left(\frac{dS}{dT}\right)_p dT + T\left(\frac{dS}{dp}\right)_T dp + vdp = 0 \tag{7.5}$$

Using fourth Maxwellian relation, Eq. 7.5 becomes

$$T\left(\frac{dS}{dT}\right)_p dT - T\left(\frac{dv}{dT}\right)_p dp + vdp = 0$$

so that
$$T\left(\frac{dS}{dT}\right)_p dT = \left[T\left(\frac{dv}{dT}\right)_p - v\right] dp$$

or
$$C_p dT = \left[T\left(\frac{dv}{dT}\right)_p - v\right] dp$$

or
$$\left(\frac{dT}{dp}\right)_H = \frac{1}{C_p}\left[T\left(\frac{dv}{dT}\right)_p - v\right] \tag{7.6}$$

The quantity $(dT/dp)_H$ is called the cooling coefficient produced by throttling process. In throttling process, dp is negative. If this is cooling effect, then dT is also negative. This makes the right-hand side positive. If the right-hand side is negative, it is a heating effect.

For a perfect gas obeying the relation $pv = RT$,

$$\left(\frac{dv}{dT}\right)_p = \frac{R}{p}$$

$$T\left(\frac{dv}{dT}\right)_p = \frac{RT}{p} = v$$

Hence, with a perfect gas

$$\left(\frac{dT}{dp}\right)_H = 0$$

Now $$dH = TdS + v\,dp$$

or $$\left(\frac{dH}{dp}\right)_T = T\left(\frac{dS}{dp}\right)_T + v$$

or $$\left(\frac{dH}{dp}\right)_T = -T\left(\frac{dv}{dT}\right)_p + v$$

or $$T\left(\frac{dv}{dT}\right)_p - v = -\left(\frac{dH}{dp}\right)_T$$

Substituting the values in Eq. 7.6, we get

$$\left(\frac{dT}{dp}\right)_H = -\frac{1}{C_p}\left(\frac{dH}{dp}\right)_T \tag{7.7}$$

or $$dT = -\frac{1}{C_p}\frac{(dH)}{(dp)}_T\,dp \tag{7.8}$$

Equation 7.8 gives “differential effect” due to throttle expansion.
Equation 7.6 can also be written as follows:

$$\left(\frac{dT}{dp}\right)_H = -\frac{T^2}{C_p}\frac{d}{dT}\left(\frac{v}{T}\right)$$

or $$dT = \left(\frac{dT}{dp}\right)_H = -\frac{T^2}{C_p}\frac{d}{dT}\left(\frac{v}{T}\right)dp$$

or $$\Delta T = \int_{p_A}^{p_B}\frac{T^2}{C_p}\frac{d}{dT}\left(\frac{v}{T}\right)dp \tag{7.9}$$

Equation 7.9 gives the "integral effect" of cooling due to throttle expansion.

Again from Eq. 7.6,

$$C_p\left(\frac{dT}{dp}\right)_H = T\left(\frac{dv}{dT}\right)_p - v$$

Using Maxwell's fourth relation, this becomes

$$C_p\left(\frac{dT}{dp}\right)_H = -T\left(\frac{dS}{dp}\right)_T - v \tag{7.10}$$

now

$$TdS = du + pdv$$

or

$$T\left(\frac{dS}{dp}\right)_T = \left(\frac{du}{dp}\right)_T + p\left(\frac{dv}{dp}\right)_T$$

Substituting the values in Eq. 7.10, we get

$$C_p\left(\frac{dT}{dp}\right)_H = -\left(\frac{du}{dp}\right)_T - p\left(\frac{dv}{dp}\right)_T - v$$

$$C_p\left(\frac{dT}{dp}\right)_H = -\left(\frac{du}{dp}\right)_T - \frac{d}{dp}(pv)_T \tag{7.11}$$

The first term on the right of Eq. 7.11 gives the deviation from Joule's law according to which

$$\left(\frac{du}{dp}\right)_T = 0$$

for a perfect gas.

The second term gives the deviation from perfect gas law, according to which pv = constant at constant temperature.

Hence, Joule–Thomson's cooling effect shows that no gas is perfect in the true sense of the term. That gases actually deviate from the perfect gas law is proved conclusively by Amagat's isothermals in the (pv, p) space (Fig. 7.3).

The locus of the point of minimum values of $p\ v$ is shown by the dotted curve. Over this dotted curve,

$$\left(\frac{d(pv)}{dp}\right)_T = 0$$

For a perfect gas, the (pv, p) curve should be parallel to the pressures axis.

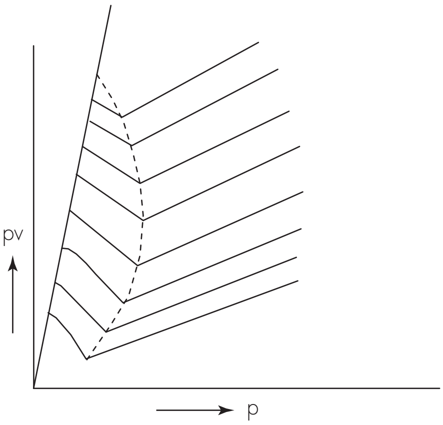

Fig. 7.3 Amagat's isothermals

7.4 Calculation of Cooling Co-efficient from Van der Waals' Equation

To determine the cooling co-efficient, we have to use equation of state of real gases. We proceed to calculate the cooling co-efficient with the help of Van der Waals' equation of state

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

Differentiating this with respect to T at constant pressure, we get

$$(v-b)\left[-\frac{2a}{v^3}\left(\frac{dv}{dT}\right)_p\right]+\left(p+\frac{a}{v^2}\right)\left(\frac{dv}{dT}\right)_p=R$$

or
$$\left(\frac{dv}{dT}\right)_p\left[\frac{2a}{v^3}(b-v)+\left(p+\frac{a}{v^2}\right)\right]=R$$

or
$$\left(\frac{dv}{dT}\right)_p\left[\frac{2a}{v^3}(b-v)+\frac{RT}{v-b}\right]=R$$

or
$$\left(\frac{dv}{dT}\right)_p=\frac{R}{\dfrac{2a}{v^3}(v-b)-\dfrac{RT}{b-v}}=\frac{Rv^3(b-v)}{2a(b-v)^2-RTv^3}$$

$$\left(\frac{dT}{dp}\right)_H=\frac{1}{C_p}\left[\frac{RTv^3(b-v)}{2a(v-b)^2-RTv^3}-v\right]$$

$$=\frac{1}{C_p}\left[\frac{RTv^3(b-v)-2av(b-v)^2+RTv^4}{2a(v-b)^2-RTv^3}\right]$$

$$=\frac{v}{C_p}\left[\frac{RTv^2b-2a(v-b)^2}{2a(v-b)^2-RTv^3}\right]$$

$$=\frac{v}{C_p}\frac{b-\dfrac{2a}{RTv^2}(v-b)^2}{\dfrac{2a}{RTv^2}(v-b)^2-v}$$

This is the cooling effect as deduced from Van der Waals' equation.

or
$$\left(\frac{dT}{dp}\right)_H=\frac{1}{C_p}\frac{b-\dfrac{2a}{RTv^2}(v-b)^2}{\dfrac{2a}{RTv^3}(v-b)^2-1} \tag{7.12}$$

Since a and b are small quantities in comparison with v, Eq. 7.12 can be put as

$$\left(\frac{dT}{dp}\right)_H = \frac{-b+\dfrac{2a}{RT}}{C_p}$$

The cooling co-efficient Eq. 7.12 is sometimes put in a different form.
Differentiating Van der Waals' equation with respect to T at constant pressure, we get

$$\frac{d}{dT}\left[\left(p+\frac{a}{v^2}\right)(v-b)\right] = R$$

or
$$(v-b)\left(-\frac{2a}{v^3}\right)\left(\frac{dv}{dT}\right)_p + \left(p+\frac{a}{v^2}\right)\left(\frac{dv}{dT}\right)_p = R$$

or
$$\left(\frac{dv}{dT}\right)_p \left(p+\frac{a}{v^2}-\frac{2a}{v^2}+\frac{2ab}{v^3}\right) = R$$

or
$$\left(\frac{dv}{dT}\right)_p = \frac{R}{p-\dfrac{a}{v^2}+\dfrac{2ab}{v^3}}$$

$$C_p\left(\frac{dT}{dp}\right)_H = \frac{RT}{p-\dfrac{a}{v^2}+\dfrac{2ab}{v^3}} - v$$

$$= \frac{\left(p+\dfrac{a}{v^2}\right)(v-b) - pv + \dfrac{a}{v} - \dfrac{2ab}{v^2}}{p-\dfrac{a}{v^2}+\dfrac{2ab}{v^3}}$$

$$C_p\left(\frac{dT}{dp}\right)_H = \frac{-bp+\dfrac{2a}{v}-\dfrac{3ab}{v^2}}{p-\dfrac{a}{v^2}+\dfrac{2ab}{v^3}}$$

The cooling co-efficient will be zero, if

$$p = \frac{2a}{bv} - \frac{3a}{v^2}$$

or
$$p = \frac{a}{b^2}\left[2\left(\frac{b}{v}\right) - 3\left(\frac{b}{v}\right)^2\right] \tag{7.13}$$

$$p = 27p_c\left[2\left(\frac{b}{v}\right) - 3\left(\frac{b}{v}\right)^2\right] \text{since } p_c = \frac{a}{27b^2}$$

$$\pi = 27\left[2\left(\frac{b}{v}\right) - 3\left(\frac{b}{v}\right)^2\right] \text{since } \pi = \frac{p}{p_c}$$

Thus, cooling co-efficient depends on temperature. It a1so depends on *a* and *b* which are characteristics of the particular gas experimented on. At a given temperature, the cooling co-efficient depends on the nature of the gas. The experiments of Joule and Thomson show that the cooling effect diminishes as the temperature rises.

This also follows from Eq. 7.12. It is expected that at a particular temperature, the cooling effect would vanish. This would happen when the numerator of Eq. 7.12 is equal to zero, that is, when

$$b = \frac{2a}{RT}\left(1 - \frac{b}{v}\right)^2 \tag{7.14}$$

or at temperature

$$T_0 = \frac{2a}{Rb}\left(1 - \frac{b}{v}\right)^2 \tag{7.15}$$

It can be proved that this point corresponds to the minimum point on the Amagat (pv, p) isothermal as follows:

Writing Van der Waals' equation of state in the form

$$pv = \frac{RTv}{v-b} - \frac{a}{v}$$

For minimum value of (pv, p) curve, we must have

$$\left[\frac{d(pv)}{dp}\right]_T = 0$$

or

$$-\frac{RTv}{(v-b)^2}\frac{dv}{dp} + \frac{RT}{v-b}\frac{dv}{dp} + \frac{a}{v^2}\frac{dv}{dp} = 0$$

or

$$\left[\frac{a}{v^2} - \frac{RTb}{(v-b)^2}\right]\left(\frac{dv}{dp}\right)_T = 0$$

Since $\left(\frac{dv}{dp}\right)_T \neq 0$, we must have

$$\frac{a}{v^2} - \frac{RTb}{(v-b)^2} = 0$$

or

$$RT\frac{b}{a} = \frac{(v-b)^2}{v^2} = \left(1 - \frac{b}{v}\right)^2$$

This temperature is only half of that obtained by the other method. This is of the same form as Eq. 7.15. Hence, the pressure and volume at the temperature at which the cooling effect vanishes can be obtained from the co-ordinates of the minimum point of Amagat's curve. Evidently, the locus of minimum points on Amagat's curves of different isothermals is the curve over which the Joule–Thomson cooling effect vanishes.

The pressure and volume corresponding to the temperature at which cooling effect vanishes can also be obtained from calculation. For this purpose, we transform Eq. 7.15 in terms of reduced co-ordinates π, θ, and ϕ where $\pi = p/p_C$, $\theta = T/T_C$, and $\phi = v/v_C$, p_C, T_C and v_C being the critical pressure, temperature and volume, respectively. We have

$$T_c = \frac{8a}{27Rb}, \ p_c = \frac{a}{27b^2}, \text{ and } v_c = 3b$$

Substituting the values a and b in terms of critical constants in Eq. 7.15,

$$T_0 = \frac{2a}{Rb}\left(1 - \frac{b}{v}\right)^2$$

we get

$$T_0 = \frac{27}{4}T_c\left(1 - \frac{1}{3}\frac{v_c}{v}\right)^2$$

or

$$\frac{T_0}{T_c} = \frac{27}{4}\left(1 - \frac{1}{3\varphi}\right)^2$$

or

$$\theta_0 = \frac{27}{4}\left(1 - \frac{1}{3\varphi}\right)^2$$

To obtain the values of π and ϕ, we substitute this value of θ in the reduced equation of state

$$\theta = \frac{3}{8}\left(\pi + \frac{3}{\varphi^2}\right)\left(\varphi - \frac{1}{3}\right)$$

This gives

$$\frac{27}{4}\left(1 - \frac{1}{3\varphi}\right)^2 = \frac{3}{8}\left(\pi + \frac{3}{\varphi^2}\right)\left(\varphi - \frac{1}{3}\right)$$

or

$$9\left(1 - \frac{1}{3\varphi}\right)^2 = \frac{1}{2}\left(\pi + \frac{3}{\varphi^2}\right)\left(\varphi - \frac{1}{3}\right)$$

or

$$9\left(\frac{3\varphi - 1}{3\varphi}\right)^2 = \frac{1}{2}\left(\pi + \frac{3}{\varphi^2}\right)\left(\frac{3\varphi - 1}{3}\right)$$

or

$$3\frac{(3\varphi - 1)}{\varphi^2} = \frac{1}{2}\left(\pi + \frac{3}{\varphi^2}\right)$$

or
$$\frac{9\varphi - 3}{\varphi^2} = \frac{\pi}{2} + \frac{3}{2\varphi^2}$$

or
$$\pi = \frac{9(2\varphi - 1)}{\varphi^2} \tag{7.16}$$

This is a quadratic equation in ϕ and there are two real roots for each value of π. Substituting these pairs of values of π and ϕ in the reduced equation of state, we get two corresponding values of θ for which the cooling effect is zero. The roots of the equation

$$\varphi^2 - \frac{18\varphi}{\pi} + \frac{9}{\pi} = 0$$

are
$$\varphi = \frac{\frac{18}{\pi} \pm \sqrt{\left(\frac{18}{\pi}\right)^2 - \frac{36}{\pi}}}{2} \tag{7.17}$$

The two roots will be equal if

$$\left(\frac{18}{\pi}\right)^2 = \frac{36}{\pi} \quad \text{or} \quad \pi = 9 \quad \text{or} \quad p = 9p_c$$

The two equal roots of ϕ are then $\phi = 1$.

The corresponding value of θ is

$$\theta = \frac{3}{8}(9+3)\times\frac{2}{3} = \frac{3}{8}\times 12\times\frac{2}{3} = 3$$

This gives $T = 3T_C$

Thus at a pressure $9p_C$, there is only one temperature at which the cooling co-efficient is zero.

We can also express the equation of the inversion curve in terms of π and θ. For this purpose, we use Eqs 7.13 and 7.15. These are

$$T_0 = \frac{2a}{Rb}\left(1 - \frac{b}{v}\right)^2$$

and
$$p = \frac{a}{b^2}\left[2\left(\frac{b}{v}\right) - 3\left(\frac{b}{v}\right)^2\right]$$

or
$$\theta = \frac{27}{4}\left(1 - \frac{b}{v}\right)^2$$

and
$$\pi = 27\left[2\left(\frac{b}{v}\right) - 3\left(\frac{b}{v}\right)^2\right]$$

Putting $x = (b/v)$, these equations become

$$(1-x)^2 = \frac{4\theta}{27} \tag{7.18}$$

and
$$2x - 3x^2 = \frac{\pi}{27} \tag{7.19}$$

From Eq. 7.18,
$$x = 1 - \frac{2\sqrt{\theta}}{3\sqrt{3}}$$

Substituting the value in Eq. 7.19, we get

$$\frac{\pi}{27} = 2\left(1 - \frac{2\sqrt{\theta}}{3\sqrt{3}}\right) - 3\left(1 - \frac{2\sqrt{\theta}}{3\sqrt{3}}\right)^2 \tag{7.20}$$

$$= -1 + \frac{8\sqrt{\theta}}{3\sqrt{3}} - \frac{4\theta}{9}$$

or
$$\pi = -27 + 12\sqrt{12\theta} - 12\theta$$

or
$$= (9 - \sqrt{12\theta})(\sqrt{12\theta} - 3) \tag{7.21}$$

Equation 7.21 is the equation of a parabola.

To bring out the idea more clearly, we put Eq. 7.16 in terms of reduced Amagat co-ordinates. For this purpose, we put

$$y = \pi\phi \ \text{ and } \ x = \pi \ \text{ so that } \ \phi = \frac{y}{x}$$

Substituting these values in Eq. 7.16, we get

$$x\left(\frac{y}{x}\right)^2 = 9\left(\frac{2y}{x} - 1\right)$$

or
$$y^2 - 18y + 9x = 0 \tag{7.22}$$

This curve is a parabola and is shown in Fig. 7.4 for $x = 0$, $y = 0$ or 18. Hence, it passes through the origin. The co-ordinates of the apex A of the parabola is obtained from the equation $dx/dy = 0$

Differentiating Eq. 7.22 with respect x, we get

$$2y\frac{dy}{dx} - 18\frac{dy}{dx} + 9 = 0$$

or
$$\frac{dy}{dx}(2y - 18) = -9$$

or
$$\frac{dx}{dy} = -\frac{1}{9}(2y - 18) = 0 \tag{7.23}$$

This gives

$$\left.\begin{array}{l} y=9\\ x=9\end{array}\right) \text{ or } \begin{array}{l}\pi\phi=9\\ \pi=9\end{array} \text{ or } \left.\begin{array}{l}\phi=1\\ \pi=9\end{array}\right) \tag{7.24}$$

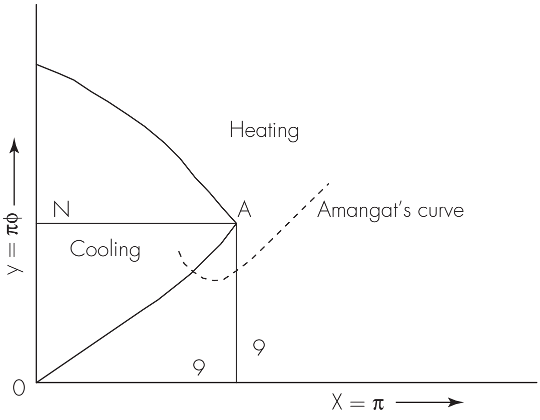

Fig. 7.4 Inversion curve

Thus for all pressures less than $9p_c$, there are two temperatures at which there is no cooling effect.

From Eq. 7.12, there will be cooling on expansion if

$$b < \frac{2a}{RT}\left(1-\frac{b}{v}\right)^2$$

or

$$T < \frac{2a}{Rb}\left(1-\frac{b}{v}\right)^2$$

or

$$\theta_0 < \frac{27}{4}\left(1-\frac{1}{3\phi}\right)^2 \tag{7.25}$$

or

$$\frac{3}{8}\left(\pi+\frac{3}{\phi^2}\right)\left(\phi-\frac{1}{3}\right) < \frac{27}{4}\left(1-\frac{1}{3\phi}\right)^2$$

or

$$\frac{1}{2}\left(\pi+\frac{3}{\phi^2}\right)\left(\phi-\frac{1}{3}\right) < \frac{9(3\phi-1)^2}{9\phi^2}$$

or

$$\pi < \frac{9(2\phi-1)}{\phi^2} \tag{7.26}$$

or

$$\pi\phi^2 < 9(2\phi-1)$$

or

$$y^2 < 18y - 9x \tag{7.27}$$

where

$$x = \pi,\ y = \pi\phi$$

or

$$y^2 - 18y + 9x < 0$$

or

$$(y-\alpha)(y-\beta) = \text{negative}$$

where α and β are the roots of the equation.

$$y^2 - 18y + 9x = 0$$

so that

$$\alpha = \frac{18+\sqrt{18^2-36x}}{2} \tag{7.28}$$

and
$$\beta = \frac{18 - \sqrt{18^2 - 36x}}{2} \tag{7.29}$$

Similarly, there will be heating on expansion if

$$(y - \alpha)(y - \beta) = \text{a positive quantity} \tag{7.30}$$

A line ABCD (Fig. 7.5) drawn parallel to the y axis will cut the parabola at two points B and C with values of y equal to β and α, respectively. For any point P within BC, y is greater than β but less than α.

So that
$$(y - \alpha)(y - \beta) = \text{negative}$$

Hence at states of the substance represented by a point inside the parabola, the substance cools by throttle expansion.

If the point P lies within AB, then y is less than β and less than α so that

$$(y - \alpha)(y - \beta) \text{ is positive}$$

Similarly if P lies within CD, then also the expression

$$(y - \alpha)(y - \beta) \text{ is positive}$$

Hence for all points lying outside the parabola, there is heating on expansion.

The parabola, therefore, represents the curve of inversion. On passing through the parabola along a line parallel to the y axis or along a line of constant pressure starting at a very low value of y, the heating co-efficient diminishes and it becomes zero on the parabola. The substance then cools down on expansion. Temperatures corresponding to points on the parabola are called temperatures of inversion.

Critical temperature of Hydrogen is about 33 K. Hence for Hydrogen the apex of the parabola is at 3 × 33 = 99 K. Ordinary temperatures being far above this temperature, the thermodynamic state of Hydrogen at room temperature lies out side the region enclosed by the parabola. Hence it lies in the region of warming on throttle expansion. Hence hydrogen must be cooled below 100 K to produce cooling effect.

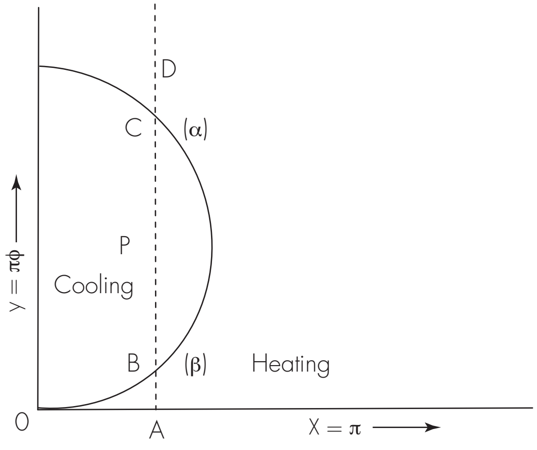

Fig. 7.5 Inversion curve

The critical temperature of Helium is 50 K. Hence unless helium be cooled below 100 K the cooling co-efficient of helium can never be positive. The critical temperature of Oxygen is 135 K. The corresponding apex of the parabola is at 3 × 135 = 405 K, room temperature is far below 405 K. Hence at ordinary temperature it shows cooling effect.

This explains the anomaly of hydrogen and helium.

7.5 CONDITION FOR LIQUEFACTION OF GASES

It appears from the characteristics of isothermals for different gases obtained from experiments of Amagat and others that for every gas there is a limiting value of temperature called the critical temperature above which a gas can never be liquefied by pressure alone, however high the pressure may be. So, the essential condition of liquefaction is that the temperature of the gas must be below its critical temperature. Table 7.1 shows the values of critical temperature and pressure of some gases.

Below the critical temperature, a gas can be liquefied by compression during which the pressure remains constant. The further the temperature is lowered below the critical temperature, the less is the pressure required for liquefaction.

Hence, the problem of liquefaction of a gas involves the problem of production of low temperatures. The methods of production of low temperatures are as follows:

Evaporative cooling: It is the rapid evaporation of a liquid placed in a chamber which is thermally insulated. A liquid can be made to boil at any temperature by reducing its superincumbent pressure by means of a pump. The latent heat of evaporation is absorbed from the boiling liquid which is, therefore, cooled.

By adiabatic expansion or external work method: This is usually done with the help of an expansion engine. It consists of a cylinder provided with a piston, an inlet and an outlet valve. Highly compressed gas enters the cylinder whenever the inlet valve is opened. The valve closes quickly and the gas continues to expand doing work on the piston. This work is mechanically absorbed by means of a drive rod and crankshaft arrangement and is used for driving other machineries such as dynamo. At the end of the expansion, the outlet valve opens and the gas at a constant lower pressure is pushed out of the cylinder and is ready to take up the next charge from the high pressure line.

The indicator diagram is shown in Fig. 7.6. In this figure, the opening of the inlet valve is marked by the point *A*. At *B*, the inlet valve closes. At *C* the outlet valve opens, which closes at the point *D*. The path *DA* gives the changes of pressure of the next charge of the gas. The pressure gradually rises till it is sufficient to force the inlet valve open, when the next cycle of operations begin.

Table 7.1 Some characteristic values of important gases

Gas	T_c (K)	p_c (atm)	a (dynes,cm^4/mole^2)	b (cm^3/mole)	Normal Boiling point
CO_2	304.2	73.00	3.64×10^{12}	42.5	–
Xe	289.8	58.22	–	–	–
Kr	209.4	54.24	–	–	–
A	150.7	48.00	1.27×10^{12}	36	–
O_2	154.0	49.7	1.49×10^{12}	32.2	90.1
N_2	126.0	33.49	1.36×10^{12}	38.3	77.3
Ne	44.8	26.88	0.207×10^{12}	24	27.17
H_2	33.2	12.8	0.25×10^{12}	26.7	20.40
He	5.25	2.26	0.035×10^{12}	23.6	4.19

The total amount of work done in the process of adiabatic expansion is $C_v (T_2 - T_1)$.

The total change of enthalpy in the adiabatic expansion is

$$\int_2^1 dH = \int_{p_2}^{p_1} vdp \tag{7.31}$$

From the relation $dQ = C_p dT - vdp$ for perfect gas

$$vdp = C_p dT$$

Since $dQ = 0$,

$$\therefore H_1 - H_2 = \int_{p_2}^{p_1} vdp = \int_2^1 C_p dT = C_p (T_1 - T_2)$$

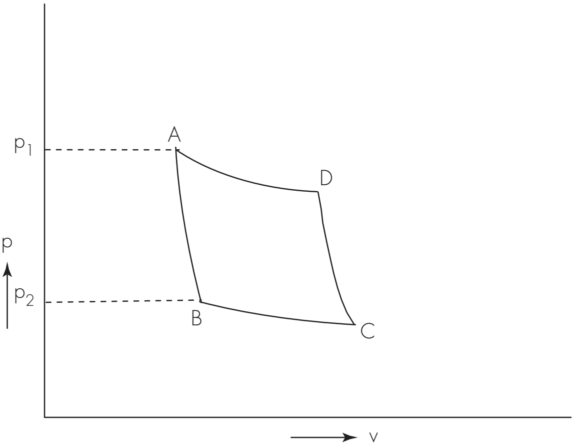

Fig. 7.6 Indicator diagram of expansion engine

The change of temperature of the gas in the adiabatic expansion from pressure p_1 and p_2 is

$$T_1 - T_2 = T_1 \left[1 - \left(\frac{p_1}{p_2} \right)^{\frac{1-\gamma}{\gamma}} \right] \tag{7.32}$$

Difficulties of expansion engines: Cylinder expansion method of cooling is not convenient at low temperatures. In Claude's expansion engine, the cylinder is heat insulated and lubricants used inside the cylinder to maintain the piston gas tight are frozen up on account of low temperature. This difficulty is overcome by using impregnated leather cups specially prepared for the purpose.

Heylandt's expansion engine is not heat insulated. It is maintained approximately at room temperature. It is run at high speed so that the expanded gas is quickly swept out of the cylinder before it can warm up by conduction from walls of the cylinder.

In Kapitza's expansion engine, a quantity of compressed gas entering the cylinder (about 4 per cent) is made to flow out of the cylinder through shallow longitudinal grooves on the surface of the piston of the lubricant.

The throttle expansion method: The difficulties mentioned above limit the efficiency of the expansion engine. Hence, the last bit of cooling for liquefaction is done with the Joule–Thomson expansion valve or throttle expansion valve. When highly compressed gas is allowed to expand to a lower pressure through a fine orifice, it cools, the consequent lowering of temperature which is given by

$$dT = \frac{T^2}{C_p} \frac{d}{dT} \frac{(v)}{T} dp$$

In adiabatic expansion, the entropy of the gas remains constant; in throttle expansion, the enthalpy of the gas remains unaltered. For every gas, there is a minimum temperature above which the gas can never be cooled by throttle expansion. This temperature is called the temperature of inversion. The inversion temperature is nearly three times the critical temperature of the gas. Critical temperatures of some common gases are given in Table 7.1. From this table, the inversion temperatures can be calculated. It follows that air, oxygen, CO_2 can be cooled by throttle expansion at room temperatures but the temperatures of hydrogen and helium must be below about 100 K and 15 K to be cooled by throttle expansion. In order that the gas may be liquefied by pressure, it must be cooled below its critical temperature by adiabatic expansion or throttle expansion or by the combination of both these processes.

The drop of temperature due to fall of pressure from p_1 to p_2 by passing through the throttle valve is less than that produced by adiabatic expansion in the expansion engine. However on account of the difficulties of realization of the external work method, the two types of processes have nearly the same efficiency.

Distinction between adiabatic and Joule–Thomson (Joule–Kelvin) expansion.

Joule–Thomson (Joule–Kelvin) Expansion	**Adiabatic Expansion**
(i) Enthalpy ($H = u + pv$) remains constant. Expansion is called isenthalpic.	(i) Entropy $\left(=\sum \frac{dQ}{T}\right) =$ remains constant. Expansion is called isentropic.
(ii) In this expansion, the vessel containing the gas is made of heat insulating material; so, no heat can enter or leave the system.	(ii) This type of expansion is so rapid that no heat exchange is possible with the surroundings.
(iii) In this expansion, cooling is comparatively less because external work is done by the gas against the intermolecular force of attraction when the gas is real; in the case of perfect gas, no external work is done as there is no intermolecular force.	(iii) In adiabatic expansion cooling is comparatively large as external work is done which derives energy from the internal energy of the gas molecules; so, there is always a cooling effect whether the gas is real or perfect.
(iv) At inversion temperature, there is no temperature change; cooling occurs below inversion temperature and heating above inversion temperature.	(iv) This expansion always involves cooling.
(v) The work done in overcoming intermolecular attraction can not be utilized for useful purpose.	(v) In this expansion, work done can be utilized to serve useful purposes.
(vi) This expansion, though adiabatic in nature, passes through non-equilibrium states from initial equilibrium state to final equilibrium state. It is associated with internal mechanical irreversibility as viscosity, friction, eddies are set up in the neighbourhood of the plug.	(vi) In this expansion, the system passes through equilibrium state from the initial to the final state which can be expressed in terms of thermodynamic coordinates at any instant.

7.6 REGENERATIVE COOLING

To produce cumulative cooling effect, the expanded gas is made to flow out as a counter current through a double-walled pipe whose inner wall is constituted by the inlet pipe leading the gas on the expansion engine. The double-walled pipe is wound as a helix on a large cone-shaped stainless steel form. The coil is placed inside a vacuum chamber.

The whole system thus formed is called the heat interchanger. The inner tube is connected to the inlet valve of the expansion engine while the outer tube is connected to the exhaust valve of the engine. The incoming gas is progressively cooled by the gas flowing out through the double- walled chamber.

Figure 7.7 shows the change of temperature suffered by a given mass of gas as it flows in and out of an interchanger in the steady state. In this figure, *AB* is the length of the interchanger, *AC* (= T_A) is the temperature of the gas just before it enters the interchanger, *EB* is its temperature before entering the valve. The temperature of the gas falls to *DB* (= T_B) after passing through the valve, on account of Joule–Thomson cooling effect. On passing out of the interchanger, the temperature of the gas again rises to T_A. If p_A and p_B be the pressures of the gas at the points *A* and *B*, then the total fall of temperature is

$$\Delta T = \frac{T^2}{C_p}\int_{p_A}^{p_B} \frac{d}{dT}\frac{(v)}{T}\,dp \tag{7.33}$$

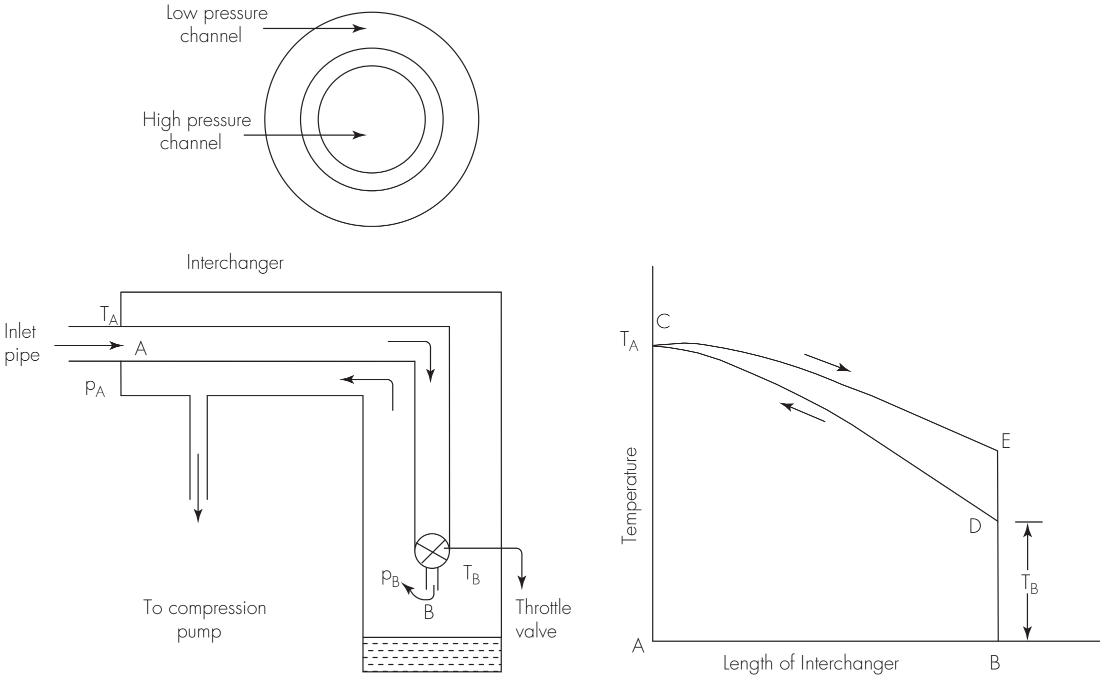

Fig. 7.7 Schematic representation of regenerative cooling

7.6.1 Efficiency of The Liquefier

Let the pressure and temperature of the gas just before it enters the interchanger be p_A and T_A, respectively. After throttle expansion, let its temperature and pressure fall to T_B and p_B. If the interchanger is perfect, $T_A = T_B$. Under this condition, the total heat of the gas before entering the interchanger is equal to that of the liquefied gas and that of the gas leaving the interchanger. Let a fraction $\in$ of the gas be liquefied when unit mass of the gas is forced through the nozzle. Let H_A, H_B and H_C be the total heats per unit mass of the gas before it enters the interchanger at A just before it passes out of the throttle at B and that of the liquefied gas.

Since H remains constant in a throttling process,

$$H_A = (1-\in)H_B + \in H_C$$

$$\in = \frac{H_B - H_A}{H_B - H_C} \tag{7.34}$$

The fraction $\in$ is called the efficiency of the liquefier. In the steady state of the interchanger, the values of p_B, T_B, p_C, T_C and T_A depends on the design of the liquefier. Hence, the yield can be varied by varying the input pressure. From Eq. 7.34, efficiency $\in$ is maximum, when H_A is minimum, H_B and H_C being constants.

This occurs when

$$\left(\frac{dH_A}{dp}\right)_T = 0 \tag{7.35}$$

From the Joule–Thomson differential effect,

$$dT = \frac{1}{C_p}\left(\frac{dH}{dp}\right)_T dp \tag{7.36}$$

Hence, for maximum value of efficiency, dT must be equa1 to zero. This means that for maximum yield, the input pressure must lie on the inversion curve. To obtain maximum yield, a knowledge of the inversion curve and of H as a function of p and T is necessary.

7.7 METHOD OF ADIABATIC DEMAGNETIZATION

A sketch of the apparatus used for adiabatic demagnetization is shown in Fig. 7.8. The substance S a paramagnetic salt of $Gd_2(SO_4)8\ H_2O$ or $FeNH_4,(SO_4)12\ H_2O$ is pressed into a sphere or ellipsoid. It is coated with a thin layer of stop-cock grease to prevent oxidation or dehydration. It is suspended by silk thread at the centre of the secondary coils which is used for measurement of susceptibility inside a calorimeter immersed in boiling helium at a temperature of about 1 K. This in turn is surrounded by a bath of liquid nitrogen. The whole system is placed between the pole pieces of electromagnet. To perform the experiment, the calorimeter is filled with helium at a pressure of 1 mm of Hg.

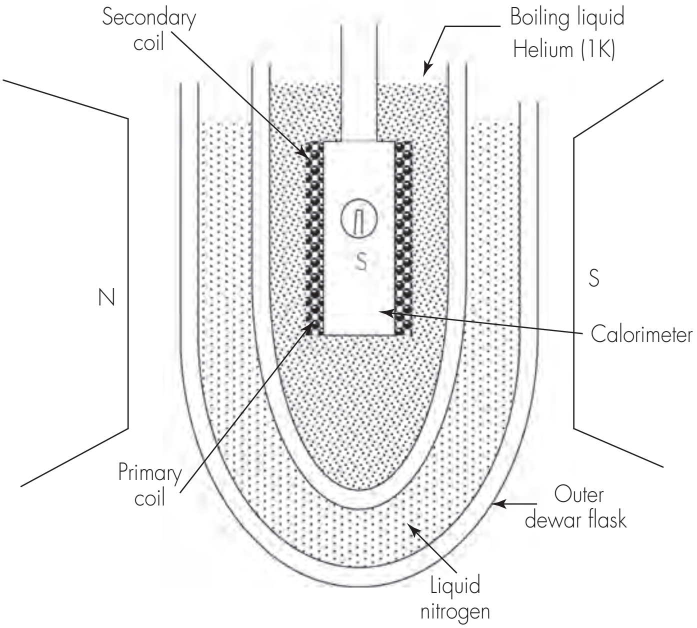

Fig. 7.8 Sketch of the apparatus used for adiabatic demagnetization

The magnetic field of 10.000 to 30.000 oersteds is then put on. That produces a rise in temperature of the specimen. When the temperature has become steady, the gas is pumped out of the calorimeter. Field is then turned off and the magnet completely removed from the neighbourhood of the cryostat when the temperature of the specimen is reduced. The fall of temperature is measured from the deflection of a ballistic galvanometer connected to the secondary coils.

7.7.1 Theory of The Method

Any cause which tends to bring order to a disordered system reduces the entropy of the system. The paramagnetic salts used in this experiment contains magnetic dipoles (better electron spin moments) which are oriented at random even at 1 K.

These moments are orderly arranged by the application of the magnetic field. Hence, magnetic field strength H is another parameter which must be added to the entropy function. Thus,

$$S = f(H, p, T) \tag{7.37}$$

so that,

$$dS = \left(\frac{dS}{dH}\right)_{p,T} dH + \left(\frac{dS}{dp}\right)_{T,H} dp + \left(\frac{dS}{dT}\right)_{H,p} dT \tag{7.38}$$

The process of magnetization or demagnetization is conducted at constant pressure so that $dp = 0$.

Hence,
$$dS = \left(\frac{dS}{dH}\right)_{p,T} dH + \left(\frac{dS}{dT}\right)_{H,p} dT \tag{7.39}$$

If the process is adiabatic, $dS = 0$

$$\left(\frac{dT}{dH}\right)_{S,p} = -\frac{\left(\frac{dS}{dH}\right)_{p,T}}{\left(\frac{dS}{dT}\right)_{H,p}} \tag{7.40}$$

Now
$$\left(\frac{dS}{dT}\right)_{H,p} = \frac{1}{T}\left(\frac{dQ}{dT}\right)_{H,p} = \frac{C_{H,P}}{T} \tag{7.41}$$

Hence,
$$\left(\frac{dT}{dH}\right)_{S,p} = -\frac{T}{C_{H,P}}\left(\frac{dS}{dH}\right)_{p,T} \tag{7.42}$$

The total energy per mole of the magnetic substance is given by

$$dU = TdS + HdI - pdv \tag{7.43}$$

writing $(pdv - HdI)$ for dW, I being the intensity of magnetization. In that case, the thermodynamic potential takes the following form

$$G = U - TS + pv - HI \tag{7.44}$$

so that

$$dG = dU - TdS - SdT + pdv + vdp - HdI - IdH \tag{7.45}$$

Substituting the value for dU from Eq. 7.43, we get

$$dG = -S\ dT + vdp - IdH \tag{7.46}$$

Expressing G as a function of p, T and H,

$$dG = \left(\frac{dG}{dp}\right)_{T,H} dp + \left(\frac{dG}{dH}\right)_{p,T} dH + \left(\frac{dG}{dT}\right)_{p,H} dT \tag{7.47}$$

Comparing with Eq. 7.46, we get

$$\left(\frac{dG}{dT}\right)_{p,H} = -S, \quad \left(\frac{dG}{dp}\right)_{T,H} = v, \quad \left(\frac{dG}{dH}\right)_{p,T} = -I$$

Differentiating S with respect to H and I with respect to T, we get

$$-\frac{dS}{dH} = \frac{d^2G}{dHdT}; -\frac{dI}{dT} = \frac{d^2G}{dTdH}$$

so that
$$\left(\frac{dS}{dH}\right)_{p,T} = \left(\frac{dI}{dT}\right)_{p,H} \tag{7.48}$$

Again, $I = \chi H$, where χ is the susceptibility per mole

$$\left(\frac{dI}{dT}\right)_{p,H} = H\left(\frac{d\chi}{dT}\right)_{p,H} \tag{7.49}$$

Hence from Eq. 7.48,

$$\left(\frac{dS}{dH}\right)_{p,T} = \left(\frac{dI}{dT}\right)_{p,H} = H\left(\frac{d\chi}{dT}\right)_{p,H}$$

Substituting the value in Eq. 7.42, we get

$$\left(\frac{dT}{dH}\right)_{S,p} = -\frac{TH\left(\frac{d\chi}{dT}\right)_{p,H}}{C_{p,H}} \tag{7.50}$$

In this case of paramagnetic salt,

$$\chi = \frac{A}{T}$$

where A is Curie constant

Hence,
$$\frac{d\chi}{dT} = -\frac{A}{T^2}$$

Substituting the value in Eq. 7.50, we get

$$\left(\frac{dT}{dH}\right)_{S,p} = -\frac{HA}{TC_{p,H}} = \text{a positive quantity} \tag{7.51}$$

Hence, the substance is heated by increasing the magnetizing field. Conversely by reducing the magnetizing field, the temperature of the paramagnetic salt is lowered.

The lowest temperature attained by the method of adiabatic demagnetization is 0.0034 K.

It is evident from Eq. 7.51 that the lower the temperature T, the greater is the amount of cooling by demagnetization.

Simon desorption method: In this method, helium gas is allowed to be absorbed by charcoal at 14 K; on desorption of the gas, sufficiently lower temperature can be obtained.

Adiabatic compression of liquid helium II: When liquid helium initially at any temperature below 2.19 K is compressed adiabatically, its temperature falls. By this method, temperature well below 1 K can be obtained.

By forcing liquid helium II through fine capillaries: Adiabatically at temperature below 2.19 K, temperature below 1 K can be obtained.

By nuclear demagnetization: Nucleus of many atoms possess magnetic moment which is very small in comparison with magnetic moments of paramagnetic salt. By adiabatic nuclear demagnetization, low temperature of the order of 10^{-6} K can be obtained.

7.8 LIQUEFACTION OF AIR

7.8.1 Linde's Process

Air is a mixture of hydrogen and oxygen and some percentage of carbon dioxide and moisture. Critical temperatures of oxygen and nitrogen are 154 K and l26 K, respectively. In order that they may be cooled by throttle expansion, the temperatures of oxygen and nitrogen must be below 462 K and 378 K, respectively. It can be cooled by throttle expansion at room temperatures under suitable pressure. As already stated, for a given liquefier the efficiency can be altered only by changing the input pressure and input temperature. Another factor which determines the efficiency is the work done in compression. The magnitude of this work is $RT[\log_e p_1 - \log_e p_2]$ when the gas is compressed isothermally from pressure p_1 to p_2.

Hence for greater efficiency, p_2 must not be very small. The theoretical optimum input pressure at temperature −40 °C is 210 atmospheres. In Linde's process, the input pressure is 200 atmospheres and input temperature is −40 °C and value of p_2 is 40 atmospheres. The air expands through the throttle value to a pressure of 40 atmospheres.

A sketch of apparatus explaining Linde's process is shown in Fig. 7.9.

Here, air is first freed from CO_2 and moisture by passing through a tower of lime and potassium hydroxide. It is then compressed to a pressure of 200 atmospheres by a compression pump. The heat generated by compression is removed by a water cooler. The gas at room temperature is then led through an ammonium refrigerator where its temperature falls to −40 °C. The gas at 200 atmospheres and at −40 °C then expands to 40 atmospheres through the heat interchanger cooling the inflowing gas

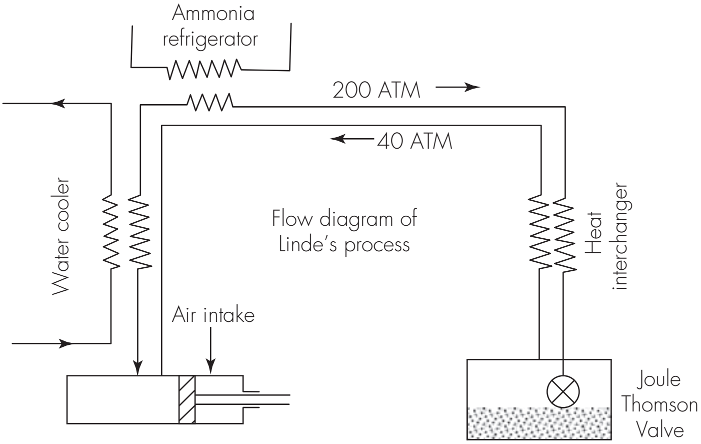

Fig. 7.9 Sketch of Linde's apparatus

regeneratively till it liquefies. The liquefied air is stored up in a Dewar's flask. Liquid air thus contains a mixture of liquid nitrogen and oxygen. The normal boiling points of N_2 and O_2 are 77.32 K and 90.19 K, respectively. Nitrogen being more volatile than oxygen, it is quickly evaporated and after sometime the liquid contains only pure oxygen.

7.8.2 Claude's Method

In this method, air compressed to 40 atmospheres enters the interchanger I maintained at −80 °C by way of the inlet tube *A* as shown in Fig. 7.10. At the point *P* gas divides, a fraction $(1 - M)$ passing to the expansion engine and the remaining portion *M* at reduced pressure passing through the interchangers at II and III.

The fraction $(1 - M)$ of the gas is allowed to expand to 1 atmosphere and is thereby cooled. This cooled gas flows out by way of the tube *Q* through the interchangers I and II and cools the incoming gas.

The fraction *M* of the gas at reduced pressure flows through the interchangers II and III and is cooled below the critical temperature of the gas but not to its normal boiling point under 1 atmosphere. As a result, some quantity of the gas condenses in the interchangers II and III at a temperature higher than the normal boiling point of the liquid. It then passes through the valve and its pressure falls to 1 atmosphere. The liquid collects in the chamber and cool vapour passes through the interchangers thereby cooling the inflowing gas.

The corresponding change in entropy of the flowing mass of gas is shown in Fig. 7.11.

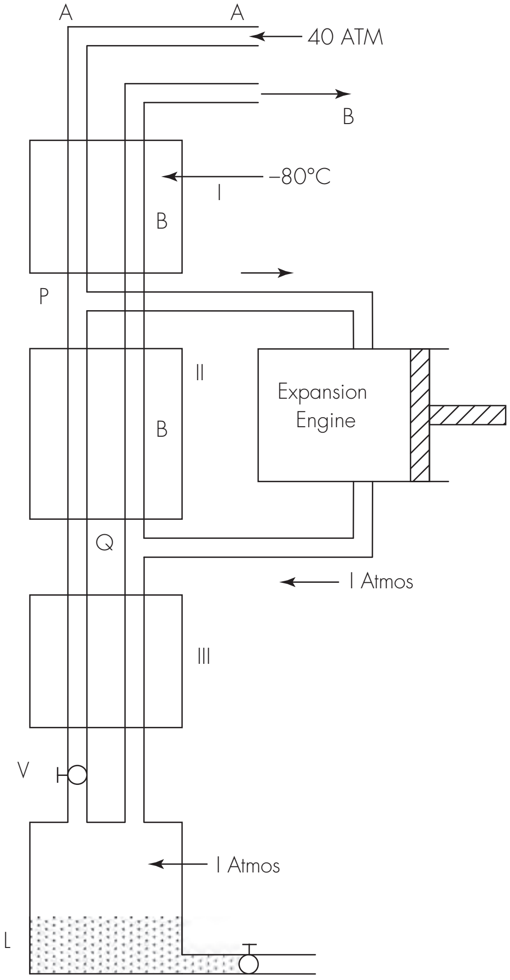

Fig. 7.10 Sketch of Claude's apparatus

7.8.3 Heylandt's Method

This method is based on the same principle as Claude's and differs from it only in details. In Heylandt's method, the interchanger 1 is omitted. Air enters liquefier at a pressure of 200 atmospheres. The fraction (1 − M) of the gas passes into the expansion engine. After expansion, the temperature of the gas still remains above critical temperature.

The corresponding change in entropy of the gas flowing in and out of the liquefier is shown in Fig. 7.12.

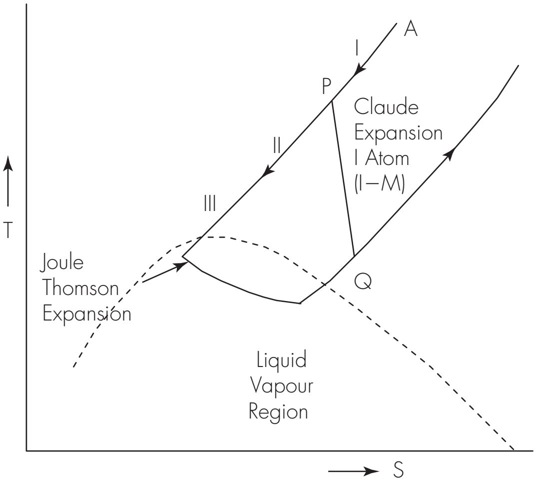

Fig. 7.11 Schematic representation of entropy change in Claude's process

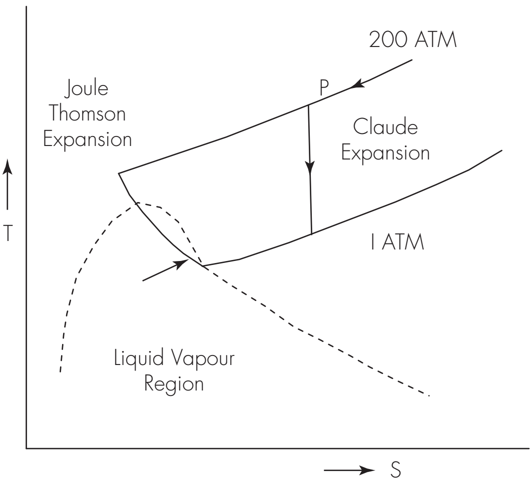

Fig. 7.12 Schematic representation of entropy change in Heylandt's process

7.9 LIQUEFACTION OF HYDROGEN

Critical temperature of hydrogen is 33.2 K. Hence, it must be cooled below about 100 K in order that it may be cooled by throttle expansion. The optimum input temperature and pressure for maximum yield of liquid hydrogen is between 63 K and 80 K and 160 atmospheres, the gas expanding to 1 atmosphere.

Figure 7.13 shows the flow diagram for hydrogen of the liquefier of the Mond laboratory of the Royal Society at Cambridge. In this apparatus, two separate circulations are used, which are as follows:

1. one that is used mainly for cooling the apparatus;
2. other where hydrogen to be liquefied flows through the path marked

(i) Pure hydrogen at 160–170 atmospheres enters the tube 1. It flows through the interchanger *A*, then through a bath of nitrogen boiling under reduced pressure at 66 K. It then passes through the regenerator coil *D* and finally expands through the value *E* to a pressure of 1 atmosphere. A small quantity of the gas liquefies and collects in the container *F*.

When it is about one-third full, it passes by way of the tube 4 to the coil in the container *G* where it evaporates and the cold vapour passes out through the tube 2 into a compressor which compresses the gas to 160 to 170 atmospheres and returns the gas to the tube 1. By such circulation, the temperature of the interchangers is continually lowered.

(ii) Commercial hydrogen at a pressure of 3 to 4 atmospheres is led through the pipe 3 into the interchanger *A* then successively through the bath of boiling nitrogen and the regenerator coil *D*. It then enters the interchanger *G* whose temperature is 20 K. At this temperature, it liquefies under a pressure of 3 atmospheres and condenses on the coil in *G*. The liquid is pushed through the tube 5 and is drained off at the valve *H* into a suitable container. Any impurity

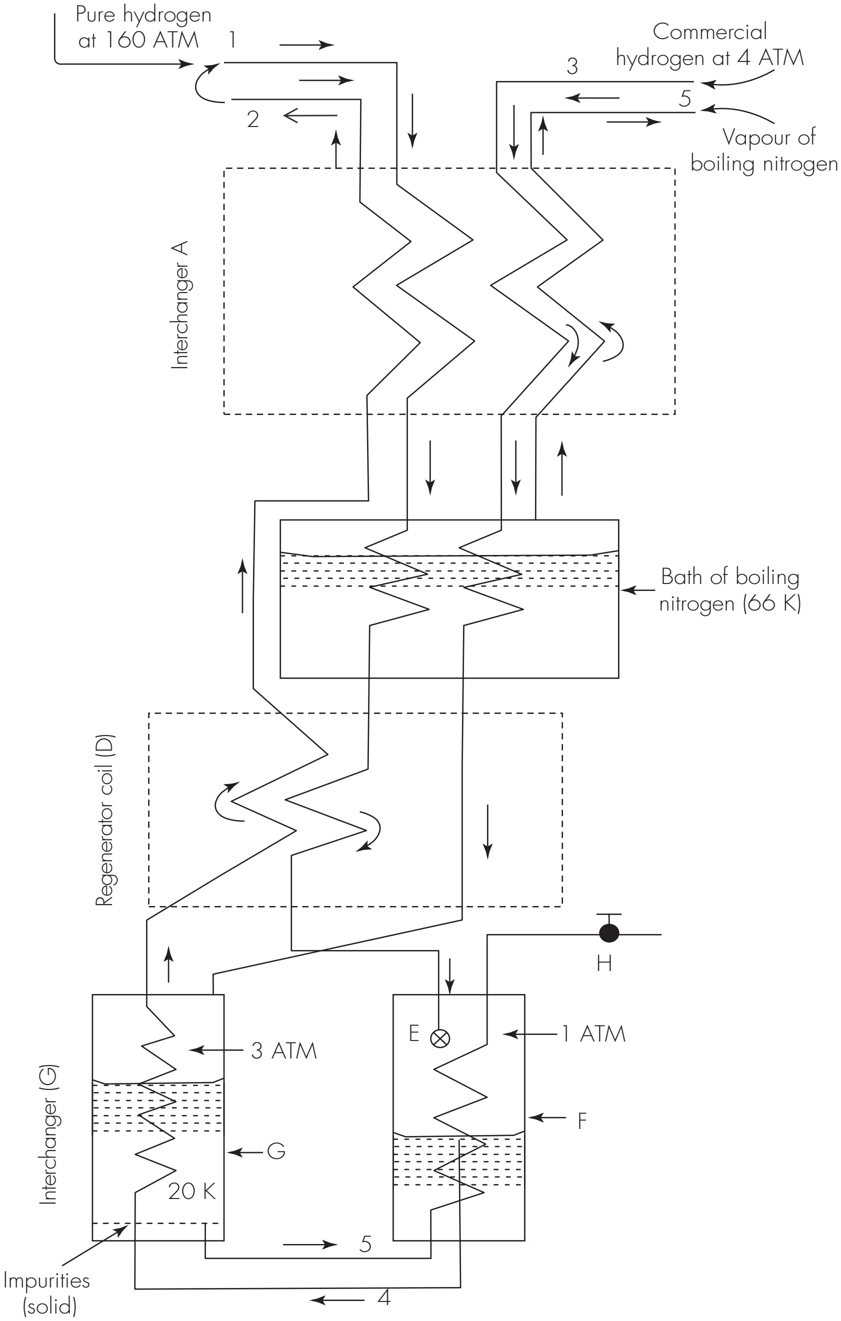

Fig. 7.13 Flow diagram for hydrogen to be liquified

present in the commercial hydrogen solidifies and collects at the bottom of *G* and removed at the end of the run. The whole liquefier is enclosed in a metal case maintained at a high vacuum.

7.10 LIQUEFACTION OF HELIUM

The critical temperature of helium is 5 K. Hence, it must be precooled below 15 K in order that it may be cooled by throttle expansion below its critical temperature. The optimum input pressure for helium is 30 atmospheres for an input temperature of 15 K and expansion to 1 atmosphere.

In the Kapitza helium liquefier at the Mond laboratory, Cambridge, helium is first led through a reducing valve and then through charcoal immersed in liquid air to remove impurities. It then passes through a bath of liquid hydrogen. The gas then passes through the inner tube of the interchanger and expands to 1 atmosphere at the throttle valve. The vapour of the gas then escapes out of the liquefier through the outer tube of the interchanger.

Figure 7.14 shows the flow diagram of Kapitza's helium liquefier working on Heylandt's principle employing expansion engine. At helium temperatures, no grease can be used. This difficulty was overcome by Kapitza by leaving just sufficient space between the cylinder and the piston to avoid friction. By accelerating the compression stroke, the amount of gas escaping through the space between the cylinder and the piston could be made negligible. The great advantage of the method is that it requires no liquid hydrogen for precooling purposes. Theoretically, no precooling is necessary at all in this apparatus for liquefaction of helium. But this would require uncommonly large dimension of the apparatus. Hence to increase efficiency, the gas is cooled by liquid nitrogen alone.

Pure helium enters the liquefier by tube 1 at 30 atmospheres. It then passes through the interchanger *A* and then through the bath of boiling nitrogen. A portion of the gas is then led through the expansion engine in the interchanger *B* where it expands to 2.2 atmospheres. The expanded gas passes through the interchanger *C* and escapes into atmosphere by way of tube 2. The remaining portion of the gas then passes through the interchanger *C* at 15–18 atmospheric pressure where it is cooled to 9 K. The final temperature drop to 4.2 K is obtained by expansion at the throttle valve. The vapour of liquid helium passes out of the liquefier by way of tube 2. The vapour of boiling nitrogen is led out into the atmosphere by way of tube 3 through the interchanger *A*.

7.10.1 Simon's Single Expansion Method of Liquefaction of Helium

In this apparatus, helium is compressed to about 150 atmospheres through the tube 1 and kept in *A* (Fig. 7.15). It is cooled to the temperature of liquid hydrogen which is vigorously pumped till it solidifies when its temperature falls to about 11 K. It is then thermally insulated from the surrounding. By opening a valve, the gas is then allowed to expand slowly to 1 atmosphere. The temperature of the container A then falls and about 75 per cent of the volume of *A* is then filled with liquid helium. The liquid can then be drained off through the outer tube.

The ranges of temperature covered by different liquids are indicated in Table 7.2. The range covered by each liquid is evidently the differences of temperature between its normal boiling point and the boiling point under reduced pressure limited by its triple point at which temperature the liquid solidifies.

The gap between oxygen and hydrogen (−218 to −253) has been bridged by Kamerlingh Onnes by using hydrogen vapour cryostat. The other gap between −259 and −269 could be similarly covered by using helium vapour cryostat.

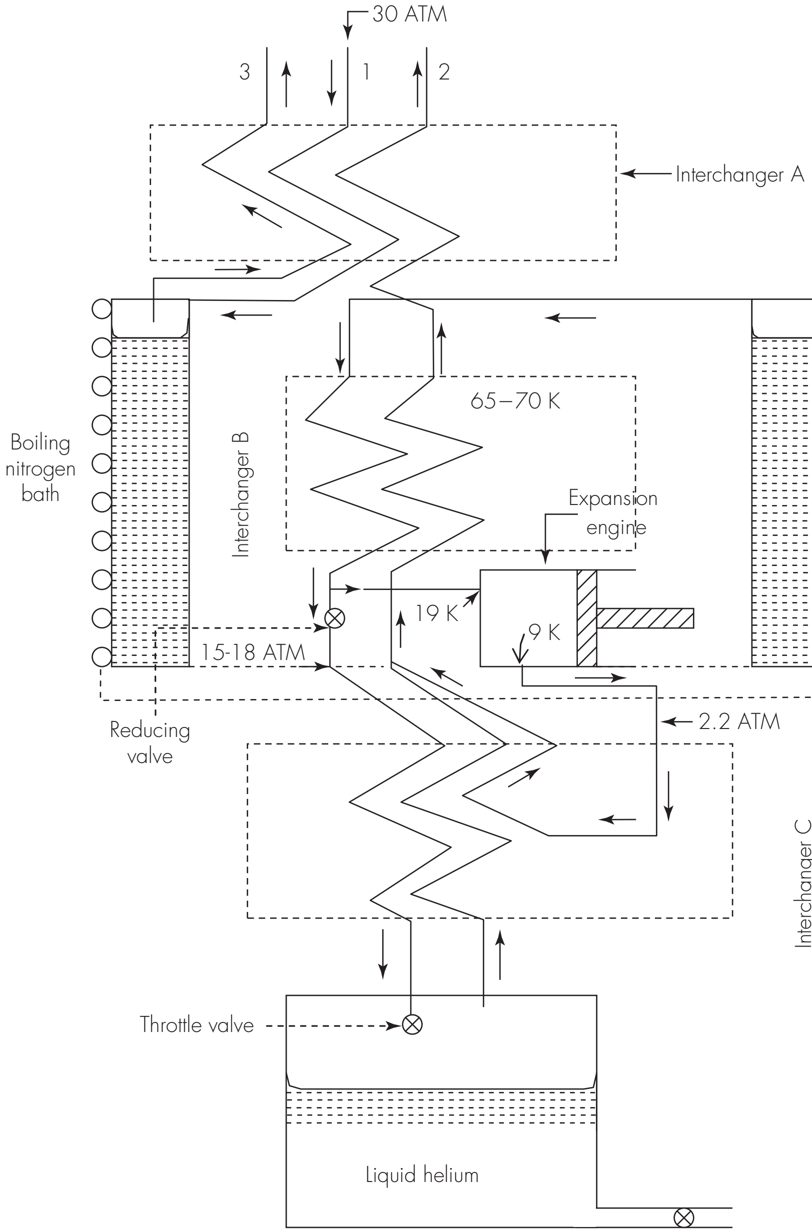

Fig. 7.14 Flow diagram of Kapitza's helium liquefier

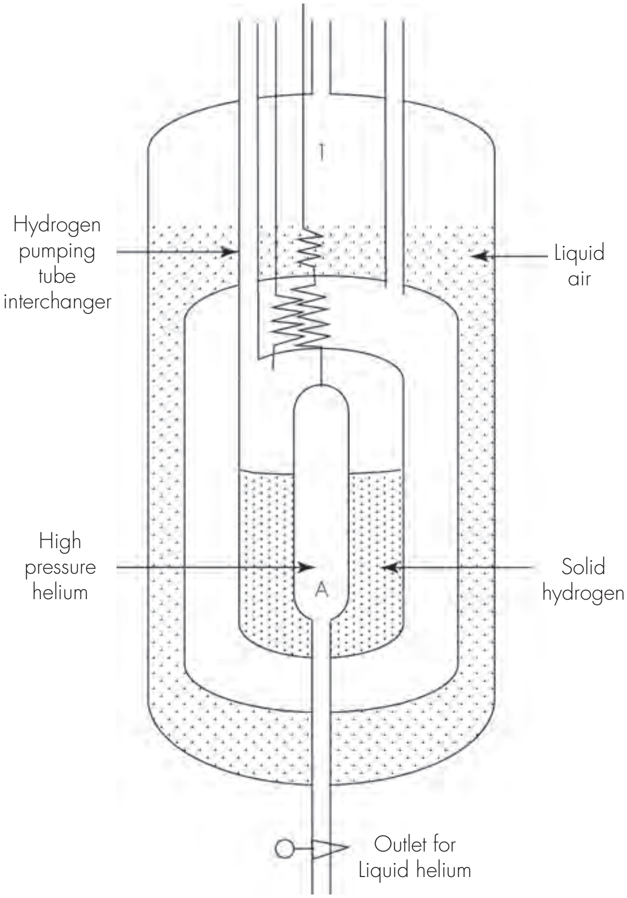

Fig. 7.15 Simon's apparatus for liquifaction of helium

Table 7.2 Characteristic temperatures of some liquids

Substance	Boiling point (normal) °C	Triple point °C
Methyl chloride	−24.1	−103.6
Nitrous oxide	−89.8	−102.4
Ethylene	−103.7	−169.0
Methane	−161.4	−183.1
Oxygen	−182.9	−218.4
Nitrogen	−195.8	−209.9
Hydrogen	−252.76	−259.14
Helium	−268.83	

7.11 PROPERTIES OF LIQUID HELIUM

Helium was first obtained in liquid form by Kamerlingh Onnes in 1908 as a colourless, mobile and very volatile liquid boiling at 4.22 K under 1 atmosphere pressure. All attempts to solidify helium by boiling under reduced pressure failed; for even under a pressure of 0.013 mm of Hg (corresponding temperature 0.82 K), it remained in liquid state. Helium was first obtained in the solid state by Keesom in 1926 by the combined effects of high pressure and low temperature. He found that helium melts at 4 K under a pressure of 126 kg/cm^2. According to Simon, melting point of helium is 42 K under a pressure of 5600 atmospheres. Evidently, liquid helium contracts on freezing. Critical temperature and pressure of liquid helium are 5.3 K and 1718 cm, respectively.

Density of liquid helium: Density of liquid helium rises by about 20 per cent as the temperature falls from 4.2 K to 2.19 K. Below 2.19 K, density of liquid helium decreases and then remains practically constant.

Dielectric constant: Dielectric constant of liquid helium increases up to 2.19 K. Below this temperature, it suddenly decreases.

Specific heat: Specific heat of liquid helium shows a similar variation. It rises to a pronounced maximum at 2.19 K and then falls abruptly as the temperature rises. It then continues to rise till 4.1 K and then falls. It follows that the heat content ($C_v dT$) and, therefore, entropy of liquid helium diminishes as temperature diminishes. Hence below 2.19 K, the molecules of liquid helium are in highly ordered state.

Latent heat of vapourization: Latent heat of vapourization of liquid helium shows no abrupt change at 2.19 K. Latent heat of vapourization of liquid helium between 1.5 K and 3.0 K is 5.5 cal/gm only. This explains the extreme volatility of liquid helium.

The λ-point: These abrupt changes in physical properties of liquid helium led Keesom and Wolfke to suggest that helium changes from one phase to another at 2.19 K. These two phases are called He I and He II. The transition temperature is called the λ-point. Liquid helium, unlike other liquids, does not possess any triple point where solid, liquid and vapour phases meet. The curves representing different phases of helium are shown in Fig. 7.16.

The diagram shows that the solid liquid line and the liquid vapour line are connected by the line *AB* called the λ line. This means that the change from phase I to phase II occurs at different temperatures under different pressures. The coordinates of the point *A* are 1.75 K and 30 atmospheres. The condition of maximum density of liquid helium persists all along the λ line. The solid phase of helium can not be attained for pressures less than 25 atmospheres. The absence of any abrupt change in the value

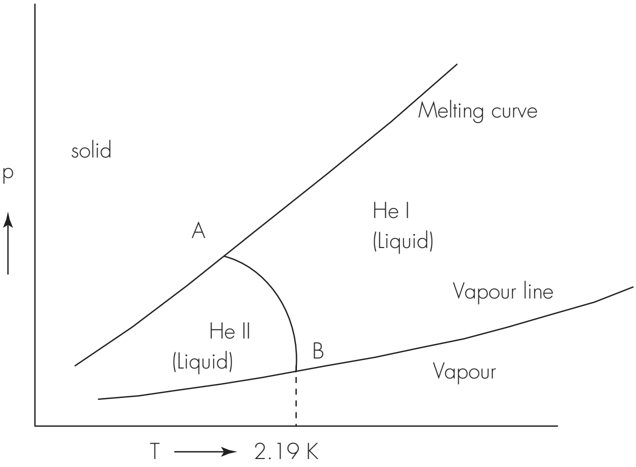

Fig. 7.16 Different phases of helium

of latent heat at 2.19 K indicates that no heat is evolved or absorbed at the transition point between the two phases.

There is nothing very remarkable about He I. But He II possesses abnormal properties which have nothing in common with properties of other substances. Hence, it may be looked upon as the fourth state of matter.

Helium II is a superfluid: Unlike other liquids, viscosity of liquid helium decreases as the temperature diminishes. Viscosity of He I decreases from 29 to 18 micropoises within the temperature range 4.0 to 2.2 K. For He II, viscosity diminishes from 23 to 1.2 micropoises as the temperature falls from 2.18 to 1.2 K. This stands in marked contrast with that of liquid hydrogen (200 micropoises at 15 K) and water (10,000 micropoises at 293 K). It can flow through extremely fine channels with a complete absence of viscous drag.

Film flow of He II: If liquid helium II is placed in two concentric vessels, the surfaces of the liquid in the two vessels automatically adjust themselves to the same level. In this case, a thin film of liquid helium 3.5×10^{-6} cm thick creeps over the wall of the vessel and thereby transports liquid from one vessel into the other.

Thermal conductivity of liquid helium: The thermal conductivity of liquid He I is quite normal and that of liquid He II varies with the temperature gradient. It shows a maximum value at 1.9 K. This maximum value reaches the astonishing figure of 1900 cal/degree cm sec. This is 3×10^7 times greater than that of He I and about 2000 times greater than that of copper at room temperature. It falls to a low value of 2×10^{-3} cal/degree cm sec at 0.2 K.

The fountain effect: Figure 7.17 shows a U tube open at both ends tightly packed with emery powder. One limb of the U tube is connected to a fine capillary tube. When the U tube is immersed in liquid He II and is illuminated by a lamp, a jet of the liquid is projected to a height of several centimetres out of the capillary tube while liquid helium is sucked into the U tube through the emery powder. This effect is explained by the fact that whenever a temperature gradient is established in He II, a pressure gradient is always produced.

The reverse of fountain effect has also been observed; whenever there is a pressure gradient in liquid He II, there is always a temperature gradient. Thus if liquid He II is forced through emery powder as shown in Fig. 7.17, the temperature of the jet is less than that of the liquid in the bath.

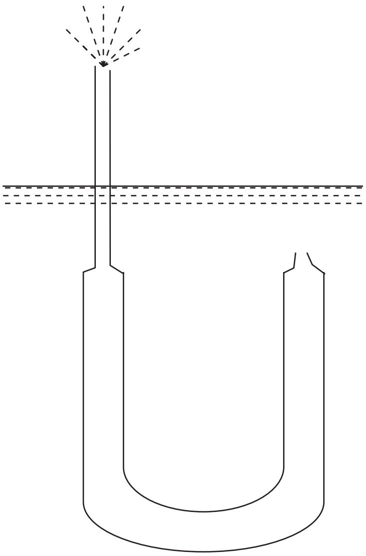

Fig. 7.17 Fountain effect

7.12 MEASUREMENT OF LOW TEMPERATURE

The normal hydrogen pressure thermometer can be used for measurement of low temperature down to −259 °C. For measurement of low temperatures down to −270 °C, normal helium thermometers are used. To convert the readings to absolute scale, the readings of these thermometers must be extrapolated to vanishingly small pressures. For measurement of still lower temperatures—4.2 K to 0.9 K—the zero point pressure of 10 cm to 0.2 cm of mercury is employed and the mercury manometer is replaced by the Pirani or the hot wire manometer. Some uncertainty arises on account of thermal molecular pressure at such low temperatures.

7.12.1 Secondary Thermometers

For measurement of low temperatures, secondary thermometers such as resistance thermometer, thermocouple and vapour pressure thermometers are very convenient and they give reliable results. These thermometers are calibrated by comparison with standard gas thermometers. The following fixed points (in absolute scale) are used for this purpose—melting point of Hg (−38.87), the sublimation point of CO_2 (−78.51), the boiling point of oxygen (−182.97), and boiling point of hydrogen (−252.75).

The resistance thermometers, platinum resistance thermometers become insensitive below −258 °C. From 0 ° to 190 °C; the resistance of the thermometer is represented by the formula

$$R_\theta = R_0[1 + a\theta + b\theta^2 + c(\theta - 100)\theta^3]$$

The constants R_0, a, b and c are determined by calibration at the boiling point of oxygen, the ice point, the steam point and sulphur point (444.6 °C).

Between −193 and −258, no simple formula represents the relation between temperature and resistance. The readings of the thermometer are, therefore, to be compared with those of a gas thermometer at as many points as possible.

At hydrogen temperatures, thermometers of gold and lead can be used with advantage. Pure metals become supra conductors at helium temperatures, but resistance of alloys vary appreciably below 5 K. Resistance thermometer of annealed phosphor bronze wire is sufficiently sensitive from 5 K to 1 K. At helium temperatures, carbon resistance thermometers in the form of graphite rod or carbon ink line drawn on glass may be used. Its resistance increases with the fall in temperature.

The Thermocouple: The copper constant couple can be employed to measure temperatures down to −258 °C. The following formula given by Nernst holds within the range 100 K to 15 K:

$$C = 31.32 \log_e \left(1 + \frac{T}{90}\right) + 10^{-7} T^4 \text{ microvolt}$$

At hydrogen temperatures, gold silver couple is more sensitive than copper constant couple. At very low temperatures, a couple of 1 at. per cent of cobalt in gold and 1 at. per cent of gold in silver is very sensitive.

Vapour pressure thermometers: The pressure of vapour in equilibrium with its liquid depends only on temperature. It does not, therefore, require any of the troublesome corrections which are so essential for mercury-in-glass or gas thermometers since the changes in the volume of the container has no effect on the pressure exerted by the vapour.

A scheme of the vapour pressure manometer shown in Fig. 7.18 is such that one arm of the manometer con-

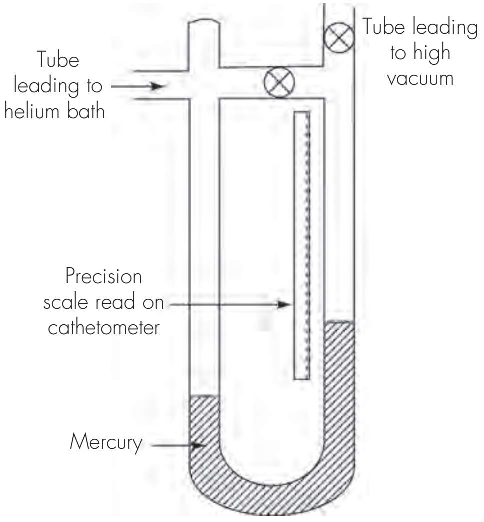

Fig. 7.18 Scheme of vapour pressure manometer

taining mercury is completely pumped out while the other arm is connected by a gas tight tube to a bulb placed inside the cryostat. The bulb contains the liquefied gas whose vapour pressure is to be measured.

The manometer is read with a cathetometer and a precision scale. For vapour below 1 mm of mercury, a Mcleod gauge is used for comparison. With wide manometer tubes, the effect of thermal molecular pressure is small. It should be noted that the pressure shown by the manometer is the saturated vapour pressure corresponding to the temperature of the coldest part of the thermometer.

The relation between vapour pressure and temperature is obtained from the integration of Clapeyron's equation

$$\log_e p = -\frac{A}{T} + B\log_e T - CT + K$$

Values of the constants A, B, C and K are different for different ranges of temperature and for different substances.

Magnetic thermometer: Below 1 K, vapour pressure thermometer does not serve any useful purpose. This is because the vapour pressure of helium is too small below 1 K; further, the Kundsen effect makes accurate measurement impossible. The safest method of measurement of such low temperatures is to use the magnetocalorie effect of paramagnetic salts which produces refrigeration. The method depends on Curie's law

$$\chi = \frac{A}{T}$$

where χ is the susceptibility at temperature T. Hence from change of susceptibility of a paramagnetic salt, change of temperature can be deducted. This temperature depends on the validity of Curie's law. Hence, it is called Curie temperature and it is represented by T^*. This can be translated into the absolute temperature by the relation

$$T = \left(\frac{dQ}{dS}\right)_{H=0} = \left(\frac{dQ/dT^*}{dS/dT^*}\right)_{H=0}$$

The procedure requires two plots: one, entropy against T^* and the other heat content against T^*. The entropy against T^* is obtained from the relation

$$\left(\frac{dS}{dH}\right)_{p,T} = \left(\frac{dI}{dT}\right)_{p,H}$$

or

$$S_{T_O H} = S_{T_O H=0} + \int_0^H \left(\frac{dI}{dT}\right)_{H=0} dH$$

To obtain the plot of Q against T^*, we supply heat to the specimen and measure T^* continuously. Some experiments used carbon heater on glass capsule containing the specimen for this purpose. Others used γ - radiations from radioactive substance for the purpose of heating.

The apparatus for the measurement of susceptibility consists of an induction coil (Fig. 7.19). The primary of the coil is wound on the heat exchange gas tube containing the specimen. The secondary consists of two coils wound on the primary, each containing equal number of turns, but wound in opposite directions. They, thus, annul the induction effect due to the primary, but only allow the current induced by the specimen to pass through the ballistic galvanometer.

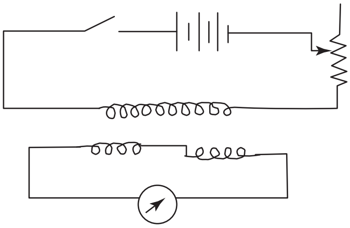

Fig. 7.19 Apparatus to measure susceptibility

7.13 MEASUREMENT OF SPECIFIC HEAT AT LOW TEMPERATURES

A cryostat for experiment at low temperature is shown in Fig. 7.20. It consists of a Dewar's flask containing liquid nitrogen. Inside this flask, there is another Dewar's flask containing liquid helium. A metal ring with taper end is sealed to the inner flask. This is connected to a metal cap through rubber gaskets. Experimental equipments are placed inside a thin-walled metal tube of Monel or super nickel hung from the metal cap by a fibre. Since helium can diffuse through pyrex glass, provision is made to pump out the gas from the double-walled region of the inner flask.

Figure 7.21 shows a calorimeter developed by Keesom for the measurement of specific heat of metals at helium temperatures. Inside the block of metal under test, there is a tapped recess into which the core of the calorimeter is screwed. The core contains a constantan and a phosphor bronze resistance thermometer and a constantan heater.

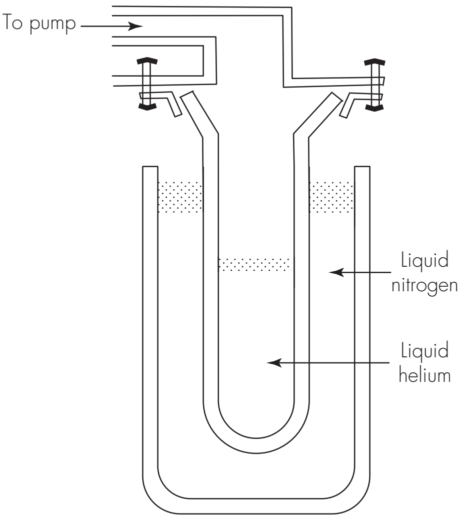

Fig. 7.20 Cryostat for experiment at low temperature

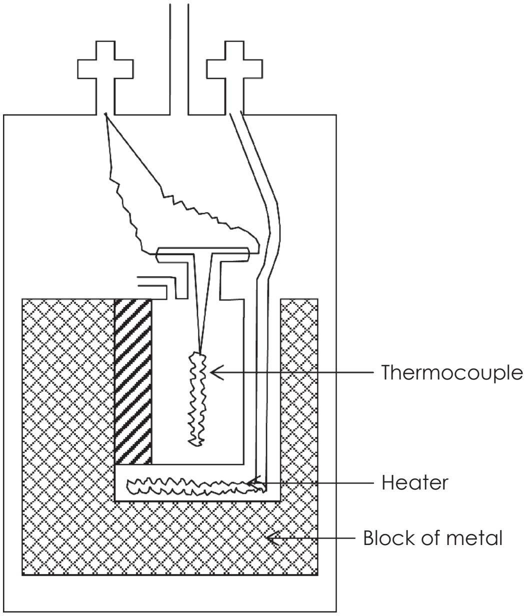

Fig. 7.21 Keesom's calorimeter for measurement of specific heat of metal at helium temperature

The block is placed in a metal casing which is immersed in liquid helium. To perform the experiment, the calorimeter is allowed to cool to the temperature of the bath. The space surrounding the calorimeter is then evacuated. Current is then passed through the heating coil and time and temperature are recorded at regular intervals during and after the period of heating. The energy input is determined from current, voltage and time of heating.

For measurement of specific heat of powder, the type of calorimeter shown in Fig. 7.22 is used. The calorimeter is of thin sheet of silver or copper. The heating coil is wound round the outer wall of the calorimeter. The calorimeter containing powder is sealed off with helium at a low pressure to increase the conductivity of the powdered mass. The same instrument can be used for the measurement of specific heat of solidified gas.

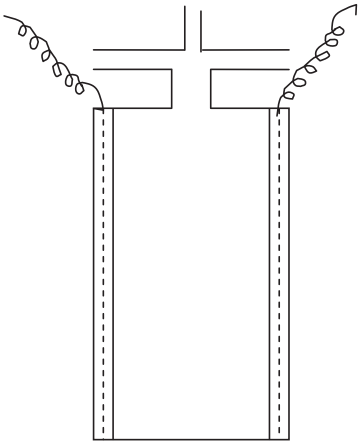

Fig. 7.22 Calorimeter used for measurement of specific heat of powder.

7.13.1 Measurement of Specific Heat of Gases at Low Temperatures

Scheel and Heuse continuous flow method: The continuous flow method of measurement of specific heat of a gas is illustrated by Fig. 7.23. The gas to be experimented upon enters the calorimeter by the open end *A*. It then flows through the spiral *S* and then through the double-jacketed chamber and finally discharged into the atmosphere through the end *B*. The temperature of the inflowing gas is measured by the pt. thermometer P_1. It is then heated by the heating coil *H*. The temperature of the heated gas is measured by the platinum thermometer P_2. The flow tube is surrounded by a glass jacket which is silvered in the inner wall and maintained at high vacuum to reduce loss of heat by radiation. The whole chamber is immersed in a bath of specific temperatures.

Eucken and Hiller vacuum calorimeter method: The apparatus shown in Fig. 7.24 was employed by Eucken and Hiller for the measurement of specific heat of hydrogen at low temperatures. The gas was compressed in a small steel bulb at a pressure of 150 atmospheres through the capillary tube K. The heating coil of constantan was wound on the outside of the bulb. The temperature of the gas was measured by the change of resistance of a platinum wire wound on the bulb *A*.

The bulb *A* was surrounded by a metal cylinder *B* maintained at the same temperature as *A* by current through another heating coil wound on *B*. By this guard ring method, the loss of heat due to radiation was eliminated.

The quantity of temperature of *A* and *B* was indicated by a thermocouple whose junctions were attached to *A* and *B*. The calorimeter was placed inside a glass jacket silvered on the inside and maintained at high vacuum.

7.14 REFRIGERATING MECHANISM

It is the mechanism of artificially maintaining a reservoir at a fixed desired temperature lower than that of the surrounding which is done by extracting heat from a cold reservoir with as little work as possible, applied externally. If a device takes heat Q_2 from cold body at temperature T_2 and gives out heat Q_1 to the surrounding or hot body at temperature T_1, the excess of heat Q_1 over Q_2 is the work *W* applied on the device, then the coefficient of performance is defined as

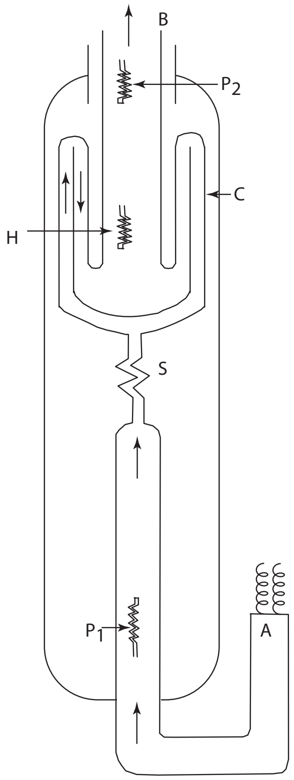

Fig. 7.23 Scheel and Heuse continuous flow method of measurement of specific heat of gas

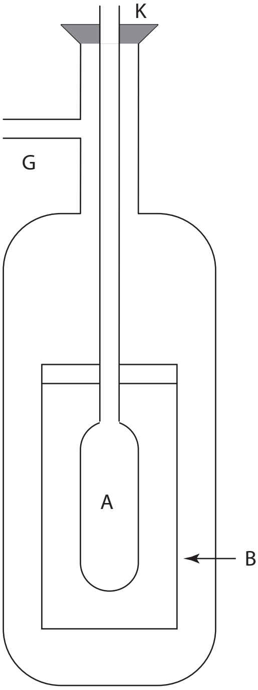

Fig. 7.24 Eucken and Hiller vacuum calorimeter for measurement of specific heat of hydrogen

$$\in = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

At temperatures above 10°C, bacteria increase greatly at a rapid rate. Food materials such as cooked food or raw materials such as fish, egg, meat, milk, fruit, vegetables, etc. become harmful in hot weather. If they are kept in a contrivance of lower temperature, they remain intact for long time. Such contrivance is known as refrigerator. For keeping medicines, vaccines and injectibles in their proper utility, they are kept in refrigerators. Refrigerators are used in long journey vehicles such as ships, planes, trains. Fishing ships must be equipped with ice-making plants by the help of refrigerators to keep the catch safe from decay as their voyages continue for long time. Air conditioning in residential houses, public halls, cinema houses, factories such as rubber, textiles, spinning mills is affected by refrigerators. Scope of refrigeration is very vast ranging from household refrigerators to cargo vessels where the refrigerated holds are kept many degrees bellow 0 °C for various purposes. Commercial refrigeration is generally used to indicate the technique for keeping goods at low temperatures; this is an important trade in the US, the UK and countries of European Union, this trade is also in the process of growth in tropical countries.

The principle of refrigeration is manifested in several ways such as: (1) cooling of a liquid by rapid evaporation, the liquid is called refrigerant which should have high latent heat of vapourization so that a small quantity of it on evaporation may produce desired effect; it should have low boiling point, (2) at NTP, the refrigerant should be a vapour but coluld be easily liquefied by cooling and compressing, (3) the vapour pressure in the evaporator section should exceed atmospheric pressure to prevent air from mixing in which case the passage will be obstructed, (4) compression pressure for liquefaction of the vapour in condenser unit should not be very large; otherwise vapour will have a tendency to leak, (5) the part of the machine should be short and heavy, (6) specific volume of vapour should be small so that a small compressor will serve the purpose. Sometimes, adiabatic expansion method of cooling is also used in conjunction.

Some general refrigerants are ammonia, sulphur dioxide, carbon dioxide, methyl chloride, ethyl chloride and freon. In massive refrigerating plants for manufacturing ice, ammonia is usually used as the refrigerant and they are also known as ammonia plants. But in household refrigerators such as frigidaires, sulphur dioxide or freon is used.

There are two types of refrigerating machines—electrolux refrigerators—absorption type and frigidaire—compression type.

7.14.1 Electrolux Refrigerator: Absorption Type

The absorption type of refrigerator was constructed first by Carsre; the schematic diagram is shown in Fig.7.25. The boiler *A* contains strong ammonia solution which is heated by *J*. The gaseous ammonia passes into the condenser *B* through spiral coil *D*, the coil is surrounded by cold water in *B*. Ammonia gas becomes liquefied here and the liquid is forced through the valve *V* on to the spiral coil *E* in the chamber *C*. Liquid ammonia evaporates here by taking the latent heat from the brine solution in *C* where the refrig-

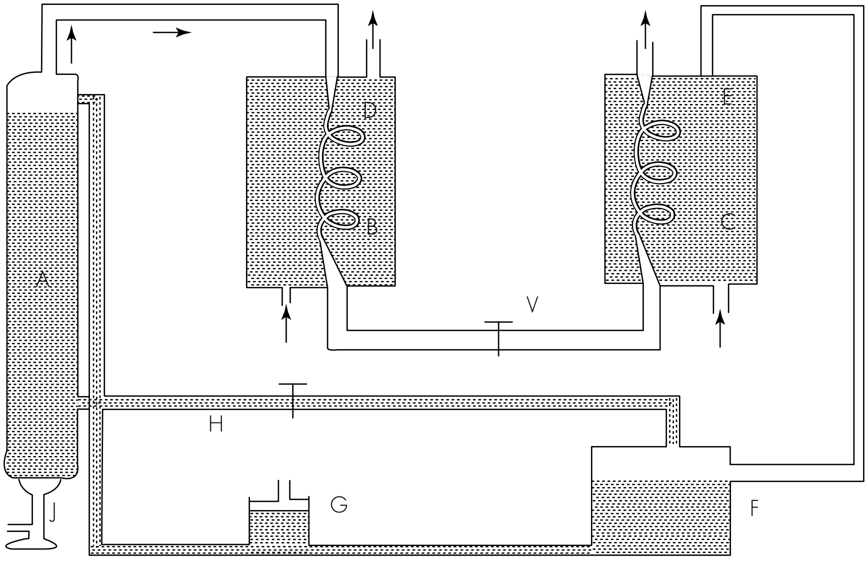

Fig. 7.25 Schematic diagram of absorption type of refrigerator

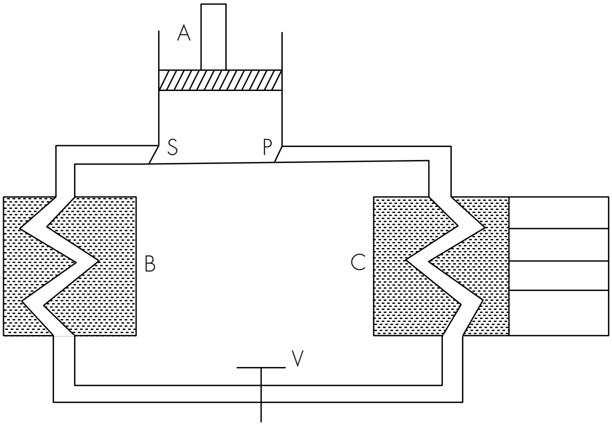

Fig. 7.26 Working principle of the compression type of refrigerator

erator chamber is placed. From the coil *E*, the ammonia gas is absorbed in *F* by dilute ammonia solution which is manipulated by valve *H* and is then pumped on the top of the boiler *A* by means of pump *G*. This cycle is repeated so that the refrigerator runs continuously. The wanted low temperature in the refrigerator is obtained by regulating the valve *V*, which manipulates the desired difference of pressure in the coils *D* and *E*.

In an improvised version of electrolux refrigerator, the use of the valve and pump is done away with liquid ammonia being evaporated at reduced pressure by hydrogen gas, the concentrated ammonia solution being transferred to the boiler by convection current.

7.14.2 Frigidaire Refrigerator: Compression Type

The working principle of the compression type of refrigerator is illustrated in Fig. 7.26. A suitable refrigerant, usually liquefiable sulphur dioxide, is made to evaporate under reduced pressure which produces the required cooling; the generated vapour is then compressed and cooled into the liquid state. This process is repeated. The machine consists of the following parts: (i) a pump *A*, (ii) condenser *B*, (iii) evaporator *C* associated with refrigerator *R* and (iv) a valve *V*.

As the piston of the pump *A* moves up, the pressure within the long copper spiral tube, in which the liquid refrigerant evaporates extracting latent heat from the adjacent refrigerator R, falls and the low pressure vapour is drawn in through the valve *P*. When the piston moves down, vapour is compressed and passes to the condenser *B* through valve *S* and gets liquefied in condenser *B*; the liquid then passes through the valve *V* and falls in pressure, and evaporates in *C* extracting latent heat from the refrigerator *R*. The low pressure vapour is again drawn in the pump and the cycle continues.

The working of the vapour compression machine is represented by the indicator diagram as shown in Fig. 7.27 where pressure and volume of the refrigerant are represented along *Y* and *X* axis of the indicator diagram,

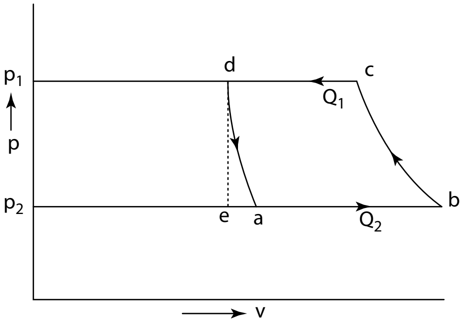

Fig. 7.27 Indicator diagram representing the working of vapour compression machine

respectively. During the passage of the cycle *ab*, the liquid is evaporated extracting heat Q_2 at temperature T_2 of the refrigerator; during *bc*, the vapour is adiabatically compressed; during *cd*, the vapour is liquefied at condenser *B*, Q_1 heat is transferred at temperature T_1 and pressure p_1 and finally during da, adiabatic expansion of the liquid through valve *V* is made.

Since the cycle is reversible; from Carnot's principle, $Q_1/T_1 = Q_2/T_1$ and coefficient of performance $\in$ is given by

$$\in = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

In actual machine, $\in$ is less as the expansion chamber is absent; expansion of liquid through valve *V* follows path de instead of *da*.

7.15 AIR CONDITIONING MACHINE

It is found that proper working and living conditions of human being necessitates certain criteria such as temperature, moisture content, clearness and circulation of air should be conducive to human health and comfort. The technique by which this is done is known as air conditioning. Air should be free from any type of impurity such as gaseous material, tobacco and bad odour. All these factors increase the efficiency of people working in offices and factories; this is also used to create ideal conditions necessary for producing and processing of certain goods. American Society of Heating and Ventilating Engineers have recommended the following data for average comfort conditions:

(a) Temperature—17° to 22°C in winter and 19° to 24°C in summer.
(b) Relative humidity—30 to 65%.
(c) Air movement—4.5 to 15 m per minute.
(d) Fresh air to be introduced—25% of total air circulation.

This will keep fresh air free from bad odour and harmful components. Relative humidity plays an important role in human comfort for at a particular temperature if the relative humidity is high, we feel warm and if it is low, we feel cold because evaporation from our body and abstraction of heat thereby depends on relative humidity. The comfort condition differs from people to people, season to season and country to country depending on the latitudes.

7.15.1 Summer Air Conditioning

This type of air conditioning requires suitable arrangement for cooling, dehumidifying, cleaning of air and proper ventilation. The evaporator of a refrigerator is kept at suitable position of closed space requiring summer air conditioning; evaporator is a series of zigzag copper tubing finned with thin copper sheets for increasing the effective area of cold surface. A suction pump draws fresh air through a filter which precipitates particles of dust, smoke, etc. as they are carriers of harmful bacteria. This air is passed from one end of the cooling coils to the other end through the fins and thus gets cooled. Moisture content exceeding comfort limit is precipitated on the fins and drained out. This is known as dehumidification; for less moisture content, humidification arrangement is to be made. There are devices controlling the cooling and ventilation. The power of the refrigerating machine depends on the size of the closed space, heat conduction through walls and roof, number of persons in the room, outside air entering the room and heat producing articles. If the walls and roof are carefully covered with bad conducting materials like masonite and calotex, cost of air conditioning will be less.

7.15.2 Winter Air Conditioning

In winter, temperature and relative humidity are generally less. Winter air conditioning necessitates heating and humidifying. Air sucked through filter is passed over heating coil, which increases the temperature of air. This air is simultaneously humidified by spraying water on the heating coil and is then supplied to the air-conditioning space; the exhausted air is again conditioned with sucking air.

7.16 EFFECTS OF CHLOROFLUORO CARBONS (CFCS) ON OZONE LAYER

Earth's atmosphere is a mixture of gases and vapours of which some are fixed components such as nitrogen, oxygen, argon, carbon dioxide, neon, krypton, hydrogen, nitrogen oxide, xenon and helium 3; and some are variable components like ozone, sulphur dioxide, nitrogen peroxide, methane and iodine. The atmosphere is divided into troposphere, stratosphere, thermosphere, ionosphere and magnetosphere according to height and their characteristics. The layer nearest to the earth's surface is called troposphere; it is about 17 km above equator, 9 km at latitude 50 ° and 6 km at poles. In this region, concentration of ozone is very small—nearly 0.02 parts per million in non-urban areas and less in urban areas but at higher altitudes in stratosphere, its concentration is higher. Ozone is an allotropic form of the element oxygen. Common oxygen molecule contains two atoms of oxygen while ozone molecule contains three atoms of oxygen. Ozone is formed by photochemical action on atmospheric oxygen at stratosphere. This ozone absorbs solar ultraviolet radiation helping life on earth and also raising the temperature with height forming a stable layer which restrains vertical mixing to such an extent that gases injected into this region may remain there for years together. Ozone layer, being thinnest at the equatorial region, allows more ultraviolet radiation to reach earth's surface in the torrid region. That is why, people in this region are black and suffer from skin cancer. So, we see that the presence of ozone in lower atmosphere closer to earth contributes to air pollution and causes damage to human tissue; but its presence in the stratosphere is absolutely vital for life where ozone concentration is nearly ten parts per million.

The decrease in ozone concentration has tremendous adverse effects on earth. Volcanic eruptions and cosmic rays indirectly reduces ozone; besides this, human activities are also responsible for reduction of ozone concentration. Nuclear explosions and supersonic aircrafts flying at altitudes nearly 28 km, release of chlorofluoro carbons (CFCs) are believed to reduce ozone concentration. CFCs made up of chlorine, fluorine and carbon are so chemically inert that once they are released in the atmosphere, they rise to the stratosphere where sun's ultraviolet rays break down CFCs releasing their chlorine content which is the main cause of ozone depletion. Ozone absorbs 2400 to 3200 angstrom wavelength of sun's rays. Above 30 km, oxygen molecule is dissociated into oxygen atoms during day time by ultraviolet photons $O_2 + h\nu \rightarrow O + O$ by $\lambda < 2400$ angstrom.

This oxygen atom then forms ozone by $O + O_2 + M \rightarrow O_3 + M$ where M is arbitrary molecule required to conserve energy and momentum in the reactions. Electric discharge reactions including lightning and electric sparks from motors also convert oxygen into ozone.

Chloro fluoro methanes $CFCl_3$ (Freon 11) and CF_2Cl_2 (Freon 12) are responsible for ozone depletion, their atmospheric life time is about 80 years. Even if their production is halted, the effect will be felt upto 80 years. The importance of this ozone layer at about 30 km above earth's surface is that it absorbs most of the lethal shorter ultraviolet wavelengths of the sun. If these rays penetrate the ozone layer, life would not be possible on earth.

Scientists reported a large hole in the ozone layer over Antarctica in early 1980s. Level of ozone is dropping regularly by the use of man-made chemicals containing CFCs used as coolants in refrigerators, air conditioners and fire extinguishers. These are introduced because of their non-poisonous, non-inflammable and highly stable nature; they are used in blowing plastic foams in spray canes and cleaning computer circuits also. A thorough research shows that such CFC molecule destroys ten million ozone molecules.

When a similar hole was reported to appear over thickly populated northern hemisphere, rich nations of Europe and North America were set into action which resulted into Montreal Protocol. It was decided to eliminate 90 per unit ozone destroying substance by 2000. Developing countries were given a grace period of 10 years. The nations of the world should think over postponement of these practices which are self destructing in favour of "sustainable development", as the environmentalists call it. There should be a compromise between modern technology and the corresponding environmental damage jeopardizing the prospect of future generation.

7.17 Applications of Substances at Low Temperature

Mysteries are the actions of science and its followers, i.e., researchers. There is no end of scientific achievements; when one thinks that limit has been reached, new horizons emerge. The low temperature domain has provided researchers wide field to tread. Normally, electricity flows through a conductor which waste nearly 50 per cent of the power produced. Scientists are trying to get rid of this phenomenon by looking after carriers of electric current which can be made super conductive so that this waste of energy is avoided. Dutch physicist Heike Kamerlingh Onnes (1853–1926) discovered superconductivity in 1911 while studying the variation of electrical resistance of mercury with temperature. He observed that at temperature near absolute zero, the resistance drops to a very low value making it superconductive; this temperature is called transition temperature or superconducting temperature. In 1833, W. Meissner and R. Ochsenfild discovered that a superconductor placed in a not too high magnetic field expelled the field from the interior of superconductor. This phenomenon is called Meissner effect. Helium liquefies at 4.2 K producing low temperature region for studying such phenomena. A new technological revolution with a potential input as great as industrial revolution creeps in. Superconductivity is a broad area serving many fields, opening up amazing possibilities. Bullet trains now move at a tremendous speed on cushions of magnetism. High power small size electric cars, miniaturized computers which are more powerful, safer nuclear reactors yielding many times more energy, cheap diagnostic aids of extra dimensions are just a few examples in this regard. A new world opens up with chemical compounds showing super conductivity at liquid nitrogen temperature where production is not so costly as liquid helium, lead, tin, mercury, etc., originally known to be super conductive at low temperature, lose this characteristic as soon as enough current is made to flow to generate sufficient magnetic field but alloys of oxides of niobium and titanium known as ceramics posses superconductivity. Later Karl Alek Muller of IBM's Zurich laboratory tried metallic oxides at higher transition temperature; Paul C.W. Chu of Houston University took up the study along with different scientists of the world including India. They are trying with rare earth element, India and China have world's largest rare earth's material's deposit and this process is still going on.

One of the surprising features at low temperature is superfluidity. Generally, fluids possess viscosity which means they tend to resist relative motion between their layers as if different layers are moving with different velocities. Viscous forces appear in tending to slow down the faster moving layers and to increase the velocity of slower moving layers. But liquid helium II has zero viscosity. This has been discussed in Section 7.11. Cryogenics (the study of materials and phenomena at temperature close to absolute zero) has revealed a new dimension in the area of low temperature. Quick freezing by liquid nitrogen has enhanced taste, texture, aroma, nutritive value and appearances of food articles in addition to reduced degradation by bacteriological, enzymatic, oxidative and chemical reactions. This cryogenic freezing system is more economical than ordinary system and is handy for refrigerated transportation of marine food, fruits, vegetables and other perishable foods. A new blood freezing technique developed with liquid nitrogen is now used for storing blood for months or even years and may be used to store marrow cells. Some diseases such as Parkinson's and other disorders of involuntary movement can be treated by cryosurgery. Tumours can be frozen and removed. Cryosurgery can be used in tonsillectomies and in the removal of cataracts of eyes. The gases burnt in the refineries or oil fluids uselessly can be liquefied by cryogenic methods and transported to the residents of remote corners of our country which do not have the facility of city gas lines. Liquid methane can reduce the cost of supersonic flights by one-third. Research on application of substances at low temperature is going on in premier research laboratories in India like National Physical Laboratory, New Delhi; Tata Institute of Fundamental Research and Bhaba Atomic research Centre, Mumbai; Indian Institute of Science, Bengaluru; Indian Association for the Cultivation of Science, Jadavpur; Cryogenic Centre at Jadavpur University; Department of Physics and Astrophysics at University of Delhi, Solid State Physics Laboratory, Delhi; and IITs. Amusing mankind friendly results are awaited.

SOLVED PROBLEMS

Q 1. Calculate the temperature of inversion of hydrogen where cooling effect would vanish from the following data assuming that the gas obeys Van der Waals' equation.

Critical temperature of hydrogen = 33.18 K

Critical pressure of hydrogen = 12.80 atmospheres

Ans. We have

$$p_c = \frac{a}{27b^2} \qquad T_c = \frac{8}{27}\frac{a}{bR}$$

∴

$$\frac{T_c}{p_c} = \frac{8}{27}\frac{a}{bR} \times \frac{27b^2}{a} = \frac{8b}{R}$$

or

$$b = \frac{R}{8}\frac{T_c}{p_c} = \frac{83.15\times10^6\times33.18}{8\times12.8\times76\times13.6\times981} = 28.16$$

Density of hydrogen = 0.08987 gm/litre

Gram- Molecular Volume of hydrogen $= v = \dfrac{2000}{0.08987}$ cc

Substituting the value in Eq. 7.15, $T_o = \dfrac{2a}{Rb}\left(1 - \dfrac{b}{v}\right)^2$

$$= \frac{2\times27}{8}\times33.18\left(1 - \frac{28.16\times.08987}{2000}\right)^2$$

$$=\frac{27}{4}\times 33.18(I-.0013)^2$$

or $$T_o = 223.8K$$

Q 2. In the case of saturated steam, the specific heat at 150 °C is − 0.674 calories, critical temperature of steam = 374 °C, for steam $p_c = 218.5$ atmospheres, $v_c = 0.00248$ cc, $a = 0.0110$ atmospheres $(suv)^2/gm^2$ (suv is the volume of 1 gm of specified gas at N.T.P; for a pure gas, it is equal to about 22415 *cc* divided by the molecular weight of the gas),

$$b = 0.00136\frac{suv}{gm},\ R = 0.00369568\frac{atm(suv)}{gm\deg}$$

Calculate the change of temperature per atmosphere drop of pressure of steam by throttle expansion.

Ans. We know $$\left(\frac{dT}{dp}\right)_H = \frac{-b+\dfrac{2a}{RT}}{C_p}$$

$$\left(\frac{dT}{dp}\right)_H = \frac{0.00136\left(\dfrac{suv}{gm}\right) - \dfrac{2\times 0.011\dfrac{atm\ (suv)^2}{gm^2}}{0.003696\dfrac{atm\ (suv)}{gm\ (\deg)}\times 423\deg}}{\dfrac{0.674}{0.024205}\dfrac{atm\ (cc)}{gm\ (\deg)}}$$

$$= \frac{\left(0.00136 - \dfrac{2\times 0.011}{0.003696\times 423}\right)\dfrac{suv}{gm}}{\dfrac{0.674}{0.024205}\dfrac{atm\ (cc)}{gm\ (\deg)}}$$

$$= \frac{0.00136 - \dfrac{0.022}{0.003696\times 423}}{\dfrac{0.674}{0.024205}}\frac{\deg}{atm} = -0.000456\frac{\deg}{atm}$$

Thus saturated steam on throttle expansion becomes superheated and, therefore, unsaturated. By adiabatic expansion of steam in the cylinder of a boiler, it condenses on the walls of the cylinder. This produces considerable loss of heat. By allowing steam to pass through a throttle before entering the cylinder, this loss of heat is very much reduced. This process is known as “wire drawing”.

Q 3. Taking the gas constant R to be 8.3×10^7 ergs/°C, calculate $\left(\dfrac{dT}{dp}\right)_H$ for the oxygen gas at 0 °C from the following data:

$$a = 1.36 \times 10^6 \text{ atmospheres}$$

$$b = 32 \text{ cc}$$

$$C_p = 7.03$$

$$J = 4.18 \times 10^7 \text{ ergs/cal}$$

Ans. We know

$$\left(\frac{dT}{dp}\right)_H = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

$$= \frac{1}{7.03 \times 4.18 \times 10^7}\left(\frac{2 \times 1.36 \times 10^6 \times 76 \times 981 \times 13.6}{8.3 \times 10^7 \times 273} - 32\right)$$

$$= 0.31\,°\text{C per atm. per cm}^2$$

Q 4. Calculate the change in enthalpy when a gram molecule of a gas is isothermally compressed from 1 atmosphere to 20 atmospheres. Given $\mu = 1.08$, $C_p = 8.6$ and $J = 4.18 \times 107$ ergs/cal.

Ans. We know

$$\left(\frac{dH}{dp}\right)_T = \mu C_p$$

The change in enthalpy

$$= -\int_{p_2}^{p_1} \mu C_p dp = -\mu C_p (p_1 - p_2)$$

$$= 1.08 \times 8.6 \times 4.2 \times 10^7 \times 19 \times 1.013 \times 10^6$$

$$= 750.8 \times 10^6 \text{ joules}$$

Q 5. Given T_c for helium = 5.26 K, find the inversion temperature.

Ans. We know

$$T_i = \frac{27}{4} T_C = \frac{27}{4} \times 5.26 = 35.5 \text{ K}$$

Q 6. The Van der Walls' constants a and b for one mole of hydrogen are $a = 0.245$ litre^2 × atm/mole^2 and $b = 2.67 \times 10^{-2}$ litre/mole. Calculate the temperature of inversion. Atmospheric pressure may be approximately taken to be 10^6 dynes/cm^2 and R = 2 cal/mole K.

Ans. Now

$$a = 0.245 \text{ litre}^2 \times \text{atm/mole}^2$$

$$= 0.245 \times 10^6 \times 10^6 \text{ cm}^4 \text{ dyne/mole}^2$$

$$b = 2.67 \times 10^{-2} \text{ litre/mole}$$

$$= 2.67 \times 10^{-2} \times 10^3 \text{ cc/mole}$$

$$T_i = \frac{2a}{bR} = \frac{2 \times 0.245 \times 10^{12}}{26.7 \times 2 \times 4.2 \times 10^7} = 220 \text{ K}$$

Q 7. Calculate the drop in temperature produced by adiabatic throttling in case of oxygen when the pressure is reduced by 50 atmospheres. Initial temperature is 27 °C, a = 1.32 litre^2 × atmosphere/mole^2 and $b = 3.12 \times 10^{-2}$ litre per mole. Atmospheric pressure may be approximately taken to be 10^6 dynes per cm^2 and R = 2 cal/mole K.

Ans. We know

$$\left(\frac{dT}{dp}\right) = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

or

$$T_1 - T_2 = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)(P_1 - P_2)$$

Since oxygen is a diatomic gas, $C_p = \frac{7}{2}R = 7$ cal/mole K

Change in temperature

$$= \frac{1}{7 \times 4.2 \times 10^7}\left(\frac{2 \times 1.32 \times 10^{12}}{2 \times 4.2 \times 10^7 \times 300} - 31.2\right) \times 50 \times 10^6$$

$$= 12.5 \text{ K}$$

Q 8. What would be the cooling in the above case if the expansion were reversible doing external work, γ being 1.4 and initial and final pressures are 51 atmospheres and 1 atmosphere, respectively?

Ans. We know

$$T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}}$$

$$300\,(51)^{\frac{1-1.4}{1.4}} = T_2 (1)^{\frac{1-1.4}{1.4}}$$

$$\therefore \qquad T_2 = 300(51)^{\frac{-.4}{1.4}} = 97.4 \quad \text{K}$$

The drop in temperature = 300 − 97.4 = 202.6 K

PROBLEMS

1. Calculate the temperature of inversion for hydrogen (H_2) if the critical temperature is 22 K.

   Ans. 148.5 K

2. Calculate the temperature of inversion of oxygen (O_2) when

   a = 1.32 litre^2 × atmosphere per mole^2 and

   $b = 3.12 \times 10^{-2}$ litres per mole.

   Ans. 1048 K

3. Calculate the drop in temperature produced by the adiabatic throttling expansion of air from 215 atmospheres to 1.2 atmospheres, the air being initially at 0 °C. What would be the cooling if the expansion were reversible doing external work? Assume that air obeys Van der Waals' equation with

$a = 13.4 \times 10^5$ atmospheres $\times$ cm^6 per gm mole and

$b = 36.5$ cc/gm. mole and

$C_p = 6.95$ cal per gm. mole

$\gamma = 1.4$

Ans. 61.8 °C, 211 °C

4. Given the values of Van der Waals' constants a and b for argon to be 1.35 atm. litre^2/mole^2 and 3.2×10^{-2} litre/mole, respectively, calculate the critical temperature, inversion temperature and the Boyle temperature of the gas.

Ans. $T_c = 152.6$ K
$T_i = 1030$ K
$T_b = 514.3$ K

QUESTIONS

1. Distinguish between Joule–Thomson cooling and adiabatic cooling.
2. What is Joule–Thomson cooling effect? Deduce the theory.
3. Describe different methods of liquefaction of gases.
4. Describe adiabatic demagnetization method of production of low temperature. Give the theory.
5. Describe the method of liquefaction of hydrogen.
6. Describe the method of liquefaction of helium.
7. Give a brief account of measurement of low temperature.
8. Give a description of the porous plug experiment of Joule and Thomson. Discus the results and indicate their significance for liquefaction of gases.
9. Explain the principle of regenerative cooling and describe a method of liquefying air based on it.
10. Describe the methods of measuring low temperatures.
11. What is Joule–Thomson effect? Obtain an expression for the cooling produced assuming that the gas obeys Van der Waals' equation. Why do hydrogen and helium show a heating effect at ordinary temperature?
12. Describe briefly a method of liquefying helium and state some of the important changes in the physical properties of a substance near absolute zero.

Chapter 8

FIRST LAW OF THERMODYNAMICS

8.1 Principle of Conservation of Energy

It states that the sum total of the energy of the universe is an invariant; it can only transform into different forms. This principle forms the fundamental postulate in Physics. Regarding the forms of energy, we have the following categories:

1. The mechanical energy, which may be kinetic or potential corresponding to mechanical work which is measured by mechanical force × displacement.
2. The non-mechanical energy such as heat, light, electrical and magnetic energies.

In thermodynamics, we deal only with the relation between two forms of energy—heat and mechanical work. The quantitative law of transformation of mechanical work into heat is given by the Joule's law

$$W = J \times Q$$

where W is the amount of mechanical work done by a body in ergs and Q is the quantity of heat given out or absorbed by the body in calories. J is the constant of proportionality called the Joule's equivalent or mechanical equivalent of heat. Its value is 4.18×10^7 ergs per calorie.

8.2 The Thermodynamic State and Thermodynamic Co-ordinates

The properties of a body which can be perceived by our senses are called physical properties. In any physical change of a body caused by heat, it is the pressure, volume and temperature of the body that changes. These properties of the body are measurable quantities. The thermodynamic state of a body can be measured by certain physical measurable properties of the body, suggested more or less by our sense perception. These measurable properties of the body which specify the thermodynamic state are called the thermodynamic co-ordinates of the body. The fundamental co-ordinates in thermodynamics are (1) pressure (p), (2) volume (v) and (3) temperature (θ). In addition to these co-ordinates, there are other co-ordinates which can be derived from these fundamental or primary co-ordinates such as entropy, free energy, enthalpy, thermodynamic potential and so on. We shall call these co-ordinates secondary or derived co-ordinates. Since temperature of a body is measured either by the change of volume or change of pressure, the three fundamental or primary co-ordinates are not independent. In fact, any one of these co-ordinates can be expressed in terms of the other two. Hence out of the three fundamental co-ordinates, only two can vary independently.

So that,

$$dp = \frac{\partial p}{\partial v} dv + \frac{\partial p}{\partial \theta} d\theta$$

$$dv = \frac{\partial v}{\partial p} dp + \frac{\partial v}{\partial \theta} d\theta$$

$$d\theta = \frac{\partial \theta}{\partial p} dp + \frac{\partial \theta}{\partial v} dv$$

These three co-ordinates (p, v, θ) only define the state of matter in bulk or the so-called macroscopic state and they require no special assumption concerning the structure of matter composing the body.

8.2.1 Thermodynamic Equilibrium

The thermodynamic state of a body is specified by mathematical relation connecting the thermodynamic co-ordinates. That mathematical relation is called the equation of state of the body. It is to be noted that an equation of state does not refer to a changing state; in fact, the thermodynamic co-ordinates which define the state of a body are not measured while they are changing. As such, they are not functions of time. An equation of state specifies an equilibrium state or balanced state. Since the equation of state is defined by pressure (force per unit area), volume and temperature, any state of equilibrium in thermodynamics implies both mechanical and thermal equilibrium. By thermal equilibrium of a body, we mean a state of the body in which it is neither giving out nor absorbing any heat. A body is in mechanical equilibrium when it has no displacement.

Nevertheless, we often use thermodynamic co-ordinates to describe a process of continuous change of thermodynamic states. The justifying assumption for such procedure is that at all times during which the change is taking place, the system undergoing change is supposed to be infinitely near an equilibrium state. An infinitely slow process of change of state like the above is called *quasistatic process*. Evidently, it is only an ideal process. When we represent physical states of a body by a graph (such as the p–v diagram), our object is to find the value of pressure when the volume acquires a given value when both the volume and pressure are not changing, that is, when they are in equilibrium state.

A cyclic process is a process in which a substance undergoes a series of changes in the form of expansion and compression, and finally comes back to the initial stage.

A process in which the system is thermally insulated and has no communication of heat or work with its surroundings is called an isolated process.

8.2.2 Zeroth Law of Thermodynamics

It states that if two bodies A and B are each separately in thermal equilibrium with a third body C, then A and B are also in thermal equilibrium with each other. This law provides the basis for temperature measurement.

8.3 SPECIFIC HEATS AND LATENT HEATS

As already stated, thermodynamics deals with the transformation of heat energy into mechanical work and vice versa. By the application of heat, to a body, the thermodynamic state of the body changes and therewith the thermodynamic co-ordinates defining the state also change. Let dp, dv and $d\theta$ be the infinitesimally small changes in pressure, volume and temperature of the body as a result of absorption of small quantity of heat dQ. Then from change of any two of these co-ordinates, the quantity of heat absorbed dQ can be calculated. The change in the remaining thermodynamic co-ordinates can be obtained from the changes of the two co-ordinates with the help of the equation of state.

Thus,

$$dQ = k\,d\theta + \ell\,dv \tag{8.1}$$

$$dQ = k'\,d\theta + \ell'\,dp \tag{8.2}$$

$$dQ = P\,dp + V\,dv \tag{8.3}$$

where k, ℓ, k', l', P and V are constants.

To obtain the meaning of the constant k, we put $dv = 0$. A process which takes place at constant volume is called an *isochore* or *isovolumic process*. Under this condition, Eq. 8.1 gives for a body of unit mass,

$$k = \left(\frac{dQ}{d\theta}\right)_v$$

Hence, the constant k is called the *specific heat of the substance at constant volume*. We shall represent it by C_v. Thus, $k = C_v$.

To find the meaning of ℓ, we put $d\theta = 0$ in Eq. 8.1 so that the process is isothermal. Under this condition,

$$\ell = \left(\frac{dQ}{dv}\right)_\theta$$

Under this condition, the heat dQ absorbed by the body does not raise its temperature but only changes its volume. Hence, ℓ must be latent heat. We shall call ℓ *latent heat of isothermal expansion*.

To find the meaning of k', we put $dp = 0$. A process in which pressure remains constant is called *isobaric process*.

Under this condition,

$$k' = \left(\frac{dQ}{d\theta}\right)_p$$

Hence, k' is the *specific heat of the substance at constant pressure*. We shall represent it by C_p.

Thus, $k' = C_p$

To find the meaning of ℓ' , we put $d\theta = 0$ in Eq. 8.2.

This gives

$$\ell' = \left(\frac{dQ}{dp}\right)_\theta$$

Under this condition, the heat absorbed by the body does not change its temperature but only changes the pressure. Hence, ℓ' must be latent heat. We shall call ℓ' the latent heat of isothermal increase of pressure.

To find the value of P in Eq. 8.3, we put $dv = 0$ so that

$$P = \left(\frac{dQ}{dp}\right)_v$$

This can be written as

$$P = \left(\frac{dQ}{d\theta}\right)_v \left(\frac{d\theta}{dp}\right)_v = \frac{\left(\frac{dQ}{d\theta}\right)_v}{\left(\frac{dp}{d\theta}\right)_v}$$

or $P = C_v/\alpha$ where α = co-efficient of pressure variation at constant volume.

To find the value of V, we put $dp = 0$ in Eq. 8.3 so that

$$V = \left(\frac{dQ}{dv}\right)_p$$

This can be written as

$$V = \left(\frac{dQ}{dv}\right)_p = \left(\frac{dQ}{d\theta}\right)_p \left(\frac{d\theta}{dv}\right)_p = \frac{\left(\frac{dQ}{d\theta}\right)_p}{\left(\frac{dv}{d\theta}\right)_p}$$

or $V = C_p/\beta$ where β = co-efficient of volume variation at constant pressure.
For a perfect gas, $\alpha = \beta$ so that $P = C_v/\alpha$ and $V = C_p/\beta$
Equations 8.1–8.3 can now be written in the following forms

$$dQ = C_v d\theta + \ell\, dv$$

$$dQ = C_p d\theta + \ell'\, dp$$

$$dQ = \frac{C_v}{\alpha} dp + \frac{C_p}{\beta} dv$$

or $$\alpha dQ = C_v dp + C_p dv \quad \text{for a perfect gas.}$$

The constants k, ℓ, k', ℓ', P and V are not independent. In Eq. 8.1, the quantity of heat absorbed dQ produces changes in volume and temperature only. In Eq. 8.2, the same quantity of heat only serves to effect a change in temperature and pressure. If in both cases the quantity of heat supplied be the same, then

$$kd\theta + \ell dv = k'd\theta + \ell' dp \tag{8.4}$$

Expressing p as a function of v and θ so that

$$dp = \left(\frac{dp}{dv}\right)_\theta dv + \left(\frac{dp}{d\theta}\right)_v d\theta$$

and substituting the value in the above equation, we get

$$kd\theta + \ell dv = k'd\theta + \ell'\left[\left(\frac{dp}{dv}\right)_\theta dv + \left(\frac{dp}{d\theta}\right)_v d\theta\right]$$

This is true when $dv = 0$ so that

$$k = k' + \ell'\left(\frac{dp}{d\theta}\right)_v \tag{8.5}$$

when $$d\theta = 0,\ \ell = \ell'\left(\frac{dp}{dv}\right)_\theta \tag{8.6}$$

Expressing v as a function of θ and p,

$$dv = \left(\frac{dv}{dp}\right)_\theta dp + \left(\frac{dv}{d\theta}\right)_p d\theta$$

and substituting the value in Eq. 8.4,

$$kd\theta + \ell\left[\left(\frac{dv}{dp}\right)_\theta dp + \left(\frac{dv}{d\theta}\right)_p d\theta\right] = k'd\theta + \ell'dp$$

This is true when $dp = 0$. This gives

$$k + \ell\left(\frac{dv}{d\theta}\right)_p = k' \tag{8.7}$$

Putting $$d\theta = 0,\ \ell\left(\frac{dv}{dp}\right)_\theta = \ell' \tag{8.8}$$

In the same way, equating Eqs 8.1 and 8.3, we get

$$kd\theta + \ell dv = Pdp + Vdv \tag{8.9}$$

If p is the function of v and θ, then

$$kd\theta + \ell dv = Vdv + P\left[\left(\frac{dp}{dv}\right)_\theta dv + \left(\frac{dp}{d\theta}\right)_v d\theta\right]$$

Putting $dv = 0$,

$$k = P\left(\frac{dp}{d\theta}\right)_v \tag{8.10}$$

Putting $d\theta = 0$,

$$\ell = V + P\left(\frac{dp}{d\theta}\right)_\theta \tag{8.11}$$

Putting θ as a function of p and v, and substituting the values in Eq. 8.9, we get

$$k\left[\left(\frac{d\theta}{dp}\right)_v dp + \left(\frac{d\theta}{dv}\right)_p dv\right] + \ell dv = Pdp + Vdv$$

Putting $$dp = 0, \quad k\left(\frac{d\theta}{dv}\right)_p + \ell = V \tag{8.12}$$

Putting $$dv = 0, \quad k\left(\frac{d\theta}{dp}\right)_v = P \tag{8.13}$$

Similarly equating Eqs 8.2 and 8.3, we get other sets of relations between the constants. Thus, it proves the relations

$$k'\left(\frac{d\theta}{dp}\right)_v + \ell' = P \tag{8.14}$$

$$k'\left(\frac{d\theta}{dv}\right)_p = V \tag{8.15}$$

8.4 THE ENERGY EQUATION

The sum total of energy of a system may be divided into two parts—(1) *the internal energy* and (2) *the external energy*.

The internal energy consists of the kinetic energy of molecular motion and potential energy of intermolecular forces. The external energy of a system is measured by the work which would be performed by the system in expanding to a state of infinite rarity starting from its present state. This work is performed by the pressure exerted by the body.

The work done by an expanding fluid can be easily calculated as: let us suppose that a small element of surface dS of the fluid moves through a distance dn in the outward direction normally. If p is the pressure of the fluid, the work done in this displacement is $p\ ds\ dn = p\ dv$

The total work done by the fluid in small displacement is the sum of contributions from all elements of surface which are moved. Work done by a substance as its state changes in the p–v space from the point A to the point B along AB is $\int_{v_1}^{v_2} pdv$. Since the amount of work done is determined by the shape of the path AB, dW is not a perfect differential.

Calling U and W the internal and external energies respectively, the total energy of a body in any configuration is

$$E = U + W \tag{8.16}$$

where U is measured from a state in which the internal energy is zero. This state of the body is not known. Hence, the actual internal energy of a body is an indeterminate quantity. Fortunately, we are concerned only with changes of energy and not with actual quantity of energy when a body passes from one state to another. Hence, any arbitrary state of external and internal energies can be taken as the standard state for our calculation.

Let us suppose that a quantity of heat energy dQ is absorbed by a body from an external source as a consequence of which the pressure, volume and temperature of the body change. Let us suppose that after this absorption of energy, the body again assumes a steady state. Let us suppose that in the new state, U changes to $U + dU$ and W changes to $W + dW$. By the principle of conservation of energy,

$$dQ = dE = dU + dW \tag{8.17}$$

This equation is known as the energy equation.

Since $$dW = p\,dv,$$

the energy equation for a fluid takes the following form

$$dQ = dU + p\,dv \tag{8.18}$$

This energy equation is known as *the first law of thermodynamics.*

In the energy equation, dQ represents that part of energy which is absorbed or given out by a body in the process of change from one state to another. In other words, dQ refers to energy transferred across the boundary of the body.

8.4.1 *dU* is a Perfect Differential

The change of internal energy of a body as it passes from state A to state B depends only on the initial and final states, and not on the path or manner of change of state.

If not, let the difference of energy of a body in the transition from the state A to the state B along the path I (Fig. 8.1) be less than that along the path II. Then, the effect of bringing the body from A to B along path I and back from B to A along the path II would be an increase of energy of the surroundings. But the system has been brought back to precisely the same state as at the beginning, for the thermodynamic state of a body is a single valued function of any two of the thermodynamic co-ordinates (p, v and θ).

Hence, energy must have been created which is contrary to the principle of conservation of energy. Expressed in mathematical language, this means that dU is a perfect differential.

8.4.2 *dQ* is Not a Perfect Differential

In the energy equation, dU is a perfect differential and dW is not a perfect differential. Hence, dQ is not a perfect differential.

The change of thermodynamic state of the body in the states A and B can be defined in terms of any two of the thermodynamic co-ordinates—p, v and θ.

If U is regarded as a function of θ and v, that is, in the θ–v space, then

$$dU = \left(\frac{dU}{d\theta}\right)_v d\theta + \left(\frac{dU}{dv}\right)_\theta dv \tag{8.19}$$

If U is regarded as a function of θ and p, that is, in the θ–p space, then

$$dU = \left(\frac{dU}{d\theta}\right)_p d\theta + \left(\frac{dU}{dp}\right)_\theta dp \tag{8.20}$$

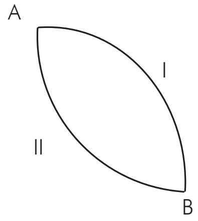

Fig. 8.1 Representation of Internal Energy

8.4.3 Joule's Experiment

The apparatus (Fig. 8.2) consisted of two stout cylinders immersed under water contained in a vessel.

One of these cylinders contained air under high pressure, and the other was exhausted of air. The two vessels communicated with each other by means of a pipe provided with a stop-cock. The temperature of water was measured by a sensitive thermometer.

On opening the stop cock, the compressed gas rushed into the vacuum without doing any external work. When equilibrium was attained, the thermometer recorded no change in temperature. Hence, the results of experiment were $dW = 0$, $d\theta = 0$. No external work was done because the gas rushed into vacuum.

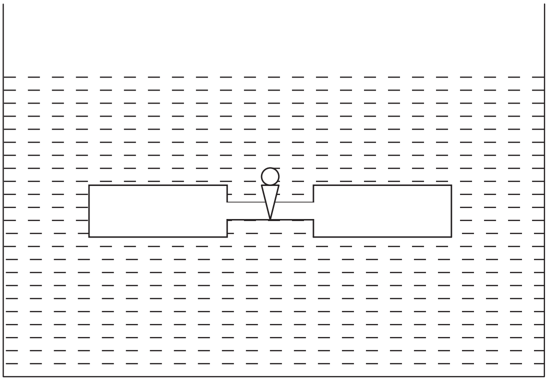

Fig. 8.2 Joule's experiment

Since the apparatus was thermally isolated, $dQ = 0$.

Hence from the first law of thermodynamics, $dU = 0$ eqn. (8.17)

Substituting $dU = 0$ and $d\theta = 0$ in Eq. 8.19, we get

$$\left(\frac{dU}{dv}\right)_\theta = 0 \tag{8.21}$$

Substituting these values in Eq. 8.20, we get

$$\left(\frac{dU}{dp}\right)_\theta = 0 \tag{8.22}$$

Hence, internal energy U does not change when the volume and the pressure change at constant temperature. Internal energy of a given quantity of a gas must depend only on temperature.

In other words, $U = f(\theta)$

The experiment of Joule as described above is not very accurate since the thermal capacity of the apparatus employed was too large to produce any readable difference of temperature by the small quantity of heat that might have been developed. Later on, Joule and Thomson repeated this experiment with a very improved form of apparatus and actually detected a difference of temperature.

Eqs 8.21 and 8.22 can, therefore, be used only in connection with an ideal gas or the so-called perfect gas which obeys the relation $pv = R\theta$.

8.4.4 Forms of Energy Equation

From Eq. 8.19,

$$dU = \left(\frac{dU}{d\theta}\right)_v d\theta + \left(\frac{dU}{dv}\right)_\theta dv$$

Substituting the values in Eq. 8.18, we get

$$dQ = \left(\frac{dU}{d\theta}\right)_v d\theta + \left[\left(\frac{dU}{dv}\right)_\theta + p\right] dv \tag{8.23}$$

If the volume remains constant so that $dv = 0$,

$$dQ = \left(\frac{dU}{d\theta}\right)_v d\theta$$

So that

$$\left(\frac{dQ}{d\theta}\right)_v = \left(\frac{dU}{d\theta}\right)_v = C_v \tag{8.24}$$

Thus, the rate of variation of internal energy with temperature at constant volume is the same as the specific heat of the substance at constant volume. Hence, Eq. 8.23 can be written as

$$dQ = C_v d\theta + \left[\left(\frac{dU}{dv}\right)_\theta + p\right] dv \tag{8.25}$$

Comparing Eq. 8.25 with Eq. 8.1, we find

$$\ell = \left(\frac{dU}{dv}\right)_\theta + p$$

Equation 8.25 is the most general form of energy equation for a perfect gas,

$$\left(\frac{dU}{dv}\right)_\theta = 0, \text{ so that } \ell = p$$

Hence for a perfect gas, the energy equation 8.25 reduces to

$$dQ = C_v d\theta + pdv \tag{8.26}$$

The energy equation can be put in another form.
Expressing U as a function of p and θ, we get

$$dQ = \left(\frac{dU}{dp}\right)_\theta dp + \left(\frac{dU}{d\theta}\right)_p d\theta + pdv \tag{8.27}$$

For a perfect gas, $\left(\frac{dU}{dp}\right)_\theta = 0$ Eq. 8.22

so that $dQ = \left(\frac{dU}{d\theta}\right)_p d\theta + pdv$

or $\left(\frac{dQ}{d\theta}\right)_p = \left(\frac{dU}{d\theta}\right)_p + p\left(\frac{dv}{d\theta}\right)_p$

or $$C_p = \left(\frac{dU}{d\theta}\right)_p + p\left(\frac{dv}{d\theta}\right)_p \tag{8.28}$$

Expressing v as a function of p and θ, we get

$$dv = \left(\frac{dv}{dp}\right)_\theta dp + \left(\frac{dv}{d\theta}\right)_p d\theta$$

Substituting the values in Eq. 8.27, we get

$$dQ = \left[\left(\frac{dU}{d\theta}\right)_p + p\left(\frac{dv}{d\theta}\right)_p\right] d\theta + \left[\left(\frac{dU}{dp}\right)_\theta + p\left(\frac{dv}{dp}\right)_\theta\right] dp \tag{8.29}$$

If $dp = 0, \quad \left(\frac{dQ}{d\theta}\right)_p = \left(\frac{dU}{d\theta}\right)_p + p\left(\frac{dv}{d\theta}\right)_p = C_p$

Hence, $$dQ = C_p d\theta + \left[\left(\frac{dU}{dp}\right)_\theta + p\left(\frac{dv}{dp}\right)_\theta\right]dp \tag{8.30}$$

Comparing Eq. 8.30 and Eq. 8.2, we find

$$\ell' = \left(\frac{dU}{dp}\right)_\theta + p\left(\frac{dv}{dp}\right)_\theta$$

For a perfect gas, $$\left(\frac{dU}{dp}\right)_\theta = 0 \text{ so that } \ell' = p\left(\frac{dv}{dp}\right)_\theta$$

For a perfect gas, $$pv = R\theta \text{ so that } \left(\frac{dv}{dp}\right)_\theta = -\frac{v}{p}$$

So that for a perfect gas, $\ell' = -v$

Hence for a perfect gas, Eq. 8.30 reduces to

$$dQ = C_p d\theta - vdp \tag{8.31}$$

For a perfect gas,

$$dQ = C_v d\theta + pdv$$

If the same quantity of heat dQ is applied to the gas at constant pressure,

$$dQ = C_p d\theta - vdp$$

$\therefore$ $$C_p d\theta - vdp = C_v d\theta + pdv$$

or $$(C_p - C_v)d\theta = pdv + vdp = Rd\theta$$

$\therefore$ $$C_p - C_v = R \tag{8.32}$$

8.4.5 Dependence of C_p and C_v of a Perfect Gas on Pressure and Volume at Constant Temperature

By Eq. 8.24, $$C_v = \left(\frac{dU}{d\theta}\right)_v$$

Regarding C_v as function of v and θ,

$$\frac{d}{dv}(C_v) = \frac{d^2U}{dvd\theta} = \frac{d}{d\theta}\left(\frac{dU}{dv}\right)_\theta = 0 \text{ for a perfect gas.}$$

$\therefore$ For perfect gas, C_v does not change with v.

Further, $\frac{d}{dv}(C_p)-\frac{d}{dv}(C_v)=0$ from Eq. 8.32

$$\therefore \qquad \frac{d}{dv}(C_p)=0$$

Hence for a perfect gas, C_p does not change with v.

A perfect gas obeys the relation $p_v = R\theta$, giving

$$\left(\frac{dv}{d\theta}\right)_p = \frac{R}{p}$$

Hence, Eq. 8.28 reduces to

$$C_p = \left(\frac{dU}{d\theta}\right)_p + R \tag{8.33}$$

Differentiating Eq. 8.33 with respect to p,

$$\frac{d}{dp}(C_p)=\frac{d^2U}{dpd\theta}=\frac{d^2U}{d\theta dp}=\frac{d}{d\theta}\left(\frac{dU}{dp}\right)_\theta=0$$

for a perfect gas. Hence for such a gas, C_p does not change with p.

Further from Eq. 8.32,

$$\frac{d}{dp}(C_p)-\frac{d}{dp}(C_v)=0$$

$$\frac{d}{dp}(C_v)=0$$

Hence for a perfect gas, C_v is independent of p.

8.4.6 Meyer's Method of Determining *J*

One cc of air at N.T.P. weighs 0.001293 gm. Hence, specific volume of air $v_0 = 1/0.001293$ cc.

Normal pressure $P_0 = 76\times 13.6\times 981$ dynes/sq cm

Specific gas constant $R=\frac{1013000}{0.001293\times 273}$ ergs/degree

For air, $C_p = 0.238$ cal/gm, $C_v = 0.17$ cal/gm

Since R is expressed in ergs and C_p, C_v in calories,

$$C_p - C_v = \frac{R}{J}$$

$$J = \frac{R}{C_p - C_v} = \frac{1013000}{0.001293 \times 273 \times 0.066} = 4.2 \times 10^7 \text{ ergs/cal}$$

To prove that for an adiabatic change, pv^γ = constant where $\gamma = \frac{C_p}{C_v}$ in the case of a perfect gas.

From Eq. 8.26, $$dQ = C_v d\theta + pdv$$

and from Eq. 8.31 $$dQ = C_p d\theta - vdp$$

In an adiabatic process, $dQ = 0$; so that Eqs 8.26 and 8.31 reduce to

$$C_v d\theta = -pdv$$

and $$C_p d\theta = vdp$$

or $$\frac{C_p}{C_v} = -\frac{vdp}{pdv}$$

or $$\gamma \frac{dv}{v} = -\frac{dp}{p}$$

Integrating $\gamma \log_e v = -\log_e p + \log_e k$ where $\log_e k$ is the constant of integration

Hence, $pv^\gamma = k =$ constant

Equation 8.32 is known as the adiabatic equation of state of a perfect gas.

Since every state defined by the thermodynamic co-ordinates is an equilibrium state, the state must confirm to the equation $pv = R\theta$.

Substituting $p = \frac{R\theta}{v}$ in Eq. 8.32,

$$\frac{R\theta}{v} v^\gamma = \text{constant}$$

$$\theta v^{\gamma - 1} = \text{constant}$$

Also substituting $v = R\theta/p$ in Eq. 8.32,

$$p \frac{R^\gamma \theta^\gamma}{p^\gamma} = \text{constant}$$

or $$\theta^\gamma p^{1-\gamma} = \text{constant} \tag{8.34}$$

A useful form of Eq. 8.34 is given below:

Taking logarithm of Eq. 8.34, we get

$$(1-\gamma)\log_e p + \gamma \log_e \theta = \text{constant}$$

Differentiating this equation, we get

$$(1-\gamma)\frac{dp}{p}+\gamma\frac{d\theta}{\theta}=0$$

or
$$d\theta=\frac{\gamma-1}{\gamma}\frac{dp}{p}\theta \tag{8.35}$$

In the special case where the pressure is 1 atmosphere and the temperature 0 °C, such as often happens above the surface of the earth, an adiabatic change of pressure by 1 mm produced a temperature change given by

$$=\frac{1.41-1}{1.41}\times\frac{1}{760}\times 273=\frac{273}{3.4\times 760}=0.106\ ^\circ\text{C}$$

8.5 ATMOSPHERE IN CONVECTIVE EQUILIBRIUM

The temperature of the atmosphere falls as one rises up in the atmosphere. This is due to the fact that the hot air from the lower level expands as it rises, such expansion being more or less adiabatic.

Consider a mass of air enclosed in a cylindrical space of height *dh* and unit cross section. Let the pressure at the two faces of the cylinder be *p* and *p* + *dp,* respectively (Fig. 8.3).

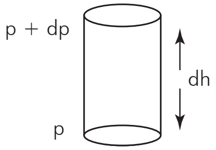

Fig. 8.3 Variation of pressure with height

This change in pressure *dp* is due to the weight of the column of air enclosed in the cylinder so that

$$dp=-g\rho\,dh \tag{8.36}$$

The negative sign means that the pressure diminishes as the height increases. Let *m* be the mass of air in the cylinder, then by the gas equation if the mean pressure of air in the cylinder be *p* and *v* the volume of air in the cylinder

$$pv=\frac{m}{M}R\theta$$

where *R* is the universal gas constant and *M*, the molecular weight of the gas. The last equation gives

$$p=\frac{m}{v}\frac{R\theta}{M}\quad=\rho\frac{R\theta}{M} \tag{8.37}$$

Substituting the value of ρ in Eq. 8.36, we get

$$dp=-g\frac{pM}{R\theta}dh \tag{8.38}$$

From Eq. 8.35, the change of temperature when the pressure changes by *dp* is

$$d\theta=\frac{\gamma-1}{\gamma}\frac{dp}{p}\theta$$

or
$$dp = \frac{\gamma p}{\gamma - 1}\frac{d\theta}{\theta} \tag{8.39}$$

Equating Eqs 8.38 and 8.39, $-g\frac{pM}{R\theta}dh = \frac{\gamma p}{\gamma - 1}\frac{d\theta}{\theta}$

$\therefore$
$$\frac{d\theta}{dh} = -\frac{\gamma - 1}{\gamma}\frac{gM}{R} \tag{8.40}$$

For air, $\gamma = 7/5$, $g = 980.665$, $M = 28.88$, $R = 8.214 \times 10^7$

so that
$$\frac{d\theta}{dh} = -9.8 \times 10^5\,\text{deg/cm} = -9.8\,\text{deg/km}$$

This value is slightly higher than the observed value. The difference is due to condensation of water vapour in the mass of expanding air.

8.6 THE ISOTHERMAL AND ADIABATIC CURVES

The curve showing the relation between pressure and volume of a given mass of gas when the temperature is constant is called its isothermal curve. It is represented by the equation

$$pv = \text{constant}$$

The curve showing the relation between pressure and volume of a given mass of gas when the flow of heat into or out of the gas is stopped is called its adiabatic curve.

It is represented by the equation

$$pv^\gamma = \text{constant}$$

where
$$\gamma = \frac{C_p}{C_v}$$

If isothermal and adiabatic curves be plotted on the same p–v diagram (Fig. 8.4), then the adiabatic curve would be steeper than the isothermal curve. For, at the point of intersection P, the slope of the isothermal curve is

$$\tan\theta_1 = \frac{dp}{dv}$$

Now, $pdv + vdp = 0$

$$\frac{dp}{dv} = -\frac{p}{v} \tag{8.41}$$

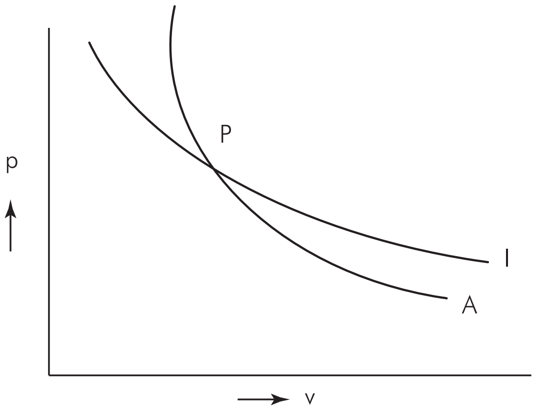

Fig. 8.4 Isothermal and adiabatic curve in *p*–*v* diagram

The slope of the adiabatic curve is obtained by differentiating the relation

$$pv^{\gamma} = \text{constant}$$

This gives $$p\gamma v^{\gamma-1}\,dv + v^{\gamma}\,dp = 0$$

or $$\gamma p\,dv + vdp = 0$$

so that $$\frac{dp}{dv} = -\gamma\frac{p}{v} \qquad (8.42)$$

8.6.1 Work Done in Isothermal Expansion

Total work done by a gas in expanding under pressure p isothermally from a volume v_1 to a volume v_2 is

$$W = \int_{v_1}^{v_2} pdv$$

By gas laws, $pv = R\theta$

so that $$p = \frac{R\theta}{v}$$

Hence, $$W = R\theta\int_{v_1}^{v_2}\frac{dv}{v}$$

or $$W = R\theta\log_e\frac{v_2}{v_1} \qquad (8.43)$$

8.6.2 Work Done in Adiabatic Expansion

In case of adiabatic change, $pv^{\gamma} = $ constant. Let p_1, v_1 and p_2, v_2 be the initial and final values of pressure and volume of the mass of the gas, respectively. If p and v are the pressure and volume in an intermediate stage, then

$$p_1v_1^{\gamma} = p_2v_2^{\gamma} = pv^{\gamma} \text{ so that } p = \frac{p_1v_1^{\gamma}}{v^{\gamma}}$$

Work done by the gas in expanding from v_1 to v_2 is

$$W = \int_{v_1}^{v_2} pdv = p_1v_1^{\gamma}\int_{v_1}^{v_2}\frac{dv}{v^{\gamma}}$$

or
$$W = p_1 v_1^{\gamma} \left(\frac{v^{1-\gamma}}{1-\gamma} \right)_{v_1}^{v_2}$$

$$= \frac{p_1 v_1^{\gamma}}{1-\gamma} \left(v_2^{1-\gamma} - v_1^{1-\gamma} \right)$$

$$= \frac{1}{1-\gamma} \left(p_1 v_1^{\gamma} v_2^{1-\gamma} - p_1 v_1 \right)$$

or
$$W = \frac{1}{1-\gamma}(p_2 v_2 - p_1 v_1) = \frac{R}{1-\gamma}(\theta_2 - \theta_1) \tag{8.44}$$

Work done in adiabatic change can also be expressed in another way; from the energy equation,

$$dQ = C_v d\theta + dW$$

Since
$$dQ = 0, dW = -C_v d\theta$$

Hence,
$$\int_1^2 dW = -C_v \int_1^2 d\theta$$

$$W_2 - W_1 = -C_v(\theta_2 - \theta_1) = C_v(\theta_1 - \theta_2) \tag{8.45}$$

8.6.3 Adiabatic and Isothermal Elasticities of a Perfect Gas

By definition of bulk modulus, the isothermal elasticity is $E_\theta = -v(dp/dv)_\theta$ and adiabatic elasticity is $E_s = -v(dp/dv)_s$.

For perfect gas, pv = constant if θ is constant; so that

$$pdv + vdp = 0$$

$$E_\theta = -v\left(\frac{dp}{dv}\right)_\theta = p$$

For perfect gas, pv^γ = constant ($dQ = 0$)

So that
$$\gamma p v^{\gamma - 1} dv + v^\gamma dp = 0$$

$\therefore$
$$E_s = -v\left(\frac{dp}{dv}\right)_s = \gamma p$$

$\therefore$
$$\frac{E_s}{E_\theta} = \gamma = \frac{C_p}{C_v}$$

8.6.4 The Most General Equation Relating to Specific Heats of a Substance

From Eq. 8.24,
$$C_v = \left(\frac{dU}{d\theta}\right)_v = \left(\frac{dU}{dp}\right)_v \left(\frac{dp}{d\theta}\right)_v$$

$$\therefore \qquad \left(\frac{dU}{dp}\right)_v = C_v \left(\frac{d\theta}{dp}\right)_v$$

Differentiating U and θ, v was maintained constant. Accordingly, the resulting equation must be a function of v.

Now,
$$\frac{d}{dv}\left(\frac{dU}{dp}\right) = \frac{d}{dv}\left[C_v\left(\frac{d\theta}{dp}\right)\right]$$

$$= \frac{d\theta}{dp}\frac{d}{dv}(C_v) + C_v \frac{d^2\theta}{dvdp}$$

From Eq. 8.28,
$$C_p = \left(\frac{dU}{d\theta}\right)_p + p\left(\frac{dv}{d\theta}\right)_p$$

$$= \left(\frac{dU}{dv}\right)_p \left(\frac{dv}{d\theta}\right)_p + p\left(\frac{dv}{d\theta}\right)_p$$

$$= \left(\frac{dv}{d\theta}\right)_p \left[\left(\frac{dU}{dv}\right)_p + p\right]$$

or
$$\left(\frac{dU}{dv}\right)_p = C_p\left(\frac{d\theta}{dv}\right)_p - p$$

$$\frac{d}{dp}\left(\frac{dU}{dv}\right)_p = \left(\frac{d\theta}{dv}\right)_p \frac{d}{dp}(C_p) + C_p \frac{d}{dp}\left(\frac{d\theta}{dv}\right)_p - 1$$

Since
$$\frac{d^2U}{dvdp} = \frac{d^2U}{dpdv}$$

$$\frac{d\theta}{dp}\frac{d}{dv}(C_v) + C_v\frac{d^2\theta}{dvdp} = \frac{d\theta}{dv}\frac{d}{dp}(C_p) + C_p\frac{d^2\theta}{dpdv} - 1$$

or
$$(C_p - C_v)\frac{d^2\theta}{dvdp} - \frac{d\theta}{dp}\frac{d}{dv}(C_v) + \frac{d\theta}{dv}\frac{d}{dp}(C_p) = 1$$

For a perfect gas,
$$\frac{d}{dv}(C_v) = \frac{d}{dp}(C_p) = 0$$

Since $$pv = R\theta, \ \left(\frac{d\theta}{dv}\right)_p = \frac{p}{R} \text{ and } \frac{d}{dp}\left(\frac{d\theta}{dv}\right) = \frac{1}{R}$$

∴ $$C_p - C_v = R$$

SOLVED PROBLEMS

Q 1. 1 gm of ice at normal pressure is changed in to 1 gm of water at 0 °C. What is the change in the internal energy?

Ans. We have $$dU = dQ - dW$$

Now, $$dQ = 80 \times 4.2 \times 10^7 = 3.4 \times 10^9 \text{ ergs}$$

$$dW = -76 \times 13.6 \times 981 \times \frac{1}{11} = -0.092 \times 10^6 \text{ ergs}$$

∴ $$dU = (3.4 \times 10^3 + 0.092) \times 10^6 = 34 \times 10^8 \text{ ergs}$$

Q 2. 1 cc of water at 100 °C and normal pressure is changed into 1 gm of steam whose volume is 1649 cc at the same temperature and pressure. Find the change in internal energy.

Ans. $dQ = 536 \times 4.2 \times 10^7 = 2.25 \times 10^{10}$ ergs

$$dW = 76 \times 13.6 \times 981 \times 1649 = 1.67 \times 10^9 \text{ ergs}$$

$$dW = dQ - dW = 2.25 \times 10^{10} - 1.67 \times 10^9 = 20.83 \times 10^9 \text{ ergs}$$

Q 3. A mass of air is suddenly compressed to 1/10 of its original volume adiabatically; find the temperature immediately after the compression. The original temperature is 20 °C.

Ans. For the same mass of gas, we have

$$\theta_1 v_1^{\gamma - 1} = \theta_2 v_2^{\gamma - 1}$$

Here, $$\theta_1 = 273 + 20 = 293, \quad v_2 = \frac{v_1}{10}$$

$$\theta_2 = \theta_1 \left(\frac{v_1}{v_2}\right)^{\gamma - 1} = 293(10)^{0.41} = 753 \text{ K}$$

Q 4. Over the surface of the earth at a height, the temperature is 0 °C and pressure is 1 atmosphere. What will be the change in temperature due to adiabatic change of pressure by 1 mm?

Ans. We know that $d\theta$ is the change in temperature.

$$d\theta = \frac{\gamma - 1}{\gamma}\frac{dp}{p}\theta = \frac{1.41 - 1}{1.41}\frac{1}{760} 273 = 0.106 \text{°C}$$

Q 5. A tyre is pumped to a pressure of 2 atmospheres at 15 °C when it suddenly bursts. Calculate the resulting drop in temperature.

Ans. We know that
$$\frac{\theta_2}{\theta_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$

Here,
$$\theta_1 = 273 + 15 = 288$$
$$p_1 = 2 \text{ atm}$$
$$\theta_2 = 288\left(\frac{1}{2}\right)^{\frac{1.4-1}{1.4}} = 288\left(\frac{1}{2}\right)^{\frac{0.4}{1.4}} = 236.2 \text{ K}$$

$\therefore$ Drop in temperature $= 288 - 236.2 = 51.8$

Q 6. A volume of gas at 15 °C expands adiabatically until its volume is doubled. Find the resultant temperature given that $\gamma = 1.4$.

Ans. Here, we are to use $\theta v^{\gamma-1} =$ constant.

or
$$\theta_1 v_1^{\gamma-1} = \theta_2 v_2^{\gamma-1}$$
$$\theta_1 = 273 + 15 = 288, \quad v_2 = 2v_1$$

$\therefore$
$$\theta_2 = \theta_1\left(\frac{v_1}{v_2}\right)^{\gamma-1} = \frac{288}{2^{0.4}} = 218.3 \text{ K}$$

Q 7. What pressure would be required to compress dry air at the standard pressure and temperature into 1/50 of its volume (a) slowly and (b) suddenly? What would be the resultant rise in temperature? ($\gamma = 1.4$)

Ans. (a) If the compression is done slowly, the change will be isothermal and we should use the relation $pv =$ constant.

$$p_1v_1 = p_2v_2 \qquad p_2 = \frac{p_1v_1}{v_2} = 1, \quad \frac{v_1}{\frac{v_1}{50}} = 50 \text{ atm}$$

There will be no rise in temperature

(b) If the compression is done suddenly, the change will be adiabatic and we should use the relation pv^γ constant.

or
$$p_1v_1^\gamma = p_2v_2^\gamma$$

or
$$p_2 = p_1\left(\frac{v_1}{v_2}\right)^\gamma = 1\left(\frac{v_1}{\frac{v_1}{50}}\right)^{1.4} = 50^{1.4} = 239 \text{ atmosphere}$$

To calculate the rise of temperature, we should use the relation $\theta v^{\gamma-1}$ = constant.

$$\theta_1 v_1^{\gamma-1} = \theta_2 v_2^{\gamma-1}$$

$$\therefore \qquad \theta_2 = \theta_1\left(\frac{v_1}{v_2}\right)^{\gamma-1} = 273\left(\frac{v_1}{\frac{v_1}{50}}\right)^{1.4-1} = 273(50)^{0.4} = 1305\text{ K}$$

Q8. Calculate the rise of temperature when a gas for which $\gamma = 1.5$ is compressed to 8 times its original pressure, assuming the initial temperature to be 300 K.

Ans. Here, we are to use the relation

$$p^{1-\gamma}T^{\gamma} = \text{constant}$$

So,
$$p_1^{1-\gamma}T_1^{\gamma} = p_2^{1-\gamma}T_2^{\gamma}$$

or
$$T_2 = T_1\left(\frac{p_1}{p_2}\right)^{\frac{1-\gamma}{\gamma}} = 300\left(\frac{p_1}{8p_1}\right)^{\frac{1-1.5}{1.5}} = 300\left(\frac{1}{8}\right)^{-\frac{0.5}{1.5}}$$

$$= 300(8)^{\frac{0.5}{1.5}} = 300(8)^{\frac{1}{3}} = 600\text{ K}$$

So, the rise in temperature is 300 K.

Q9. A gram molecule of a gas at 127 °C expands isothermally until its volume is doubled. Find the amount of work done.

Ans. Work done in isothermal expansion from v_1 to v_2 is

$$R\theta 2.303\ \log_e \frac{v_2}{v_1}$$

$$W = R\theta 2.303\ \log_e \frac{v_2}{v_1}$$

$$= 8.31\times 10^7 \times 400 \times 2.303\ \log_e \frac{2v_1}{v_2} = 2.3\times 10^{10}\text{ ergs}$$

Q10. Air at 17 °C and 76 cm of mercury pressure expands isothermally until its volume is doubled and then adiabatically until it is redoubled. Find the final temperature and pressure ($\gamma = 1.4$).

Ans. When air expands isothermally, we use the relation pv/θ = constant. Let the pressure be p when the volume is doubled, then

$$\frac{76v}{290} = \frac{p2v}{290}$$

or $\qquad p = 38$ cm of mercury

So when air expands isothermally, the final pressure is 38 cm of mercury and final temperature = 290 K.

Next, air expands adiabatically; then, the relation $\theta v^{\gamma-1}=$ constant is used to find the resultant temperature.

So, $$290(2v)^{0.4}=T(4v)^{0.4}$$

$\therefore$ $$T=290\left(\frac{2v}{4v}\right)^{0.4}=219.8\text{ K}$$

To find the pressure, we use pv^{γ} constant.

$$38(2v)^{\gamma}=p(4v)^{\gamma}$$

$$p=38\left(\frac{2v}{4v}\right)^{\gamma}=14.4\text{ cm of mercury}$$

Q11. One gram of hydrogen occupies 11.1 litres at 0 °C and 76 cm of mercury. What is the work done by the gas if heated to 1 °C at constant pressure and how much heat must be supplied to it in the process, if its specific heat at constant volume is 2.411?

Ans. When 1 gm of hydrogen occupying 11.1 litres at 0 °C and 76 cm of mercury is heated to 1 °C at constant pressure, its volume will be 11.1 × 274/273 litres.

$$\text{The work done } = p_1v_1\log_e\frac{v_2}{v_1}$$

$$=76\times13.6\times981\times11100\times2.303\ \log_e\frac{274}{273}$$

$$=4.147\times10^{7}\text{ erg}$$

$$\text{Heat supplied } = c_v dT+\text{ work done}$$

$$=2.411\times1+\frac{4.147\times10^{7}}{4.2\times10^{7}}$$

$$2.411+0.987=3.398\text{ cal}$$

Q12. Find the work done in compressing adiabatically 1 gm of air initially at N.T.P to half its original volume, ρ for air at N.T.P = 0.0001293 gm /cc, $\gamma=1.4$, atmospheric pressure = 10^6 dynes.

Ans. As 1 gm of air is considered, we have $pv=r\theta$

$$r=\frac{pv}{\theta}=\frac{10^{6}}{0.0001293\times273}$$

Final temperature after adiabatic compression is found from $\theta_1 v_1^{\gamma-1}=\theta_2 v_2^{\gamma-1}$

$$\therefore \qquad \theta_2 = \theta_1\left(\frac{v_1}{v_2}\right)^{\gamma-1} = 273\left(\frac{v_1}{\frac{v_1}{2}}\right)^{0.4} = 360\ \text{K}$$

Work done in adiabatic compression is

$$W = \frac{r(\theta_2-\theta_1)}{\gamma-1} = \frac{10^6(360-273)}{0.0001293\times 273\times 0.4} = 6.167\times 10^9\ \text{ergs}$$

Q13. Calculate the change in internal energy when 5 gm of air is heated from 0 °C to 10 °C, specific heat at constant volume for air = 0.172 cal/gm.

Ans. The change in internal energy $= mc_v d\theta$

$$= 5\times 0.172\times 10 = 8.6\ \text{cal}$$

Q14. 10^3 cc of a gas at N.T.P expands to double its volume at constant pressure. How many calories of heat have been supplied to it? ρ for the gas is 1.29 gm/litre and $c_v = 0.168$ cal/gm.

Ans. We know that for such change,

$$\frac{p_1v_1}{\theta_1} = \frac{p_2v_2}{\theta_2}$$

$$\frac{p_1 10^3}{273} = \frac{p_1 2\times 10^3}{\theta_2} \qquad \therefore \theta_2 = 2\times 273 = 546\ \text{K}$$

Again, $pv = r\theta$

$$\text{or} \qquad r = \frac{pv}{\theta} = 76\times 13.6\times\frac{981\times 10^3}{273\times 1.29} = 0.0688$$

$$c_p = c_v + r = 0.168 + 0.068\ \text{cal} = 0.236\ \text{cal}$$

$$Q = mc_p d\theta = 1.29\times 0.236\times(546-273) = 83.3\ \text{cal}$$

Q15. One gm mole of argon is expanded isothermally and reversibly at 30 °C from 1 litre to 10 litres. Calculate the maximum work done.

Ans. We know that the work done in isothermal expansion

$$= R\theta\times 2.303\times\log\frac{v_2}{v_1}$$

$$= 8.31\times 10^7\times 303\times 2.303\times\log 10 = 5.8\times 10^{10}\ \text{ergs}$$

Q16. Calculate the amount of heat absorbed by 2.6 litres of neon at N.T.P. if it is allowed to expand 4 times its own volume at 0 °C.

Ans. For 1 gm mole of a gas, the work done in isothermal expansion

$$= R\theta \times 2.303 \times \log \frac{v_2}{v_1}$$

Since volume of 1 gm mole is 22.4 litres, the work done by 2.6 litres of neon is

$$\frac{2.6}{22.4} \times 8.31 \times 10^7 \times 273 \times 2.303 \times \log 4 = 86.82 \text{ calories}$$

Q17. A certain gas at constant temperature obeys the equation $(p + a/v^2)(v - b) = K = \text{constant}$. Calculate the work done when this gas expands from v_1 to v_2.

Ans. We have

$$\left(p + \frac{a}{v^2}\right)(v - b) = K$$

or

$$p = \frac{K}{v - b} - \frac{a}{v^2}$$

The work done $= \int_{v_1}^{v_2} p\,dv = \int_{v_1}^{v_2} \frac{K}{v - b} dv - \int_{v_1}^{v_2} \frac{a}{v^2} dv$

$$= K[\log_e (v - b)]_{v_1}^{v_2} + \left(\frac{a}{v}\right)_{v_1}^{v_2} = K \log_e \frac{v_2 - b}{v_1 - b} + a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

Q18. Immediately after explosion of an atom bomb, the ball of fire produced had a radius of hundred metres and a temperature of 10^5 K. What will be the appropriate temperature when the ball expands adiabatically to 1000 metres radius ($\gamma = 1.66$)?

Ans. Initial volume $= \frac{4}{3}\pi(10^4)^3$

Final volume $= \frac{4}{3}\pi(10^5)^3$ cc

Initial temperature $\theta_1 = 10^5$ K

We know $\theta_1 v_1^{\gamma-1} = \theta_2 v_2^{\gamma-1}$

$$\therefore \quad \theta_2 = \theta_1 \left(\frac{v_1}{v_2}\right)^{\gamma-1} = 10^5 \left(\frac{\frac{4}{3}\pi 10^{12}}{\frac{4}{3}\pi 10^{15}}\right)^{1.66-1} = 6310 \text{ K}$$

Q19. A gas occupying 1 litre at 80 cm of Hg pressure is expanded adiabatically to 1190 cc. If the pressure falls to 60 cm of Hg in this process, deduce the value of γ.

Ans. We know that
$$p_1 v_1^\gamma = p_2 v_2^\gamma$$

or
$$\frac{p_1}{p_2} = \left(\frac{v_2}{v_1}\right)^\gamma$$

or
$$\frac{80}{60} = \left(\frac{1190}{1000}\right)^\gamma = 1.19^\gamma$$

Taking log,
$$\log_e \frac{8}{6} = \gamma \log_e 1.19$$

or
$$\gamma = \frac{\log_e 8 - \log_e 6}{\log_e 1.19} = 1.65$$

PROBLEMS

1. A given volume of helium is at 0 °C and is expanded suddenly to twice its volume. Find the temperature after expansion, assume $\gamma = 1.67$.

Ans. 172 K

2. Dry air is compressed at 27 °C to one third its volume. Find the resulting rise of temperature.

Ans. 165.6 °C

3. Calculate the final temperature when a given mass of a gas at 0 °C is suddenly compressed to a pressure 20 times the initial pressure ($\gamma = 1.42$).

Ans. 662 K

4. Dry air enclosed at 25 °C and atmospheric pressure is suddenly compressed to half its volume. Find the resulting temperature and pressure ($\gamma = 1.4$).

Ans. 2.638 atm, 393 K

5. A quantity of air at normal temperature is compressed (a) slowly, (b) suddenly to 1/10 of its volume. Find the rise in temperature if any in each case.

Ans. (a) nil, (b) 412.8 K

6. Calculate the rise in temperature of a gas ($\gamma = 1.5$) which is compressed to 27 times the original pressure, the initial temperature being 27 °C.

Ans. 600

7. In a certain process, 500 calories of heat are supplied to a system and at the same time 200 joules of work is done on it. What is the increase in initial energy?

Ans. 547.8 cal

8. A certain volume of dry air at N.T.P is expanded to three times its volume under (a) isothermal condition and (b) adiabatic condition. Calculate in either case, the final pressure and temperature ($\gamma = 1.4$).

Ans. (a) 25.3 cm of mercury, 0 °C
(b) 16.32 cm of mercury, −97 °C

9. An ideal gas is compressed isothermally and reversibly at 27 °C from 1 atmosphere to 10 atmospheres. Calculate the amount of work required for this change if the quantity of gas is 1 gm mole. (R = 8.3 *J*/deg mole)

Ans. 5.7×10^{10} ergs

10. What is the maximum work obtained when 600 gm of mercury vapour is allowed to expand at 500 °C from 6 atmospheres to 3 atmospheres?

Ans. 1.33×10^{11} ergs

11. A litre of dry air at N.T.P is allowed to expand to a value of 3 litres (a) very slowly, (b) very quickly. Calculate the work done in each case.

Ans. (a) 1.114×10^{9} ergs (b) 8.99×10^{8} ergs

12. Eight grams of helium gas occupying 4 litres at 0 °C is quasistatically compressed to 1 litre at constant temperature. Assuming that the gas is perfect, calculate the work done.

Ans. 63×10^{9} ergs

13. One mole of Van der Waals' gas at 27 °C was isothermally expanded from 2 litres to 20 litres. Calculate the work done, given $a = 1.42 \times 10^{12}$ dyne.cm^4 per mole and b = 30 cc per mole.

Ans. 5.76×10^{10} ergs

14. The equation of state for CO_2 is given by $p(\upsilon - nb) = n\mathrm{R}T$, n being number of gm moles. Calculate maximum work done when 11 gm of CO_2 expands isothermally at 47 °C from 5 litres to 25 litres; given $b = 40$ cc per mole.

Ans. 1.07×10^{10} ergs

QUESTIONS

1. Discuss the principle of conservation of energy. Explain thermodynamic state, thermodynamic coordinates, thermodynamic equilibrium and quasistatic processes.
2. State first law of thermodynamics and explain its importance.
3. What are internal and external energies? Internal energy of a gas depends on what characteristics of the gas, explain.
4. Explain why a gas has two kinds of specific heats. Show that the difference between two specific heats is equal to gas constant.
5. How do the specific heats of a gas depend on pressure and volume at constant temperature?
6. What is meant by adiabatic change? Deduce expressions for such changes relating to pressure, volume and temperature.
7. How does temperature fall with height?
8. What do you mean by isothermal and adiabatic changes? Show their nature in the $p - v$ diagram.
9. Deduce expressions for work done in isothermal expansion and adiabatic expansion.
10. Discuss adiabatic and isothermal elasticities of a perfect gas.

Chapter 9

THE SECOND LAW OF THERMODYNAMICS

9.1 LIMITATIONS OF THE FIRST LAW OF THERMODYNAMICS

All experimental methods developed so far for the investigation of the law of equivalence of heat and mechanical work are only methods of conversion of mechanical work into heat and not heat into mechanical work. The law of equivalence is

$$\frac{dW}{J} = dQ \tag{9.1}$$

This is the first law of thermodynamics in restricted sense and is applicable only when mechanical work is converted into heat. When heat is converted into work,

$$dQ = \frac{dW}{J}$$

except under some special circumstances to be developed later on. The natural law of conversion is

$$dQ = dU + \frac{dW}{J} \tag{9.2}$$

Equation 9.2 implies that out of the total quantity of heat dQ, only a part is converted into mechanical work and the balance is used to increase the internal energy of the body.

Thus though heat and mechanical work are only different forms of energy which can be mutually converted into each other without any loss of total quantity, yet we know from experience that they do not obey the same quantitative law of conversion. *By law of nature, all mechanical work can be converted into heat but all heat cannot be converted into mechanical work.*

9.2 THE SPONTANEOUS PROCESS

The conversion of mechanical work into heat is spontaneous. Thus when two blocks of wood are rubbed together, both of them become heated and this happens without our intervention thereby converting the mechanical work into heat. But these two blocks when placed together will not rub against each other, though each of them has a good stock of energy in the form of heat. So, *conversion of heat into mechanical work is not a spontaneous process*; otherwise, ocean-going vessels would no longer need to carry large quantities of fuel. The ocean itself has an immeasurable store of energy in the form of heat and this heat could be spontaneously converted into mechanical work of moving the vessel against the friction of water. Such conversion would not be a violation of the principle of energy; yet, it never happens in nature.

All natural processes are spontaneous and all spontaneous processes are only one sided transformations. Thus,

1. All material bodies, once set in motion, continue to move in the same direction with constant speed.
2. Heat flows of itself from warm to colder bodies.
3. Bodies fall off themselves from high to lower gravitational level.
4. Gas flows from region of high pressure to that of lower pressure.
5. Positive electricity flows from high to lower potential region.
6. Salts tend to separate from their saturated solutions as crystals.
7. Two gases placed in contact tend to diffuse into each other.
8. An under-cooled liquid tends to freeze out.
9. Chemical reaction between two ingredients proceeds in a particular direction.
10. All mechanical works are spontaneously converted into heat.

In the process of spontaneous change, the system undergoing change does not exchange its energy with the surroundings so that the sum total of its energy remains constant. If any exchange of energy with the surroundings takes place, it occurs only as a result of the spontaneous process rather than a necessary accompaniment because the process would certainly take place even if the exchange of energy was artificially prevented. Thus, a mass of compressed gas would spontaneously expand if the superincumbent pressure is reduced.

In the process of expansion the temperature of the gas would, of course, fall below that of the surroundings. As a result, heat would flow into the gas from the surroundings. If the vessels containing the gas were thermally isolated, the flow of heat might be prevented; but, that would not stop the free expansion of the gas.

Since, in a spontaneous change, the energy of the system undergoing change remains unaltered, the system does not produce any external work, that is, a body external to the system does not get any energy. Thus a freely falling pile-driver maintains its energy constant during its fall, though the energy of the falling body changes form. *Work can be derived from a natural or spontaneous process only when the natural process is resisted.* Thus the pile-driver, on falling on a pile, drives the pile into the earth and at the same time the pile-driver is brought to rest.

Any cause which tends to resist a natural or spontaneous process is a force.* The product of this force and the distance over which the force acts retarding the progress of the process is a measure of the amount of mechanical work done against the force.

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*This should be the most general definition of a force of which the Newtonian definition is only a particular case.

Other examples of mechanical work obtained from natural processes are:

Water flows of itself from high to a lower level. To obtain mechanical work out of this flow, it must be checked by a suitably installed turbine. Positive electricity flows from high to lower potential. Mechanical work can be derived by placing an electric motor in the path of flow of electricity. The energy of electric current is converted into heat by placing a resistor in the path of flow of electricity. Hydrogen and oxygen combine together at a suitable temperature to form water. Through the medium of a galvanic cell, such combination may be made to yield useful work.

Heat flows of itself from a high to a lower temperature. Main concern of thermodynamics is to obtain mechanical work out of this spontaneous flow of heat. Any interposed mechanism through which a continuous supply of mechanical work is obtained from heat is called a *heat engine.*

9.3 THE HEAT ENGINE

The main organs of a heat engine are as follows:

1. A source at high temperature.
2. A sink or refrigerator at lower temperature.
3. The working substance. The heat of the source, instead of flowing directly from the source to the sink, passes through the medium of the working substance producing certain changes of the thermodynamic state of the substance.

From the change of the thermodynamic coordinates, the work done by the substance is obtained from the relation $W = \int_{v_1}^{v_2} pdv$ where v_1 and v_2 are the initial and final volumes of the working substance, before and after the changes respectively. The balance of heat drawn from the source which is not converted into mechanical work by the engine is discharged to the sink.

The organ of the heat engine where heat is actually converted into mechanical work is called the cylinder. The theoretical cylinder consists of a stout cylindrical vessel with non-conducting wall and provided with a piston of insulating material enclosing some quantity of the working substance. This is a gas since a given quantity of heat produces greatest change in volume and pressure of a gas. The other end of the cylinder is closed by a conducting disc which may be placed in contact with the source or the sink. The piston is subjected to an external pressure to balance the tendency of the gas to expand.

9.3.1 How to Obtain Maximum Amount of Work?

From the point of view of economy, our main problem is to determine the conditions under which maximum quantity of work can be derived from a given quantity of heat supplied by the source. It appears that to obtain maximum supply of work, all the heat must be drawn by the working substance only and the only changes produced by heat in the working substance should be changes in pressure and volume and nothing else. In actual engine, in addition to the work of expansion, the heat is spent in many other ways; these are as follows:

1. A part of the energy is used up to change the internal energy of the substance.
2. A part is lost by conduction through the walls of the cylinder and through the piston unless these are made of perfectly non-conducting materials and the piston.
3. Some energy is spent as work required in overcoming friction of the piston against the wall of the cylinder. Friction always opposes motion and work done against friction is spontaneously

converted into heat which is dissipated into space. So, this is an irrecoverable loss. Hence to obtain maximum amount of work, the moving part must be frictionless.

4. Some energy is spent to generate kinetic energy of moving parts of the system. If the difference of pressure on the two sides of the piston is large, the piston would move with accelerated motion. To generate this acceleration, some amount of energy must be spent. Further on account of rapid expansion, there would be local variations of pressure throughout the cylinder which set up eddies in the working substance. The energy of these eddies is finally converted into heat.

To avoid this waste of energy, the difference of pressure on the two sides of the piston should be as small as possible.

To produce work, heat must be drawn from the source by the working substance. As such, the temperature of the working substance must be lower than that of the source. To produce maximum amount of work, the temperature of the working substance must not, however, be sensibly lower than that of the source.

This can be proved as follows:

Let the temperature of the source be θ and that of the working substance θ', and let $\theta > \theta'$. If the heat is drawn at temperature θ, the path of change of state of the working substance is given by the isothermal AB corresponding to temperature θ (Fig. 9.1). Under this condition, the work done by the substance is represented by the area ABCD.

If the heat is drawn at temperature θ', the work done is represented by area A′B′CD, where A′B′ is the isothermal corresponding to temperature θ'. Since A′B′CD is less than ABCD, work done at temperature θ' is evidently less than the work done at temperature θ. Hence to produce maximum amount of work, the temperature θ' must be as nearly equal to θ as possible. In the limiting case, the source and the working substance must be in thermal equilibrium to obtain maximum amount of work.

This also follows easily from Eq. 8.43 of Chapter 8

$$W = R\theta \log_e \frac{v_2}{v_1}$$

This means that for a given expansion ratio (v_2/v_1), W is directly proportional to θ. Hence for maximum work, the value of θ must be the highest available, that is, it must be as nearly equal to the temperature of the source as possible. Hence the process of expansion of the working substance must be isothermal,

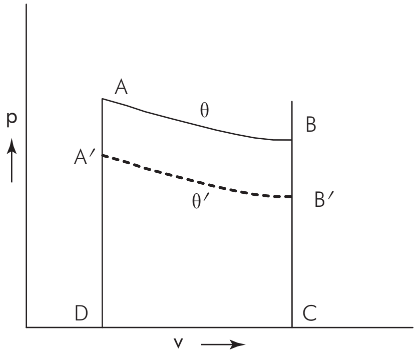


Fig. 9.1 Indicator diagram

corresponding to the temperature of the source. In order that the process may be isothermal, the system giving out heat and the system receiving heat must be partitioned by a perfectly conducting wall. Other wise, a difference of temperature will have to be maintained on the two sides of the partition wall to make the heat flow into or out of the working substance through the partition wall. Under these circumstances, the heat cannot be drawn by the working substance at the same temperature as the source.

9.3.2 Conditions of Obtaining Maximum Amount of Work

Thus to derive maximum amount of mechanical work out of the working substance, work must be performed under the following conditions:

1. The cylinder and the piston must be of zero heat capacity.
2. The moving parts of the cylinder must be frictionless.
3. The walls of the cylinder and the piston must be made of perfectly non-conducting material.
4. The base of the cylinder forming the partition wall between the source or sink and the working substance must be made of perfectly conducting material.
5. At every stage of the operation, the mechanical forces acting on the two faces of the piston must differ by an amount which is just sufficient to make the piston move in the desired direction.
6. At every stage of the operation, the temperature of the working substance must be only slightly lower than that of the source while it is receiving heat and only slightly higher than that of the sink while giving out heat.

In other words to obtain maximum amount of work, the whole process must be a succession of equilibrium or quasi-static state, the substance passing from one state to the other by steps of infinitesimally small changes so that the process is perfectly continuous in the mathematical sense.

9.3.3 Reversible Operation

Such an operation as described above is evidently reversible because by reversing the forces and the directions of the flow of heat, the whole operation may be traced back in the opposite sense so that the substance passes through the same states as in the direct process, but in the reverse order. Such reversal implies that the amount of heat received and the work done in each infinitesimal step of the reverse process is the same as in the direct process, heat being parted with where—in the direct process—it was received and work being done upon the substance by some external agency where—in the direct process—it did work. In any thermodynamic process, not only the system undergoing change but also the system external to it participates unless the system is thermally isolated. Hence, the condition of exact reversibility requires further that the system undergoing change and that external to it must be in the same state at the end of the reversal as at the beginning of the direct process. If at the end of the reversal there is a permanent change somewhere else, then the process is not exactly reversible.

A thermodynamic operation is reversible, if it satisfies the conditions (1) to (6) given in the previous section which are also the conditions for maximum yield of mechanical work. Conversely, a thermodynamic operation can yield maximum amount of mechanical work from a given quantity of heat only if the operation is reversible.

The method of obtaining maximum amount of work from a given quantity of heat as described above is only an idealized method, for the conditions of reversibility demand that the process be carried out infinitely slowly with substances possessing uncommon physical properties. These conditions can never be realized in any real experimental process; but, they can at least be approached. In the exposition of thermodynamics, we shall very often discuss such idealized experiments to derive results which are nevertheless, valid. This is because the departures of the real substances from these ideal properties do not affect the argument; rather in the case of certain irregularities, they actually reinforce the argument. A reversible process is not an imaginary process; rather, it is to be regarded as the limit of actually realizable process.

9.3.4 Cyclic Operation

The ideal engine discussed earlier satisfies the condition of reversibility (1) to (6). So, it produces maximum amount of mechanical work. Nevertheless, some amount of heat must be used up to change the internal energy of the working substance. To convert the whole heat into mechanical work, dU must be made equal to zero. Since dU is a perfect differential, it would be zero if the substance is made to work in a closed path. This has the additional advantage that by making the working substance traverse a closed path, a continuous supply of power equal to area of the cycle into the number of cycles traversed per second can be obtained.

9.3.5 The Carnot's Engine

Black's discovery that heat was a measurable quantity made it possible for Watt to develop the steam engine on scientific lines. The industrial problem was how to obtain maximum quantity of work from a given quantity of heat. The search for this led to the discovery of the ideal engine by Sadi Carnot.

Carnot's engine was imagined to be constructed as follows:

1. The cylinder was made of perfectly non-conducting material whose thermal capacity is zero.
2. The piston was made of perfectly non-conducting material of zero thermal capacity. It moved inside the cylinder without friction.
3. The base of the cylinder was made of perfectly conducting material.
4. In addition, there was a moveable disc of perfectly non-conducting material by which the base could be covered.
5. The source and the sink had infinite thermal capacity.

Heat was all taken in by the working substance at the temperature θ_1 of the source and given to the sink at the temperature θ_2 of the sink. Throughout the entire operation, the working substance was supposed to be in mechanical equilibrium with the external forces and the thermal equilibrium with the source to the sink. The engine so constructed satisfied the conditions for production of maximum quantity of mechanical work and was, therefore, perfectly reversible.

To make the engine work in a closed cycle, the two isothermal curves corresponding to temperatures θ_1 and θ_2 of the source and the sink, respectively must be connected by two adiabatic lines in order that the working substance may not exchange heat with the surroundings. The substance changed its temperature from θ_2 to θ_1 or from θ_1 to θ_2 by adiabatic compression or expansion. This enabled the working substance to take in and reject heat at the ends of the adiabatic changes only without taking or rejecting any heat in the process of change of temperature. The Carnot's engine is, thus, a four-stroke engine. Its construction and the details of operation in different strokes are described below.

In Fig. 9.2 EF is the cylinder, P is the piston, S is the source, R is the refrigerator, D is the insulating disc, ab and cd are the two isothermals at temperatures θ_1 and θ_2, bc and ad are the two adiabatics connecting the two isothermals. The diagram abcd is called the indicator diagram.

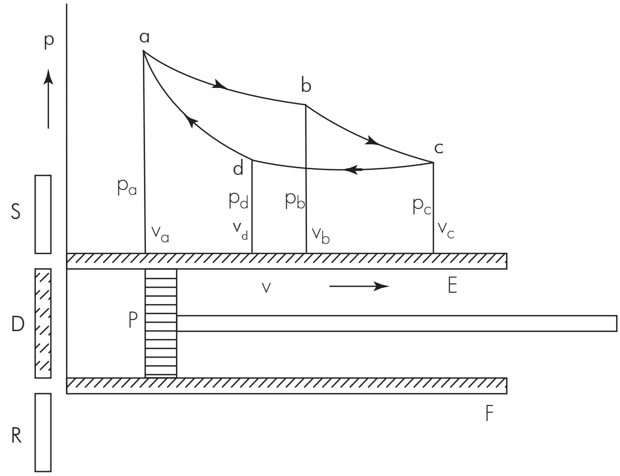


Fig. 9.2 Working of Carnot's engine

For the working substance of the engine, we shall take a perfect gas. This will not affect the arguments in any way; for it will be proved later on that any substance can be used as working substance without any loss of efficiency.

The different strokes of the engine and their characteristics are tabulated in Table 9.1.

Total work done by the working substance

=(Area *ab* $v_b v_a$ + Area *bc* $v_c v_b$) − (Area *dc* $v_c v_d$ + Area *ad* $v_d v_a$)

= Area *abcd* of the cycle

Since in a cyclic operation there is no change of internal energy,

work done = $Q_1 - Q_2$ = area *abcd* of the cycle.

Since the working substance is a perfect gas, work done in the cycle is

$$R\left(\theta_1 \log_e \frac{v_b}{v_a} - \theta_2 \log_e \frac{v_c}{v_d}\right) = Q_1 - Q_2$$

Table 9.1 Characteristics of different strokes of Carnot's engine

Stroke	Base of the cylinder	Path of change	Initial state	Final state	Heat drawn	Work done by the substance
I	In contact with source (S)	ab, isothermal expansion	p_a, v_a, θ_1 (State at *a*)	p_b, v_b, θ_1 (State at *b*)	Q_1	$R\theta_1 \log_e v_b/v_a$ (area ab $v_b v_a$)
II	Insulated by D	bc, adiabatic expansion	p_b, v_b, θ_1 (State at *b*)	p_c, v_c, θ_2 (State at *c*)	0	$C_v(\theta_1 - \theta_2)$ (area bc $v_c v_b$)
III	In contact with sink (R)	cd, isothermal compression	p_c, v_c, θ_2 (State at *c*)	p_d, v_d, θ_2 (State at *d*)	Q_2	$R\theta_2 \log_e v_d/v_c$ (area dc $v_c v_d$)
IV	Insulated by D	da, adiabatic compression	p_d, v_d, θ_2 (State at *d*)	p_a, v_a, θ_1 (State at *a*)	0	$C_v(\theta_2 - \theta_1)$ (area ad $v_d v_a$)

Efficiency of an engine is defined by

$$\eta = \frac{\text{Heat converted into work}}{\text{Heat drawn from the source}} = \frac{Q_1 - Q_2}{Q_1}$$

$$= \frac{\text{Area of the cycle (abcd)}}{\text{Heat drawn from the source}}$$

In the case of a perfect gas, there is no change of internal energy in an isothermal process. This is because internal energy is a function of temperature only. Hence, the heat drawn or the isothermal process is equal to the amount of work done, or

$$Q_1 = R\theta_1 \log_e \frac{v_b}{v_a}$$

Total amount of work done in the whole cycle is obtained by addition of works done in the last column of Table 9.1.

$$W = R\left(\theta_1 \log_e \frac{v_b}{v_a} - \theta_2 \log_e \frac{v_c}{v_d}\right)$$

Hence,
$$\eta = \frac{\theta_1 \log_e \frac{v_b}{v_a} - \theta_2 \log_e \frac{v_c}{v_d}}{\theta_1 \log_e \frac{v_b}{v_a}} \tag{9.3}$$

Now the points *a* and *b* are on the same isothermal,

$$p_a v_a = p_b v_b \quad \therefore \frac{v_b}{v_a} = \frac{p_a}{p_b} \tag{9.4}$$

Again *c* and *d* are on the same isothermal,

$$p_c v_c = p_d v_d \quad \therefore \frac{v_c}{v_d} = \frac{p_d}{p_c} \tag{9.5}$$

Again *a* and *d* are on the same adiabatic,

$$p_a v_a^\gamma = p_d v_d^\gamma \tag{9.6}$$

Similarly,
$$p_b v_b^\gamma = p_c v_c^\gamma \tag{9.7}$$

From Eqs 9.6 and 9.7,
$$\left(\frac{v_b}{v_a}\right)^\gamma \frac{p_b}{p_a} = \left(\frac{v_c}{v_d}\right)^\gamma \frac{p_c}{p_d}$$

Substituting for p_b/p_a and p_c/p_d from Eqs 9.4 and 9.5,

$$\left(\frac{v_b}{v_a}\right)^{\gamma}\left(\frac{v_a}{v_b}\right)=\left(\frac{v_c}{v_d}\right)^{\gamma}\left(\frac{v_d}{v_c}\right)$$

or

$$\left(\frac{v_b}{v_a}\right)^{\gamma-1}=\left(\frac{v_c}{v_d}\right)^{\gamma-1} \text{ or } \frac{v_b}{v_a}=\frac{v_c}{v_d}$$

Substituting the value in Eq. 9.3, we get for efficiency

$$\eta=\frac{\theta_1-\theta_2}{\theta_1}=\frac{Q_1-Q_2}{Q_1} \tag{9.8}$$

Thus in trying to convert as much heat into mechanical work as possible, it is the temperature that limits our power and only $Q_1(\theta_1 - \theta_2/\theta_1)$ quantity of heat is converted into work.

Reversible Carnot's Engine: The Carnot's engine as described in the previous section is evidently reversible, since the engine satisfies all the conditions of reversibility. In the direct cycle heat is drawn from the source, a part of which is converted into mechanical work (equal to the area of the cycle) *done by the substance* and the rest is delivered to the sink. In the reverse operation heat is drawn from the sink, same amount of work is *done upon the substance* and the sum of the heat energy drawn and the work done is transferred to the source. Direct process is spontaneous process, heat flowing of itself from high to lower temperature through the engine. As a result, some amount of work becomes available. In the reverse process, heat is conveyed from lower to higher temperature by *doing work on* the engine.

The characteristics of the different strokes of the reversed Carnot's cycle are tabulated in Table 9.2.

Table 9.2 Characteristics of different strokes of reversed Carnot's cycle

Stroke	Base of the cylinder	Path of change	Initial state	Final state	Heat drawn	Work done by working substance
I	Insulated by D	ad, adiabatic expansion	p_a, v_a, θ_1	p_d, v_d, θ_2	0	$C_v\,(\theta_1 - \theta_2)$ area ad $v_d v_a$
II	In contact with refrigerator (R)	dc, isothermal expansion	p_d, v_d, θ_2	p_c, v_c, θ_2	Q_2 from refrigerator	$+R\theta_2 \log_e v_c/v_d$ area dc $v_c v_d$
III	Insulated by D	cb, adiabatic compression	p_c, v_c, θ_2	p_d, v_d, θ_1	0	$C_v\,(\theta_2 - \theta_1)$ area cb $v_b v_c$
IV	In contact with source (S)	ba, isothermal compression	p_b, v_b, θ_1	p_a, v_a, θ_1	Q Given to the source	$R\theta_1 \log_e v_a/v_b$ area *ba* $v_a v_b$

At the end of the reversal, the source, the sink and the working substance are brought to the same state as at the beginning of the direct process. Thus, writing $r = v_b/v_a = v_c/v_d$, with

Carnot's Cycle (direct)	Carnot's Cycle (reverse)
Work done by the gas = $R(\theta_1 - \theta_2) \log_e r$	Work spent on gas = $R(\theta_1 - \theta_2) \log_e r$
Heat taken from source = $R\theta_1 \log_e r$	Heat given to source = $R\theta_1 \log_e r$
Heat given to sink = $R\theta_2 \log_e r$	Heat taken from sink = $R\theta_2 \log_e r$

Hence after the reversal, total heat taken from the source is zero, total heat taken from the sink is zero, and the total work done by the working substance is zero. Since the process is, by assumption, quasistatic, the work done by the working substance is the same as that done against the external forces. Hence at the end of the reversal, total work done by external forces is zero. Thus, by reversal, there is no permanent change anywhere. Hence, the whole process is perfectly reversible.

9.3.6 Are Spontaneous Processes Reversible?

In the Carnot's engine, working in the direct way, heat flows from the hot body (source) to the cold body (sink) through the engine. As a result, some amount of mechanical work is obtained. We have seen that the process is perfectly reversible.

Let us now examine whether the spontaneous flow of heat from a hot body (A) to a cold body (B) *without any impediment* is reversible. The only changes effected at the end of such flow are: (1) the hot body has lost some amount of heat (Q) and (2) the cold body has gained the same amount (Q) of heat. Further, there has been no exchange of energy with the surroundings.

To restore the original condition, the heat absorbed by the cold body must be transferred *in toto* to the hot body.

Now, heat does not flow of itself from the cold to the hot body. A Carnot's engine driven backwards is to be employed for such transference of heat from the cold to the hot body. Let this engine draw Q quantity of heat from the cold body and by expenditure of work W, let it deliver $(Q + W)$ quantity of heat to the hot body. The heat equivalent Q' of the work W is then to be removed from the hot body to a separate reservoir.

The two bodies A and B are now in the same state as at the beginning. The conversion of work W into equivalent amount of heat Q' (where $W = J\,Q'$) is spontaneous and is effected without any change in the external objects. The backward drive of Carnot's engine has, however, been effected at the expense of work done by some external force; as for example, by displacement of some weights to lower level. Hence the reversal is necessarily accompanied by certain changes in the external objects, namely (1) movement of some weights to lower level, and (2) gain of some heat Q' by the reservoir. The process is, therefore, not reversible.

It may be argued that the heat of the reservoir might be utilized to raise the weights to their original level thereby restoring the surrounding objects to their initial states. This requires the whole quantity of heat Q' to be converted to mechanical work, which is impossible.

Even if it was possible to convert the whole quantity of heat to mechanical work without any supply of energy from outside, that would amount to the realization of the perpetual motion machine because mechanical work is spontaneously converted into work.

Let us take another example: an ideal gas spontaneously expands into vacuum without exchange of energy with the surroundings and without any change of temperature of the gas.

To bring the gas back to its initial state, it must be compressed by a piston loaded by suitable weights so as to be in pressure equilibrium at every stage of compression. The heat developed by compression must be allowed to flow into a reservoir so that at every instant, the temperature of the gas is not sensibly different from what it was at the beginning. Under these conditions, the gas returns exactly to its original state if it is compressed to its initial volume.

This reversal has been effected at the expense of some changes of state in the outside objects, namely (1) some weights have moved to lower levels and (2) a reservoir has gained heat. To restore the surroundings to its initial state, the heat of the reservoir may be converted into mechanical work of raising the weights to their original level. But, this is impossible.

To take another example, let us consider the chemical process

$$\mathrm{Zn} + \mathrm{CuSO_4\,(Aq)} = \mathrm{ZnSO_4\,(Aq)} + \mathrm{Cu} + \mathrm{Q}$$

This means that when 65.4 gm of zinc is placed in equivalent amount of $CuSO_4$ solution, we get 63.6 gm of copper in equivalent amount of $ZnSO_4$ solution and also some quantity of heat Q, since the process is exothermic. This is a spontaneous process and there is no exchange of heat or matter with the surroundings.

To get back the reacting ingredients out of the products of reaction at the initial temperature, the heat of reaction must first be removed to a reservoir. The zinc sulphate solution may then be taken in a voltameter with a copper anode and zinc cathode. On passing a feeble current through the voltameter, zinc is deposited on the cathode and (SO_4) ion is deposited on the copper anode converting it to $CuSO_4$ which passes into solution. Time allowed for electrolysis should be just sufficient to liberate one gm- equivalent of zinc. The system has now returned to its initial state but that at the expense of some changes in state of the surrounding objects; namely (1) a reservoir has gained heat and (2) a battery has lost some amount of energy.

To restore the surrounding to its original state, the heat of the reservoir may be converted into mechanical work of running a dynamo to restore the electrical energy to the battery. But, it is not possible.

9.4 THE SECOND LAW OF THERMODYNAMICS

In all the examples discussed in Section 9.3, the possibility of exact reversal depends on the possibility of conversion of heat of a single source directly into mechanical work without effecting other changes. Experience teaches us that such conversion is not possible; otherwise, it would be possible to construct a machine which would give continuous supply of work without any expenditure of energy which contradicts the principle of conservation of energy. This impossibility has been stated as a law known as the second law of thermodynamics.

9.4.1 Kelvin's Statement of the Second Law

It is impossible for an inanimate material agency to derive (continuous) mechanical effects from any portion of matter by cooling it below the temperatures of coldest of surrounding objects.

9.4.2 Planck's statement

"It is impossible to construct an engine which working in a complete cycle will produce no effect other than the raising of a weight and the cooling of a hot reservoir".

These two statements can be combined into one equivalent statement known as Kelvin Planck's statement of the second law of thermodynamics.

9.4.3 Kelvin Planck's Statement

It is impossible to construct an engine which operating in a cycle has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work."

9.4.4 Clausius' Statement of the Second Law

It is impossible for a self-acting* machine, unaided by external agency, to transfer heat from a body at lower temperature to a body at higher temperature.

The word continuous is very significant: A compressed gas in a cylinder, if allowed to flow, can drive a fan. In the process of expansion, the gas cools. It would, thus, appear that mechanical work can be obtained by cooling the gas. This is not a violation of the second law. But by this method, work cannot be obtained continuously.

Maxwell's demon: Maxwell devised an ingenious and elusory violation of the second law of thermodynamics as stated in the form that it is not possible for an isolated mass at uniform temperature and pressure throughout to create any difference of temperature and pressure within itself by itself. The idea of Maxwell's demon as an imaginary being can, however, create a difference of temperature and pressure within the mass in the following way. Putting a partition inside the mass, the demon which can recognize the faster and slower moving molecules can direct the faster moving molecules in one chamber and the slower moving molecules in the other producing an apparent violation of the second law. Now, the demon which can recognize the molecules as discrete particles is no longer a part and parcel of the mass itself; it is a body external to the given mass and accordingly its performance is not a violation of the second law.

9.5 CARNOT'S THEOREM

All reversible engines working between the same limits of temperature must have the same efficiency.

Proof (A): If not, let an engine *S* be more efficient than an engine *R* (Fig. 9.3). This means that by drawing the same quantity of heat from the source, the work W_S produced by S is greater than the work W_R produced by *R*. Accordingly, *S* can be made to drive *R* backwards.

Let the quantity of heat drawn by *S* from the source be Q. Then, the quantity of heat given by *S* to the refrigerator is $(Q - W_s)$. Let the quantity of working substance in *R* be so adjusted that in each reverse cycle, it returns the same quantity of heat Q to the source. If Q' is the quantity of heat drawn by *R* from the refrigerator,

then $$Q = Q' + W_R \text{ or } Q' = Q - W_R$$

Hence in each cycle, heat drawn from the refrigerator is

$$(Q - W_R) - (Q - W_S) = W_S - W_R = \text{a positive quantity}$$

---

*A self-acting machine is one which can work without any permanent change in the apparatus itself; in other words, the course of changes which it undergoes during an operation must be such that it can resume its original state without external aid and thus perform cycles, repeating its operations any number of times.

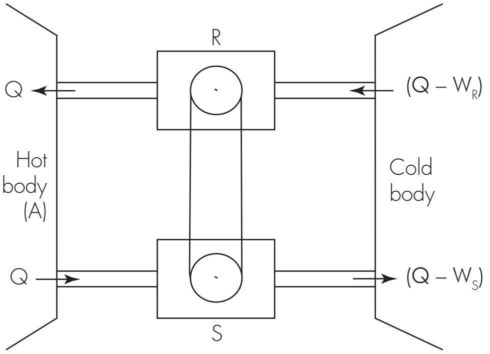


Fig. 9.3 Scheme representing Carnot's theorem

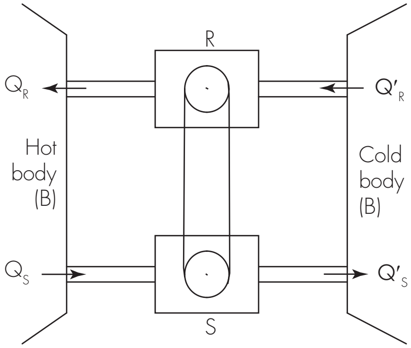


Fig. 9.4 Another schematic representation of Carnot's theorem

while the heat drawn from the source is zero. Then by drawing heat from a colder body, the combined engine can produce continuous supply of mechanical work. This violates the second law of thermodynamics in the form stated by Kelvin.

Proof (B): Let the quantities of working substance in the two engines be so adjusted that each would do the same amount of work (W) in spite of their difference of efficiencies.

Let S drive R backwards. Let the heat drawn by S from the source be Q_S and that given to the refrigerator be Q'_S (Fig. 9.4).

Let the heat drawn by R from the refrigerator be Q'_R and that given to the source be Q_R.

Then, the efficiency of S is

$$\frac{W}{Q_S} = \frac{Q_S - Q'_S}{Q_S}$$

Since R is reversible, efficiency of R in the reverse cycle is the same as that in the direct cycle so that efficiency of R is

$$\frac{W}{Q_R} = \frac{Q_R - Q'_R}{Q_R}$$

By assumption, $W = Q_S - Q'_S = Q_R - Q'_R$

If S is more efficient than R, then

$$\frac{Q_s - Q'_s}{Q_s} > \frac{Q_R - Q'_R}{Q_R}$$

or

$$\frac{1}{Q_s} > \frac{1}{Q_R}$$

Hence,

$$Q_R > Q_s$$

$\therefore$

$$Q'_R > Q'_S$$

Hence, regarding the coupled engines as a single transformer, heat gained by source is $(Q_R - Q_S)$, and heat removed from the sink is $(Q'_R - Q'_S)$ and both of these quantities are positive. Thus, by this operation, the source gets continually hotter and the sink continually colder without any work being done on the whole. This is violation of the second law of thermodynamics as stated by Clausius.

Hence, no other engine *S* can be more efficient than a reversible engine *R* when both of them work between the same limits of temperature. In other words when the source and the receiver of heat are given, a reversible heat engine is as efficient as any engine working between them can be.

Further, let both engines be reversible. Then the same argument shows that neither can be more efficient than the other. Hence, all reversible heat engines taking in and rejecting heat at the same two temperatures are equally efficient. Under these circumstances, the efficiency of a reversible engine is the maximum possible.

The two methods of proof based on two statements of the second law of thermodynamics as given by Kelvin and Clausius lead to the same result. Hence, both the statements must be equivalent.

9.6 Efficiency of A Carnot's Engine is Independent of Nature of the Working Substance

Let us have two Carnot's engines *X* and *Y* (Fig. 9.5) working with two substance *x* and *y* between two limits of temperature θ_1 and θ_2 $(\theta_1 > \theta_2)$ independently.

Let the engine *X* draw Q_1 quantity of heat at θ_1 and reject Q_{x2} quantity of heat at θ_2 after doing W_x amount of work when running independently. Let the engine *Y* draw Q_1 quantity of heat at θ_1 and reject Q_{y2} quantity of heat at θ_2 after doing W_y amount of work when running independently

Then by the first law,

$$Q_1 = Q_{x2} + W_x$$

and

$$Q_1 = Q_{y2} + W_y$$

so that

$$Q_{y2} + W_y = Q_{x2} + W_x$$

$$\text{Efficiency of } X = \frac{W_x}{Q_1} \quad \text{efficiency of } Y = \frac{W_y}{Q_1}$$

In the first instance, let us suppose that *Y* is more efficient than *X* so that $W_y > W_x$ so that $Q_{x2} > Q_{y2}$. Let the two engines *X* and *Y* be coupled together and let the engine *Y* drive the engine *X* backwards. By adjusting the quantity of working substance, the engine *X* may be made to draw Q_{x2} quantity of heat from the refrigerator and deliver $Qx_2 + Wx = Q_1$ quantity of heat to the source where W_x is the work done upon the substance *x*.

The source, at the end of the cycle, has lost no heat. The heat drawn from the refrigerator is $(Q_{x2} - Q_{y2})$ and the amount of work done by the substance is $(W_y - W_x)$, which is positive.

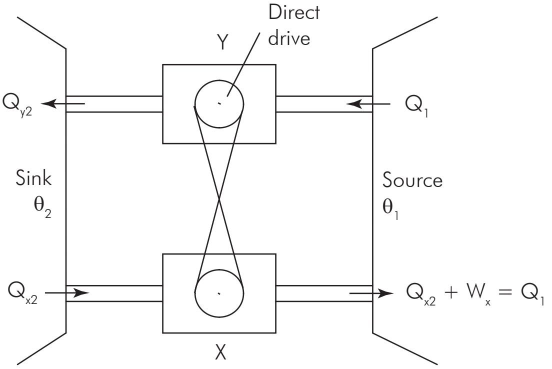


Fig. 9.5 Carnot's engine

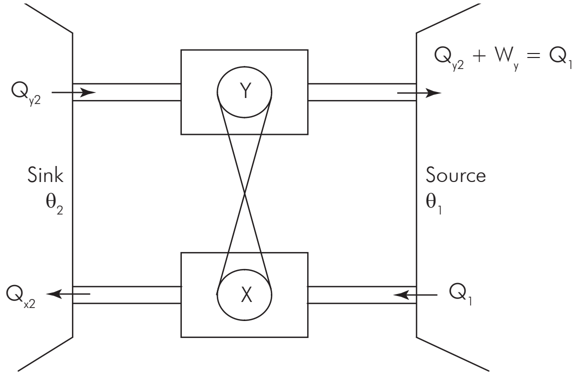


Fig. 9.6 Another scheme of Carnot's engine

Thus, at the end of the compound cycle, a certain amount of work has been derived at the expense of equivalent quantity of heat drawn from the refrigerator. This is violation of the second law of thermodynamics in the form given by Kelvin. Thus, our original assumption must be wrong. Hence, Y cannot be more efficient than X.

Next, let us suppose that X is more efficient than Y so that $W_x > W_y$. This requires ($Q_{y2} > Q_{x2}$). Let the two engines X and Y be coupled together and let the engine X drive Y backwards. The engine Y driven backwards would draw Q_{y2} quantity of heat from the refrigerator and deliver ($Q_{y2} + W_y = Q_1$) quantity of heat to the source, W_y being the amount of work done upon the substance y (Fig. 9.6).

The source at the end of the combined cycle has lost no heat. The quantity of heat drawn from the refrigerator at the end of the cycle is ($Q_{y2} - Q_{x2}$) and the amount of work done by the substances is ($W_x - W_y$), which is positive. Thus, we get a certain amount of work at the expense of heat drawn from the refrigerator. This is violation of the second law of thermodynamics. Hence, X cannot be more efficient than Y.

Therefore, the efficiency of engine X cannot be different from that of Y. Hence, the original assumption must be wrong. Thus, efficiency of Carnot's engine is independent of nature of the working substance. In this sense, Carnot's engine is said to be absolute engine.

9.7 THE THERMODYNAMIC OR KELVIN SCALE OF TEMPERATURE

We have seen that a Carnot's engine is made up of a working substance, source and a sink maintained at two different temperatures. We have proved that the efficiency of Carnot's engine is independent of nature of the working substance. It must, therefore, depend only on the temperatures θ_1 and θ_2 of the source and the sink, respectively. Thus, efficiency is

$$\eta = \frac{W}{Q} = f_1(\theta_1, \theta_2) = \frac{Q_1 - Q_2}{Q_1}$$

where W is the work done per cycle and Q_1 is the heat drawn at temperature θ_1 and Q_2 is the heat rejected at temperature θ_2. In other words,

$$\eta = 1 - \frac{Q_1}{Q_2} = f_1(\theta_1, \theta_2)$$

so that

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2)$$

Let another Carnot's engine work between temperatures θ_2 and θ_3 ($\theta_2 > \theta_3$). By adjusting the amount of working substance, let the second engine take in heat Q_2 at θ_2 and reject heat Q_3 at θ_3; then by the same argument as above,

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3)$$

Now, suppose an engine works between temperatures θ_1 and θ_3 taking in heat Q_1 at θ_1 and rejecting heat Q_3 at θ_3.

Then $$\frac{Q_1}{Q_3} = F(\theta_1, \theta_3)$$

But $$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3}$$

Or $$F(\theta_1, \theta_3) = F(\theta_1, \theta_2)\, F(\theta_2, \theta_3)$$

This equation is true only if $F(\theta_1, \theta_2)$ is of the form $f(\theta_1)/f(\theta_2)$

Thus, we get the relation

$$\frac{Q_1}{Q_2} = \frac{F(\theta_1)}{F(\theta_2)} \tag{9.9}$$

Representing $f(\theta)$ by T, the above relation takes the form

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

9.7.1 Thermodynamic Absolute Temperature

Lord Kelvin proposed the following definition of absolute temperature:

The quantities of heat taken in and rejected by a reversible engine working with a given source and refrigerator are proportional to two quantities which are functions of temperatures of the source and refrigerator. These quantities are the thermodynamic temperatures of the source and the refrigerator.

The thermodynamic temperature so defined is absolute in the sense that the scale of this temperature is independent of properties of any gas or other substance, real or imaginary.

The efficiency of Carnot's engine is

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

where T_1 and T_2 are the thermodynamic temperatures of the source and the refrigerator, respectively. Efficiency of Carnot's engine working with an ideal gas has already been proved to be

$$\eta = 1 - \frac{\theta_2}{\theta_1}$$

where θ_1 and θ_2 are the temperatures of the source and the refrigerator, respectively. These temperatures appear in the equation of state

$$pv = R\theta$$

of an imaginary perfect gas. This equation is the basis of a scale in which equal intervals of temperature are defined as those which correspond to equal amounts of expansion of a perfect gas under constant pressure. This scale of temperature is called the *perfect gas scale.* It follows that the temperatures measured by the perfect gas scale agree with those measured by the thermodynamic scale. Henceforth by absolute scale of temperature, we shall mean the perfect gas scale or the thermodynamic scale.

The zero of the thermodynamic scale: From the equations

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \text{and} \quad \eta = 1 - \frac{T_2}{T_1}$$

if $\eta = 1$, then $T_2 = 0$ so that $Q_2 = 0$

This gives the following definition of zero of thermodynamic scale of temperature: if the refrigerator of a reversible engine is kept at the absolute zero of temperature, then the engine working with this refrigerator and a source at any arbitrary higher temperature would convert all the heat drawn from the source into mechanical work so that the efficiency of the engine is unity.

Graduation of the thermodynamic scale of temperature: Let $A_1A_2A_3A_4 \ldots B_1B_2B_3B_4 \ldots$ be two adiabatics for the working substance of a Carnot's engine (Fig. 9.7). Divide the space between these adiabatics into equal areas by isothermals A_1B_1, A_2B_2, A_3B_3 and A_4B_4. Let the temperature of these isothermals be T_1, T_2, T_3, T_4, respectively. Let a chain of reversible engines be provided each working with one of the intervals of temperature $(T_1 - T_2)$, $(T_2 - T_3)$, $(T_3 - T_4)$ and so on for its range, and each handing on to the engine below it the heat which it rejects so that the heat rejected by the first forms the supply of the second and so on.

Then, the efficiencies of the different engines are

$$\frac{T_1 - T_2}{T_1}, \frac{T_2 - T_3}{T_2}, \frac{T_3 - T_4}{T_3} \ldots\ldots$$

Amount of heat supplied to them are Q_1, $Q_1(T_2/T_1)$, $Q_1(T_3/T_1)\ldots$ (Q_1 = heat drawn by the first engine).

Amount of work done by different engines are $Q_1(T_1 - T_2/T_1)$, $Q_1(T_2 - T_3/T_1)$, $Q_1(T_3 - T_4/T_1)\ldots$ Since by assumption the areas between the successive isothermals are the same, the works done in successive intervals are equal. Hence,

$$T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \ldots\ldots\ldots$$

Each of the equal intervals is, thus, a measure of the degree in the absolute scale.

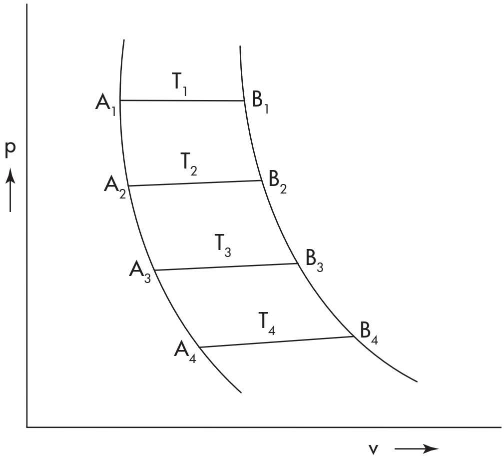


Fig. 9.7 Carnot's cycle

Rankine's statement of the second law: Conversely, "if the absolute temperature of any uniformly hot substance be divided into any number of equal parts, the effects of these parts in causing work to be performed are equal". This is Rankine's statement of the second law of thermodynamics.

9.8 CENTIGRADE SCALE AND ABSOLUTE SCALE

In order that the thermodynamic scale chosen above may agree with the two fixed points of the centigrade scale, we take 373 engines in the chain, the top temperature of the chain being taken to be the boiling point of water under 760 mm Hg pressure. Then it takes 100 steps to come down to the melting point of ice and 273 more steps to convert the remaining heat of work to reach the zero of the absolute scale.

9.8.1 The Centigrade Scale of Temperature

In the centigrade scale of temperature, the melting point of ice under normal pressure of 760 mm of mercury is taken to the zero of the scale and the boiling point of water at 760 mm pressure is taken as 100 °C. The interval between these two fixed points is divided into 100 equal parts, each division being called a degree. We shall represent the centigrade temperature by θ.

No two liquid thermometers based on the centigrade scale agree among themselves throughout the entire range. Hence, necessity was felt to have a standard thermometer to serve as a basis for comparison between the scales of different temperatures.

The isometric hydrogen pressure centigrade scale: In 1887, an international congress of weights of measures decided to use as standard for measurement of temperature the constant volume hydrogen thermometer in which pure hydrogen gas was used as the thermometric substance. Since the co-efficient of cubical expansion of a gas depends on pressure of the gas, the temperature and pressure of the gas filling the bulb of the thermometer had to be specified.

The standard or normal hydrogen thermometer is a constant-volume thermometer whose bulb is fitted with pure hydrogen at 0 °C and 1000 mm Hg pressure.

In this thermometer, each degree is measured by 1/100th of change of pressure of the gas at constant volume between 0 °C and 100 °C. Let p_0, p_{100} and p_θ be the pressure of the gas at 0 °C, 100 °C and θ°C, respectively then

$$p_\theta = \frac{(p_{100} - p_0)\theta}{100} + p_0$$

This can be proved as follows.

Let the equation of $p - \theta$ curve (Fig. 9.8) be $p = m\theta + c$ when $\theta = 0$, $p = p_0$ so that $c = p_0$

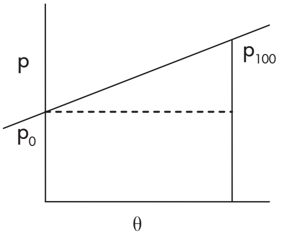


Fig. 9.8 p-q curve

Also, $m = (p_{100} - p_0)/100 \therefore p_\theta = \frac{(p_{100} - p_0)}{100}\theta + p_0$

$$\text{so that } \theta = \frac{(p_\theta - p_0)\times 100}{p_{100} - p_0} \qquad (9.10)$$

The pressure co-efficient of a gas at constant volume is

$$\alpha_p = \frac{1}{p_0}\left(\frac{dp}{d\theta}\right)_v$$

or $$dp = \alpha_p \; p_0 d\theta$$

or $$\int_{p_0}^{p_{100}} dp = \alpha_p \; p_0 \int_0^{100} d\theta \text{ if } \alpha_p \text{ is constant}$$

or $$p_{100} - p_0 = \alpha_p \; p_0 \times 100$$

or, $$\alpha_p = \frac{p_{100} - p_0}{100 p_0}$$

At 1000 mm Hg pressure, the accepted value of α_p for hydrogen is 0.0036626/°C
Substituting the value in Eq. 9.10,

$$\theta = \frac{p_\theta - p_0}{\alpha_p \; p_0} = \frac{p_\theta - 1000}{0.0036626 \times 1000}$$

or $$\theta = \frac{p_\theta - 1000}{3.6626} \text{ degree centigrade} \tag{9.11}$$

It follows that the pressure of the gas is reduced as its temperature diminishes. There must, therefore, exist a temperature at which the gas does not exert any pressure. According to the kinetic theory of gases, this is the temperature at which the molecules of the gas have no translational motion. This temperature is obtained by putting $p_\theta = 0$ in Eq. (9.11). Its value is

$$\theta_0 = -\frac{1000}{3.6626} = -273.03°\text{C}$$

This is, of course, a hypothetical temperature because the gas liquefies long before the zero degree temperature is reached.

Temperature scale of which the zero is taken at −273.03 is called the absolute hydrogen pressure scale. We shall represent absolute hydrogen temperature by

$$= \theta + 273.03$$

where θ is the centigrade temperature. Temperatures of ice point and steam point under normal pressure are, according to hydrogen temperature scale, + 273.03 and 373.03°.

In 1927, the international temperature scale was introduced. This is the ideal scale based on thermodynamic considerations or the thermodynamic scale identical with the ideal gas scale. An ideal gas obeys the equation of state

$$pv = f(\tau) \tag{9.12}$$

where τ is the temperature measured on the ideal gas scale. For a constant volume thermometer with an ideal gas as thermometric substance, $(dp/d\tau)_{v=0}$ is constant and equal to A (say).

Differentiating Eq. 9.12 with v constant ($= v_0$), we get

$$v_0\left(\frac{dp}{d\tau}\right)_{v=v_0} = \frac{d}{d\tau}[f(\tau)]_{v=v_0} = v_0 A$$

or $$d\left[f(\tau)\right] = v_0 A d\tau = R d\tau \quad \text{where } R = v_0 A$$

or $$f(\tau) = R\tau + C$$

where C is the constant of integration which must be of the same nature as $R\tau$. Let us put it as $C = RT_0$, then

$$f(\tau) = R(\tau + T_0)$$

Hence, $$pv = f(\tau) = R(\tau + T_0) \tag{9.13}$$

Evidently for a constant volume thermometer, p would vanish when $\tau = -T_0$. Taking $-T_0$ as the zero of the ideal gas scale and reckoning temperature from this absolute zero, Eq. 9.12 becomes

$$pv = RT \quad \text{where} \quad \mathrm{T} = \tau + T_0$$

It will be proved later on that $T_0 = 273.16$. Hence on the absolute thermodynamics scale, the melting point of ice under normal pressure is 273.16.

9.9 CONVERSION OF REAL GAS THERMOMETER SCALE TO PERFECT GAS THERMOMETER SCALE OR ABSOLUTE THERMODYNAMIC SCALE

No real gas obeys the equation of state of a perfect gas

$$pv = RT$$

But, any real gas approaches the perfect gas in the limit when the pressure of the gas is infinitesimally small. Accordingly to translate the readings of a real gas scale (such as the hydrogen scale), they are to be extrapolated to the limit of vanishingly small pressures. This is done as follows:

For a real gas, we can use the following equation of state:

$$pv = A + Bp + Cp^2 + \ldots\ldots \tag{9.14}$$

where the constants A, B, C, …. are functions of temperature.

Taking the constant volume at 0 °C equal to v_o, Eq. 9.14 for a constant volume thermometer with volume maintained at v_o can be written as

$$\left.\begin{aligned} p_0 v_0 &= A_0 + B_0 p_0 + C_0 p_0{}^2 + \ldots\ldots \\ p_{100} v_0 &= A_{100} + B_{100} p_{100} + C_{100} p_{100}^2 + \ldots\ldots \\ p_\theta v_0 &= A_\theta + B_\theta p_\theta + C_\theta p_\theta{}^2 + \ldots\ldots \end{aligned}\right\} \tag{9.15}$$

where p_0, p_{100}, and p_θ are pressures of volume v_0 of the gas at 0°, 100° and θ°.

If the unit of pressure is 10 mm of Hg, then *B/A* is of the order of 10^{-3} unit and *C/A* is of the order of 10^{-5} to 10^{-6} unit. If p is small, then the last set of equations become

$$\left.\begin{aligned} p_0 v_0 &= A_0 + B_0 p_0 \\ p_{100} v_0 &= A_{100} + B_{100} p_{100} \\ p_\theta v_0 &= A_\theta + B_\theta p_\theta \end{aligned}\right\} \tag{9.16}$$

Substituting in Eq. 9.10 the values of Eq. 9.16, we get

$$\theta = \frac{100(p_\theta - p_0)}{p_{100} - p_0} = 100 \times \frac{(A_\theta - A_0) + (B_\theta p_\theta - B_0 p_0)}{(A_{100} - A_0) + (B_{100} p_{100} - B_0 p_0)} \tag{9.17}$$

The corresponding temperature as p approaches zero is evidently the absolute temperature T so that

$$T = \mathrm{Lim}_{p\to 0}\theta \frac{(A_\theta - A_0)}{(A_{100} - A_0)} \times 100$$

Equation 9.17 can be put as

$$\theta = 100 \times \frac{(A_\theta - A_0)\left[1 + \left(\dfrac{B_\theta p_\theta - B_0 p_0}{A_\theta - A_0}\right)\right]}{(A_{100} - A_0)\left[1 + \left(\dfrac{B_{100} p_{100} - B_0 p_0}{A_{100} - A_0}\right)\right]}$$

$$= \mathrm{Lim}_{p\to 0}\theta \left[1 + \frac{B_\theta p_\theta - B_0 p_0}{A_\theta - A_0} - \frac{B_{100} p_{100} - B_0 p_0}{A_{100} - A_0}\right]$$

$$\mathrm{Lim}_{p\to 0}\theta - \theta = \mathrm{Lim}_{p\to 0}\theta \left[\frac{B_{100} p_{100} - B_0 p_0}{A_{100} - A_0} - \frac{B_\theta p_\theta - B_0 p_0}{A_\theta - A_0}\right] \tag{9.18}$$

The correction $(\mathrm{Lim}_{p\to 0}\theta - \theta)$ can be calculated if the constants A, B are known from the isotherms of the thermometric gas. But, the correction term involves $\mathrm{Lim}_{p\to 0}\theta$. Hence, it is convenient to use the method of successive approximations. For this purpose, the observed temperature θ given by Eq. 9.17 is first substituted for $\mathrm{Lim}_{p\to 0}\theta - \theta$ in the correction term and $\mathrm{Lim}_{p\to 0}\theta$ is calculated. This gives the first approximate value of $\mathrm{Lim}_{p\to 0}\theta$. This is then introduced in the correction term and the second approximate value of $\mathrm{Lim}_{p\to 0}\theta$ is obtained.

9.9.1 Extension of Carnot's Cycle

A Carnot's cycle is bounded by two isothermals and two adiabatics so that all heat is taken in at one temperature and given out at another lower temperature. In all practical cycles, heat is not taken in or given out at the same temperature. An actual cycle is not as simple as Carnot's cycle. Nevertheless, a cycle of any contour can be broken up into a large number of infinitesimally small Carnot's cycles by very close isothermals and adiabatics as shown in Fig. 9.9.

It will be observed that in traversing any two elementary adjacent cycles in the same direction, the common adiabatic separating the two cycles is traversed twice in opposite directions. Hence, the net amount of work done along the common adiabatic is zero. The only uncompensated work that is left out in traversing all the elementary cycles in the same direction is that done along isothermals separating two contiguous adiabatics.

In the limit when the adiabatics are indefinitely close together, the lengths of the isothermals lying between two consecutive adiabatics would coincide with the lengths of the contour lines intercepted by the same adiabatics. Hence, the net amount of work done is represented by area bounded by the given contour line.

Evidently, the algebraic sum of quantities of heat drawn and rejected by the engines in traversing all the elementary cycles in the same direction reversibly must be equal to zero, or

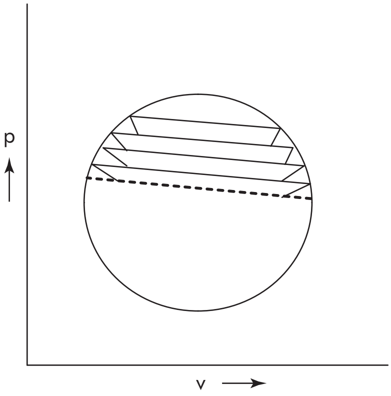


Fig. 9.9 Extension of Carnot's cycle

$$\sum \frac{\Delta Q}{T} = 0 \quad (9.19)$$

where the summation extends over the whole contour line of the given cycle. In the limit when the adiabatic lines are indefinitely close together, the summation is replaced by the closed integral

$$\oint \frac{dQ}{T} = 0 \tag{9.20}$$

Equation 9.20 is known as the theorem of Clausius.

9.10 ENTROPY

The quantity dQ/T is called the change of entropy. Thus in any thermodynamic process, when any quantity of heat dQ is given out by a substance at absolute temperature T, the entropy of the substance is reduced by dQ/T. Since the quantity of heat dQ absorbed or emitted in any thermodynamic process depends on the *mass and specific heat* of the substance, the entropy depends on the mass and nature of the substance emitting or absorbing heat. As a result, the entropy of a substance is reckoned per unit mass of the substance and it is different for different substances.

As in dealing with internal energy, we take an arbitrary starting point at which the entropy of a substance is taken a zero; what we are concerned with is not the absolute value entropy in a given thermodynamic state but the change of entropy as a substance passes from one state to another.

The entropy of unit mass of a substance is defined by dQ/T. Each of the quantities dQ and T are scalar. Hence, entropy must also be a scalar quantity. Its unit is erg/degree. The name Rank was suggested by Rankine for the unit of entropy.

We have already seen that in trying to convert as much of heat energy into mechanical work as possible, it is the temperature that limits our power of conversion. In the most perfect type of engine (the Carnot's engine), the maximum amount of work that can be obtained from a given quantity of heat Q_1 drawn from a source at temperature T_1 is

$$Q_1 - Q_2 = Q_1 \frac{T_1 - T_2}{T_1} = \frac{Q_1}{T_1}(T_1 - T_2)$$

where Q_2 is the quantity of heat given to the refrigerator at temperature T_2. Further,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

In this respect, entropy is analogous to the gravitational weight of a body. In passing down the temperature interval ($T_1 - T_2$), the entropy Q_1/T_1 of given mass of a substance at temperature T_1 does not change (provided the change is reversible) while it does an amount of mechanical work $Q_1/T_1(T_1 - T_2)$; just as a given quantity (mg) of water in falling down a height ($h_1 - h_2$) can supply an amount of work mg ($h_1 - h_2$) though its mass remains unaltered. Further as we shall prove, like work in gravitational field, entropy is independent of path of change.

In developing his idea of the most perfect engine, Carnot thought that heat was an incompressible fluid which could neither be created nor destroyed. According to Carnot this imaginary fluid in falling from the temperature level of the source to that of the refrigerator supplied the amount of work done by the engine, the quantity of heat remaining constant. This led to much controversy since later researches proved that heat was not indestructible and that it could be obtained from mechanical work. We now know that it is not heat but entropy which is analogous to falling mass of water in regard to its power of doing mechanical work.

9.10.1 Entropy of a Heterogeneous System

If unit mass of a substance absorbs Q quantity of heat in passing from state A to state B, then a mass m of the same substance will absorb mQ quantity of heat in the same transformation. Hence, its change of entropy would be mQ/T where T is the absolute temperature at which the change takes place.

If we have a heterogeneous system consisting of different bodies of masses $m_1, m_2, m_3 \ldots$ and of entropies per unit mass $S_1, S_2, S_3 \ldots$ measured from any arbitrary zero, and at temperatures $T_1, T_2, T_3 \ldots$, respectively, then the entropy of the system as a whole is

$$S = m_1S_1 + m_2S_2 + m_3S_3 + \ldots\ldots\ldots$$

The average entropy of the system per unit mass may, therefore, be defined as

$$\bar{S} = \frac{S}{\sum m} = \frac{\sum mS}{\sum m} \qquad (9.21)$$

The theorem of Clausius states that the total change of entropy of a substance in any closed reversible cyclic process is zero. This can be true only when the change of entropy in a given transformation depends on the initial and final states and is independent of the path of change. This can also be proved as follows:

Imagine a reversible operation taking place along the path APB and a closed reversible cycle to be completed by a process conducted along the path BQA (Fig. 9.10). Then, the total change of entropies along the paths APB and BQA is

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ}{T} = \oint \frac{dQ}{T} = 0$$

by the theorem of Clausius, since the cycle is supposed to be reversible.

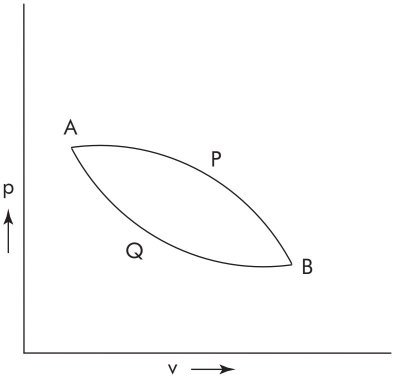


Fig. 9.10 Two reversible paths of operation joining the initial and final states of a system

Let ARB be some other reversible path joining A and B.

Let X be the change of entropy along the path ARB. Then considering the paths ARB and BQA, the total change of entropy along these paths are

$$X+\int_B^A \frac{dQ}{T}=\oint \frac{dQ}{T}=0$$

$$\int_A^B \frac{dQ}{T}+\int_B^A \frac{dQ}{T}=X+\int_B^A \frac{dQ}{T}$$

$$\therefore \qquad X=\int_A^B \frac{dQ}{T}$$

This is true for every other reversible path connecting A and B.

Hence, dQ/T must be a perfect differential

or
$$\frac{dQ}{T}=dS$$

where dS is the change of entropy so that

$$\int_A^B \frac{dQ}{T}=S_B-S_A \tag{9.22}$$

Evidently, $\int_A^B \frac{dQ}{T}$ can be evaluated only when the transformation from the state A to the state B is reversible.

9.10.2 The Integrating Factor

In the energy equation

$$dQ = dU + dW$$

dU is a perfect differential, but dW is not a perfect differential. But on multiplying both sides of the energy equation by $1/T$, it becomes a perfect differential; thus,

$$\frac{dQ}{T}=\frac{dU}{T}+\frac{dW}{T}=dS \tag{9.23}$$

Hence, $1/T$ is the integrating factor of the energy equation.

9.10.3 Change of Entropy Along an Adiabatic

A system undergoing any adiabatic change does not exchange any heat energy with the surroundings. Hence in an adiabatic process, $dQ = 0$; so that along an adiabatic line, $dS = 0$. Adiabatic lines are, therefore, lines of constant entropy or isentropies.

There is a perfectly definite change of entropy when a given substance passes from one adiabatic line to another, by any path connecting the adiabatic lines. This can be proved as follows:

Let ad and bc be two adiabatics specified by entropies S_1 and S_2, respectively (Fig. 9.11). Connect these two adiabatics by isothermal lines ab and dc corresponding to temperatures T_1 and T_2, respectively.

If Q_1 and Q_2 are the heats absorbed from *a* to *b* and from *d* to *c* in a reversible process, then change of entropy along *ab* is Q_1/T_1 and that along *dc* is Q_2/T_2.

But since *abcd* forms a Carnot's cycle,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

If *a* and *c* be connected by a line *ac*, then change of entropy along *ac* is the sum of change of entropy along *ad* plus the change of entropy along *dc*. But, change of entropy along *ad* is zero.

Therefore, change of entropy along *ac* = change of entropy along $dc = \frac{Q_2}{T_2} = \frac{Q_1}{T_1}$

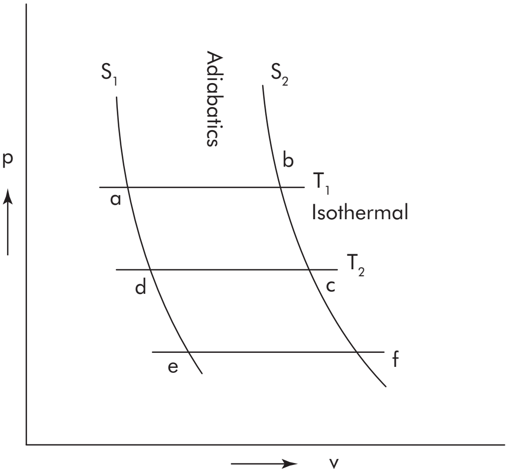


Fig. 9.11 Entropy change representation

If we move from the isentropic S_1 to the isentropic S_2 along the path af, then the total change of entropy from a to f is the change of entropy from a to e and from e to f. But, change of entropy from a to e is zero. Hence, the change of entropy from a to $f = Q_3/T_3$ where Q_3 is the heat drawn reversibly at T_3. But, the cycle abfe is the Carnot's cycle.

Therefore, $$\frac{Q_3}{T_3} = \frac{Q_1}{T_1}$$

∴ Change of entropy along each path is Q_1/T_1.

Entropy of given mass of a substance may be defined as that physical property of the substance which does not change when the substance undergoes an adiabatic transformation.

9.10.3 Clausius' Theorem Considered as Second Law

The theorem of Clausius

$$\oint \frac{dQ}{T} = 0$$

for a closed reversible cyclic process has been obtained merely as a generalization of the equation

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

which applies to a simple Carnot's cycle. The latter equation is based on the fact that the efficiency of Carnot's engine is the maximum attainable efficiency. To prove this, the only principle adopted is the second law of thermodynamics. Hence, Clausius' theorem may properly be regarded as the mathematical expression for the second law of thermodynamics.

Conversely, if Clausius' theorem represents the second law of thermodynamics, it ought to be possible to deduce the second law from this theorem. This can be done as follows:

Let a body pass through a closed cyclic operation so that the entropy at the end of the operation is the same as at the beginning. If, in the process of transformation, an amount of heat dQ_1 has been taken in at temperature T_1 and if dQ_2 has been given out at temperature T_2 then, in order that the entropy may remain unaltered, the exchange of heat must take place in such a way that

$$\frac{dQ_1}{T_1} = \frac{dQ_2}{T_2}$$

If T_2 is less than T_1, then dQ_2 must be less than dQ_1.

This means that the amount of heat gained by the cold body must be less than that lost by the hot body so that the work is done during the cycle by drawing heat from the warm body and giving it in part to the colder body. This is the second law of thermodynamics.

9.10.4 Changes of Entropy in Irreversible and Reversible Processes

The theorem of Clausius states that the change of entropy in a closed reversible cyclic process is zero. As already stated a reversible process is an equilibrium process, the working substance being at the temperature of the source when it is taking in heat and at the temperature of the refrigerator when it is giving out heat. Considering a simple Carnot's cycle, let T_1 and T_2 be the temperature of the source and the refrigerator, respectively (Fig. 9.12). If the process is irreversible, that is, if it is a non-equilibrium process, then the working substance is at a lower temperature τ_1 than the temperature T_1 of the source when it is receiving heat and at a higher temperature τ_2 than the temperature T_2 of the refrigerator when it is giving out heat. Let Q_1 be the quantity of heat received by the working substance at temperature τ_1 and let Q_2 be the quantity of heat given out by the working substance at temperature τ_2. Now, heat lost by the source is equal to that gained by the working substance and that gained by the sink is equal to that lost by the working substance.

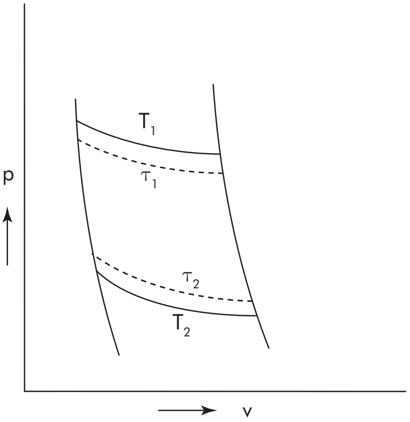


Fig. 9.12 Schematic presentation of entropy change in irreversible and reversible process

Hence, the gain of entropy of the working substance $= \dfrac{Q_1}{\tau_1} - \dfrac{Q_2}{\tau_2}$

Loss of entropy of the source $= \dfrac{Q_1}{T_1}$

Gain of entropy of the refrigerator $= \dfrac{Q_2}{T_2}$

Then, the total gain of entropy of the system consisting of the source, sink and the working substance is

$$\left[\left(\frac{Q_1}{\tau_1} - \frac{Q_2}{\tau_2}\right) + \frac{Q_2}{T_2}\right] - \frac{Q_1}{T_1} = \left(\frac{Q_1}{\tau_1} - \frac{Q_1}{T_1}\right) + \left(\frac{Q_2}{T_2} - \frac{Q_2}{\tau_2}\right)$$

$$= Q_1\left(\frac{1}{\tau_1} - \frac{1}{T_1}\right) + Q_2\left(\frac{1}{T_2} - \frac{1}{\tau_2}\right) = \text{a positive quantity}$$

since $T_1 > \tau_1$ and $\tau_2 > T_2$.

Applying this method of proof to all the elementary Carnot's cycles constituting a given closed cyclic operation, we conclude that the entropy of the entire system taking part in a given irreversible cyclic operation tends to increase.

Hence in a *closed irreversible cyclic operation*,

$$\oint \frac{dQ}{T} > 0 \tag{9.24}$$

We have already proved that Carnot's cycle is perfectly reversible and that the temperature of the working substance is the same as that of the source when it is receiving heat.

Further since the heat gained by the working substance is the same as that lost by the source, the gain of entropy of the working substance is equal to the loss of entropy by the source. It can be similarly proved that the loss of entropy by the working substance, when it is giving out heat, is the same as the gain of entropy of the refrigerator. Hence, the total gain of entropy of the system consisting of the source, sink and the working substance is equal to zero. Applying this method of proof to all elementary Carnot's cycles constituting a given closed reversible cyclic operation, we conclude that the total gain of entropy of the entire system taking part in a closed reversible cyclic operation is zero. In other words, for a *closed reversible cyclic process*

$$\oint \frac{dQ}{T} = 0$$

We have already proved that all natural or spontaneous processes are irreversible. Hence, *we may define entropy as that physical property which increases in all natural or spontaneous processes.* Taking the whole universe as one isolated system, we may enunciate a general principle – *the entropy of the universe tends towards a maximum value*. In a spontaneous process the total energy of the system undergoing change remains constant though it may transform. So, energy is not a measure of the magnitudes of spontaneous changes in nature. Such changes can only be measured by change of the physical property of the system which we call entropy.

Condition of reversibility: Every process occurring in nature is accompanied by an increase in the sum of entropies of all bodies which take part in any manner in the process.

If an isolated system goes from a state A to another state B without any change of entropy of the system, then the process must be reversible; for if it were irreversible, the entropy must have increased. If in the process of change, the entropy in the state B were greater than in the state A, then the process must have been irreversible; for if it had been reversible, there would have been no change of entropy. When applied to any process occurring in an isolated system, the equality or inequality of entropy of the system in the two states is not on1y the necessary but also the sufficient condition for the reversibility or irreversibility of the process.

Available energy of motivity: In Carnot's reversible cycle, the amount of mechanical work done by the working substance is

$$W = J(Q_1 - Q_2) = JQ_1\left(1 - \frac{Q_2}{Q_1}\right) = JQ_1\left(1 - \frac{T_2}{T_1}\right)$$

where Q_1 is heat drawn at absolute temperature T_1 and Q_2 is the heat rejected at absolute temperature T_2. According to the first law of thermodynamics, the dynamic value of the quantity of heat Q_1 drawn from the source is $J\,Q_1$. But its practical value is $JQ(1 - T_2/T_1)$. This practical value of heat is called the *motivity of heat* or *the available energy* from the amount of heat Q_1. If the refrigerator is at the absolute zero of temperature ($T_2 = 0$), then the motivity of heat Q_1 is equal to its dynamical value JQ_1. This is the maximum possible value of motivity or energy available from the Q_1 amount of heat.

Dissipation of energy: Let T and T_o be the temperatures of the hottest and coldest body of a system, respectively. Let a Carnot's engine draw dQ quantity of heat from the body at temperature T and reject the unused heat to the body at temperature T_o. Then, the motivity of the system under the given condition is

$$dQ\left(1-\frac{T_o}{T}\right)$$

Instead of rejecting heat to the coldest body at temperature T_o, let heat dQ' be rejected to a body at an intermediate temperature T'.

A Carnot's engine working between temperatures T' and T_o and drawing in heat dQ' at T' would produce

$$dQ'\left(1-\frac{T_o}{T'}\right)$$

units of mechanical work. Hence, motivity still remaining in dQ' is

$$dQ'\left(1-\frac{T_o}{T'}\right)$$

Hence, the loss in motivity or energy available for performance of external work due to transference of heat to a body at intermediate temperature T' is

$$dQ\left(1-\frac{T_o}{T}\right)-dQ'\left(1-\frac{T_o}{T'}\right)$$

$$= dQ - dQ' - T_o\left(\frac{dQ}{T}-\frac{dQ'}{T'}\right)$$

Considering any closed cyclic transformation as made up of large number of small elementary cycles bounded by two isothermals and two adiabatics as in Carnot's cycle, the loss in motivity for the entire cycle is

$$Q - Q' - T_o\oint\frac{dQ}{T}$$

where Q and Q' are the total quantities of heat taken in and rejected during the cycle.

If the process is reversible, $\oint dQ/T = 0$ and the loss in motivity is $Q - Q'$. If the process is irreversible, $\oint dQ/T > 0$ = a positive quantity and the loss in motivity is greater than that for reversible cycle.

Now, all natural processes are irreversible. Hence in all practical cases of cyclic transformation, a quantity of heat energy of magnitude dQ/T is lost. This waste of availability is called dissipation. Hence, "entropy of the universe tends towards a maximum value" means that "the availability of energy tends towards a minimum value". This is known as the *1aw of degradation of energy*. This means that in all natural transformations, energy is transformed to a less useful form.

9.10.5 Entropy and Available Energy

Maximum work obtainable from heat Q_1 taken from a body of fixed composition and volume at temperature T_1 is

$$W = Q_1 - Q_2 = Q_1\left(1 - \frac{T_2}{T_1}\right)$$

where T_2 is the lowest temperature available for the refrigerator of a reversible engine. The balance of heat Q_1 which is not converted into work, that is, $Q_2 = Q_1\, T_2/T_1$ is the *unavailable energy* given up as heat to the refrigerator. It is proportional to the lowest available temperature T_2 and inversely proportional to the temperature of the source from which Q_1 is taken. The quantity Q_1/T_1 is the entropy of the quantity of heat Q_1 at temperature T_1. Hence,

$$\text{Entropy} = \frac{\text{unavailable energy}}{\text{lowest available temperature}}$$

If the lowest available temperature is fixed, then entropy and unavailable energy must increase together. Therefore, increase of entropy means *diminution of available energy* or *dissipation of energy*.

9.10.6 Entropy of an Ideal Gas

In an infinitesimal change of reversible process undergone by a mole of perfect gas involving a certain amount of external work *pdv*

$$dQ = C_v dT + pdv,$$

change of entropy in the process is

$$dS = \frac{dQ}{T} = C_v \frac{dT}{T} + \frac{p}{T} dv$$

For an ideal gas, $pv = RT$ so that $\frac{p}{T} = \frac{R}{v}$
R being the universal gas constant,

$$dS = C_v \frac{dT}{T} + R\frac{dv}{v} \tag{9.25}$$

Total change of entropy as the gas passes from the state A to state B is

$$S_B - S_A = C_v \int_{T_A}^{T_B} \frac{dT}{T} + R\int_{v_A}^{v_B} \frac{dv}{v}$$

or

$$S_B - S_A = C_v \log_e \frac{T_B}{T_A} + R\log_e \frac{v_B}{v_A} \tag{9.26}$$

Equation 9.26 gives change of entropy due to change in temperature and volume only.
Equation 9.25 can be expressed in other forms as follows:

In the state A, $$p_A v_A = RT_A \tag{9.27}$$

In the state B, $$p_B v_B = RT_B \tag{9.28}$$

This gives $$\frac{T_B}{T_A} = \frac{p_B v_B}{p_A v_A}$$

Substituting the value in Eq. 9.26, we get

$$S_B - S_A = C_v \log_e \frac{p_B}{p_A} + C_v \log_e \frac{v_B}{v_A} + R \log_e \frac{v_B}{v_A}$$

$$= C_v \log_e \frac{p_B}{p_A} + (C_v + R) \log_e \frac{v_B}{v_A}$$

or $$S_B - S_A = C_v \log_e \frac{p_B}{p_A} + C_p \log_e \frac{v_B}{v_A} \tag{9.29}$$

Equation 9.29 gives change of entropy due to change of pressure and volume only.

Again from Eqs 9.27 and 9.28,

$$\frac{v_B}{v_A} = \frac{T_B}{T_A} \frac{p_A}{p_B}$$

Substituting the value in Eq. 9.25,

$$S_B - S_A = C_v \log_e \frac{T_B}{T_A} + R \log_e \frac{T_B}{T_A} + R \log_e \frac{p_A}{p_B}$$

$$= (C_v + R) \log_e \frac{T_B}{T_A} + R \log_e \frac{p_A}{p_B}$$

or $$S_B - S_A = C_p \log_e \frac{T_B}{T_A} + R \log_e \frac{p_A}{p_B} \tag{9.30}$$

Equation 9.30 gives change of entropy due to change in temperature and pressure only.

Integrating Eq. 9.25, we get

$$S = C_v \log_e T + R \log_e v + c \tag{9.31}$$

Here, c is the constant of integration. It must be of the nature of S. Hence, it must depend on the quantity and nature of the substance.

From equation of the perfect gas $pv = RT$, we get

$$S = C_v \log_e T + R \log_e \frac{RT}{p} + c$$

$$= C_v \log_e T + R \log_e \frac{T}{p} + R \log_e R + c$$

or $$S = C_v \log_e T + R \log_e \frac{T}{p} + k \tag{9.32}$$

where $k = R \log_e R + c$. Evidently, it depends on the quantity and nature of the gas.

Also, $$S = C_v \log_e T + R \log_e T - R \log_e p + k$$

$$= (C_v + R) \log_e T - R \log_e p + k$$

or $$S = C_p \log_e T - R \log_e p + k \tag{9.33}$$

9.10.7 Entropy of Mixture of Perfect Gases

Consider n_1, n_2, n_3 ……. moles of perfect gases numbered 1, 2, 3 …… etc. mixed up in a volume v at the same temperature T. Let p_1, p_2, p_3 ……. be the partial pressure of these gases and let p be the resultant pressure. Let C_{v1}, C_{v2}, C_{v3} ……. be the specific heats of these gases at constant volume. Then, the entropy of the mixture is

$$S = n_1 \left[C_{v1} \log_e T + R \log_e \left(\frac{T}{p_1} \right) + k_1 \right]$$

$$+ n_2 \left[C_{v2} \log_e T + R \log_e \left(\frac{T}{p_2} \right) + k_2 \right]$$

$$+ n_3 \left[C_{v3} \log_e T + R \log_e \left(\frac{T}{p_3} \right) + k_3 \right]$$

$$+ \dots\dots\dots\dots\dots\dots$$

or $$S = \sum n_1 \left[C_{v1} \log_e T + R \log_e \left(\frac{T}{p_1} \right) + k_1 \right]$$

where the summation extends over all the numbered gases.

Now, $$p_1 = \frac{n_1 RT}{v}, p_2 = \frac{n_2 RT}{v}, p_3 = \frac{n_3 RT}{v} \text{ and so on}$$

By Dalton's law of partial pressures,

$$p = p_1 + p_2 + p_3 + \dots\dots$$

$$= \frac{RT}{v}(n_1 + n_2 + n_3 + \dots\dots)$$

or
$$p = \frac{RT}{v}\sum n$$

or
$$\frac{RT}{v} = \frac{p}{\sum n}$$

This gives
$$p_1 = \tfrac{n_1}{\sum n} p;\, p_2 = \tfrac{n_2}{\sum n} p;\, p_3 = \tfrac{n_3}{\sum n} p \text{ and so on}$$

or
$$p_1 = C_1 p;\, p_2 = C_2 p;\, p_3 = C_3 p \text{ and so on}$$

where C_1, C_2, C_3 …… are concentrations of gases 1, 2, 3…, respectively.

Hence, the entropy of the mixture is

$$S = \sum n_1 \left(C_{v_1} \log_e T + R \log_e \frac{T_1}{C_1 p} + k_1 \right) \tag{9.34}$$

9.10.8 Changes of Entropy in Spontaneous Processes

We have seen that all spontaneous processes are irreversible. Accordingly in all such processes, there must be an increase of entropy. We proceed to illustrate this by some examples:

(a) *Expansion of gas into vacuum*. The entropy of *n* moles of a perfect gas is given by Eq. 9.31

$$S = n\left(C_v \log_e T + R \log_e v + c\right)$$

Let the volume of the gas before and after expansion be v_1 and v_2, respectively. By Gay Lussac's experiment, there is no change of temperature after expansion. Let S_1 and S_2 be the entropies of the gas before and after expansion, then

$$S_1 = n\left(C_v \log_e T + R \log_e v_1 + c\right)$$

and
$$S_2 = n\left(C_v \log_e T + R \log_e v_2 + c\right)$$

The change of entropy is

$$S_2 - S_1 = nR \log_e \frac{v_2}{v_1} \tag{9.35}$$

Since $v_2 > v_1$, the right hand side of Eq. 9.35 must be positive. So, S_2 must be grater than S_1.

(b) *Change of entropy due to diffusion*. Diffusion is a spontaneous process. Let n_A and n_B moles of two perfect gases *A* and *B* initially at the same temperature *T* and at the same pressure *p* be separated by a porous partition. They will diffuse into one another. Let C_{vA} and C_{vB} be the specific heats of these gases at constant volume. Then, the entropy of the gases A and B before diffusion is given by Eq. 9.32.

$$S_1 = n_A \left[C_{vA} \log_e T + R \log_e \left(\frac{T}{p} \right) + k_A \right]$$

$$+n_B\left[C_{vB}\log_e T+R\log_e\left(\frac{T}{p}\right)+k_B\right]$$

Let C_A and C_B be the molar concentrations of the two gases after complete diffusion. The two gases after diffusion will evidently be at the same pressure p. Then, the entropy of the mixture is given by Eq. 9.34.

$$S_2=n_A\left[C_{vA}\log_e T+R\log_e\left(\frac{T}{pC_A}\right)+k_A\right]$$

$$+n_B\left[C_{vB}\log_e T+R\log_e\left(\frac{T}{pC_B}\right)+k_B\right]$$

Hence, the change of entropy by diffusion is

$$S_2-S_1=R\left[n_A\log_e\left(\frac{T}{pC_A}\right)+n_B\log_e\left(\frac{T}{pC_B}\right)\right]$$

$$-R\left[n_A\log_e\left(\frac{T}{p}\right)+n_B\log_e\left(\frac{T}{p}\right)\right]$$

or

$$S_2-S_1=R\left[n_A\log_e\left(\frac{1}{C_A}\right)+n_B\log_e\left(\frac{1}{C_B}\right)\right] \tag{9.36}$$

All the quantities on the right hand side of Eq. 9.36 are necessarily positive. Hence, S_2 must be grater than S_1.

(c) *Change of entropy by equalization of temperature*. Let a quantity of heat Q flow from a body A at higher temperature T_1 to a body of B at lower temperature T_2. Then, the loss of entropy of A is (Q/T_1) and the gain of entropy B is (Q/T_2) . Hence, the gain of entropy of A and B taken together is

$$Q\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Since $T_1 > T_2$, there is a positive gain of entropy. The spontaneous processes of conduction, convection and radiation by which equalization of temperature is effected involve flow of heat, unaltered in quantity, from one body to another. Hence in all these processes, there must be increase of entropy.

"All spontaneous changes are attended by increase of entropy and, therefore, by diminution of available energy. Hence, all changes would cease when the available energy of a system is a minimum or its entropy a maximum."

9.10.9 The Temperature–Entropy Diagram

The entropy is a very useful and important property of matter in bulk. Hence, it can be used as a thermodynamic co-ordinate for specifying the physical state of a body in the process of thermodynamic change. Entropy is, of course, a derived thermodynamic co-ordinate since it can always be expressed in terms of the fundamental co-ordinates (p, v and T).

Let ab be any portion of a curve representing the change of state of a substance in the S–T space (Fig. 9.13). The area of the shaded strip is $T\,dS$ But,

$$T\,dS = dQ$$

Hence, the whole area abcd under the curve ab is

$$\int T ds = \int dQ$$

where the integration is to extend within assigned limits.

Hence, the whole area under the curve is equal to the total quantity of heat taken in as the substance passes from the state a to the state b. For a closed cycle,

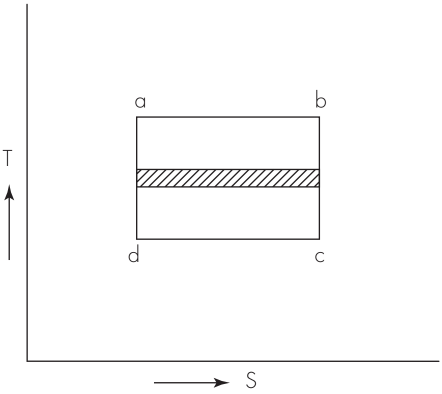


Fig. 9.13 Entropy temperature diagram

$$\oint TdS = Q_2 - Q_1$$

where Q_1 is the heat taken in and Q_2 is the heat given out. Since the substance returns to its initial state,

$$Q_1 - Q_2 = W = \text{the total work done in the cycle}$$

Hence, temperature–entropy diagram has the property in common with the p–v diagram in that the area enclosed by a curve measures the work done in a complete cycle provided the cycle is reversible.

Carnot's Cycle on the temperature–entropy diagram. In an isothermal operation, temperature remains constant.

Hence, isothermal must be parallel to S-axis in the S–T space (Fig. 9.14). Adiabatic lines must be parallel to the T-axis. Thus, Carnot's cycle bounded by two adiabatic and two isothermal lines must be a rectangle in the temperature–entropy diagram. Area of this rectangle is equal to the work done in the cyclic operation.

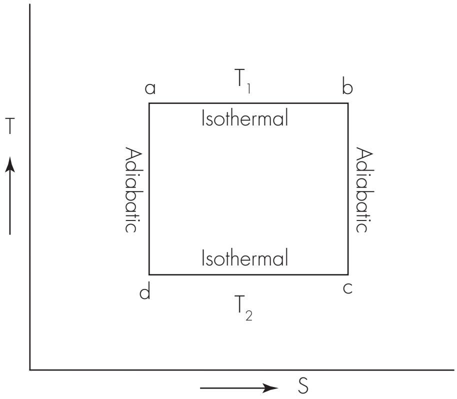


Fig. 9.14 Carnot's cycle scheme on entropy temperature diagram

9.11 CALCULATION OF EFFICIENCY OF RANKINE'S CYCLE

We shall first calculate the amount of work done. In the forward motion of the piston (AB portion of the curve in (Fig. 9.15)), a volume v_{S1} of the steam enters the cylinder at constant pressure p_1. Hence, work done in operation AB is $p_1\, v_{S1}$. In the operation CD, a volume v_{S2} of steam is forced out of the cylinder at constant pressure p_2. Hence, the total work done is $p_2 v_{S2}$. Total work done in the operations AB and CD is $(p_1 v_{S1} - p_2 v_{S2})$.

In the case of adiabatic expansions, amount of work done is equal to the change in internal energy. Let U_{S1} and U_{S2} be the internal energies of vapour in the state B and of the mixture of vapour and condensed drops in the state C. Then, the change in internal energy from state B to state C is $(U_{S1} - U_{S2})$. Hence, the total amount of work done in the operations AB, BC and CD is

$$\begin{aligned}&(U_{S1} - U_{S2}) + (p_1 v_{S1} - p_2 v_{S2})\\ &= (U_{S1} + p_1 v_{S1}) - (U_{S2} + p_2 v_{S2})\\ &= H_{S1} + H_{S2}\end{aligned}$$

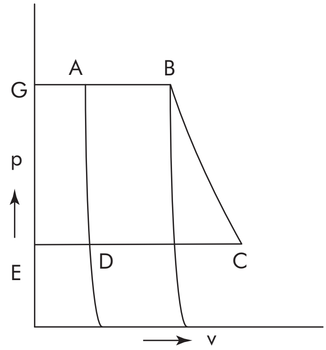


Fig. 9.15 Rankine's cycle

The work done by the auxiliary pump is to be subtracted from this. Hence, the total work done in the cycle is

$$H_{S1} + H_{S2} - (p_1 - p_2)v_w$$

Since the auxiliary pump must work in a complete cycle for the production of continuous work, this requires an additional expenditure of work represented by area ABCD = $(p_1 - p_2)v_w$ where v_w is the volume of condensed water. The cycle of operation is called the Rankine's cycle. The useful work done in the complete cycle is the area GBCE. Rankine's cycle is also an ideal cycle to which all practical cycles attempt to approach.

9.11.1 Calculation of Heat Drawn

Heat is drawn by the working substance in the transition from the state of water in the condenser at temperature T_2 and under vapour pressure of water at T_2 to the state of steam at temperature T_1 of the boiler and under pressure p_1 inside the boiler. This transition is made up of following three distinct operations:

1. Increasing the pressure of water in the condenser from p_2 to p_1 at constant volume (neglecting small change of volume due to change of pressure).
2. Increasing the temperature of water from T_2 to T_1.
3. Evaporating the mass of water at temperature T_1 and pressure p_1.

Let H_{w2} be the total heat of water in the condenser at pressure p_2 and temperature T_2. Work done in the operation (1) is $v_w(p_1 - p_2)$. Heat equivalent of this amount of work is absorbed by water so that the total heat after the stage (1) is $[H_{w2} + v_w(p_1 - p_2)]$. The operations (2) and (3) are effected at constant pressure p_1. Hence if H_{S1} is the total heat after operation (3), then the net amount of heat drawn in the operation AB is

$$H_{S1} - H_{w2} - v_w\left(p_1 - p_2\right)$$

Hence, the efficiency of Rankine's cycle is

$$\eta = \frac{H_{S1} + H_{S2} - \left(p_1 - p_2\right)v_w}{H_{S1} - H_{w2} - \left(p_1 - p_2\right)v_w}$$

Values of total heats of water and steam can be obtained from steam tables.

9.12 EFFICIENCY OF DIESEL CYCLE

9.12.1 Ideal Diesel Cycle

The ideal diesel cycle is a constant pressure cycle (Fig. 9.16).

The cycle consists of two adiabatics: AB, CD, and two constant pressure lines: AD and BC. At A, the cylinder is completely filled with air at nearly atmospheric pressure drawn along the path EA. It is then compressed adiabatically along AB. At B, the oil valve opens and the fuel is injected. It ignites and the air expands at constant pressure till the point C is reached. The oil valve is closed and the volume expands adiabatically along CD. At D, the exhaust valve opens and pressure drops to atmospheric pressure. The spent charge then flows into the atmosphere along AE.

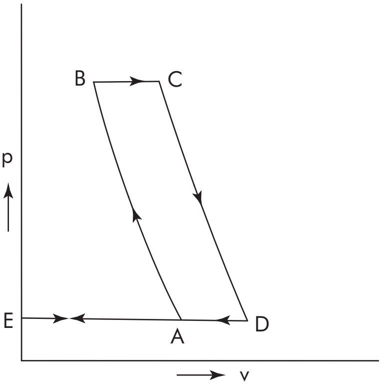


Fig. 9.16 Ideal diesel cycle

We shall suppose that the work done along EA and AE balance one another.

Let v_A, v_B, v_C and v_D be the volumes at A, B, C and D, respectively; and let T_A, T_B, T_C and T_D be the corresponding temperatures. The characteristics of the different operations are tabulated in Table 9.3.

Work done during the cycle = total heat entry

$$= C_p\left[(T_C - T_B) - (T_D - T_A)\right]$$

$$\text{Efficiency} = \qquad \eta = \frac{C_p\left[(T_C - T_B) - (T_D - T_A)\right]}{C_p(T_C - T_B)}$$

$$= 1 - \frac{T_D - T_A}{T_C - T_B}$$

$$\text{Now,} \qquad \left.\begin{aligned} v_A^{\gamma-1} T_A &= v_B^{\gamma-1} T_B \\ v_D^{\gamma-1} T_D &= v_C^{\gamma-1} T_C \end{aligned}\right\} \qquad \therefore \left(\frac{v_A}{v_D}\right)^{\gamma-1} \frac{T_A}{T_D} = \left(\frac{v_B}{v_C}\right)^{\gamma-1} \frac{T_B}{T_C}$$

Table 9.3 Characteristics of different operations of ideal diesel cycle

Temperature	Path of change	Heat entry	Work done by
Rising from T_A to T_B	AB	0	$-C_p(T_B - T_A)$
Rising from T_B to T_C	BC	$C_p(T_C - T_B)$	$p_B(v_C - v_B)$
Falling from T_C to T_D	CD	0	$C_P(T_C - T_D)$
Falling from T_D to T_A	DA	$-C_v(T_D - T_A)$	$p_D(v_D - v_A)$

Since AD and BC are constant pressure lines,

$$\left.\begin{aligned}\frac{v_A}{v_D} &= \frac{T_A}{T_D}\\ \frac{v_B}{v_C} &= \frac{T_B}{T_C}\end{aligned}\right\} \quad \frac{T_A}{T_D} = \frac{T_B}{T_C} \text{ or } \frac{T_D}{T_C} = \frac{T_A}{T_B} = \frac{T_D - T_A}{T_C - T_B}$$

Hence, efficiency $\qquad \eta = 1 - \dfrac{T_A}{T_B} = 1 - \left(\dfrac{v_B}{v_A}\right)^{\gamma - 1} = 1 - \left(\dfrac{1}{r}\right)^{\gamma - 1}$

calling $\qquad r = \dfrac{v_A}{v_B}$

Hence, efficiency = 1 − (ratio of temperatures at the beginning and at the end of adiabatic compression)

9.12.2 Actual Diesel Cycle

Consideration of mechanical simplicity makes it impossible to carry the expansion CD right down to the atmospheric pressure (the former cycle requires a very large volume for the cylinder) and in actual diesel engine, the exhaust valve opens earlier. Under the condition, the indicator diagram is shown in Fig. 9.17. The characteristics of successive operations in the cycle are tabulated in Table 9.4.

Hence, work done = total heat entry

$$= C_p\,[(T_c - T_B) - C_v(T_D - T_A)]$$

Efficiency $\quad = \eta = \dfrac{C_p[(T_C - T_B) - C_v(T_D - T_A)]}{C_p(T_C - T_B)}$

$$= 1 - \frac{C_v(T_D - T_A)}{C_p(T_C - T_B)} = 1 - \frac{T_D - T_A}{\gamma(T_C - T_B)}$$

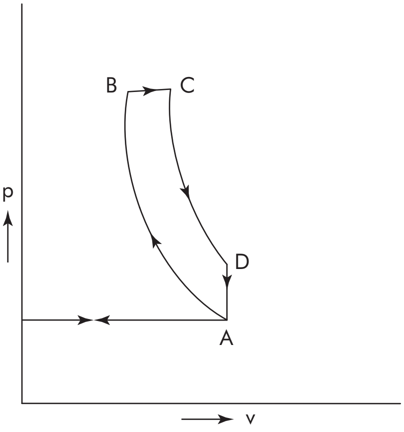


Fig. 9.17 Actual diesel cycle

Table 9.4 Characteristics of successive operations of actual diesel cycle

Temperature	Path of change	Heat entry	Work done by
Rising from T_A to T_B	AB	0	$-C_v(T_B - T_A)$
Rising from T_B to T_C	BC	$C_p(T_C - T_B)$	$p_B(v_C - v_B)$
Falling from T_C to T_D	CD	0	$C_v(T_C - T_D)$
Falling from T_D to T_A	DA	$-C_v(T_D - T_A)$	0

This result is usually expressed in terms of volume changes. Thus, let

$$\frac{V_A}{V_B} = r \quad \text{and} \quad \frac{V_C}{V_B} = \rho$$

Since the points A and B lie on the same adiabatic,

$$v_A^{\gamma-1} T_A = v_B^{\gamma-1} T_B$$

or
$$T_B = \left(\frac{v_A}{v_B}\right)^{\gamma-1} T_A = r^{\gamma-1} T_A$$

Since the pressure at B and C is same,

$$\frac{T_C}{T_B} = \frac{v_C}{v_B} = \rho \qquad T_C = \rho\ T_B = \rho r^{\gamma-1} T_A$$

Also,
$$v_D^{\gamma-1} T_D = v_C^{\gamma-1} T_C$$

and
$$v_A^{\gamma-1} T_A = v_B^{\gamma-1} T_B$$

Hence,
$$\left(\frac{v_D}{v_A}\right)^{\gamma-1} \frac{T_D}{T_A} = \left(\frac{v_C}{v_B}\right)^{\gamma-1} \frac{T_C}{T_B}$$

But,
$$v_D = v_A$$

Hence,
$$\frac{T_D}{T_A} = \rho^{\gamma-1} \frac{T_C}{T_B} = \rho^{\gamma-1} \rho = \rho^{\gamma}$$

$$T_D = \rho^{\gamma} T_A$$

Substituting the values of T_C, T_D and T_B in terms of T_A,

We get efficiency
$$= 1 - \frac{\rho^{\gamma} T_A - T_A}{\gamma\left(\rho r^{\gamma-1} T_A - r^{\gamma-1} T_A\right)}$$

$$= 1 - \frac{T_A\left(\rho^{\gamma} - 1\right)}{\gamma r^{\gamma-1} T_A \left(\rho - 1\right)}$$

$$= 1 - \left[\frac{\left(\rho^{\gamma} - 1\right)}{\gamma\left(\rho - 1\right)}\right] \frac{1}{r^{\gamma-1}}$$

If ρ is very small,

efficiency $\eta = 1 - \frac{1}{\gamma}\left(\frac{1}{r}\right)^{\gamma-1}$

9.13 EFFICIENCY OF OTTO CYCLE

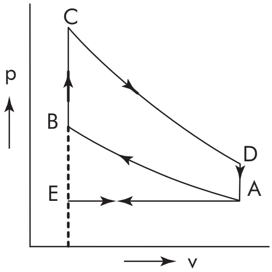


Fig. 9.18 Otto cycle

The indicator diagram for an Otto cycle is as shown in Fig. 9.18. It may be assumed that the work done in filling the cylinder with charge represented by EA and that of exhausting the cylinder along AE balance each other.

We shall represent the volumes and temperatures at points A, B, C, D by V_A, V_B, V_C, V_D and T_A, T_B, T_C, T_D, respectively.

Table 9.5 gives full description of the different operations.

The work done by the engine in one cycle is

$$= C_v\left[(T_C - T_D) - (T_B - T_A)\right] = C_v\left[(T_C - T_B) - (T_D - T_A)\right]$$

$$= C_v(T_C - T_B)\left[1 - \frac{T_D - T_A}{T_C - T_B}\right]$$

In the indicator diagram,

$$\left.\begin{aligned} v_D &= v_A \\ v_C &= v_B \end{aligned}\right\} \quad \frac{v_A}{v_B} = \frac{v_D}{v_C} = \rho$$

Further since the points C and D are on the same adiabatic,

$$v_C^{\gamma-1} T_C = v_D^{\gamma-1} T_D$$

Since B and A are on the same adiabatic,

$$v_B^{\gamma-1} T_B = v_A^{\gamma-1} T_A$$

$$\frac{T_A}{T_B} = \left(\frac{v_B}{v_A}\right)^{\gamma-1} \quad \text{and} \quad \frac{T_D}{T_C} = \left(\frac{v_C}{v_D}\right)^{\gamma-1}$$

$$\therefore \qquad \frac{T_A}{T_B} = \frac{T_D}{T_C} = \frac{T_D - T_A}{T_C - T_B}$$

Hence, the work done by the engine in one cycle is $= C_v(T_C - T_B)\left(1 - \frac{T_A}{T_B}\right)$

Table 9.5 Characteristics of different operations of Otto cycle

Temperature	Path of change	Heat entry	Work done by
Rising from T_A to T_B	AB	0	$-C_v(T_B - T_A)$
Rising from T_B to T_C	BC	$C_v(T_C - T_B)$	0
Falling from T_C to T_D	CD	0	$C_v(T_C - T_D)$
Falling from T_D to T_A	DA	$-C_v(T_D - T_A)$	0

Heat drawn by the engine is $C_v\left(T_C - T_B\right)$
Hence, the efficiency of the Otto engine is

$$\eta = \frac{\text{Work done}}{\text{Heat drawn}} = 1 - \frac{T_A}{T_B} = 1 - \left(\frac{1}{\rho}\right)^{\gamma - 1}$$

9.14 THIRD LAW OF THERMODYNAMICS

In 1906, Nernst proposed a new theorem called heat theorem derived from thermodynamic considerations supported by a series of experimental evidences on dealing with atomic heat at low temperature. Its importance is very great and, hence, it is known as the third law of thermodynamics. It states, "the heat capacities of all solids tend to zero as the absolute zero is approached and that the internal energies and entropies of all substances become equal there, approaching their common value asymptotically tending to zero." It follows neither from the 1st law, law of conservation of energy nor from the second law, law of transmutability of energy giving rise to the nature of a new law called the third law of thermodynamics, the consequence of which is that absolute zero temperature can never be attained.

SOLVED PROBLEMS

Q 1. A Carnot's engine whose low temperature reservoir is at 27 °C has an efficiency of 40%. What should be the temperature of high temperature reservoir? What should be the temperature of the latter if the efficiency is to be raised to 60%?

Ans. We know that $\eta = \frac{T_1 - T_2}{T_1}$

or $$0.4 = \frac{T_1 - 300}{T_1}$$

or $$0.4\,T_1 = T_1 - 300$$

or $$0.6T_1 = 300$$

or $$T_1 = 500\text{ K}$$

Again, $$0.6 = \frac{T - 300}{T}$$

or $0.6T = T - 300$ or $0.4T = 300, T = 750\ {}^\circ k$

Q 2. A Carnot's engine working between 0 °C and 100 °C takes up 840 joules from the high temperature reservoir. Calculate the work done, heat rejected and the efficiency.

Ans. Work done $= Q_1 - Q_2 = Q_1 - Q_1\frac{T_2}{T_1} = Q_1\frac{T_1 - T_2}{T_1}$

$$= 840\frac{373 - 273}{373} = 225 \text{ joules}$$

$$\text{Heat rejected} = Q_2 = Q_1\frac{T_2}{T_1} = \frac{840}{4.2}\frac{273}{373} = 146 \text{ calories}$$

$$\text{Efficiency} = \frac{T_1 - T_2}{T_1} = \frac{373-273}{373} = 26.8\%$$

Q 3. Liquid oxygen boils at 90 K and liquid hydrogen at 20 K. What is the efficiency of a reversible engine working between heat reservoirs at these two temperatures? If the same efficiency is required for an engine with a cold reservoir at 27 °C, what must be the temperature of the source?

Ans. Efficiency $= \dfrac{90-20}{90} = \dfrac{70}{90} = 0.77$

$$\eta = \frac{7}{9} = \frac{T-300}{T} \text{ or } 7T = 9T - 2700 \text{ or } 2T = 2700$$

$\therefore \quad T = 1350$ K

Q 4. A reversible engine works in a Carnot's cycle between the temperatures 100 °C and 0 °C. If the work done in the cycle is 1200 kilogram metres, find the quantity of heat in calories taken at higher temperatures.

Ans. Now, $\dfrac{Q_1}{T_1} = \dfrac{Q_2}{T_2} = \dfrac{Q_1 - Q_2}{T_1 - T_2} = \dfrac{W}{T_1 - T_2}$

$$Q_1 = W\frac{T_1}{T_1 - T_2} = \frac{1200\times 10^5 \times 980}{4.18\times 10^7}\frac{373}{100} = 10490 \text{ cal}$$

Q 5. Assuming that a domestic refrigerator can be regarded as a reversible engine working between the temperatures of melting ice and the room temperature of 17 °C, calculate the efficiency and the energy that must be supplied to freeze 1 kg of water already at 0 °C.

Ans. The refrigerator takes heat from a cold body and rejects heat to a hot body and does some work which is reckoned as negative.

$$\text{Efficiency} = -\frac{W}{Q} = \frac{290-273}{273} = 5.86\%$$

To freeze 1 kg of water at 0 °C, 80,000 calories of heat must be taken away from water at 273 K

$$-\frac{W}{80{,}000} = \frac{17}{273}$$

$$W = 2.092\times 10^{11} \text{ ergs}$$

Q 6. An engine works in a Carnot's cycle between the temperature 100 °C and 0 °C. Calculate the work done in the cycle in ergs, if the quantity of heat taken in at the higher temperature is 10^4 calories.

Ans. We know that $\dfrac{Q_1}{T_1} = \dfrac{Q_2}{T_2} = \dfrac{Q_1 - Q_2}{T_1 - T_2} = \dfrac{W}{T_1 - T_2}$

$$\therefore \qquad W = \frac{Q_1}{T_1}(T_1 - T_2) = \frac{10^4 \times 4.2 \times 10^7 \times 100}{373}\,\text{ergs}$$

$$= 1.1 \times 10^{11}\ \text{ergs}$$

Q 7. A Carnot's engine develops 100 h.p and operates between 27 °C and 227 °C. What is the heat supplied? What is the heat rejected? What is its thermal efficiency?

Ans. Thermal efficiency $= 1 - \dfrac{T_2}{T_1} = 1 - \dfrac{Q_2}{Q_1}$

$$= 1 - \frac{300}{500} = 0.4 = 40\%$$

Power developed by the engine = 100 h.p

$$= 100 \times 746\ \text{watts} = \frac{100 \times 746}{4.2}\ \text{calories/sec}$$

If Q_1 is the heat supplied, then

$$Q_1 = \frac{100 \times 746}{4.2} \times \frac{100}{40}\ \text{cal/sec} = 4.44 \times 10^4\ \text{cal/sec}$$

Again,
$$1 - \frac{Q_2}{Q_1} = 0.4$$

$$\frac{Q_2}{Q_1} = 1 - 0.4 = 0.6$$

$$Q_2 = Q_1 \times 0.6 = 4.44 \times 10^4 \times 0.6 = 2.66 \times 10^4\ \text{cal/sec}$$

Q 8. A Carnot's cycle is performed by a litre of air ($\gamma = 1.4$) initially at 327 °C and at a pressure of 12 atmospheres. Each stage represents a compression or expansion in the ratio 1:6. Calculate the lowest temperature, net work delivered and efficiency of the cycle.

Ans. The lowest temperature will be reached by adiabatic expansion. To calculate the lowest temperature, we use the relation

$$T_1 v_1^{\gamma - 1} = T_2 v_2^{\gamma - 1}$$

or
$$T_2 = T_1 \left(\frac{v_1}{v_2}\right)^{\gamma - 1} = \frac{600}{6^{0.4}} = 293\ \text{K}$$

Work is done in following four stages:

1. Work done by the gas in isothermal expansion at $T_1 = R'T_1 \log_e(v_2 / v_1)$

2. Work done by the gas in adiabatic expansion $= R'(T_1 - T_2)/\gamma - 1$

3. Work done on the gas in isothermal compression $= R'T_2 \log_e(v_2 / v_1)$.

4. Work done on the gas in adiabatic compression $= R'(T_1 - T_2)/\gamma - 1$

Net work done by the gas

$$W = R'T_1 \log_e \frac{v_2}{v_1} + \frac{R'(T_1 - T_2)}{\gamma - 1} - R'T_2 \log_e \frac{v_2}{v_1} + \frac{R'(T_1 - T_2)}{\gamma - 1}$$

$$= R'(T_1 - T_2)\log_e \frac{v_2}{v_1}$$

Again, we know that $pv = R'T$ where $p = 12$ atm, $v = 1$ litre, $T = 600$ K.

$$\therefore \qquad R' = \frac{pv}{T} = \frac{12 \times 1.013 \times 10^6 \times 10^3}{600} = 2.026 \times 10^7$$

$$W = 2.026 \times 10^7 (600 - 293) \times 2.303 \times \log_e 6$$

$$= 1.11 \times 10^{10} \text{ ergs}$$

Efficiency $\qquad = 1 - \frac{T_2}{T_1} = 1 - \frac{293}{600} = 51.2\%$

Q 9. An engine consumes 4 lbs of coal per horse power per hour. The heat developed by combustion of 1 lb of coal is capable of converting 15 lbs of water at 100 °C into steam at 100 °C. What percentage of heat produced is wasted? [Latent heat of steam 964.8 B. Th. U per lb]

Ans. The heat developed by combustion of 4 lbs of coal

$$= 4 \times 15 \times 964.8 \text{ B. Th. U} = 4 \times 15 \times 964.8 \times 778 \text{ ft lbs}$$

Work done by the engine per horse power hour $= 33000 \times 60$ ft lbs

Efficiency $= \frac{W}{Q} = \frac{33000 \times 60}{4 \times 15 \times 964.8 \times 778} = 4.3\%$

So, 4.3% of the heat is converted into work; hence, 95.7% of heat is wasted.

Q10. In a test on a gas engine, it was found that the gas consumption was 16.3 cubic feet of gas per minute when the brake horse power is 31 b.h.p. The heating value of the gas used was 500 B. Th. U per cubic feet and mechanical efficiency was 72%. What is the indicated thermal efficiency?

Ans. Mechanical efficiency $= \frac{B.H.P}{I.H.P}$

$$\therefore \qquad I.H.P = \frac{B.H.P}{M.E} = \frac{31}{0.72}$$

Input power $= 16.3 \times 500 \times 778$ ft.lb.

$$= \frac{16.3 \times 500 \times 778}{33000} \text{ HP}$$

$$\text{Indicated thermal efficiency} = \frac{\dfrac{31}{0.72}}{\dfrac{16.3 \times 500 \times 778}{33000}}$$

$$= \frac{31 \times 33000}{0.72 \times 16.3 \times 500 \times 778} = 22.4\%$$

Q11. What should be horse power of a steam engine which consumes 200 lbs of coal per hour, assuming that all the heat supplied is turned into useful work? (1 lb of coal gives 12500 B. Th. U, J is equivalent to 770 ft lbs per B. Th. U).

Ans. Heat produced per hour $= 12500 \times 200\,\text{B.Th.U}$

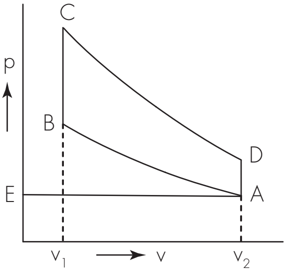
Equivalent work $= 12500 \times 200 \times 770$ ft.lb.per hr

$$\text{Horse power} = \frac{12500 \times 200 \times 770}{60 \times 33000} = 909.1$$

Q12. During the initial suction of an otto engine, the petrol vapour and air are sucked in at atmospheric pressure and temperature. If the atmospheric temperature is taken as 340 K and the temperature after the compression stroke as 612 K, calculate the adiabatic expansion ratio, assuming the ratio of specific heats at constant pressure and at constant volume to be 1.4. Hence, find the efficiency of the engine. If after the constant volume ignition, the temperature rises to 2040 K, what is the maximum pressure in the engine in atmospheres?

Ans. Let us draw the indicator diagram

From the adiabatic AB,



$$T_A V_2^{\gamma - 1} = T_B V_1^{\gamma - 1}$$

$$\therefore \quad \frac{T_A}{T_B} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{1}{\rho}\right)^{\gamma-1} = \frac{T_D}{T_C}$$

$$\therefore \quad \rho = \left(\frac{T_B}{T_A}\right)^{\frac{1}{\gamma - 1}} = \left(\frac{612}{340}\right)^{\frac{1}{0.4}} = 4.5 \text{ approx}$$

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma - 1} = 44\%$$

From the adiabatic CD, $p_C^{1-\gamma} T_C^{\gamma} = p_D^{1-\gamma} T_D^{\gamma}$ or $p_C = \left(\frac{T_D}{T_C}\right)^{\frac{\gamma}{1-\gamma}} p_I$

From AD, $\frac{p_D v_2}{T_D} = \frac{p_A v_2}{T_A}$ or $p_D = \frac{T_D}{T_A} p_A$

$$\therefore \qquad p_C = \left(\frac{T_D}{T_C}\right)^{\frac{\gamma}{1-\gamma}} \frac{T_D}{T_A}\, p_A = \rho^{\gamma}\, \frac{T_C}{T_B}\, p_A$$

$$= (4.5)^{1.4}\, \frac{2040}{612} = 27 \text{ atmospheres}$$

Q13. In an engine of constant pressure ignition type, the temperatures at the beginning and at the end of the ignition are 915 K and 2040 K, respectively and the adiabatic expansion ratio is 12.6 . Calculate the efficiency of the engine. ($\gamma = 1.39$)

Ans. $\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma - 1} \frac{x^{\gamma} - 1}{\gamma(x-1)}$ where $\rho = 12.6$ and $x = \frac{2040}{915} = 2.23$

$$= 1 - \left(\frac{1}{12.6}\right)^{0.39} \frac{(2.23)^{1.39} - 1}{1.39(2.23 - 1)} = 0.554$$

Q14. The expansion ratio of a diesel engine is 15 and to start with the compression stroke, it contains air at 15 lb/sq. inch and 520 K. Calculate the pressure and temperature at the end of the stroke.

Ans. $p_1 = 15\,\text{lb/sq.inch},\ v_1/v_2 = 15,\ T_1 = 520\text{ K}$

Now, $\qquad p_1 v_1^{\gamma} = p_2 v_2^{\gamma}$

$$p_2 = p_1\left(\frac{v_1}{v_2}\right)^{\gamma} = 15(15)^{1.4} = 15^{2.4} = 664.6\,\text{lb/in}^2$$

and from $\qquad T_1 v_1^{\gamma - 1} = T_2 v_2^{\gamma - 1}$

$$T_2 = T_1\left(\frac{v_1}{v_2}\right)^{\gamma - 1} = 520(15)^{0.4} = 1536\text{ K}$$

PROBLEMS

1. Calculate the efficiency of Carnot's engine working between 100 °C and 0 °C.

Ans. 26.8%

2. A Carnot's engine is operated in the reverse direction as a refrigerator between 300 K and 450 K. If it receives 1000 calories of heat from the reservoir at 300 K, what is the amount of heat delivered at 450 K.

Ans.1500 calories

3. A Carnot's engine has a low temperature reservoir at 7 °C with efficiency of 40%. It is desired to increase the efficiency to 50%. By how many degrees should the temperature of the high temperature reservoir be increased?

   Ans. 93.3 °C

4. An engine works in a Carnot's cycle between 27 °C and 127 °C and the work output per cycle is 300 kgm-meters. Calculate the heat supplied to the engine from the source.

   Ans. 2803 calories

5. A Carnot's engine has a low temperature reservoir at 12 °C and has an efficiency of 40%. It is desired to increase the efficiency to 60%. By how many degree centigrade should the temperature of the reservoir at the higher temperature be increased?

   Ans. 237.5 °C

6. An engine works in a Carnot's cycle between the temperatures 100 °C and 15 °C. If the work done in the cycle is 400 kgm-meters, how much heat measured in calories is taken in at the upper temperatures?

   Ans. 4.1×10^3 calories

7. Calculate the efficiency of a reversible heat engine working between the temperatures 167 °C and 57 °C.

   Ans. 25%

8. A Carnot's engine works between temperatures 100 °C and 10 °C. Calculate its efficiency. When will its efficiency be 100%?

   Ans. 24.13%, $T_2 = 0$ K

9. A Carnot's engine whose hot body temperature is 227 °C takes 200 calories of heat at this temperature and rejects 150 calories to the cold body. What is the temperature of the latter?

   Ans. 102 °C

10. Heat supplied to a Carnot's engine working between 0 °C and 100 °C is 1000 calories. How much useful work can be done by the engine?

    Ans. 268 calories

11. Calculate the efficiency of a diesel engine for which the adiabatic compression ratio $r = 17$, the adiabatic expansion ratio $e = 5$. and $\gamma = 1.4$

    Ans. 50%

12. An engine works in a Carnot's cycle between the temperatures 100 °C and 10 °C. If the work done in the cycle is 1000 kgm-meters, find how much heat measured in calories is taken in at the higher temperature?

    Ans. 9680 cal

13. A Carnot's engine with sink at 10 °C has an efficiency of 30%. By how many degrees the temperature of the source should be changed to increase its efficiency to 50%?

    Ans. 162 K

QUESTIONS

1. Give the enunciation of the second law of thermodynamics as given by Clausius as well as by Kelvin. Show that the two actually mean the same thing.
2. Explain the terms: reversible process and reversible cycle. Describe Carnot's cycle. Is the efficiency of the Carnot's cycle dependent on the nature of the working substance?
3. Describe a Carnot's engine. Draw the p-v indicator diagram for a cycle of its operations between two given temperatures and deduce from it the thermal efficiency of the engine.
4. State and explain the significance of the second law of thermodynamics. Show that the efficiency of a reversible engine is maximum.
5. Show that no engine can be more efficient than the reversible Carnot's engine.
6. How did Kelvin arrive at the absolute scale of temperature? Show that the ideal gas scale and the absolute scale are identical. How is the absolute scale realized in practice?
7. Define entropy. What is its physical significance? Show that entropy remains constant in a reversible process and increases in an irreversible process.
8. Derive an expression for the change of entropy of a gm molecule of a gas during an isothermal expansion.
9. Explain the concept of reversible and irreversible process. Show that the efficiency of a reversible engine is a maximum.
10. Show that the second law of thermodynamics enables us to define a scale of temperature independent of the properties of any working substances. How is the scale realised in practice?
11. Describe a Diesel engine and deduce an expression for its efficiency. Can the Carnot's engine be realized in practice?
12. Describe with diagrams an Otto engine and deduce an expression for its efficiency.

Chapter 10

THERMODYNAMIC RELATIONS

10.1 Maxwell's Relations

The two fundamental principles of thermodynamics are as follows:

1. The first law of thermodynamics represented by the energy equation

$$dQ = dU + dW \tag{10.1}$$

2. The second law of thermodynamics represented by the equation of Clausius

$$dQ = TdS \tag{10.2}$$

In these equations, the quantities U, W and S are functions of the thermodynamic co-ordinates p, v and T of which only two are independent variables. From these equations, other useful relations between the four co-ordinates p, v, T and S can be obtained. Out of these four co-ordinates, only two can vary independently. Hence, any two of these co-ordinates only can be expressed in terms of the remaining two co-ordinates. The equations thus obtained are called Maxwell's relations. We shall represent the two independent variables by x and y. They can subsequently be replaced by any two of the four co-ordinates, that is, p, v, T and S.

From Eqs 10.1 and 10.2, we get

$$T\ dS = dU + dW = dU + p\ dv$$

or

$$dU = T\ dS - p\ dv \tag{10.3}$$

Since S and v are both functions of x and y,

$$\therefore \qquad dS = \frac{\partial S}{\partial x} dx + \frac{\partial S}{\partial y} dy$$

$$dv = \frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy$$

Substituting the values of dS and dv in Eq. 10.3,

$$dU = T\left(\frac{\partial S}{\partial x} dx + \frac{\partial S}{\partial y} dy\right) - p\left(\frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy\right)$$

$$= \left(T\frac{\partial S}{\partial x} - p\frac{\partial v}{\partial x}\right)dx + \left(T\frac{\partial S}{\partial y} - p\frac{\partial v}{\partial y}\right)dy$$

Since U is a function of x and y,

$$dU = \frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial y} dy$$

Hence,

$$\frac{\partial U}{\partial x} = T\frac{\partial S}{\partial x} - p\frac{\partial v}{\partial x}$$

and

$$\frac{\partial U}{\partial y} = T\frac{\partial S}{\partial y} - p\frac{\partial v}{\partial y}$$

Since U is a function of x and y,

$$\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)$$

or

$$\frac{\partial}{\partial y}\left(T\frac{\partial S}{\partial x} - p\frac{\partial v}{\partial x}\right) = \frac{\partial}{\partial x}\left(T\frac{\partial S}{\partial y} - p\frac{\partial v}{\partial y}\right)$$

or

$$\frac{\partial T}{\partial y}\frac{\partial S}{\partial x} + T\frac{\partial^2 S}{\partial y \partial x} - \frac{\partial p}{\partial y}\frac{\partial v}{\partial x} - p\frac{\partial^2 v}{\partial y \partial x}$$

$$= \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} + T\frac{\partial^2 S}{\partial x \partial y} - \frac{\partial p}{\partial x}\frac{\partial v}{\partial y} - p\frac{\partial^2 v}{\partial x \partial y}$$

or

$$\frac{\partial T}{\partial y}\frac{\partial S}{\partial x} - \frac{\partial p}{\partial y}\frac{\partial v}{\partial x} = \frac{\partial T}{dx}\frac{\partial S}{\partial y} - \frac{\partial p}{\partial x}\frac{\partial v}{\partial y} \qquad (10.4)$$

From Eq. 10.4, we can deduce some important relations by substituting for x and y any two of the variables S, p, T and v.

Relation I: Let $x = S$ and $y = v$

Then, $$\frac{\partial S}{\partial x} = 1 \quad \text{and} \quad \frac{\partial v}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0 \quad \text{and} \quad \frac{\partial v}{\partial x} = 0 \ \text{ since } x \text{ and } y \text{ are independent.}$$

Substituting the values in Eq. 10.4, we get

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial S}\right)_v \tag{10.5}$$

or $$-\left(\frac{\partial T}{\partial v}\right)_s = T\left(\frac{\partial p}{\partial Q}\right)_v \tag{10.6}$$

Equation 10.6 means that the fall of temperature per unit increase of volume during an adiabatic transformation is equal to the increase of pressure per unit increase of entropy at constant volume.

Relation II: Let $x = T$ and $y = v$

Then, $$\frac{\partial T}{\partial x} = 1 \quad \text{and} \quad \frac{\partial v}{\partial y} = 1$$

Also, $$\frac{\partial T}{\partial y} = 0 \quad \text{and} \quad \frac{\partial v}{\partial x} = 0$$

Substituting these values in Eq. 10.4, we get

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \tag{10.7}$$

or $$\left(\frac{\partial Q}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v \tag{10.8}$$

This means that the change of entropy per unit change of volume at constant temperature is equal to the change of pressure per unit change of temperature at constant volume. It may also be interpreted as shown in Eq. 10.8—latent heat of isothermal expansion at temperature T is equal to the absolute temperature multiplied by change of pressure per unit change of temperature at constant volume.

Let L be the latent heat required to change unit mass of the substance from state 1 to state 2, and let v_1 and v_2 be the specific volumes in the two states; then,

$$\left(\frac{\partial Q}{\partial v}\right)_T = \frac{L}{v_2 - v_1}$$

Hence, Eq. 10.8 may be written as

$$\frac{L}{v_2 - v_1} = T\left(\frac{\partial p}{\partial T}\right)_v \tag{10.9}$$

If the change of state takes place in such a way that pressure is independent of volume (as in the case of saturated vapours), then the suffix v in Eq. 10.9 may be omitted so that Eq. 10.9 may be written as

$$\frac{L}{v_2 - v_1} = T\frac{\partial p}{\partial T} \tag{10.10}$$

Equation 10.10 is known as *Clapeyron's equation*.

Relation III: Let $x = p$ and $y = S$

Then, $$\frac{\partial p}{\partial x} = 1 \quad \text{and} \quad \frac{\partial S}{\partial y} = 1$$

Also, $$\frac{\partial p}{\partial y} = 0 \quad \text{and} \quad \frac{\partial S}{\partial x} = 0$$

Substituting these values in Eq. 10.4, we get

$$\left(\frac{\partial v}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \tag{10.11}$$

or $$T\left(\frac{\partial v}{\partial Q}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \tag{10.12}$$

This means that the increase of temperature per unit increase of pressure in an adiabatic change is equal to the absolute temperature multiplied by change of volume due to unit quantity of heat supplied to the substance at constant pressure.

Relation IV: Let $x = T$ and $y = P$

Then, $$\frac{\partial T}{\partial x} = 1 \quad \text{and} \quad \frac{\partial p}{\partial y} = 1$$

Also, $$\frac{\partial T}{\partial y} = 0 \quad \text{and} \quad \frac{\partial p}{\partial x} = 0$$

Substituting these values in Eq. 10.4, we get

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \tag{10.13}$$

Now, the co-efficient of thermal expansion at constant pressure is

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

Hence, Eq. 10.13 can be written as

$$\left(\frac{\partial Q}{\partial p}\right)_T = -Tv\alpha \tag{10.14}$$

This means that in the case of substance which expands on being heated (α is positive), increase of pressure is accompanied by evolution of heat so that the heat must be taken away to keep the temperature constant.

Water below 4 °C diminishes in volume with rise of temperature (α is negative) while above 4 °C, it increases in volume with rise of temperature (α is positive). Hence below 4 °C, increase of pressure will be accompanied by cooling while above 4 °C increase of pressure would produce heating effect. This result was verified by Joule.

Rubber contracts on being heated. So for rubber, α is negative. Tension is negative pressure. Hence, putting a wire under tension or pulling it is equivalent to reduction of pressure. Hence, a rubber cord would show a fall of temperature on being pulled. Metallic wires under similar conditions would show heating effect.

10.1.1 Gibb's Heat Functions

1. *Free energy*: By combining the first and the second law of thermodynamics, we have obtained

$$dU = TdS - pdv \quad \text{Eq. (10.3)}$$

Subtracting $d(T\,S)$ from both sides of the above equation, we get

$$dU - d(T\,S) = TdS - p\,dv - d(T\,S)$$

or

$$d(U - T\,S) = T\,dS - p\,dv - T\,dS - S\,dT$$

Calling $U - T\,S = F$, this becomes

$$dF = -p\,dv - S\,dT \tag{10.15}$$

The function F is called the free energy.

2. *Enthalpy or Total Heat*: Adding $d(p\,v)$ to both sides of Eq. 10.3, we get

$$dU + d(p\,v) = TdS - pdv + d(p\,v)$$

or

$$d(U + pv) = TdS - pdv + pdv + vdp$$

Calling $U + pv = H$, the above equation reduces to

$$dH = T\,dS + v\,dp \tag{10.16}$$

The function H is called the enthalpy or free energy.

Thermodynamic potential: Performing both the above operations on Eq. 10.3, we get

$$dU - d(T\,S) + d(p\,v) = TdS - pdv - d(T\,S) + d(p\,v)$$

$$= TdS - pdv - TdS - SdT + pdv + vdp$$

or

$$d(U - ST + pv) = -SdT + vdp$$

calling

$$U - ST + pv = G,$$

we have

$$dG = -SdT + vdp \tag{10.17}$$

The function G is called the thermodynamical potential.

10.1.2 Alternative Method of Deduction of Maxwell's Relations

We have already proved that dS is a perfect differential. All the quantities of which dF, dH and dG composed are also perfect differentials. Hence, dF, dH and dG are also perfect differentials.

From Eq. 10.3, we at once obtain

$$\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_v$$

This is the first Maxwellian relation.

From Eq. 10.15 since dF is a perfect differential,

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T$$

This is the second Maxwellian relation.

From Eq. 10.16, since dH is a perfect differential,

$$\left(\frac{\partial T}{\partial p}\right)_v = \left(\frac{\partial v}{\partial S}\right)_p$$

This is the third Maxwellian relation.

From Eq. 10.17, since dG is a perfect differential,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

This is the fourth Maxwellian relation.

10.2 RELATION BETWEEN THE THERMODYNAMIC FUNCTIONS

In Eq. 10.15, F is a function of v and T; hence,

$$dF = \left(\frac{\partial F}{\partial v}\right)_T dv + \left(\frac{\partial F}{\partial T}\right)_v dT$$

By Eq. 10.15, $dF = -pdv - SdT$

Hence, $$p = -\left(\frac{\partial F}{\partial v}\right)_T \quad \text{and} \quad S = -\left(\frac{\partial F}{\partial T}\right)_v \tag{10.18}$$

Again, H is a function of S and p. Hence,

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

By Eq. 10.16, $dH = TdS + vdp$

Hence, $$T = \left(\frac{\partial H}{\partial S}\right)_p \quad \text{and} \quad v = \left(\frac{\partial H}{\partial p}\right)_S \tag{10.19}$$

G is a function of T and p. Hence,

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

By Eq. 10.17, $dG = -SdT + vdp$

Hence, $$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad \text{and} \quad v = \left(\frac{\partial G}{\partial p}\right)_T \tag{10.20}$$

Now, $$F = U - TS$$

or $$U = F + TS$$

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_v \text{ from Eq. 10.18.} \tag{10.21}$$

Equation 10.21 is called Gibb's Helmholtz equation.

Again, $$H = U + pv$$

or $$U = H - pv$$

$$U = H - p\left(\frac{\partial H}{\partial p}\right)_S \text{ from Eq. 10.19} \tag{10.22}$$

Further, $$G = (U - TS) + pv = H - TS$$

$$H = G + TS$$

$$H = G - T\left(\frac{dG}{dT}\right)_p \text{ from Eq. 10.20.} \tag{10.23}$$

Conditions of possibility of a transformation: Equations 10.3 and 10.15–10.17 relate only to isolated systems undergoing thermodynamic changes; that is, it includes all members which take part in the process of exchange of energy. In most of the physical and chemical processes with which we have to deal, the exchange of energy occurs between a system and its surroundings. To deal with such cases, we have to regard the system under consideration and that external to it as one isolated system.

Let S_i and S_e stand for entropies of the system under consideration and of that external to it. Then considering the two as one isolated system,

$$d(S_i + S_e) \geq 0$$

The sign of equality applies when the process is reversible and inequality sign holds only for irreversible processes. In an infinitesimally small change of thermodynamic state, let the internal system absorb dQ quantity of heat supplied by the surroundings and thereby do an amount of work dW on the surroundings. If, thereby, the internal energy of the given system increases by amount dU, then by the first law of thermodynamics,

$$dU_i = dQ - dW$$

We may, without any loss of generality, assume that the exchange of energy with the surroundings takes place reversibly. Then, the change of entropy of the surroundings would be

$$dS_e = -\frac{dQ}{T} = -\frac{dU_i + pdv}{T}$$

writing $dW = pdv$

Then, the total change of entropy of the systems taken as a whole is

$$dS_i = -\frac{dU_i + pdv}{T} \geq 0$$

or
$$dS_i \geq \frac{dU_i + pdv}{T}$$

or
$$TdS_i \geq dU_i + pdv \text{ or } dU_i + pdv \leq TdS_i$$

$$dU_i \leq TdS_i - pdv$$

We shall, for the sake of convenience, drop the subscript *i* and write the equation for the given internal system simply as

$$dU \leq TdS - pdv \tag{10.24}$$

U and *S* referring only to the internal system.

When a system is not isolated, spontaneous processes can take place between the system and the surroundings. Such processes, as we know, are irreversible. Hence, Eqs 10.24 to 10.26 give the conditions of possibility of a transformation.

The above result can be deduced otherwise as follows:

Let a system pass from the state *A* (Fig. 10.1) to the state *B* along the reversible path *AMB*. Along the path, the quantity *dQ*/*T* is a perfect differential so that

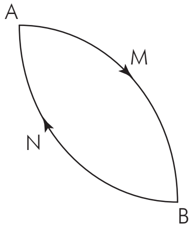


Fig. 10.1 Behaviour of a system

$$\left(\int_A^B \frac{dQ}{T}\right)_R = S_B - S_A$$

Let the same system be brought back to the state *A* along the irreversible path *BNA*. Along the path, the quantity *dQ*/*T* is not a perfect differential and cannot be evaluated. The whole cycle *AMBNA* being irreversible,

$$\left(\int_B^A \frac{dQ}{T}\right)_I + \left(\int_A^B \frac{dQ}{T}\right)_R = \left(\int_B^A \frac{dQ}{T}\right)_I + \left(S_B - S_A\right) > 0$$

or
$$\left(\int \frac{dQ}{T}\right)_I > S_A - S_B \tag{10.25}$$

or
$$\left(\int \frac{dQ}{T}\right)_I < S_B - S_A$$

Since the spontaneous processes are irreversible, we conclude that no spontaneous change is possible for which the value of the integral is greater than ($S_B - S_A$). Hence, the condition of possibility of a transformation is that the value of the integral is less than ($S_B - S_A$).

For an infinitesimally small change,

$$\frac{dQ}{T} < dS$$

or $$dQ < Tds \tag{10.26}$$

$$dU + pdv < TdS$$

or $$dU < TdS - pdv \tag{10.27}$$

For reversible change, $dU = TdS - pdv$

If the system is isolated, $dQ = 0$

so that $TdS > 0$

Also, from Eq. 10.25 if $dQ = 0$

$$S_B > S_A$$

Hence for any transformation occurring in an isolated system, the energy of the final state must always be greater than that in the initial state.

When a system is in the state of maximum entropy consistent with its energy, it cannot undergo any further change because that would result in further increase of entropy. Hence, the state of maximum entropy is the most stable state of equilibrium.

Subtracting $d(TS)$ from both sides of Eq. 10.27, we get

$$dF < -pdv - SdT$$

Adding $d(pv)$ to both sides of Eq. 10.27, we get

$$dH < TdS + vdp$$

Performing both operators on Eq. 10.27, we get

$$dG < -SdT + vdp$$

Thus for a system which is not isolated,

$$dU \leq Tds - pdv \tag{10.28}$$

$$dF \leq -pdv - SdT \tag{10.29}$$

$$dH \leq -TdS + vdp \tag{10.30}$$

$$dG \leq -SdT + vdp \tag{10.31}$$

The signs of equality hold good for the cases of reversible operations.

10.3 SPECIFIC HEAT EQUATIONS

With the help of Maxwell relations, the fundamental equations

$$dQ = C_v\, dT + l\, dv \tag{10.32}$$

and $$dQ = C_p\, dT + l'\, dp \tag{10.33}$$

can be put in a more useful form.

From Eq. 10.32 putting $dT = 0$,

$$l = \left(\frac{dQ}{dv}\right)_T = T\left(\frac{dS}{dv}\right)_T$$

By Maxwell's relation II,

$$\left(T\frac{\partial S}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v$$

$$l = T\left(\frac{\partial p}{\partial T}\right)_v$$

Hence, Eq. 10.32 takes the following form

$$dQ = C_v\ dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \tag{10.34}$$

For a perfect gas, $T\left(\frac{dp}{dT}\right)_v = p$

Hence, $dQ = C_v dT + pdv$

Again from Eq. 10.33, putting $dT = 0$

$$l' = \left(\frac{dQ}{dp}\right)_T = T\left(\frac{dS}{dT}\right)_T$$

From Maxwell's relation IV,

$$\left(T\frac{\partial S}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p$$

Hence, Eq. 10.33 takes the following form

$$dQ = C_p\ dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \tag{10.35}$$

For a perfect gas, $pv = RT$ so that $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$

Hence, $T\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT}{p} = \frac{pv}{p} = v$

so that for a perfect gas,

$$dQ = C_p\ dT - v\ dp$$

Again, $dS = \frac{dQ}{T}$

Since dS is a perfect differential,

$$\left[\frac{\partial}{\partial v}\left(\frac{C_v}{T}\right)\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)\right]_v$$

or

$$\left(\frac{dC_v}{dv}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v \tag{10.36}$$

For a perfect gas, $pv = RT$

$$\therefore \quad \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}\left[\frac{\partial}{\partial T}\left(\frac{R}{v}\right)\right]_v = 0$$

For a perfect gas,

$$\left(\frac{\partial C_v}{\partial v}\right)_T = 0$$

or C_v does not vary with v in an isothermal change.

From Eq. 10.35,

$$dS = \frac{dQ}{T} = \frac{C_p}{T}dT - \left(\frac{\partial v}{\partial T}\right)_p dp$$

Since dS is a perfect differential,

$$\left[\frac{\partial}{\partial p}\left(\frac{C_p}{T}\right)\right]_T = -\left[\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)\right]_p$$

or

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \tag{10.37}$$

For a perfect gas, $pv = RT$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \text{ and } \left[\frac{\partial}{\partial T}\left(\frac{R}{p}\right)\right] = 0 \; \therefore \left(\frac{\partial C_p}{\partial p}\right)_T = 0$$

Hence, for a perfect gas, C_p does not change with pressure in an isothermal change.

In the case of real gases if (v T) curve at constant pressure be drawn, then C_p must diminish with increase of pressure, if the curve is concave downwards and conversely.

Between temperature 0–150 °C, $\left(\frac{dC_p}{dp}\right)_T$ is positive for nitrogen and negative for CO_2.

From Eq. 10.34,

$$\left(\frac{\partial Q}{\partial T}\right)_p = C_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$

or
$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \tag{10.38}$$

Expressing p as a function of v and T,

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT$$

putting
$$dp = 0, \left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

Substituting these values in Eq. 10.38,

$$C_p - C_v = -T\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p^2 \tag{10.39}$$

$\partial p/\partial v$ is always a negative quantity. Hence, C_p is always greater than C_v. For water, $(\partial v/\partial T)_p = 0$ at 4 °C. Hence for water at 4 °C, $C_p = C_v$.

Now, the compressibility of a substance is

$$K = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

so that
$$\left(\frac{\partial v}{\partial p}\right)_T = -Kv$$

The co-efficient of cubical expansion is three times that of linear expansion (α) and

$$3\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

so that
$$\left(\frac{\partial v}{\partial T}\right)_p = 3\alpha v$$

Substituting the values $\left(\frac{\partial v}{\partial p}\right)_T$ and $\left(\frac{\partial v}{\partial T}\right)_p$ in Eq. 10.39,

$$C_p - C_v = -T\left(-\frac{1}{Kv}\right)(3\alpha v)^2$$

or
$$C_p - C_v = \frac{9\alpha^2 vT}{K} \tag{10.40}$$

It has been proved experimentally that *v/K* is approximately constant at all temperatures. Gruneisen has shown that specific heat at constant pressure is proportional to the co-efficient of linear expansion. Hence, Eq. 10.40 can be put in the following form

$$C_p = C_v + BC_p^2T \tag{10.41}$$

where *B* is a constant characteristic of the substance and it is inversely proportional to the melting point of the substance (T_s). Hence, Eq. 10.41 reduces to

$$C_p = C_v + B_0\frac{TC_p^2}{T_s} \tag{10.42}$$

Here, B_o is a universal constant. Its value is 0.0214 deg/cal. Specific heats of solids and liquids are determined at constant pressure. Eqs 10.40 and 10.42 give the specific heats at constant volume when those at constant pressure are known.

10.3.1 Specific Heat of Saturated Vapour

For saturated vapour, Eq. 10.34 can be written as

$$\left(\frac{\partial Q}{\partial T}\right)_{sat} = C_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_{sat}$$

where the suffix sat means saturation pressure. From Amagat's curve, $(\partial p/\partial T)_v$ is positive. But, $(\partial v/\partial T)_{sat}$ is positive on the liquid line and negative on the vapour line. Hence on the vapour side, the specific heat of saturated vapour is always less than C_v. In the case of steam, it is so much as to become negative. This means that heat must be removed from the vapour as the temperature rises so that the vapour may remain saturated.

For water, the following experimental data was obtained.

t°C	Volume at constant pressure	$\left(\frac{\partial v}{\partial T}\right)_p$	$\left(\frac{\partial^2 v}{\partial T^2}\right)_p$
20	1.001738		
21	1.001949	0.000211	0.000011
22	1.002171	0.000222	0.000010
23	1.002403	0.000232	0.000010
24	1.002643	0.000242	0.000010
			Mean = 0.00001

SOLVED PROBLEMS

Q 1. The melting point of pure acetic acid is 16.6 °C and this is raised by 0.0244 °C per one atmosphere increase of pressure. If 1 gm of acetic acid occupies 0.00079 litre in the solid state and 0.00095 in the liquid state at its melting point, calculate the latent heat of fusion in work units (litre-atmosphere) per gram.

Ans.

$$\frac{L}{0.00095-0.00079}=(273+16.6)\times\frac{1}{0.0244}$$

$$L=289.6\times\frac{0.00016}{0.0244}\text{ litre-atmosphere}$$

Q 2. Calculate the change in C_p of water at 22 °C.

Ans. We know

$$\left(\frac{\partial C_p}{\partial p}\right)_T=-T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

Here, $T = 273 + 22 = 295$ K

Mean value of $\left(\frac{\partial^2 v}{\partial T^2}\right)_p=0.00001=10^{-5}$

Hence, $\left(\frac{\partial C_p}{\partial p}\right)=-295\times10^{-5}$

$\therefore$ $dC_p=-295\times10^{-5}\,dp$

$$dp = 1 \text{ atmosphere} = 10^6 \text{ C. G. S. Unit}$$

$$dC_p=-29.5\times10^2\text{ C. G. S. Unit}$$

$$=-\frac{2950}{4.2\times10^7}=-7\times10^{-5}\text{ cal/degree}$$

Q 3. Calculate the specific heat of copper at constant volume at 0 °C from the following data:

Specific volume of copper at 0 °C = 0.112 litre per degree
Coefficient of linear expansion of copper = 5.01×10^{-6}
Compressibility of copper = 8×10^{-7} per atmos.
C_p of Copper = 0.0909 cal/degree

Ans. We know

$$C_p-C_v=\frac{9\alpha^2 vT}{K}$$

Substituting the data,

$$C_p - C_v = \frac{9 \times 273 \times 0.112 \times (5.01 \times 10^{-6})^2}{8 \times 10^{-7}}$$

$$= 8.63 \text{ Atoms. cc/degree}$$

To convert this into calories per degree, we must multiply this by 0.024142. This gives for copper

$$C_p - C_v = 8.63 \times 0.024142^*$$

$$= 0.208 \text{ cal/degree}$$

$$C_v = 0.298 \text{ cal/degree}$$

Q 4. Prove that the ratio of adiabatic to isothermal elasticity is equal to the ratio of specific heat at constant pressure to that at constant volume.

Ans. Adiabatic elasticity $E_S = -V \left(\frac{\partial p}{\partial v}\right)_S$

Isothermal elasticity $E_T = -V \left(\frac{\partial p}{\partial v}\right)_T$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial p}{\partial v}\right)_S}{\left(\frac{\partial p}{\partial v}\right)_T} = \frac{\left(\frac{\partial p}{\partial T}\frac{\partial T}{\partial v}\right)_S}{\left(\frac{\partial p}{\partial S}\frac{\partial S}{\partial v}\right)_T} = \frac{\left(\frac{\partial p}{\partial T}\right)_S\left(\frac{\partial T}{\partial v}\right)_S}{\left(\frac{\partial p}{\partial S}\right)_T\left(\frac{\partial S}{\partial v}\right)_T}$$

$$= \frac{-\left(\frac{\partial S}{\partial v}\right)_p\left(\frac{\partial p}{\partial S}\right)_v}{-\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial p}{\partial T}\right)_v} \text{ by Maxwell's equations.}$$

---

* $$\frac{\text{Atmos} \times \text{litre}}{\text{degree}} = \frac{76 \times 13.6 \times 981 \times 1000}{\text{degree}} \frac{\text{dynes}}{(\text{cm})^2} \times (\text{cm})^3$$

or $$= \frac{76 \times 13.6 \times 981 \times 1000}{\text{degree}} \text{erg} = \frac{76 \times 13.6 \times 981 \times 1000}{4.2 \times 10^7} \frac{\text{cal}}{\text{degree}}$$

$$\frac{\text{Atmosphere} \times \text{cc}}{\text{degree}} = 0.024142 \frac{\text{cal}}{\text{degree}}$$

$$= \frac{\left(\frac{\partial S}{\partial v}\right)_p \left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial s}{\partial p}\right)_v} = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_v} = \frac{\left(\frac{dQ}{dT}\right)_p}{\left(\frac{dQ}{dT}\right)_v} = \frac{C_p}{C_v} = \gamma$$

Q 5. The melting point of pure acetic acid is 16.6 °C and this is raised by 0.0244 °C per 1 atmosphere increase of pressure. If 1 gm of acetic acid occupies 0.00079 litre in the solid state and 0.00095 litre in the liquid state when at its melting point, calculate the latent heat of fusion in work unit (litre-atmosphere) per gram.

Ans. We know

$$\frac{L}{v_2 - v_1} = T\left(\frac{\partial p}{\partial T}\right)_v$$

or
$$\frac{L}{0.00095 - 0.00079} = (273+16.6)\ \frac{1}{0.0244}$$

$\therefore$
$$L = \frac{289.6 \times 0.00016}{0.02414} \text{ litre-atmosphere}$$

$$= 1.896 \text{ litre-atmosphere}$$

Q 6. Determine the rate of change of saturation pressure with temperature for water at 100 °C; given latent heat of water at 100 °C = 539 cal, J = 4.2 × 10^7 ergs/cal and volume of steam formed = 1670 cc.

Ans. We know

$$\frac{L}{T(v_2 - v_1)} = \left(\frac{\partial p}{\partial T}\right)_v$$

$\therefore$
$$\frac{\partial p}{\partial T} = \frac{L}{T(v_2 - v_1)} = \frac{539 \times 4.2 \times 10^7}{373(1670-1)}\ \frac{\text{erg}}{\text{deg cc}}$$

$$= 3.64 \times 10^4\ \frac{\text{erg}}{\text{deg cc}} = \frac{3.64 \times 10^4}{13.6 \times 981} \text{ cm of mercury}$$

$$= 2.7 \text{ cm of mercury}$$

Q 7. Water boils at 100.5 °C and 99.5 °C when the atmospheric pressures are 77.371 and 74.650 cm of Hg, respectively. Calculate the volume of a gram of steam at 100 °C, the latent heat being 537 cal/gm.

Ans. We know

$$\frac{L}{T\left(v_2 - v_1\right)} = \left(\frac{\partial p}{\partial T}\right)_v$$

$$\therefore \qquad (v_2 - v_1) = \frac{L}{T\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_v} = \frac{537 \times 4.2 \times 10^7}{373(77.321 - 74.650) \times 13.6 \times 981}$$

$$= \frac{537 \times 4.2 \times 10^7}{373 \times 2.721 \times 13.6 \times 981} = 1666 \text{ cc}$$

$$v_2 = v_1 + 1666 \text{ cc} = 1 + 1666 \text{cc} = 1667 \text{ cc}$$

Q 8. Calculate the specific volume of the vapour of carbon tetrachloride at the boiling point from the following data: boiling point = 77 °C at 1 atmosphere, latent heat = 46 cal/gm, density of liquid = 1.6 gm/cc, dp/dT = 23 mm of Hg/degree.

Ans. We know

$$\frac{L}{T(v_2 - v_1)} = \left(\frac{\partial p}{\partial T}\right)_v$$

$$\therefore \qquad (v_2 - v_1) = \frac{L}{T\left(\frac{\partial p}{\partial T}\right)_v} = \frac{4.6 \times 4.2 \times 10^7}{(273 + 77)2.3 \times 13.6 \times 981} = 179.9 \text{ cc}$$

$$v_2 = 179.9 + \frac{1}{1.6} = 180.525 \text{ cc}$$

Q 9. Calculate the change in temperature of the boiling point of water due to a change of pressure of 1 cm of mercury (L = 536 calories, volume of 1 gm of water at 100 °C = 1 cc, volume of 1 gm saturated steam at 100 °C = 1600 cc).

Ans. We know

$$\frac{L}{T(v_2 - v_1)} = \left(\frac{\partial p}{\partial T}\right)_v$$

or

$$= \frac{536 \times 4.2 \times 10^7}{373(1600 - 1)} = \frac{1 \times 13.6 \times 981}{dT}$$

$$\therefore \qquad dT = \text{change in temperature} = \frac{373 \times 1599 \times 13.6 \times 981}{536 \times 4.2 \times 10^7} \text{ degree}$$

$$= 0.35 \text{ degree}$$

Q 10. Napthaline melts at 80 °C. The increase in specific volume is 146 cc/gm. Assuming the latent heat of fusion to be 35.6 cal/gm, find the change in the melting point per atmosphere pressure.

Ans. We know

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{L}{T(v_2 - v_1)}$$

$$\therefore \qquad dT = \frac{T(v_2 - v_1)dp}{L} = \frac{(273+80)\times 0.146\times 76\times 13.6\times 981}{35.6\times 4.18\times 10^7}$$

$$= 0.035 \text{ per atmosphere}$$

Q 11. Calculate the change in the freezing point of water at 0 °C from the following data: $L = 79.6 \times 4.18 \times 10^7$ ergs/gm. $T = 273.16$ K, $v_1 = 1.0001$ cc (specific volume of water at 0 °C) $v_2 = 1.0908$ cc (specific volume of ice at 0 °C).

Ans. We know

$$\frac{\partial p}{\partial T} = \frac{L}{T(v_2 - v_1)}$$

or

$$dT = \frac{T(v_2 - v_1)dp}{L} = \frac{273.16(1.0001 - 1.0908)\times 1.013\times 10^6}{79.6\times 4.18\times 10^7}$$

$$\text{taking } dp = 1 \text{ atmosphere} = 76\times 13.6\times 981 = 1.013\times 10^6 \frac{\text{dyne}}{\text{cm}^2}$$

$$dT = -\,0.0075\,°\text{C}$$

This shows that the melting point of ice is lowered with increase of pressure, the lowering per atmosphere being 0.0075 °C . The pressure necessary to lower the melting point by 1 °C is 133 atmospheres.

Q 12. Deduce a relation of variation of C_v with v.

Ans. We know

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v$$

From second relation,

$$\left(\frac{\partial S}{\partial v}\right)_T = t\left(\frac{\partial p}{\partial T}\right)_v$$

As dS is a perfect differential, we may write

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial v}\right) = \frac{\partial}{\partial v}\left(\frac{\partial S}{\partial T}\right)$$

$$\frac{\partial}{\partial v}(C_v) = T\frac{\partial}{\partial v}\left(\frac{\partial S}{\partial T}\right)_v = T\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial v}\right)_T = T\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)_v = T\frac{\partial^2 p}{\partial T^2}$$

Q 13. Derive a relation of variation of C_p with p.

Ans. We know

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

From fourth relation,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

As dS is a perfect differential, we may write

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)=\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)$$

So, $$\frac{\partial}{\partial p}\left(C_p\right)=T\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial T}\right)_p=T\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T=-T\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_p=-T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

Q 14. Prove that for a perfect gas, $C_p - C_v = R$.

Ans. In the case of a perfect gas, $pv = RT$

$\therefore$ $$p=\frac{RT}{v} \text{ and } v=\frac{RT}{p}$$

So, $$\left(\frac{\partial p}{\partial T}\right)_v=\frac{R}{v} \text{ and } \left(\frac{\partial v}{\partial T}\right)_p=\frac{R}{p}$$

$$C_p-C_v=T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_v=T\frac{R}{v}\frac{R}{p}=\frac{TR^2}{RT}=R$$

Q 15. Prove that for a gas obeying Van der Waals' equation, $C_p-C_v=R\left(1+\frac{2a}{RTv}\right)$.

Ans. We have $\left(p+\frac{a}{v^2}\right)(v-b)=RT$

or $$p+\frac{a}{v^2}=\frac{RT}{v-b}$$

or $$p=\frac{RT}{v-b}-\frac{a}{v^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_v=\frac{R}{v-b}$$

Again, we have $$\frac{a}{v^2}=\frac{RT}{v-b}-p$$

or $$-\frac{2a}{v^3}\left(\frac{\partial v}{\partial T}\right)_p=\frac{R}{v-b}-\frac{RT}{(v-b)^2}\left(\frac{\partial v}{\partial T}\right)_p$$

or $$\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{RT}{(v-b)^2}-\frac{2a}{v^3}\right)=\frac{R}{v-b}$$

Now, $$C_p-C_v=T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$

$$= T\left(\frac{R}{v-b}\right)\frac{\left(\frac{R}{v-b}\right)}{\frac{RT}{(v-b)^2}-\frac{2a}{v^3}} = \frac{T\frac{R^2}{(v-b)^2}}{\frac{RT}{(v-b)^2}-\frac{2a}{v^3}}$$

$$= \frac{R}{1-\frac{2a}{v^3}\frac{(v-b)^2}{RT}} = \frac{R}{1-\frac{2a}{v^3}\frac{v^2}{RT}} \quad \text{since } b \text{ is very small } (v-b)^2 \approx v^2$$

$$= \frac{R}{1-\frac{2a}{RTv}} = R\left(1-\frac{2a}{RTv}\right)^{-1} = R\left(1+\frac{2a}{RTv}\right)$$

Q 16. Prove that for a gas obeying the relation $pv = RT + Bp$, $C_p - C_v = R + 2p\ dB/dT$.

Ans. We have $\qquad pv = RT + Bp$

$$\therefore \qquad p = \frac{RT}{v} + \frac{Bp}{v}$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v} + \frac{B}{v}\left(\frac{\partial p}{\partial T}\right)_v + \frac{p}{v}\left(\frac{\partial B}{\partial T}\right)_v$$

$$\therefore \qquad \left(\frac{\partial p}{\partial T}\right)_v\left(1-\frac{B}{v}\right) = \frac{R}{v} + \frac{p}{v}\left(\frac{\partial B}{\partial T}\right)_v$$

Again, $\qquad v = \frac{RT}{p} + B$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + \left(\frac{\partial B}{\partial T}\right)_p$$

$$\therefore \qquad C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{dT}\right)_p$$

$$= T\left[\frac{R}{p} + \left(\frac{\partial B}{\partial T}\right)_p\right]\left[\frac{\frac{R}{v} + \frac{p}{v}\left(\frac{\partial B}{\partial T}\right)_v}{1-\frac{B}{v}}\right]$$

$$= T\left[\frac{R}{p} + \left(\frac{\partial B}{\partial T}\right)_p\right]\left[\frac{R + p\left(\frac{\partial B}{\partial T}\right)_v}{v-B}\right]$$

$$= T\left[R + p\left(\frac{\partial B}{\partial T}\right)_p\right]\left[\frac{R + p\left(\frac{\partial B}{\partial T}\right)_v}{p(v - B)}\right]$$

$$= \frac{T\left[R + p\left(\frac{\partial B}{\partial T}\right)_p\right]^2}{pv - Bp} = \frac{T\left[R^2 + 2pR\left(\frac{\partial B}{\partial T}\right) + p^2\left(\frac{\partial B}{\partial T}\right)^2\right]}{RT}$$

$$= \frac{TR}{RT}\left[R + 2p\left(\frac{\partial B}{\partial T}\right)\right] \text{ neglecting } p^2\left(\frac{\partial B}{\partial T}\right)^2$$

$$= R + 2p\frac{\partial B}{\partial T}$$

Q 17. Prove that $dQ = C_p\left(\frac{\partial T}{\partial v}\right)_p dv + C_v\left(\frac{\partial T}{\partial p}\right)_v dp$.

Ans. Let Q be a function of pressure and volume $Q = f(p,v)$

$$dQ = \left(\frac{\partial Q}{\partial p}\right)_v dp + \left(\frac{\partial Q}{\partial v}\right)_p dv$$

$$= \left(\frac{\partial Q}{\partial T}\right)_v\left(\frac{\partial T}{\partial p}\right)_v dp + \left(\frac{\partial Q}{\partial T}\right)_p\left(\frac{\partial T}{\partial v}\right)_p dv$$

Now, $$C_v = \left(\frac{\partial Q}{\partial T}\right)_v \text{ and } C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$

$\therefore$ $$dQ = C_v\left(\frac{\partial T}{\partial p}\right)_v dp + C_p\left(\frac{\partial T}{\partial v}\right)_p dv$$

Q 18. If dQ denotes the amount of heat absorbed in an isothermal change, prove that $dQ = (C_p - C_v)\left(\frac{\partial T}{\partial v}\right)_p dv$

Ans. Let T be a function of p and v

$$T = f(p,v)$$

$$dT = \left(\frac{\partial T}{\partial p}\right)_v dp + \left(\frac{\partial T}{\partial v}\right)_p dv$$

For an isothermal change, $dT = 0$

$\therefore$ $$\left(\frac{\partial T}{\partial p}\right)_v dp = -\left(\frac{\partial T}{\partial v}\right)_p dv$$

$$dQ = C_v\left(\frac{\partial T}{\partial p}\right)_v dp + C_p\left(\frac{\partial T}{\partial v}\right)_p dv$$

$$= C_p\left(\frac{\partial T}{\partial v}\right)_p dv - C_v\left(\frac{\partial T}{\partial v}\right)_p dv$$

$$= (C_p - C_v)\left(\frac{\partial T}{\partial v}\right)_p dv$$

Q19. Prove that the ratio of isochoric and adiabatic pressure coefficient of expansion $= \frac{\gamma}{\gamma - 1}$.

Ans. The ratio

$$\frac{\left(\frac{\partial p}{\partial T}\right)_S}{\left(\frac{\partial p}{\partial T}\right)_v} = \frac{1}{\left(\frac{\partial T}{\partial p}\right)_S\left(\frac{\partial p}{\partial T}\right)_v}$$

$$= \frac{1}{\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial S}\right)_p}$$

$$= \frac{1}{\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial T}{\partial S}\right)_p} = \frac{T\left(\frac{\partial S}{\partial T}\right)_p}{T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p}$$

$$= \frac{C_p}{C_p - C_v} = \frac{\gamma}{\gamma - 1}$$

PROBLEMS

1. If a substance of latent heat 50 melts in vacuum at 127 °C and contracts 1/10 of its bulk while melting, at what temperature will it melt at 100 atmospheres?

   Ans. 125.06 °C

2. Calculate the specific volume of the vapour of ethyl ether at its boiling point, given BP = 346 °C at 1 atmosphere and density of liquid = 0.71 gm/cc, latent heat = 86 cal/gm, rate of increase of vapour pressure with temperature = 27 mm of mercury per °C.

   Ans. 328 cc/gm

3. Calculate the rate of increase of vapour pressure of water with temperature; given that boiling point = 100 °C, latent heat of steam = 539.4 cal/gm, specific volume of saturated steam at 100 °C = 1677 cc per gm and specific volume of water at 100 °C = 1 cc per gm and J = 4.18×10^7 erg/cal.

   Ans. 2.7 cm of Hg per °C

4. The density of iodine at the boiling point 185.3 °C is 3.71 gm/cc and *L* of vapourization is 40.9 cal/gm. If the boiling point changes by 1 °C for a change of pressure of 17 mm of Hg, calculate the specific volume of vapour.

   Ans. 164.27 cc/gm

5. Calculate the melting point of ice when it is subjected to a pressure of 100 atmospheres; given density of ice = 0.917 gm/cc, latent heat of fusion = 334 Joule/gm.

Ans. −0.745 °C

6. Calculate the boiling point of benzene under pressure of 80 cm of mercury. The normal boiling point of benzene is 80 °C, latent heat of evaporation is 380 Joules, the density of vapour at boiling point is 4 gm per litre and of the liquid is 0.9 gm per cc.

Ans. 81.2 °C

7. Calculate the value of C_v per mole of silver from the following data at 0 °C, $c_p = 0.0556$ cal/gm °C, coefficient of linear expansion = 20.5×10^{-6} per °C, bulk modulus = 1.04×10^{12} dynes/cm^2, density = 10.5 gm/cm^3, atomic weight = 107.9, J = 4.18×10^7 erg/cal.

Ans. 5.74 cal/ °C

8. Paraffin wax melts at 52.7 °C, increases in specific volume 0.125 cc, find the change in melting point per atmosphere, L = 35.35 cal/gm.

Ans. 0.028 °C

9. Find the value of dp/dT in case of water ice. Given latent heat of ice = 80 cal/gm, volume of ice per gm = 1.09 cc.

Ans. 1.36×10^8 dyne/sq cm/degree

10. Calculate the specific heat of aluminium at constant volume at 0 °C from the following data:

bulk modulus = 7.46×10^{11} dynes/cm^2
$v = 0.37$ cc per gm
α = coefficient of linear expansion = 25.6×10^{-6} per °C
$c_p = 0.201$ cal per °C

Ans. 0.19 cal per °C

11. Calculate the specific heat of mercury at constant volume from the following data:

$\alpha = 1.812 \times 10^{-4}$ per °C
$c_p = 3.33 \times 10^{-2}$ calories
$K = 3.9 \times 10^{-6}$ per atmosphere
$d = 13.6$ gm/cc

Ans. 0.03 cal per °C

12. Prove that the ratio of adiabatic and isobaric volume coefficient of expansion is $\frac{1}{1-\gamma}$.

QUESTIONS

1. Deduce Maxwell's thermodynamic relations and explain them.
2. Discuss free energy, enthalpy and thermodynamic potential. Deduce Gibb's Helmholtz equation.
3. Starting from Maxwell's relation, derive Clapeyron's equations.
4. With the help of Maxwell's thermodynamic relations derive equations involving specific heats.

Chapter 11

CONDUCTION OF HEAT

11.1 INTRODUCTION

If we hold one end of a metal rod in fire, after some time we feel hot at our hand as that heat moves from the end of the rod on fire to the other end at our hand. We have also seen that if a beaker containing water and potassium permanganate at the bottom of the beaker is heated, after some times pink lines rise from the bottom of the beaker to the top of the beaker turning round, moving towards the bottom of beaker and again moving up. Also, we have the experience of feeling hot when we stand near a furnace. These three experiences categorize three different processes of transfer of heat. The first process of transfer of heat is called *conduction* of heat. Here, heat waves move through the solid medium without actual movement of the molecules of the medium. The molecules are heated, made to vibrate vigorously transferring heat energy to the adjacent colder molecule by collision. This operation is repeated. In the second case, the movement of the pink colour shows that the water molecules carry the heat energy from one end to the other. This process is called the *convection* of heat. The last event shows that no medium is necessary for the transfer of heat. This third process of transfer of heat is called *radiation*. The first two processes are slow and require medium, and the last process is rapid and requires no medium for heat transfer.

In the first process, our sensation of hotness depends upon the material heated. Some materials are quickly heated and we feel hot in less time than by other materials which are heated less quickly. This difference is due to variation of a particular property of the material called thermal conductivity which is defined as the quantity of heat flowing per second normally through the opposite faces of a unit cube from the hotter side to the colder side when the temperature difference is unity. In CGS system, its unit is cal.cm^{-1}.sec^{-1}°C^{-1}.

11.2 RECTILINEAR FLOW OF HEAT

Let us consider a metal rod of area of cross section A whose one end is heated at a furnace (Fig. 11.1). Heat will be conducted towards the free end. The temperature at any section of the rod perpendicular to

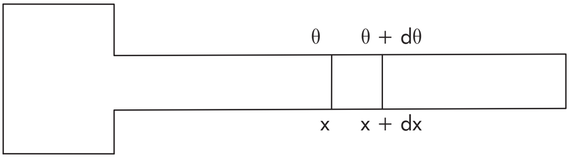


Fig. 11.1 Rectilinear flow of heat

its length increases and after some time it becomes steady; before this state, it was variable state when the temperature varied with time.

Let θ be the steady temperature at a distance x and $\theta + d\theta$ be the steady temperature at a distance $x + dx$. The quantity of heat flowing through the layer x per second is

$$Q_1 = -KA\frac{d\theta}{dx} \tag{11.1}$$

and the quantity of heat flowing through the layer $x + dx$ per second is

$$Q_2 = -KA\frac{d}{dx}\left(\theta + \frac{d\theta}{dx}dx\right) \tag{11.2}$$

Heat gained by the rod of thickness dx per second is

$$Q_1 - Q_2 = -KA\frac{d\theta}{dx} - \left[-KA\frac{d}{dx}\left(\theta + \frac{d\theta}{dx}dx\right)\right] = KA\frac{d^2\theta}{dx^2}dx \tag{11.3}$$

This heat will be used up in two ways. A part of it will raise the temperature of the rod of thickness dx and another part will be radiated from that part. If we neglect the heat lost by radiation, then the heat will be used up to heat the body. If A be the area of cross section of the body, ρ the density, c the specific heat of the material of the body and $d\theta/dt$ is the rate of rise of temperature, then we can write

$$KA\frac{d^2\theta}{dx^2}dx = Adx\,\rho c\frac{d\theta}{dt} \tag{11.4}$$

or

$$\frac{d\theta}{dt} = \frac{K}{\rho c}\frac{d^2\theta}{dx^2} = h\frac{d^2\theta}{dx^2} \tag{11.5}$$

where $h = K/\rho c$ is called the diffusivity by Kelvin and thermometric conductivity by Maxwell; it is equal to the thermal conductivity divided by thermal capacity per unit volume. It determines the rapidity with which temperature changes take place in a given rod.

In the steady state,

$$\frac{d\theta}{dt} = 0$$

So,

$$h\frac{d^2\theta}{dx^2} = 0 \text{ or } \frac{d^2\theta}{dt^2} = 0 \text{ as } h \text{ is not zero.} \tag{11.6}$$

The solution of this equation gives

$$\theta = Ax + B \tag{11.7}$$

where A and B are constants determined from the boundary conditions.

At $\quad x = 0 \quad \text{let } \theta = \theta_0 \quad (11.8)$

and at $\quad x = l \quad \text{let } \theta = \theta_1 \quad (11.9)$

From the boundary conditions, Eq. 11.7 changes to

$$\theta = \frac{\theta_1 - \theta_0}{l} x + \theta_0 \tag{11.10}$$

But if the radiation of heat is considered, then if p = the perimeter of the rod, E = emissive power of the surface, that is, the quantity of heat radiated per second per unit area per unit temperature difference, θ_e = excess temperature of the surface over the surroundings, then the heat radiated is given by $Epdx\ \theta_e$.

Now, $\theta_e = \theta - \theta_s$ where θ_s is the surrounding temperature (11.11)

$$\therefore \quad \theta = \theta_e + \theta_s$$

$$\frac{d^2\theta}{dx^2} = \frac{d^2\theta_e}{dx^2} \tag{11.12}$$

and $\quad \dfrac{d\theta}{dt} = \dfrac{d\theta_e}{dt}$ considering that θ_s remains constant (11.13)

Then, Eq. 11.4 changes to

$$KA\frac{d^2\theta_e}{dx^2}dx = Adx\,\rho c\frac{d\theta_e}{dt} + Ep\theta_e dx \tag{11.14}$$

or

$$\frac{d\theta_e}{dt} = \frac{K}{\rho c}\frac{d^2\theta_e}{dx^2} - \frac{Ep}{A\,\rho c}\theta_e$$

$$= h\frac{d^2\theta_e}{dx^2} - \mu\theta_e \text{ where } \mu = \frac{Ep}{A\,\rho c} \tag{11.15}$$

This is known as Fourier equation of one dimensional heat flow.

In the steady state, $\quad \dfrac{d\theta_e}{dt} = 0$

or

$$h\frac{d^2\theta_e}{dx^2} = \mu\theta_e \tag{11.16}$$

or

$$\frac{d^2\theta_e}{dx^2} = \frac{\mu}{h}\theta_e = \alpha^2\theta_e \tag{11.17}$$

where $$\alpha^2 = \frac{\mu}{h} = \frac{Ep/A\rho c}{K/\rho c} = \frac{Ep\,\rho c}{KA\,\rho c} = \frac{Ep}{KA}$$

Let the solution of Eq. 11.17 be $\theta_e = Ae^{mx}$ (11.18)

where A and m are constants.

Then from Eq. 11.17, $m^2 = \alpha^2$ or $m = \pm\alpha$

$$\therefore \qquad \theta_e = Ae^{\alpha x} + Be^{-\alpha x} \tag{11.19}$$

where the constants A and B are determined from boundary conditions.

At $x = 0, \theta_e = \theta_0$, source temperature excess over the surrounding (11.20)

$$x = \infty, \theta_e = 0, \tag{11.21}$$

$x = l, \theta_e = \theta_m$ farthest end temperature over the surrounding (11.22)

Using Eq. 11.20 in Eq. 11.19,

we get $$\theta_0 = A + B \tag{11.23}$$

Using Eq. 11.21 in Eq. 11.19,

we get $$0 = A\infty \quad \therefore A = 0 \tag{11.24}$$

Using Eq. 11.22 in Eq. 11.19,

we get $$\theta_m = Be^{-\alpha l} \tag{11.25}$$

From Eqs 11.23 and 11.24, $B = \theta_0$

$$\therefore \text{ Eq. 11.19 becomes } \theta_m = \theta_0 e^{-\alpha x} = \theta_0 e^{-\sqrt{\frac{Ep}{AK}}.x} \tag{11.26}$$

Distribution of temperatures along the length of the rod from the hot end is given by Eqs 11.10 and 11.26 and are graphically represented by curves I and II, respectively as shown in Fig. 11.2.

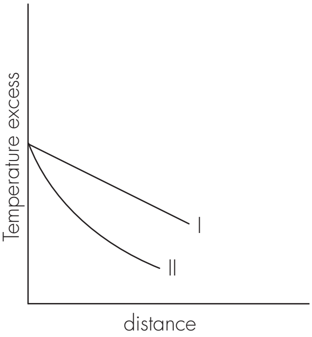


Fig. 11.2 Temperature distance curve for rectilinear flow of heat (i) considering no radiation and (ii) considering radiation

11.3 INGEN-HAUSZ'S METHOD

The experiment utilizing Eq. 11.26 was conducted due to Ingen-Hausz. In this experiment, thermal conductivities of different materials are compared and determined if that of any one material is known.

Here, several rods of different metals and of equal area of cross section and polish to ensure equal emissivity are coated with wax. One end of each of the rods is placed in an oil bath as shown in Fig. 11.3.

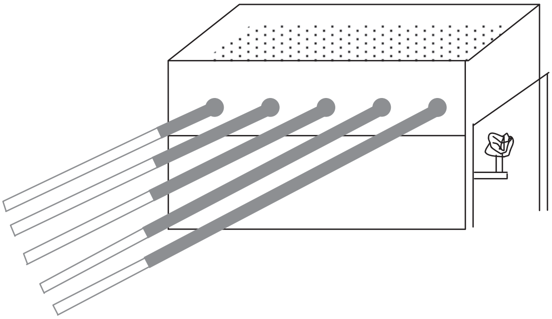


Fig. 11.3 Ingen Hausz's experiment

Heat is transferred from the end introduced into the bath towards the other end exposed outside. This causes melting of wax on the surface. At first, heat is transferred quickly in bismuth than in copper because at the variable state flow of heat depends on thermal capacity as well as thermal conductivity and as thermal capacity of bismuth is lower than that of copper. However when steady is reached, melting of wax stops. Wax melts up to that point of the rod whose steady state temperature is the melting point of wax. The lengths are measured up to which wax melts. Let l_1 be the length and K_1 be the thermal conductivity of the material of the first rod, l_2, K_2 be the similar quantities for the second rod; l_3, K_3 be the similar quantities for third rod, and so on.

Then from Eq. 11.26, we can write

$$\sqrt{\frac{Ep}{AK}}\; l = \log_e \frac{\theta_0}{\theta_m} \tag{11.27}$$

Since $\log_e \theta_0 / \theta_m$, E, p and A are same for all bars, we can write

$$\frac{l_1^2}{K_1} = \frac{l_2^2}{K_2} = \frac{l_3^2}{K_3} = \ldots\ldots = \text{constant} \tag{11.28}$$

The thermal conductivities are in the simple ratio of the square of length up to which wax melts. If the thermal conductivity of any one material is known, then that of other materials can be calculated.

11.4 EXPERIMENT OF DESPRETZ, WIEDEMANN AND FRANZ FOR COMPARISON OF CONDUCTIVITIES OF TWO DIFFERENT MATERIALS

In 1822, Despretz compared the thermal conductivities of two materials by heating one end of each of the rods made with the materials, and measuring temperature at three equidistant places of the rods. For this purpose three equidistant holes were made and filled with mercury in which mercury-in-glass thermometers were introduced for temperature measurement.

Let θ_1, θ_2, θ_3 be the temperatures at distances $x, x+a, x+2a$ from the hot end, respectively; then from Eq.11.19, we can write

$$\theta_1 = Ae^{\alpha x} + Be^{-\alpha x}$$

$$\theta_2 = Ae^{\alpha(x+a)} + Be^{-\alpha(x+a)}$$

$$\theta_3 = Ae^{\alpha(x+2a)} + Be^{-\alpha(x+2a)}$$

$$\therefore \qquad \theta_1 + \theta_3 = Ae^{\alpha x} + Be^{-\alpha x} + Ae^{\alpha(x+2a)} + Be^{-\alpha(x+2a)}$$

$$= e^{\alpha a}\left(Ae^{\alpha(x+a)} + Be^{-\alpha(x+a)}\right) + e^{-\alpha a}\left(Ae^{\alpha(x+a)} + Be^{-\alpha(x+a)}\right)$$

$$= \left(Ae^{\alpha(x+a)} + Be^{-\alpha(x+a)}\right)\left(e^{\alpha a} + e^{-\alpha a}\right)$$

$$= \theta_2(e^{\alpha a} + e^{-\alpha a})$$

or

$$\frac{\theta_1 + \theta_3}{\theta_2} = e^{\alpha a} + e^{-\alpha a} = 2n \text{ (say)} \tag{11.29}$$

Putting $y = e^{\alpha a}$ in Eq. 11.29, we have

$$y + \frac{1}{y} = 2n$$

or

$$y^2 - 2ny + 1 = 0$$

or

$$y = \frac{2n \pm \sqrt{4n^2 - 4}}{2} = n \pm \sqrt{n^2 - 1}$$

The negative sign before the radical sign is impossible since it is experimentally observed that $\theta_1 + \theta_3 / 2\theta_2 > 1$

Hence, $n > 1$.

So,

$$e^{\alpha a} = y = n + \sqrt{n^2 - 1}$$

or

$$\alpha a = \log_e(n + \sqrt{n^2 - 1})$$

$$\sqrt{\frac{Ep}{Ak}}\, a = \log_e(n + \sqrt{n^2 - 1}) \tag{11.30}$$

If the two bars are of same perimeter, area of cross section and emissivity and a is same, then we can write

$$\sqrt{\frac{K_1}{K_2}} = \frac{\log_e(n_2 + \sqrt{n_2^2 - 1})}{\log_e(n_1 + \sqrt{n_1^2 - 1})} \tag{11.31}$$

Thus by determining temperatures at three places of each rod, ratio of their thermal conductivities can be determined.

Following this rule, Wiedemann and Franz designed a more accurate apparatus.

11.5 FORBES' METHOD

It is one of the earliest methods for determination of thermal conductivity of a substance. The experiment is a tedious one. Forbes performed the experiment in 1864.

The principle of the method is that at the steady state, the quantity of heat passing through any section of a bar will be equal to the quantity of heat lost by radiation by the remaining part of the bar. Let l be the length, A be the area of cross section, ρ be the density, c be the specific heat and K be the thermal conductivity of the material of the bar. We consider a section of the bar at a distance $x = x_1$ from the hot end of the bar; then according to the theory, the quantity of heat passing through the section at $x = x_1$ per second

$$= KA\left(\frac{d\theta}{dx}\right)_{x=x_1} \tag{11.32}$$

At the steady state, the amount of heat lost by the surface of the bar per second from x to $x + dx$ is

$$Adx\,\rho c\frac{d\theta}{dt} \text{ where } \frac{d\theta}{dt} \text{ is the rate of change of temperature.}$$

So, the total amount of heat lost by radiation per second from the point $x = x_1$ to the end of the bar ($x = l$) is

$$A\,\rho c\int_{x=x_1}^{x=l}\frac{d\theta}{dt}dx \tag{11.33}$$

At steady state,

$$KA\left(\frac{d\theta}{dx}\right)_{x=x_1} = A\,\rho c\int_{x=x_1}^{x=l}\frac{d\theta}{dt}dx$$

$$\therefore \qquad K = \frac{\rho c\displaystyle\int_{x=x_1}^{x=l}\frac{d\theta}{dt}dx}{\left(\dfrac{d\theta}{dx}\right)_{x=x_1}} \tag{11.34}$$

By determining $\int_{x=x_1}^{x=l}\frac{d\theta}{dt}dx$ and $\left(\frac{d\theta}{dx}\right)_{x=x_1}$, K is determined. $\left(\frac{d\theta}{dx}\right)_{x=x_1}$ is called the static part as it is determined at the steady state of the bar and $\int_{x=x_1}^{x=l}\frac{d\theta}{dt}dx$ is called dynamic part because it is determined when the bar is radiating.

A long bar made of the material whose thermal conductivity is to be determined is heated at one end which is introduced into a hot bath of molten lead or silver (Fig. 11.4).

The other end is practically at room temperature. A number of thermometers with their bulbs introduced in the holes drilled on the bar within which a little quantity of mercury was given to make good contact between the metal and the bulbs of the thermometer indicate its temperature through out its entire length. When steady state is reached for which a few hours are required, the temperature

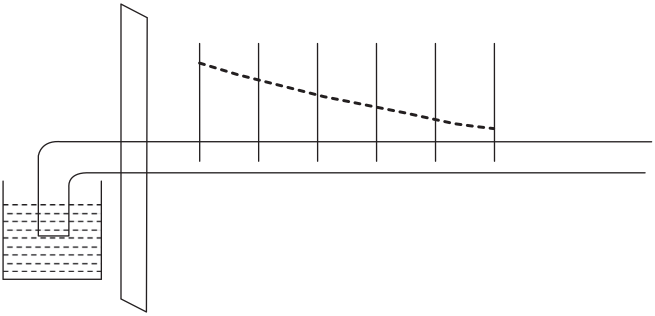


Fig. 11.4 Forbes' method

at each thermometer becomes constant and then the temperatures are noted. The distribution of steady temperature follows exponential variation as given by Eq. 11.26. The excess temperature over that of the room is plotted against distance and a curve as shown in Fig. 11.5 is obtained.

The curve meets x axis at l. A tangent is drawn at (x_1, θ) which meets x axis making an angle ϕ, then

$$\tan\phi = \left(\frac{d\theta}{dx}\right)_{x=x_1} = \frac{AB}{BC}$$

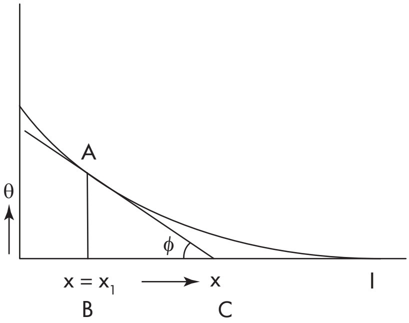


Fig. 11.5 Plot of excess temperature at different lengths of the bar

This is the static part of the experiment since it deals with the steady state of heat flow.

There is another part of the experiment called the dynamical part. In this part of the experiment another bar of the same material, short in length, otherwise similar to the previous bar is heated uniformly up to the temperature which the hot end gained in the static part experiment and it is allowed to cool by suspending in the same surroundings as that of the bar.

The excess temperature of the bar over the surroundings is noted with time and a curve is obtained as shown in Fig. 11.6. From this curve, the values of $d\theta/dt$ corresponding to various values of θ and, therefore, of x obtained in Fig. 11.5 are plotted in another curve as shown in Fig. 11.7.

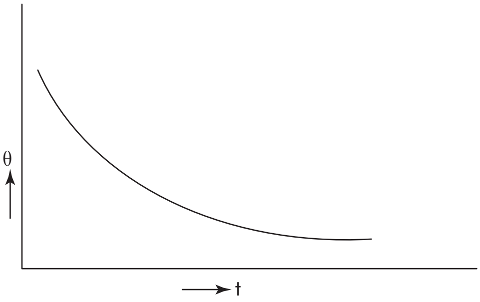


Fig. 11.6 Plot of $\theta - t$ of the same rod

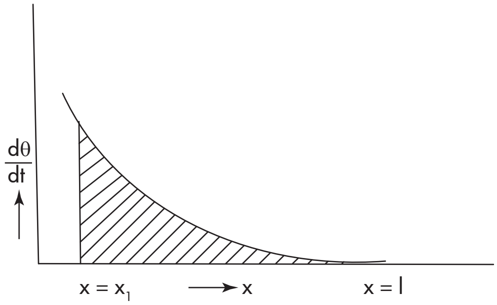


Fig. 11.7 $d\theta/dt$ vs x curve

On extrapolating the graph, it meets the x axis the corresponding value of x is l. From this graph, the value of

$\int_{x=x_1}^{x=l} \frac{d\theta}{dt} dx$, which is equal to the area of the shaded portion of the graph, is obtained and is measured by a planimeter. So, value of K can be found out from Eq.11.34 if ρ, c,

$$\frac{d\theta}{dx} (= \tan\phi) \text{ and } \int_{x=x_1}^{x=l} \frac{d\theta}{dt} dx \text{ are known.}$$

The experiment is laborious and tedious since in the static part of the experiment, six hours are needed to attain the steady state.

There are some sources of error though; they are as follows:

1. The specific heat of the metal of the bar does not remain constant as temperature changes. But specific heat is considered constant, so error appears.
2. The temperature distribution in the two cases (static and dynamic experiments) is not same.

11.6 CONDUCTIVITY OF POOR CONDUCTORS

In the case of poor conductors as the heat conduction is very small, the specimen can not be taken as bars as in the case of the good conductors because in that case the heat loss from the sides will be many times the heat conducted. Since the rate of flow of heat is proportional to the cross sectional area and inversely proportional to the thickness, substances in the form of a thin plate, sphere or cylinder will be favourable. Wood, rubber, glass, asbestos, clay and cork are poor conductors.

We shall consider here three methods of determining thermal conductivities; they are:

1. Lee's disc method
2. Spherical shell method
3. Cylindrical shell method

11.6.1 Lees' Disc Method

This method is used to measure thermal conductivity of poor conductors such as wood, ebonite, card board and asbestos. The material is taken in the form of a circular sheet B placed between a steam chamber A and solid disc C, both made of brass as shown in the Fig. 11.8.

Two thermometers are inserted in the holes drilled in the solid base of steam chamber A and the solid disc C.

As steam is passed through A the solid base gets heated, and heat is conducted to C through B. This goes on till the temperature recorded by two thermometers becomes constant. This is the steady state. Let the two steady temperatures be θ_1 and θ_2. In this state, the heat conducted through B to C is radiated by the exposed surface of C as there is no rise of temperature of thermometer T_2.

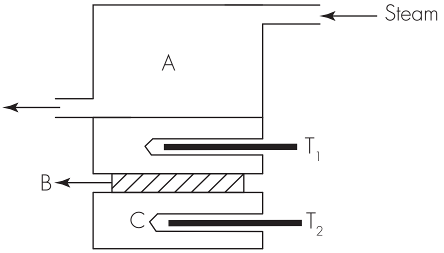


Fig. 11.8 Lees' disc method

So, we may write for the heat conducted per second

$$Q = \frac{KA(\theta_1 - \theta_2)}{d} \tag{11.35}$$

where K is the thermal conductivity of the material, A is the area of the cross section and d is the thickness of the sheet.

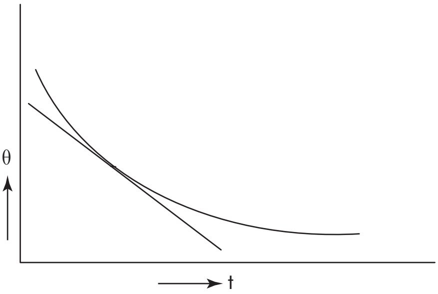


Fig. 11.9 θ – t plot to determine temperature gradient

This Q can be measured in the following way. After the steady state has reached, the steam chamber A and the sheet are withdrawn and the lower disc is heated above, say, 10 degrees of its steady value either by a burner or by putting the steam chamber directly over it. When the temperature is 10 degrees above its steady value, the sheet is again placed in between A and C. C will radiate as its temperature is higher, and its temperature is recorded at an interval of half a minute. When the temperature reaches θ_1, flow of steam is stopped and the procedure of noting the temperature of the lower disc at an interval of half a minute is continued till the temperature is below 5 degree of θ_2. The reading of θ with t is plotted as shown in Fig. 11.9.

Then at temperature θ_2, a tangent is drawn to the curve and that will give $(d\theta/dt)_{\theta = \theta_2}$

The amount of heat radiated per second from the lower slab is

$$Q = ms\left(\frac{d\theta}{dt}\right)_{\theta = \theta_2} \tag{11.36}$$

where m = mass of the lower disc and s = specific heat of the material of the lower disc.

From Eqs 11.35 and 11.36, we can write

$$K = \frac{msd\left(\frac{d\theta}{dt}\right)_{\theta = \theta_2}}{A(\theta_1 - \theta_2)} \tag{11.37}$$

Thermal conductivity of liquids can also be determined by this method with some modifications. The arrangement of the apparatus is as shown in the Fig. 11.10.

A, C, D and F are four copper discs. In between D and F, the experimental liquid is kept in L surrounded by ebonite ring E. G is a glass disc and B houses the heating coil. This combined arrangement so formed is varnished for providing uniform known emissivity. The whole thing is within a constant temperature enclosure. Heat is produced by connecting the heating coil to a constant source of electromotive force. Four thermocouples are provided to measure the temperatures of

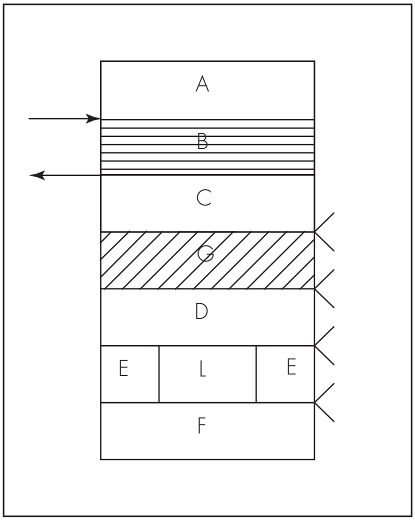


Fig. 11.10 Apparatus to measure thermal conductivity of liquids

the two faces of glass discs and the two faces of liquid trapped by ebonite ring. By heating the coil, steady temperatures recorded by the four thermocouples are noted. In the steady state, let θ_1, $\theta_{2,}$ θ_3 and θ_4 be the temperatures recorded by four thermocouples, *I* be the current flowing through the heating coil and *E* be the potential difference between the two ends of the heating coil, then we can write for the amount of heat supplied per second

$$Q = \frac{EI}{J} = \frac{KA(\theta_1 - \theta_2)}{d_g} = \frac{K_l A_l(\theta_3 - \theta_4)}{d_l} = \frac{K_e A_e(\theta_3 - \theta_4)}{d_e} \tag{11.38}$$

where K = thermal conductivity of glass

K_1 = thermal conductivity of liquid
K_e = thermal conductivity of ebonite
θ_1 = steady temperature of upper glass face
θ_2 = steady temperature of lower glass face
θ_3 = steady temperature of upper surface of ring
θ_4 = steady temperature of lower surface of ring
A = area of cross section of glass disc
A_1 = area of cross section of liquid
A_e = area of cross section of ebonite
d = thickness of glass
d_1 = thickness of liquid
d_e = thickness of ebonite

From Eq. 11.38, K_1 can be calculated. For accurate measurement, loss of heat due to radiation from the curved surface of *G*, *D* and *E* should be considered.

11.7 SPHERICAL SHELL METHOD

In spherical shell method employed by Nusselt two hollow concentric spheres, one of copper and 30 cm diameter (*A*) and the other (*B*) of aluminium and 15 cm diameter are used; the spheres can be divided into two parts and can also be united (Fig. 11.11).

The material under test such as powdered cork, charcoal and clay is placed between the intervening space of the two spheres. The source of heat is placed at *C*, which is electrically driven.

Thermocouples are provided to measure the temperatures of the material at point of different radii which will be spheres of isothermal surfaces. Thermal conductivity can be calculated from the heat generated, electrical energy spent and the temperatures at different surfaces of equal radii. The theory of the method is as follows:

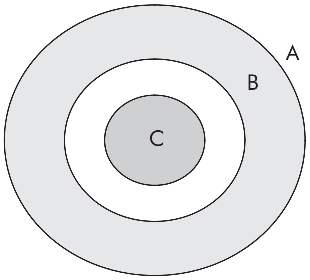


Fig. 11.11 Nusselts' apparatus

Let us consider a spherical surface of radius *r*; the quantity of heat flowing outwards through the spherical surface of radius *r* per second= $-4\pi r^2 K\, d\theta/dr$ where $d\theta/dr$ is temperature gradient. This must be equal to the amount of electrical energy (*Q*) supplied. So, we can write

$$Q = -4\pi r^2 K \frac{d\theta}{dr} \tag{11.39}$$

or
$$d\theta = \frac{-Q}{4\pi K}\frac{dr}{r^2}$$

Integrating,
$$\theta = \frac{Q}{4\pi Kr} + A \tag{11.40}$$

In the steady state, the temperature at r_1 is θ_1 and that at r_2 is θ_2 then

$$\theta_1 = \frac{Q}{4\pi Kr_1} + A \tag{11.41}$$

$$\theta_2 = \frac{Q}{4\pi Kr_2} + A \tag{11.42}$$

or
$$\theta_1 - \theta_2 = \frac{Q}{4\pi K}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{Q}{4\pi K}\left(\frac{r_2 - r_1}{r_1 r_2}\right)$$

or
$$Q = \frac{4\pi K(\theta_1 - \theta_2)r_1 r_2}{(r_2 - r_1)} = \frac{I^2 R}{J} = \frac{EI}{J} \tag{11.43}$$

where I = current flowing through heating coil of resistance R, E = potential difference between the two ends of the heating coil and J = mechanical equivalent of heat.

Knowing Q, r_1, r_2, θ_1, θ_2, K can be calculated.

11.7.1 Temperature Distribution at a Point at a Certain Time

Dividing Eq. 11.41 by r_2 and Eq. 11.42 by r_1 and then subtracting them, we get

$$\frac{\theta_1}{r_2} - \frac{\theta_2}{r_1} = \frac{A}{r_2} - \frac{A}{r_1} = A\left(\frac{r_1 - r_2}{r_1 r_2}\right)$$

or
$$A = \frac{r_1 r_2}{r_1 - r_2}\left(\frac{\theta_1}{r_2} - \frac{\theta_2}{r_1}\right) \tag{11.44}$$

From Eqs 11.40, 11.43 and 11.44, we can write

$$\theta = \frac{4\pi K(\theta_1 - \theta_2)r_1 r_2}{4\pi Kr(r_2 - r_1)} + \frac{r_1 r_2}{r_1 - r_2}\left(\frac{\theta_1}{r_2} - \frac{\theta_2}{r_1}\right) \tag{11.45}$$

This is the expression for the temperature at any spherical surface of radius r.

Rigorous proof: The simplest case of heat conduction in three dimensions is that of a sphere. With reference to Fig. 11.12, we can write for the conduction of heat in three dimensions:

$$h\left(\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2}\right) = \frac{d\theta}{dt} \tag{11.46}$$

At steady state,
$$\frac{d\theta}{dt} = 0$$

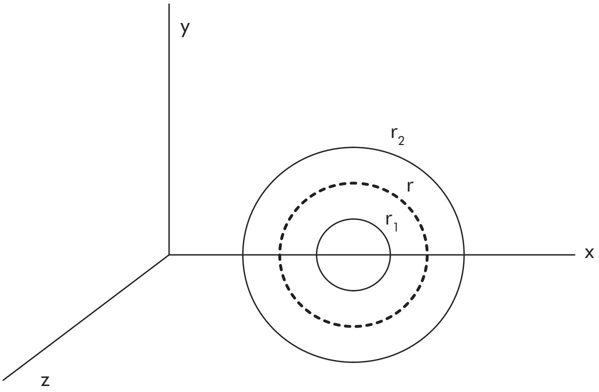


Fig. 11.12 Schematic representation of spherical shell method in cartisian coordinates

So,
$$\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}=0 \tag{11.47}$$

Quantity of heat flowing per second across the surface of radius r

$$=-4\pi r^2 K\frac{d\theta}{dr}$$

Again,
$$\frac{d\theta}{dx}=\frac{d\theta}{dr}\frac{dr}{dx} \tag{11.48}$$

or
$$\frac{d}{dx}\left(\frac{d\theta}{dx}\right)=\frac{d}{dx}\left(\frac{d\theta}{dr}\frac{dr}{dx}\right)$$

$$=\frac{d\theta}{dr}\frac{d^2r}{dx^2}+\frac{dr}{dx}\frac{d^2\theta}{dr^2}\frac{dr}{dx}$$

or
$$\frac{d^2\theta}{dx^2}=\frac{d\theta}{dr}\frac{d^2r}{dx^2}+\left(\frac{dr}{dx}\right)^2\frac{d^2\theta}{dr^2} \tag{11.49}$$

Similarly,
$$\frac{d^2\theta}{dy^2}=\frac{d\theta}{dr}\frac{d^2r}{dy^2}+\left(\frac{dr}{dy}\right)^2\frac{d^2\theta}{dr^2} \tag{11.50}$$

and
$$\frac{d^2\theta}{dz^2}=\frac{d\theta}{dr}\frac{d^2r}{dz^2}+\left(\frac{dr}{dz}\right)^2\frac{d^2\theta}{dr^2} \tag{11.51}$$

Adding

$$\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}=\frac{d\theta}{dr}\left(\frac{d^2r}{dx^2}+\frac{d^2r}{dy^2}+\frac{d^2r}{dz^2}\right)+\frac{d^2\theta}{dr^2}\left[\left(\frac{dr}{dx}\right)^2+\left(\frac{dr}{dy}\right)^2+\left(\frac{dr}{dz}\right)^2\right] \tag{11.52}$$

In the case of spherical shell,

$$r^2 = x^2 + y^2 + z^2 \tag{11.53}$$

Differentiating this with respect to x,

$$2r\frac{dr}{dx} = 2x \tag{11.54}$$

Differentiating again with respect to x,

$$r\frac{d^2r}{dx^2} + \frac{dr}{dx}\frac{dr}{dx} = 1$$

or

$$r\frac{d^2r}{dx^2} + \left(\frac{dr}{dx}\right)^2 = 1 \tag{11.55}$$

Similarly, we can get

$$r\frac{dr}{dy} = y \tag{11.56}$$

$$r\frac{d^2r}{dy^2} + \left(\frac{dr}{dy}\right)^2 = 1 \tag{11.57}$$

and

$$r\frac{dr}{dz} = z \tag{11.58}$$

$$r\frac{d^2r}{dz^2} + \left(\frac{dr}{dz}\right)^2 = 1 \tag{11.59}$$

Squaring Eqs 11.54, 11.56 and 11.58, and then adding them, we get

$$x^2 + y^2 + z^2 = r^2\left[\left(\frac{dr}{dx}\right)^2 + \left(\frac{dr}{dy}\right)^2 + \left(\frac{dr}{dz}\right)^2\right] \tag{11.60}$$

From Eqs 11.53 and 11.60,

$$\left(\frac{dr}{dx}\right)^2 + \left(\frac{dr}{dy}\right)^2 + \left(\frac{dr}{dz}\right)^2 = 1 \tag{11.61}$$

Adding Eqs 11.55, 11.57 and 11.59,

$$3 = r\left(\frac{d^2r}{dx^2} + \frac{d^2r}{dy^2} + \frac{d^2r}{dz^2}\right) + \left[\left(\frac{dr}{dx}\right)^2 + \left(\frac{dr}{dy}\right)^2 + \left(\frac{dr}{dz}\right)^2\right] \tag{11.62}$$

From Eqs 11.61 and 11.62, we get

$$r\left(\frac{d^2r}{dx^2}+\frac{d^2r}{dy^2}+\frac{d^2r}{dz^2}\right)=2$$

or
$$\frac{d^2r}{dx^2}+\frac{d^2r}{dy^2}+\frac{d^2r}{dz^2}=\frac{2}{r} \tag{11.63}$$

From Eqs 11.52, 11.61 and 11.63, we can write

$$\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}=\frac{d\theta}{dr}\frac{2}{r}+\frac{d^2\theta}{dr^2} \tag{11.64}$$

But in the steady state,
$$\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}=0$$

So,
$$\frac{d\theta}{dr}\frac{2}{r}+\frac{d^2\theta}{dr^2}=0$$

or
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\theta}{dr}\right)=0$$

or
$$\frac{d}{dr}\left(r^2\frac{d\theta}{dr}\right)=0$$

Integrating
$$r^2\frac{d\theta}{dr}=A, \tag{11.65}$$

$$d\theta=\frac{A}{r^2}dr$$

Integrating
$$\int_{\theta_1}^{\theta_2} d\theta = A\int_{r_1}^{r_2}\frac{dr}{r^2}$$

$$\theta_2-\theta_1=-A\left(\frac{1}{r_2}-\frac{1}{r_1}\right)=A\left(\frac{r_2-r_1}{r_1r_2}\right)$$

or
$$A=\frac{r_1r_2(\theta_2-\theta_1)}{(r_2-r_1)} \tag{11.66}$$

From Eqs 11.39, 11.65 and 11.66, we get

$$Q=-4\pi Kr^2\frac{d\theta}{dr}=-4\pi Kr^2\frac{A}{r^2}$$

$$=-4\pi Kr_1r_2\frac{(\theta_2-\theta_1)}{(r_2-r_1)}=4\pi K\frac{r_1r_2}{(r_2-r_1)}(\theta_2-\theta_1) \tag{11.67}$$

11.8 CYLINDRICAL SHELL METHOD

Thermal conductivity of bad conductors may also be determined by cylindrical shell method. Here, the space between two hollow cylinders of radius r_1 and r_2 is filled with the bad conducting material (saw dust, sand, fire clay, rock) (Fig. 11.13).

The source of heat lies along the axis of the cylinder so that the heat flows radially along the surface of the cylinder as the cylinder is symmetrical about its axis where the source of heat is kept. The temperatures of the cylindrical surfaces of radii r_1 and r_2 are measured by thermocouples. Let the steady temperatures be θ_1 and θ_2 corresponding to radii r_1 and r_2, respectively. As the isothermal surface is cylindrical, the amount of heat Q flowing per second through this surface of a cylinder of radius r at the steady state

$$Q = -2\pi r l K \frac{d\theta}{dr} \tag{11.68}$$

where l = length of the cylinder

K = thermal conductivity of bad conducting material

$\frac{d\theta}{dr}$ = temperature gradient

From Eq. 11.68,

$$d\theta = -\frac{Q}{2\pi l K}\frac{dr}{r} \tag{11.69}$$

Integrating Eq. 11.69, we get

$$\theta = -\frac{Q}{2\pi l K}\log_e r + A \tag{11.70}$$

where A is a constant.

If θ_1 and θ_2 are the steady temperatures at the surface of a cylinder of radius r_1 and r_2, then

$$\theta_1 = -\frac{Q}{2\pi l K}\log_e r_1 + A \tag{11.71}$$

and

$$\theta_2 = -\frac{Q}{2\pi l K}\log_e r_2 + A \tag{11.72}$$

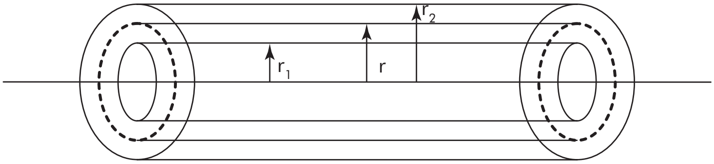


Fig. 11.13 Schematic representation of cylindrical shell method

so,
$$\theta_1 - \theta_2 = \frac{Q}{2\pi lK} \log_e \frac{r_2}{r_1} \tag{11.73}$$

or
$$Q = \frac{2\pi lK(\theta_1 - \theta_2)}{\log_e \dfrac{r_2}{r_1}} \tag{11.74}$$

Heat is produced by sending current I through the heating coil of resistance R placed along the axis of the cylinders, then $Q = I^2R/J = EI/J$ (symbols explained earlier). Then, we have

$$Q = \frac{EI}{J} = \frac{2\pi lK(\theta_1 - \theta_2)}{\log_e \dfrac{r_2}{r_1}} \tag{11.75}$$

from which K can be calculated

Temperature gradient at any point.

Multiplying Eq. 11.71 by $\log_e r_2$ and Eq. 11.72 by $\log_e r_1$ and then subtracting,

$$\theta_1 \log_e r_2 - \theta_2 \log_e r_1 = A(\log_e r_2 - \log_e r_1)$$

$\therefore$
$$A = \frac{\theta_1 \log_e r_2 - \theta_2 \log_e r_1}{\log_e r_2 - \log_e r_1} \tag{11.76}$$

Then using Eqs 11.70 and 11.75,

$$\theta = -\frac{2\pi lK(\theta_1 - \theta_2)\log_e r}{2\pi lK \log_e \dfrac{r_2}{r_1}} + \frac{\theta_1 \log_e r_2 - \theta_2 \log_e r_1}{\log_e \dfrac{r_2}{r_1}}$$

$$= \frac{1}{\log_e \dfrac{r_2}{r_1}}\left[(\theta_1 \log_e r_2 - \theta_2 \log_e r_1) - (\theta_1 - \theta_2)\log_e r\right] \tag{11.77}$$

This is the expression for temperature on cylindrical surface of radius r in the steady state.

11.8.1 Determination of Thermal Conductivity of Rubber

The required apparatus consists of a rubber tubing B, a copper boiler A for producing steam, a calorimeter C, a thermometer T and a beaker R as shown in Fig. 11.14.

The procedure of the experiment is as follows. Let m gm of water be kept in the calorimeter C of water equivalent W gm. One end of the rubber tubing is fitted at the mouth of the boiler, the other end is placed inside a beaker R. A certain length l of the rubber tubing is dipped into water in the calorimeter. Let the initial temperature recorded by the thermometer in water be θ_1. Now, the steam is produced in A by a heater and the temperature recorded by thermometer T is recorded at an interval of 3 minutes. The temperature of water rises slowly and then becomes steady at θ_2 after a certain interval of time. The amount of heat conducted through rubber in time t is

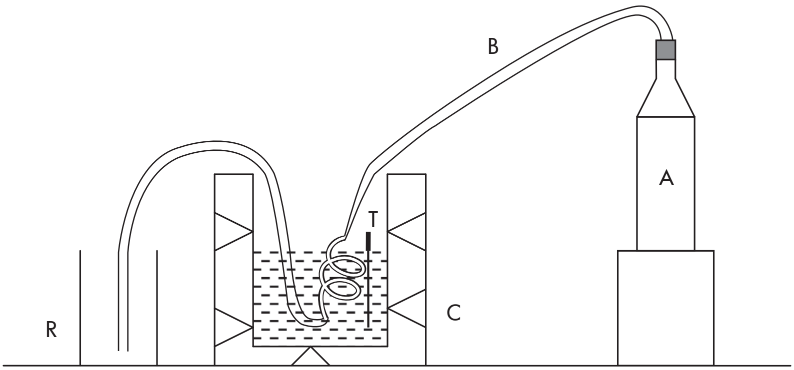


Fig. 11.14 Apparatus to determine thermal conductivity of rubber

$$Q = \frac{2\pi Kl\left(\theta - \frac{\theta_1 + \theta_2}{2}\right)t}{\log_e \frac{r_2}{r_1}} \tag{11.78}$$

where K = thermal conductivity of rubber

l = length of rubber tubing dipped in water

θ = steam temperature, the temperature at the surface of inner radius r_1

$\theta_1 + \theta_2/2$ = temperature at the surface of outer radius r_2, the average temperature of water of the calorimeter

The amount of heat gained by water and calorimeter $= w(\theta_2 - \theta_1) + m(\theta_2 - \theta_1)$

So, $$Q = \frac{2\pi Kl\left(\theta - \frac{\theta_1 + \theta_2}{2}\right)t}{\log_e \frac{r_2}{r_1}} = (w+m)(\theta_2 - \theta_1)$$

or $$K = \frac{(w+m)(\theta_2 - \theta_1)\log_e \frac{r_2}{r_1}}{2\pi l\left(\theta - \frac{\theta_1 + \theta_2}{2}\right)t} \tag{11.79}$$

To measure the radii of the rubber tube, the impression of one end of the tube is taken on a piece of paper and the inner and outer radii are measured by travelling microscope. K can be calculated by measuring temperatures and if l is known.

11.8.2 Determination of Thermal Conductivity of Glass

The experimental arrangement for the measurement of thermal conductivity of glass is shown in Fig. 11.15.

A is a steam jacket through which steam is passed. A encloses symmetrically a glass tube B through which water is allowed to flow; the initial temperature is recorded by thermometer T_1 and the temperature of outflow of water at the other end is measured by thermometer T_2. There is a spiral wire inside the glass tube B to ensure slow flow and good contact of water with the jacket.

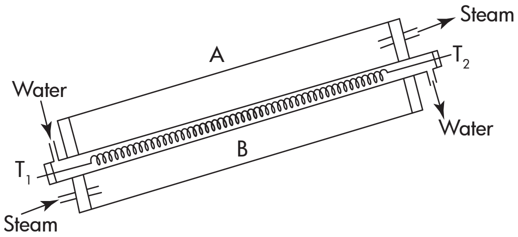


Fig. 11.15 Experimental arrangement for measurement of thermal conductivity of glass

Temperatures recorded by T_1 and T_2 are noted at regular intervals of 3 minutes as the steam is passed. The temperatures rise with time and after a considerable amount of time, the temperatures will attain constant values; let the steady temperature of inflow and outflow of water be θ_1 and θ_2, respectively. When steady state is reached, water flowing out is collected for an interval of time t; let the mass be m. The length of the glass tube exposed to steam is measured and let it be l. The internal and external radii of the glass tube are measured, let them be r_1 and r_2, respectively. The outer surface of the glass tube is at steam temperature θ and the inner surface will be at average temperature of the inflowing and outflowing water. Heat will be conducted through the glass and will be taken by flowing water. Heat conducted, Q per second, through glass is

$$Q = \frac{2\pi Kl\left(\theta - \frac{\theta_1 + \theta_2}{2}\right)t}{\log_e \frac{r_2}{r_1}}$$

The heat taken by water is $\frac{m(\theta_2 - \theta_1)}{t}$

Equating, we get

$$\frac{2\pi Kl\left(\theta - \frac{\theta_1 + \theta_2}{2}\right)t}{\log_e \frac{r_2}{r_1}} = \frac{m(\theta_2 - \theta_1)}{t}$$

$$\therefore \qquad K = \frac{m(\theta_2 - \theta_1)\log_e \frac{r_2}{r_1}}{t2\pi l\left(\theta - \frac{\theta_1 - \theta_2}{2}\right)} \qquad (11.80)$$

11.8.3 Conductivity of Gas

Determination of thermal conductivity of gases faces great difficulty as it is very small. Gases require container to be kept in, which are of larger thermal conductivity than gases. Again, two other processes of heat transfer—convection and radiation—also play an important role in the determination of thermal conductivity of gases. Scientists devised methods overcoming these difficulties. We shall describe one such method.

Laby and Hercus method: Laby and Hercus method was developed by Laby and Hercus in 1919. The arrangement of the apparatus is as shown in Fig. 11.16.

P, Q and S are copper plates. R is a guard ring made of copper. P, Q and R are heated electrically and maintained at temperature θ_1.

The gas under test is enclosed in between P, Q and S. The principle of this method is that heat is supplied electrically in P to the gas, for eliminating convection. Gas present in between Q and S conducts heat from Q to S which is taken away by water flowing below S. A guard ring R surrounds Q to make the lines of flow of heat normal to Q and is maintained at the same temperature as Q by another heater coil in R. To perform the experiment, the heaters in P, Q and R are switched on and the temperatures of Q and S are noted from thermocouples attached to them with time. After some time, the temperature will be steady; let the steady temperature of Q be θ_1 and that of S be θ_2, d is the distance of S from Q and A is the area of cross section of Q. If E and I are the potential difference and current in the heater coil, and K is the conductivity of gas, then we can write

$$\frac{EI}{J} = KA\frac{(\theta_1 - \theta_2)}{d} \tag{11.81}$$

The action due to radiation is eliminated by performing another experiment in which the electrical energy supplied is changed from EI to E ‘I’ and d is changed to d' to keep the temperature difference $\theta_1 - \theta_2$ same. Hence, the amount of heat transfer by radiation h is unchanged. So, we can write

$$\frac{EI}{J} = KA\frac{(\theta_1 - \theta_2)}{d} + h \tag{11.82}$$

$$\frac{E'I'}{J} = KA\frac{(\theta_1 - \theta_2)}{d'} + h \tag{11.83}$$

Subtracting Eqs 11.82 and 11.83, we get

$$\frac{EI - E'I'}{J} = KA(\theta_1 - \theta_2)\left(\frac{1}{d} - \frac{1}{d'}\right) \tag{11.84}$$

K can be calculated as other quantities are known.

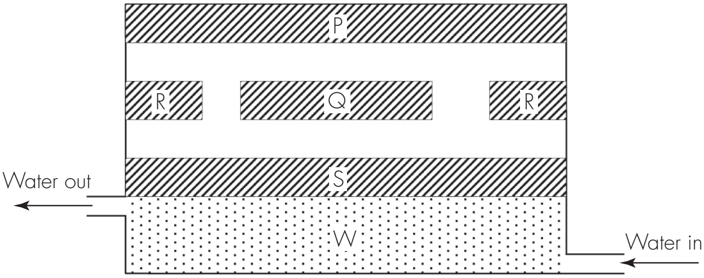


Fig. 11.16 Apparatus used by Laby and Hercus

11.9 PERIODIC FLOW OF HEAT

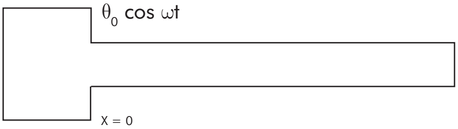


Fig. 11.17 Scheme showing periodic flow of heat

In all the considerations till now, source of heat is supplying heat at a constant rate. Now, we shall consider a source which supplies heat periodically to one end of a bar. Here, we may also include the heat loss by radiation from the surface of the bar or exclude it. Excluding radiation means that the bar is having a guard ring or jacket which is similar to the propagation of periodic temperature wave in a semi infinite solid in a specified direction. It resembles the daily and yearly temperature variation in the earth's surface.

In dealing with such problem, we consider one end of such a jacketed bar in a source whose periodic variation of temperature is given by $\theta = \theta_0 \cos \omega t, \theta$ is the temperature measured from its mean value, θ_0 is amplitude of temperature variation, ω is the pulsatance $= 2\pi n = 2\pi/\tau$ where n is the frequency and τ is the time period, t is the time. The situation is shown in Fig. 11.17.

The variation of temperature at points of the bar can be described by the diagram shown in Fig. 11.18. This diagram is meant for a general case for an unjacketed bar whose mean temperature at the source end is higher than that of the far end. For the bar under consideration, the dotted line coincides with x axis. At any given point along the bar, the temperature variation can be written in the form

$$\theta = a \cos(\omega t - \in) \tag{11.85}$$

where a = amplitude

$$\frac{\in}{\omega} = \text{time lag}$$

The time lag is due to the finite speed of propagation of the temperature wave depending on the heat capacity of the material of the bar. The amplitude decreases with distance from source end; at a large distance, the temperature of the bar becomes same as that of the surroundings.

Considering the heat flow along the x axis, let the equation be

$$\frac{d\theta}{dt} = h\frac{d^2\theta}{dx^2} \tag{11.86}$$

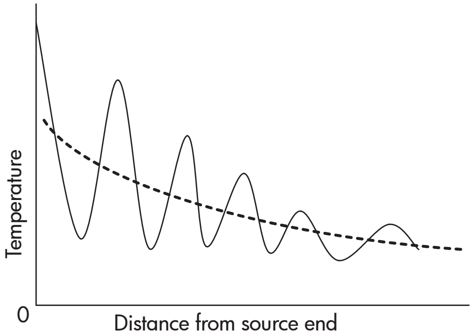


Fig. 11.18 Temperature variation at points of the bar

where $$h = \frac{K}{\rho c} = \text{diffusivity.}$$

With the conditions at $x = 0, \theta = \theta_0 \cos \omega t$

$$\text{and at } x = \propto, \qquad \theta \neq \propto$$

Let us try a solution

$$\theta = Ae^{\alpha x + i\beta t} \tag{11.87}$$

where $i = \sqrt{-1}$, A, α and β are constant.

$$\frac{d\theta}{dt} = i\beta Ae^{\alpha x + i\beta t} = i\beta\theta$$

$$\frac{d\theta}{dx} = \alpha Ae^{\alpha x + i\beta t} = \alpha\theta$$

$$\frac{d^2\theta}{dx^2} = \alpha^2 Ae^{\alpha x + i\beta t} = \alpha^2\theta$$

Putting the values in Eq. 11.86, we get

$$i\beta\theta = h\alpha^2\theta \qquad \alpha = \pm\sqrt{\frac{i\beta}{h}}$$

then from Eq. 11.87,

$$\theta = Ae^{\pm\sqrt{\frac{i\beta}{h}}x + i\beta t} \tag{11.88}$$

Again from $$(1+i)^2 = 1 + 2i + i^2 = 1 + 2i - 1 = 2i$$

$\therefore$ $$\sqrt{i} = \frac{1}{\sqrt{2}}(1+i)$$

From Eq. 11.88, we get

$$\theta = Ae^{\pm\sqrt{\frac{\beta}{2h}}(1+i)x + i\beta t}$$

or $$\theta = Ae^{-\sqrt{\frac{\beta}{2h}}(1+i)x + i\beta t} \quad \text{since } \theta \neq \infty \text{ when } x = \infty \tag{11.89}$$

$\therefore$ $$\theta = Ae^{-\sqrt{\frac{\beta}{2h}}x} \; e^{i\left(\beta t - \sqrt{\frac{\beta}{2h}}x\right)}$$

$$= Ae^{-\sqrt{\frac{\beta}{2h}}x}\left[\cos\left(\beta t - \sqrt{\frac{\beta}{2h}}x\right) + i\sin\left(\beta t - \sqrt{\frac{\beta}{2h}}x\right)\right] \tag{11.90}$$

Since the imaginary term is of no use, we get

$$\theta = Ae^{-\sqrt{\frac{\beta}{2h}}x} \cos\left(\beta t - \sqrt{\frac{\beta}{2h}}x\right) \tag{11.91}$$

At $x = 0, \theta = A \cos \beta t$

We know that at $x = 0, \theta = \theta_0 \cos \omega t$

$\therefore$ $A \cos \beta t = \theta_0 \cos \omega t$

Comparing $A = \theta_0$ and $\beta = \omega$, our Eq. 11.91 becomes

$$\theta = \theta_0 e^{-\sqrt{\frac{\omega}{2h}}x} \cos\left(\omega t - \sqrt{\frac{\omega}{2h}}x\right) \tag{11.92}$$

The equation shows that the temperature wave is travelling with a velocity $\sqrt{2\omega h}$.

If we consider radiation from the side of the bar, then our equation is

$$\frac{d\theta}{dt} = h\frac{d^2\theta}{dx^2} - \mu\theta \tag{11.93}$$

where $\mu = Ep/A\ \rho c$, the symbols having their usual meanings.

The initial conditions are:

$$\text{At } x = 0, \theta = \theta_0 \cos \omega t$$

$$\text{and at } x = \propto, \quad \theta \neq \propto$$

For solving, let us put $\theta = e^{-\mu t}\ \psi$ (11.94)

where ψ is a function of x and t

$$\frac{d\theta}{dt} = -\mu e^{-\mu t}\psi + e^{-\mu t}\frac{d\psi}{dt}$$

$$\frac{d\theta}{dx} = \frac{d\psi}{dx}e^{-\mu t}$$

$$\frac{d^2\theta}{dx^2} = \frac{d^2\psi}{dx^2}e^{-\mu t}$$

Putting these values in Eq. 11.93, we get

$$-\mu e^{-\mu t}\psi + e^{-\mu t}\frac{d\psi}{dt} = h\frac{d^2\psi}{dx^2}e^{-\mu t} - \mu e^{-\mu t}\psi$$

or $$\frac{d\psi}{dt} = h\frac{d^2\psi}{dx^2}$$

This equation can be solved as in the previous way.

11.10 ANGSTROM'S EXPERIMENT

Angstrom determined the conductivity of the material of a bar by periodically heating and cooling it. The bar was heated and cooled periodically by passing steam and water at regular intervals through a chamber at one end of the bar as shown in Fig. 11.19.

In this way, the temperature at points along the bar fluctuate periodically and on account of surface radiation the temperature amplitude diminishes as the distance from the region of supply increases.

The bar must be chosen so that it is sufficiently long to allow us to neglect the effect of terminal faces. The fluctuations should die away at a short distance from the cooler end, which thus has the same temperature as the air surrounding it. When the heating and cooling continues long enough, the periods develop themselves completely so that the mean temperature at any point of the bar maintains some constant value.

The bar was heated for 12 minutes by passing steam and cooled by passing water for 12 minutes so that the period was 24 minutes in total. Temperatures were observed at two points x and $x + l$ along the bar every minute by means of two thermocouples.

The temperature along the bar will be periodic both in distance and in time. The total effect is a propagation of heat wave which is damped, that is, the amplitude of temperature variation at any point dies away as one proceeds along the bar towards the cold end.

So, the temperature θ at any point is a function of x and t and is expected to be of the form

$$\theta(x,t) = \sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x} \sin(n\omega t + \beta_n x + \gamma_n) \tag{11.95}$$

In this case since there is no guard ring, the equation is

$$\frac{d\theta}{dt} = h\frac{d^2\theta}{dx^2} - \mu\theta \tag{11.96}$$

From Eq. 11.95,

$$\frac{d\theta}{dt} = \sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x}\, n\omega \cos(n\omega t + \beta_n x + \gamma_n)$$

$$\frac{d\theta}{dx} = \sum_{n=0}^{n=\infty} A_n(-\alpha_n) e^{-\alpha_n x} \sin(n\omega t + \beta_n x + \gamma_n)$$

$$+ \sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x}\, \beta_n \cos(n\omega t + \beta_n x + \gamma_n)$$

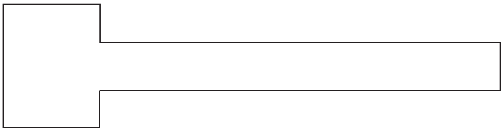


Fig. 11.19 Schematic representation of Angstrom's experiment

$$\frac{d^2\theta}{dx^2} = \sum_{n=0}^{n=\infty} A_n\left(-\alpha^2{}_n\right)e^{-\alpha_n x}\sin(n\omega t+\beta_n x+\gamma_n)$$

$$+\sum_{n=0}^{n=\infty} A_n(-\alpha_n)e^{-\alpha_n x}\ \beta_n\cos(n\omega t+\beta_n x+\gamma_n)$$

$$+\sum_{n=0}^{n=\infty} A_n(-\alpha_n)e^{-\alpha_n x}\ \beta_n\cos(n\omega t+\beta_n x+\gamma_n)$$

$$-\sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x}\ \beta^2{}_n\sin(n\omega t+\beta_n x+\gamma_n)$$

Therefore, Eq. 11.96 changes to

$$\sum_{n=0}^{n=\infty} A_n n\omega e^{-\alpha_n x}\cos(n\omega t+\beta_n x+\gamma_n)$$

$$=h\left(\sum_{n=0}^{n=\infty} A_n\alpha^2{}_n e^{-\alpha_n x}\sin(n\omega t+\beta_n x+\gamma_n)\right.$$

$$-2\sum_{n=0}^{n=\infty} A_n\alpha_n\beta_n e^{-\alpha_n x}\cos(n\omega t+\beta_n x+\gamma_n)$$

$$\left.-\sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x}\beta^2{}_n\sin(n\omega t+\beta_n x+\gamma_n)\right)$$

$$-\mu\sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x}\sin(n\omega t+\beta_n x+\gamma_n)$$

Equating coefficients of $\sin(n\omega t+\beta_n x+\gamma_n)$, we get

$$h\left(\sum_{n=0}^{n=\infty} A_n\alpha^2{}_n e^{-\alpha_n x}-\sum_{n=0}^{n=\infty} A_n\beta^2{}_n e^{-\alpha_n x}\right)=\mu\sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x}$$

or $$h(\alpha^2{}_n-\beta^2{}_n)=\mu$$

or $$\alpha^2{}_n-\beta^2{}_n=\frac{\mu}{h} \tag{11.97}$$

Equating coefficients of $\cos(n\omega t+\beta_n x+\gamma_n)$

$$\sum_{n=0}^{n=\infty} A_n n\omega e^{-\alpha_n x}=-2h\sum_{n=0}^{n=\infty} A_n\alpha_n\beta_n e^{-\alpha_n x}$$

$$n\omega=-2h\alpha_n\beta_n \qquad \therefore \alpha_n\beta_n=-\frac{n\omega}{2h} \tag{11.98}$$

From Eqs 11.97 and 11.98, α_n and β_n can be determined and the complete solution is known. To find A_n and γ_n, the temperatures at two points x and $x + l$ are determined as a function of t

$$\theta_x = \sum_{n=0}^{n=\infty} B_n \sin(n\omega t + \delta_n)$$

$$\theta_{x+l} = \sum_{n=0}^{n=\infty} B'_n \sin(n\omega t + \delta'_n)$$

where B_n, B_n', δ_n and δ_n' are constants for the two places and are given by

$$B_n = A_n e^{-\alpha_n x} \tag{11.99}$$

$$B'_n = A_n e^{-\alpha_n (x+l)} \tag{11.100}$$

$$\delta_n = \beta_n x + \gamma_n \tag{11.101}$$

$$\delta'_n = \beta_n (x+l) + \gamma_n \tag{11.102}$$

From Eq. 11.99, $\log_e B_n = \log_e A_n - \alpha_n x$

From Eq. 11.100, $\log_e B'_n = \log_e A_n - \alpha_n (x+l)$

Subtracting $$\alpha_n l = \log_e \frac{B_n}{B'_n} \tag{11.103}$$

from Eqs 11.101 and 11.102, $\delta'_n - \delta_n = \beta_n l$ (11.104)

from Eqs 11.103 and 11.104, we get

$$\alpha_n \beta_n l^2 = \left(\log_e \frac{B_n}{B'_n}\right)(\delta'_n - \delta_n)$$

$$\therefore \quad \alpha_n \beta_n = \frac{1}{l^2}\left[\left(\log_e \frac{B_n}{B'_n}\right)(\delta'_n - \delta_n)\right] \tag{11.105}$$

$$= -\frac{n\omega}{2h} \quad \text{from eqn. (11.98)}$$

So, we get

$$\frac{1}{l^2}\left(\log_e \frac{B_n}{B'_n}\right)(\delta'_n - \delta_n) = -\frac{n}{2h}\frac{2\pi}{T} = -\frac{n\pi}{hT}$$

$$\therefore \quad h = \frac{n\pi l^2}{T\left(\log_e \frac{B_n}{B'_n}\right)(\delta'_n - \delta_n)} = \frac{K}{\rho c} \tag{11.106}$$

where h = diffusivity
K = thermal conductivity
ρ = density
c = specific heat of the material

$$\therefore \qquad K = \frac{n\pi l^2 \rho c}{T\left(\log_e \frac{B_n}{B_n'}\right)(\delta_n - \delta_n')} \tag{11.107}$$

Thus, the value of K can be calculated if all the quantities on the right hand side are known.

We get as many independent values of h as there are terms in Eq. 11.95. Generally, first two or three terms are important as the coefficients diminish rapidly.

The evaluation of the constants B_n, B_n', δ_n and δ_n' can be done as follows:

$$\theta_x = \sum_{n=0}^{n=\infty} B_n \sin(n\omega t + \delta_n)$$

$$= B_0 \sin\delta_0 + B_1 \sin(\omega t + \delta_1) + B_2 \sin(2\omega t + \delta_2) + \ldots\ldots$$

In order to obtain the value of B_n, we integrate the above equation after multiplying it by $\sin(nwt)dt$

$$\int_0^{2\pi} \theta_x \sin(nwt)dt = \int_0^{2\pi} B_0 \sin\delta_0 \sin(nwt)dt + \int_0^{2\pi} B_1 \sin(wt + \delta_1)\sin(nwt)dt + \ldots\ldots\ldots$$

$$+ \int_0^{2\pi} B_n \sin^2(n\omega t + \delta_n)dt$$

On integration, all terms except the nth term in the right hand side vanish. So, we get

$$\int_0^{2\pi} \theta_x \sin(n\omega t)dt = \pi B_n \sin\delta_n$$

or

$$\frac{1}{\pi}\int_0^{2\pi} \theta_x \sin(n\omega t)dt = B_n \sin\delta_n = S_{\sin}$$

Similarly,

$$\frac{1}{\pi}\int_0^{2\pi} \theta_x \cos(n\omega t)dt = B_n \cos\delta_n = S_{\cos}$$

$$\therefore \qquad B_n^2 = S_{\sin}^2 + S_{\cos}^2 \tag{11.108}$$

and

$$\tan\delta_n = \frac{S_{\sin}}{S_{\cos}} \tag{11.109}$$

To find the values of $S_{\cos}$ and $S_{\sin}$, first the curve between θ_x and t is plotted from which a second curve between θ_x sin wt and t is plotted and a third one between θ_x cos wt and t is drawn. In these curves, the area lying between the curve and the t axis for values lying between $t = t_1$ and $t = t_1 + T$ is measured with a planimeter giving $S_{\sin}$ and $S_{\cos}$.

To find the values of B_n' and δ_n', we have to multiply by sin($n\omega t$)dt and cos($n\omega t$)dt and proceed as before. The same process has to be applied for θ_{x+1}.

11.11 CONDUCTIVITY OF EARTH'S CRUST

The periodic flow of heat is very efficient in determining the conductivity of earth's crust. The earth's surface gets heated during the day and cooled during the night. This heating and cooling causes heat wave to travel inside the earth (diurnal wave). The earth also receives more heat during summer than in winter; this causes another heat wave to pass through earth's crust having a period of one year (annual wave). We assume the wave to be simple harmonic due to which the diurnal wave comes close by this, while the annual wave departs much. The matter is equivalent to an infinite wall periodically heated and cooled at one end or to a bar provided with a guard ring which is periodically heated and cooled. For investigation of movement of temperature wave inside the earth, some thermometers are provided at different depths.

The fluctuation of temperature at any point with in the earth can be written as

$$\theta = \theta_0 e^{-\sqrt{\frac{\omega}{2h}}x} \cos\left(\omega t - \sqrt{\frac{\omega}{2h}}x\right) \tag{11.110}$$

where x is the distance of the point from the source $\omega = 2\pi/T$ and velocity of wave $= \sqrt{2\omega h}$, $\sqrt{2\omega h}$, $v = -w/\beta$ and $\alpha_n^2 - \beta_n^2 = \mu/h = 0$ in our case as radiation loss in avoided.

So, $$\alpha_n = -\beta_n$$

Now, $$\alpha_n \beta_n = -\frac{n\omega}{2h}$$

or $$\beta_n^2 = \frac{n\omega}{2h}$$

$$\beta = \sqrt{\frac{\omega}{2h}} = \sqrt{\frac{2\pi}{T2h}} = \sqrt{\frac{\pi}{Th}} \tag{11.111}$$

$$\alpha = -\beta = \sqrt{\frac{\pi}{Th}}$$

$$v = -\frac{\omega}{\sqrt{\frac{\pi}{Th}}} = \omega\sqrt{\frac{hT}{\pi}} = \frac{2\pi}{T}\sqrt{\frac{hT}{\pi}} = 2\sqrt{\frac{\pi h}{T}} \tag{11.112}$$

For daily wave, $T = 24$ hours $= 86400$ sec
Taking $h = 0.0049$ for ordinary moist soil,

$$v = 2\sqrt{\frac{3.14 \times 0.0049}{86400}} = 8.4 \times 10^{-4} \text{ cm/sec} \tag{11.113}$$

11.12 WIEDEMANN–FRANZ LAW

Wiedemann–Franz law states that the ratio of the thermal (K) to electrical conductivities (σ) is the same for all metals at the same temperature.

$$\frac{K}{\sigma} = \text{constant} \tag{11.114}$$

Lorentz extended it by adding that the value of the ratio is proportional to absolute temperature

$$\frac{K}{\sigma T} = \text{constant} \tag{11.115}$$

Drude gave a mathematical deduction based on the assumption that the presence of free electrons inside metals is responsible for the thermal and electrical conductivities. He further assumed that these free electrons behave like gas molecules and that the law of equipartition of energy is valid for them.

For deducing the law, we have to deduce thermal conductivity and electrical conductivity in terms of electrons.

Let us take the case of electrical conductivity. When a block of metal is subjected to electric field (i.e., a voltage is applied between two points of a metal block), the electron cloud will develop a drift velocity in the direction opposite to that of the field. While calculating the drift velocity, we shall neglect the Maxwellian distribution of electronic velocity and attribute to all free electrons the same speed u of thermal agitation which we shall take to be large compared with the superposed drift velocity produced by the field. Furthermore on account of small dimensions of the electrons, we shall assume that collisions between electrons occur so infrequently as to be negligible in number compared with collisions of electrons with atoms.

Let e be the charge of the electron and m be its mass; then the acceleration given to it by a field E is

$$f = \frac{eE}{m}$$

If λ is the mean free path between two successive collisions and u is the velocity of thermal agitation, then time taken per collision is λ/u.

Then, the drift velocity acquired in the course of single free path is $v = ft = f(\lambda / u) = (eE / m)(\lambda / u)$ in the direction of the field.

As the drift velocity is zero at the beginning of the free path, the mean drift velocity is half of this, that is

$$\overline{v} = \frac{1}{2}\frac{eE}{m}\frac{\lambda}{u} \tag{11.116}$$

Let us consider unit area of the metal. Thus in one second, the electrons contained in a cylinder of volume $1 \times 1 \times \overline{v} = \overline{v}$ will pass through unit area in unit time.

The total charge passing through a unit area of cross section in unit time or the current developed $J = n\overline{v}e$ where n is the number of electrons per cc and $J =$ current density $=$ the charge flowing through unit area at right angles to the direction of flow in unit time.

$$J = n\overline{v}e = \frac{1}{2}\frac{nEe^2\lambda}{mu} \tag{11.117}$$

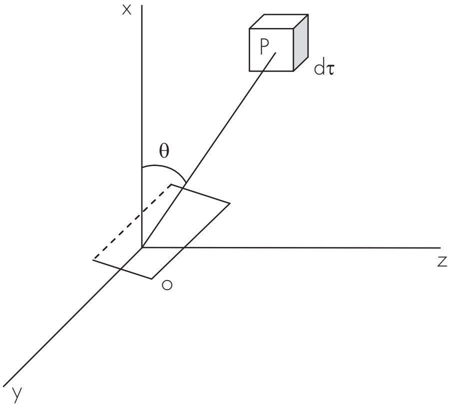


Fig. 11.20 Figure to study the Wiedemann-Franz law

Let us consider a cylinder of base area unity, and the bases are separated by unit distance. Let its resistance be ρ.

Its conductivity $= \dfrac{1}{\rho} = \sigma$

The conductivity is defined as the ratio of the current density to the electric intensity. Therefore,

$$\sigma = \frac{J}{E} = \frac{1}{2}\frac{ne^2\lambda E}{muE} = \frac{1}{2}\frac{ne^2\lambda}{mu} \tag{11.118}$$

As u varies with the square root of T, the conductivity should vary inversely with the square root of the absolute temperature; provided the other quantities appearing in this equation are constants. In pure metal, it is actually nearly proportional to the inverse first power of T.

Then, we consider the case of thermal conductivity. Let us take the origin at the centre of a unit area perpendicular to the x axis (Fig. 11.20).

Let us now consider the electrons whose free paths originate in volume element $d\tau$ at P. If n be the number of electrons per unit volume, then $nd\tau$ electrons are inside the volume element $d\tau$.

Now, we shall calculate the heat Q which passes through unit area in unit time in a metal which has temperature gradient along the x axis.

Let the collision frequency of an electron be Γ, that is, the number of collisions of an electron per second. Therefore, the total number of collisions per second due to electrons contained in the volume $d\tau$ is $\Gamma nd\tau$ and they start out on a fresh free path.

The distance of body from origin $= r$, the probability of a molecule to travel a distance r without having collision $= e^{-\frac{r}{\lambda}}$. The total number of molecules travelling a distance r without suffering collision

$$= e^{-\frac{r}{\lambda}} n\Gamma d\tau \tag{11.119}$$

As the unit area at 'o' subtends a solid angle $\cos\theta/r^2$ at P, only $\cos\theta/4\pi r^2$ of these electrons are passing through unit area at 'o'.

The number of electrons whose free paths begin at p crossing this unit area at 'o' per sec is

$$n\Gamma d\tau \frac{\cos\theta}{4\pi r^2} e^{-\frac{r}{\lambda}}$$

Let us now consider electrons contained in the ring of volume $2\pi r^2 \sin\theta d\theta dr$ (Fig. 11.21).

Let T be the temperature at the origin; then the temperature of the ring = $T + \partial \mathrm{T}/\partial \mathrm{X}\; r\cos\theta$.

According to the law of equipartition of energy, energy carried out by each electron is

$$\frac{3}{2}k\left(T+\frac{\partial T}{\partial x}r\cos\theta\right)$$

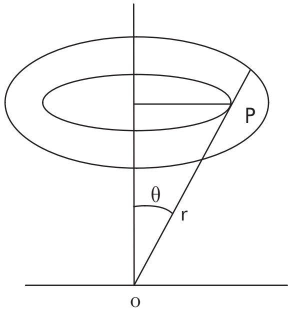


Fig. 11.21 Another figure to study the law

Therefore, the total energy carried in through the surface in the positive direction of the x axis is

$$Q=-\int_0^\infty\int_0^\pi \frac{\cos\theta}{4\pi r^2}e^{-\frac{r}{\lambda}}\, n\Gamma 2\pi r^2 \sin\theta d\theta dr\frac{3}{2}k\left(T+\frac{\partial T}{\partial x}r\cos\theta\right)$$

$$=-\frac{3}{4}nk\Gamma\int_0^\infty e^{-\frac{r}{\lambda}}dr\int_0^\pi\left(T+\frac{\partial T}{\partial x}r\cos\theta\right)\sin\theta d\theta\cos\theta$$

$$=-\frac{3}{4}nk\Gamma\int_0^\infty e^{-\frac{r}{\lambda}}\frac{2}{3}r\frac{dT}{dx}dr$$

$$=-\frac{3}{4}nk\Gamma\frac{2}{3}\frac{dT}{dx}\int_0^\infty e^{-\frac{r}{\lambda}}rdr$$

$$=-\frac{1}{2}nk\Gamma\frac{dT}{dx}\left(-r\lambda e^{-\frac{r}{\lambda}}-\lambda^2 e^{-\frac{r}{\lambda}}\right)_0^\infty$$

The first term is zero at both the limits, the second term at upper limit is zero but with lower limit it is λ^2

$$Q=-\frac{1}{2}nk\Gamma\frac{dT}{dx}\lambda^2 \tag{11.120}$$

Now, $\Gamma\lambda$ is the mean velocity due to thermal agitation, $\Gamma\lambda = u$

$$Q=-\frac{1}{2}nku\frac{dT}{dx}\lambda \tag{11.121}$$

This is the heat flowing per second in unit area in the positive direction of the x axis.

From the equation of conductivity,

$$Q=-K\frac{\partial T}{\partial x}$$

where $\partial T/\partial x$ is the temperature gradient along the positive direction of x axis and K is the thermal conductivity.

$$\therefore \qquad -K\frac{\partial T}{\partial x} = -\frac{1}{2}nku\frac{dT}{dx}\lambda$$

$$\therefore \qquad K = \frac{1}{2}nu\,\lambda k \tag{11.122}$$

$$\therefore \qquad \frac{K}{\sigma} = \frac{\frac{1}{2}nu\,\lambda k}{\frac{1}{2}\frac{ne^2\lambda}{mu}} = k\frac{u^2m}{e^2}$$

mu^2 is the twice the mean kinetic energy of an election and is equal to $3kT$ by the principle of equipartition of energy.

$$\therefore \qquad \frac{K}{\sigma} = \frac{k}{e^2}3kT = 3\left(\frac{k}{e}\right)^2 T \tag{11.123}$$

$$\therefore \qquad \frac{K}{\sigma T} = 3\left(\frac{k}{e}\right)^2 = \text{constant as } k \text{ and } e \text{ are constants}$$

$$\frac{K}{\sigma} = 3\left(\frac{1.38\times10^{-16}}{4.8\times10^{-10}}\right)^2 \times 273 = 0.68\times10^{-10}\text{ esu}$$

at a temperature of 273° absolute. Furthermore the temperature coefficient of the ratio, the increase in the ratio per unit rise in temperature divided by the value of the ratio at 0° is $1/273°\text{c} = 3.66(10)^{-3}\ /1\ °\text{c}$

It was found that at and above room temperature, the value of K/σ is nearly constant, that is, Wiedemann–Franz law is valid in that range of temperature. But at lower temperature, K/σ decreases instead of remaining constant. This law does not hold good at low temperature; from experimental results, it appears that the value of the ratio approaches to zero at 0 K. With lowering of temperature, both K and σ increase; but, the latter increases much more rapidly. Holst found that of mercury, σ becomes infinite (super conduction) while K still remains finite. Messer and Lees found that for *Cu*, the value of $K/\sigma T$ at 20 K was one-seventh of its value at room temperature.

"The variation of $K/\sigma T$ indicates that thermal conductivity is not determined only by free electrons, there must be some other agency responsible for conduction of metals. It is quite probable that the agency is the elastic binding force between different atoms as in the case of conduction through insulators."

11.13 JAEGER AND DIESSELHORST METHOD

Kohlrausch introduced a method of determining the ratio of thermal to electrical conductivity. He pointed out that a simple way of determining the thermal conductivity of a metal is to measure the temperature distribution in the metal when it is heated by an electric current. The theory of this method depends upon the fact that when a steady state has been reached, the heat gained by any element by conduction plus the heat generated by the electric current in the element is zero. This was experimentally worked out by Jaeger and Diesselhorst. The theory of this method is as follows:

Let us take the case of a solid cylinder of metal of which the thermal conductivity is to be determined. We assume that the current lines are parallel to the axes, the heat losses are negligible and the

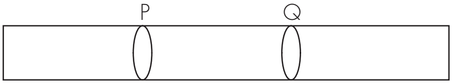


Fig. 11.22 Schematic representation of Jaeger and Diesselhorst method

flow of heat is parallel to the axis. Let x be the position coordinate of the plane P measured along the axis (Fig. 11.22).

Let v, T be the electric potential and temperature of the same plane and let $(x + dx)$ be the position coordinate of the plane Q whose electrical potential and temperature are $(v + dv)$ and $(T + dT)$, respectively. Let A be the cross section of the cylindrical bar, K and σ be the thermal and electrical conductivity. Both K and σ are the functions of the temperature and so vary along the length of the bar.

Heat flowing in unit time into the element over the area at P is equal to

$$-KA\frac{d\theta}{dx}$$

and that flowing into it over the area at Q in unit time is equal to

$$-\left[KA\frac{d\theta}{dx}+\frac{d}{dx}\left(KA\frac{d\theta}{dx}\right)dx\right]$$

The net gain of heat by conduction in unit time is, therefore,

$$A\frac{d}{dx}\left(K\frac{d\theta}{dx}\right)dx \tag{11.124}$$

The electrical energy supplied to the element in unit time is

$$i^2R = A\sigma\left(\frac{dv}{dx}\right)^2 dx \tag{11.125}$$

for $$R=\frac{dx}{A\sigma} \text{ and } i=-\frac{dv}{dx}A\sigma$$

When a steady state has been reached, the total rate of gain of heat by the element is zero; so, we have

$$A\frac{d}{dx}\left(K\frac{d\theta}{dx}\right)dx + A\sigma\left(\frac{dv}{dx}\right)^2 dx = 0$$

in case where there is no loss of heat from the sides due to radiation.

Then, $$\frac{d}{dx}\left(K\frac{d\theta}{dx}\right)+\sigma\left(\frac{dv}{dx}\right)^2 = 0$$

or $$\frac{dK}{dx}\frac{d\theta}{dx}+K\frac{d^2\theta}{dx^2}+\sigma\left(\frac{dv}{dx}\right)^2 = 0 \tag{11.126}$$

We may write $$\frac{d\theta}{dx} = \frac{d\theta}{dv}\frac{dv}{dx}$$

$$\frac{d}{dx}\left(\frac{d\theta}{dx}\right) = \frac{d^2\theta}{dx^2} = \frac{d\theta}{dv}\frac{d^2v}{dx^2} + \frac{d^2\theta}{dv^2}\left(\frac{dv}{dx}\right)^2$$

So, Eq. 11.126 changes to

$$\frac{dK}{dx}\frac{d\theta}{dv}\frac{dv}{dx} + K\frac{d\theta}{dv}\frac{d^2v}{dx^2} + K\frac{d^2\theta}{dv^2}\left(\frac{dv}{dx}\right)^2 + \sigma\left(\frac{dv}{dx}\right)^2 = 0$$

If we assume that K and σ are constants, then $dK/dx = 0$.
So, we get

$$K\frac{d\theta}{dv}\frac{d^2v}{dx^2} + K\frac{d^2\theta}{dv^2}\left(\frac{dv}{dx}\right)^2 + \sigma\left(\frac{dv}{dx}\right)^2 = 0 \tag{11.127}$$

Since the same current is flowing throughout the specimen, $i = A\sigma\, dv/dx$ is constant as both A and σ are constants; so, dv/dx = constant.

∴ $$\frac{d^2v}{dx^2} = 0$$

∴ Eq. 11.127 becomes

$$K\frac{d^2\theta}{dv^2} + \sigma = 0$$

or $$\frac{K}{\sigma}\frac{d^2\theta}{dv^2} + 1 = 0 \tag{11.128}$$

Integrating

$$\frac{K}{\sigma}\frac{d\theta}{dv} + v = -\alpha$$

Integrating again, we get

$$\frac{K}{\sigma}\theta + \frac{1}{2}v^2 = -\alpha v - \beta$$

where α and β are constants of integration.

Or $$\frac{K}{\sigma}\theta + \frac{1}{2}v^2 + \alpha v + \beta = 0 \tag{11.129}$$

Let $(\theta_1, v_1), (\theta_2, v_2), (\theta_3, v_3)$ be the temperature and potential at three points of the bar. Then, we have from Eq. 11.129

$$\frac{K}{\sigma}\theta_1 + \frac{1}{2}v_1^{\,2} + \alpha v_1 + \beta = 0 \tag{11.130}$$

$$\frac{K}{\sigma}\theta_2 + \frac{1}{2}v_2^{\,2} + \alpha v_2 + \beta = 0 \tag{11.131}$$

Subtracting, we get

$$\frac{K}{\sigma}(\theta_1 - \theta_2) + \frac{1}{2}(v_1^{\,2} - v_2^2) + \alpha(v_1 - v_2) = 0$$

or

$$\alpha = \frac{K}{\sigma}\frac{(\theta_1 - \theta_2)}{(v_2 - v_1)} - \frac{1}{2}(v_2 + v_1) \tag{11.132}$$

Multiplying Eq. 11.130 by v_2 and Eq. 11.131 by v_1, we get

$$\frac{K}{\sigma}\theta_1 v_2 + \frac{1}{2}v_1^2 v_2 + \alpha v_1 v_2 + \beta v_2 = 0$$

$$\frac{K}{\sigma}\theta_2 v_1 + \frac{1}{2}v_2^2 v_1 + \alpha v_2 v_1 + \beta v_1 = 0$$

Subtracting,

$$\frac{K}{\sigma}(\theta_1 v_2 - \theta_2 v_1) + \frac{1}{2}v_1 v_2 (v_1 - v_2) = \beta(v_1 - v_2)$$

$\therefore$

$$\beta = \frac{K}{\sigma}\frac{(\theta_1 v_2 - \theta_2 v_1)}{(v_1 - v_2)} + \frac{1}{2}v_1 v_2 \tag{11.133}$$

Equation 11.129 gives the equation of a hyperbola. Measuring temperature and electric potential at the three points $(\theta_1, v_1), (\theta_2, v_2)$ and (θ_3, v_3), if we plot them we get a curve as shown in Fig. 11.23.

The temperature will be maximum at *O* and will fall off at the two ends. Two points *A* and *B* were found where the temperatures θ_1, θ_2 will be equal due to the symmetry of the curve.

Let *A* (θ_1, v_1), *O* (θ_3, v_3) and *B* (θ_2, v_2) denote the three points, then $\theta_1 = \theta_2$ and $v_3 = v_1 + v_2 / 2$

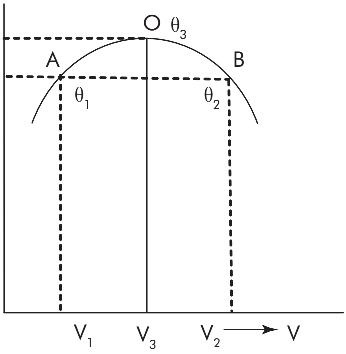


Fig. 11.23 Temperature-electrical potential curve at different points of the rod

Therefore,

$$\alpha = -v_3 \tag{11.134}$$

and

$$\beta = -K\frac{\theta_0}{\sigma}\frac{(v_1 - v_2)}{v_1 - v_2} + \frac{1}{2}v_1 v_2 \quad \text{where } \theta_1 = \theta_2 = \theta_0$$

$$= -K\frac{\theta_0}{\sigma} + \frac{1}{8}4v_1 v_2$$

$$= -K\frac{\theta_0}{\sigma} + \frac{1}{8}\left[(v_1 + v_2)^2 - (v_1 - v_2)^2\right]$$

$$= -K\frac{\theta_0}{\sigma} + \frac{1}{2}v_3^2 - \frac{1}{8}(v_1 - v_2)^2 \tag{11.135}$$

Corresponding to the point O (θ_3, v_3) Eq. 11.129 becomes

$$\frac{K}{\sigma}\theta_3 + \frac{1}{2}v_3^2 - v_3\,v_3 - \frac{K}{\sigma}\theta_0 + \frac{1}{2}v_3^2 - \frac{1}{8}(v_1 - v_2)^2 = 0$$

or

$$\frac{K}{\sigma}(\theta_3 - \theta_0) - \frac{1}{8}(v_1 - v_2)^2 = 0$$

$\therefore$

$$\frac{K}{\sigma} = \frac{1}{8}\frac{(v_1 - v_2)^2}{(\theta_3 - \theta_0)} \tag{11.136}$$

Since the temperature and potentials are parabolic in the electrically heated rod, the temperature at middle point will be maximum. In the experiment, Jaeger and Diesselhorst measured the maximum temperature. Next, they found out two points on either side of the maximum point where the temperature were the same. Actually, they measured the temperature of the middle point (θ_3) and the common temperature at the two ends of the bar (θ_0). The potential difference between the points of common temperature ($v_1 - v_2$) was also measured. Thus, K/σ can be calculated from Eq. 11.136.

In the experiment of Jaeger and Diesselhorst, the experimental rod was surrounded by a copper jacket through which water or steam was passed so as to keep the rod at a constant temperature enclosure. In this arrangement, there will be transmission of heat to the surroundings. In deriving the equation, we have neglected this transmission of heat. So, the final equation was corrected for the radial flow of heat.

Simidu modified the apparatus in such a way that radial flow of heat was taken into account, so no correction in final expression was to be applied. Figure 11.24 represents his experimental arrangement.

The experimental rod *R* is provided with a guard ring *G* consisting of a brass tube having a heating spiral H in the middle, B_1 and B_2 are the two baths at its ends. Two copper wires C_1 and C_2 are soldered at the two ends of rod *R*; B_3 and B_4 are the two water baths. *G* is a vacuum covering. A wooden chest encloses the whole apparatus.

By controlling heating current and bath temperature in such a manner that while measuring temperatures at three points I, II, III radial flow of heat was avoided. Potential difference between the point II and any one of the points I or III is measured, knowing all these K/σ can be calculated.

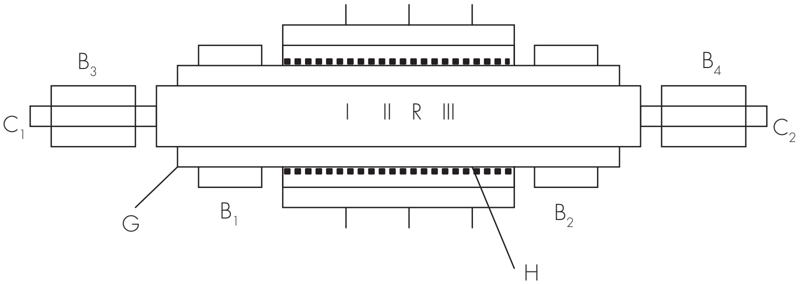


Fig. 11.24 Simidus' experimental arrangement

SOLVED PROBLEMS

Q 1. Calculate the amount of heat that will be conducted in an hour through each square centimetre of an iron plate 3 centimetre thick, its two sides being kept at the respective temperatures of 50 °C and 200 °C, thermal conductivity of iron = 0.12 cgs unit.

Ans: We know

$$Q = KA\frac{d\theta}{dx}t$$

$$\frac{0.12\times 1\times(200-50)\times 60\times 60}{3} = 21600\text{ cal}$$

Q 2. One end of a copper bar of 25 cm long, 10 sq cm in cross section is kept at 100 °C, the other end is cooled by a spiral through which water flows, the water entering the spiral at 14 °C. What must be the rate of flow of water if this end is never to rise above 20 °C when conductivity = 0. 9 cgs unit?

Ans: We know

$$Q = KA\frac{(\theta_1-\theta_2)}{d} = m(\theta_3-\theta_4)$$

$$\frac{0.9\times 10(100-20)}{25} = m(20-14)$$

$$\therefore \qquad m = \frac{9\times 80}{25\times 6} = 4.8\text{ gm per sec.}$$

Q 3. Heat is supplied to a slab of compressed cork 5 cm thick and of effective area 2 sq m by a heating coil spread over its surface. When the current in this coil is 1.18 amperes and the potential difference across its ends 20 volts, the steady temperatures of the faces of the slab are 12.5 °C and 0 °C. Assuming that the whole of the heat developed in the coil is conducted through the slab, calculate the thermal conductivity of the cork.

Ans: We know

$$\frac{EI}{J} = KA\frac{(\theta_1-\theta_2)}{d}$$

$$\frac{1.18\times 20}{4.2} = \frac{K\times 2\times 10^4\times(12.5-0)}{5}$$

$$K = \frac{1.18\times 20\times 5}{4.2\times 2\times 10^4\times 12.5} = 0.00011\text{ cgs unit.}$$

Q 4. Water passes through a glass tube 30 cm long at the rate of 165 cc per minute. It enters the tube at 20 °C and leaves at 40 °C, the outside of the tube being maintained at 100 °C. If the internal and external radii of the tube are 6 mm and 8 mm respectively, determine the thermal conductivity of glass.

Ans: We know

$$\frac{2\pi lK\left(\theta-\dfrac{\theta_1+\theta_2}{2}\right)}{\log_e\dfrac{r_2}{r_1}} = \frac{m(\theta_1-\theta_2)}{t}$$

$$\frac{2\times3.14K\times30\left(100-\frac{40+20}{2}\right)}{\log_e\frac{3}{4}}=\frac{165}{60}(40-20)$$

$$\therefore \qquad K=\frac{165\times20\times\log_e\frac{4}{3}}{60\times2\times3.14\times30\times70}=0.0012 \text{ cgs Unit}$$

Q 5. Two bars of nickel and copper of the same dimensions are coated with wax, and one end of each bar is inserted in a bath containing oil at a high temperature. When the steady state has been reached, it is found that the wax has been melted off the nickel bar to a length of 1.9 cm and of the copper bar to a length of 5 cm. Find the thermal conductivity of nickel given that K for copper = 0.92 cgs unit.

Ans: We know

$$\frac{l_1^2}{K_1}=\frac{l_2^2}{K_2}$$

$$\frac{1.9^2}{K_1}=\frac{5^2}{0.92}$$

$$\therefore \qquad K_1=\frac{0.92\times1.9^2}{5^2}=0.132 \text{ cgs unit}$$

Q 6. Equal bars of copper and aluminium are welded end to end and lagged. If the free ends of copper and aluminium are maintained at 100 °C and 0 °C respectively, find the temperature of the welded interface. Assume the thermal conductivity of copper and aluminium to be 0.92 and 0.50, respectively.

Ans: Let the temperature of the interface be θ, then

$$\frac{K_1A(100-\theta)}{d}=\frac{K_2A(\theta-0)}{d}$$

$$\frac{0.92A(100-\theta)}{d}=\frac{0.5A\theta}{d}$$

$$92-0.92\theta=0.5\theta$$

$$\therefore \qquad \theta=64.8\ ^\circ\text{c}$$

Q 7. Steam at 100 °C is passed through a rubber tube 14.6 cm length which is immersed in a copper calorimeter of thermal capacity 23 cal, containing 440 gm of water. The temperature of the water and calorimeter is found to rise at the rate of 0.19 °C every second when they are at the room temperature 22 °C. The external and internal diameters of the tube are 1 cm and 0.75 cm, respectively. Calculate the conductivity of rubber.

Ans: We know

$$\frac{2\pi Kl\left(\theta - \frac{\theta_1+\theta_2}{2}\right)t}{\log_e \frac{r_2}{r_1}} = (w+m)(\theta_2-\theta_1)$$

$$K = (w+m)\frac{(\theta_2-\theta_1)}{t}\frac{\log_e \frac{r_2}{r_1}}{2\pi l\left(\theta - \frac{\theta_1+\theta_2}{2}\right)}$$

$$= \frac{(23+440)\times .019\times \log_e \frac{1}{0.75}}{2\pi\times 14.6(100-22)} = 0.000354 \text{ cgs unit}$$

Q 8. The temperature inside a cottage is 18 °C while the outside temperature is 4 °C. How much heat is lost per hour by transmission across each square metre of wall (a) when the wall is of stone 25 cm thick and with conductivity 0.008 (b) when the wall is of steel 2 cm thick and with conductivity 0.12 (the conductivity is in cgs unit)?

Ans: We know

$$Q = KA\frac{(\theta_1-\theta_2)t}{d}$$

For stone,

$$Q = \frac{0.008\times 10^4\times(18-4)\times 60\times 60}{25} = 1.6128\times 10^5 \text{ caloreis}$$

For steel,

$$Q = 0.12\times 10^4(18-4)\times 60\times 60 = 3.024\times 10^7 \text{ calories}$$

Q 9. A slab consists of two parallel layers of different materials 4 cm and 2 cm thick and of thermal conductivities 0.54 and 0.36 cgs units, respectively. If the opposite faces of the slab are at 100 °C and 0 °C, calculate the temperature at the surface dividing the two materials.

Ans. Let θ be the temperature at the surface dividing the two materials, then at the steady state same heat is flowing; so,

$$\frac{0.5A(100-\theta)}{4} = \frac{0.36A(\theta-0)}{2}$$

or $$0.25(100-\theta) = 0.36\theta$$

∴ $$25 = 0.36\theta + 0.25\theta = 0.61\theta$$

∴ $$\theta = \frac{25}{0.61} = 41\,^\circ\text{c}$$

Q 10. The temperature at one end varies between 15 °C and 45 °C in a heating cycle of 5 hours. To what distance the temperature variation can be detected by a thermometer reading to 1/10 °C? Thermal conductivity = 0.3 cgs unit, density of the material = 7 gm/cc and specific heat = 1.

Ans. The fluctuation of temperature is represented by

$$\theta = \theta_0 e^{-\sqrt{\frac{\omega}{2h}}x} = \theta_0 e^{-bx}$$

Here, $$\theta = \frac{1}{10}\ ^\circ\text{C},\ \theta_0 = 30\ ^\circ\text{C}$$

$$b = \sqrt{\frac{\omega}{2h}} = \sqrt{\frac{2\pi}{T2h}} = \sqrt{\frac{\pi\rho c}{TK}} = \sqrt{\frac{3.14\times 7\times 1}{5\times 3600\times 0.3}}$$

∴ $$\frac{1}{10} = 30e^{-bx}$$

or $$300 = e^{bx}$$

or $$x = \frac{\log_e 300}{\sqrt{\frac{3.14\times 7}{5\times 3600\times 0.3}}} \quad \text{or} \quad x = \frac{5.7\sqrt{5\times 3600\times 0.3}}{\sqrt{3.14\times 7}} = 89.3\ \text{cm.}$$

PROBLEMS

1. A boiler has 2 cm thick plates and exposes a surface of 2 sq m to the furnace. The temperature of the outside face is kept at 105 °C. If the conductivity of the metal is 0.2 and the latent heat of steam is 540 calories per gm, find how much steam is generated in one hour?

Ans. 66.7 kg

2. A steady stream of water is flowing at the rate of 500 gm a minute through a glass tube 30 cm long, 1 cm in external diameter are 8 mm in bore, the outside of which is surrounded by steam at a pressure of 760 mm of Hg which raises the temperature from 20 °C to 30 °C as it passes through the tube. Find the thermal conductivity of glass.

Ans. 0.001315 cgs unit

3. Calculate approximately the heat passing out per minute through the walls and windows of a room 7 × 5 × 3 metres if the walls are of bricks 20 cm thick and have windows of glass 0.5 cm thick and of total area 5 sq m. The temperature of the room is 20 °C above that of the outside. The thermal conductivity of brick and of glass may be taken as 12×10^{-4} and 17×10^{-4} cgs units.

Ans. 25.225×10^4 cal

4. At the depths of 6, 12, 24 metres, the annual ranges of fluctuation of temperature are 5.6 °C, 2.8 °C, 0.7 °C, respectively. Find the velocity of propagation of the temperature wave into the earth. Also, calculate the diffusivity of the earth's crust.

Ans. 0.15 metres per day,
$0.0746\ \text{cm}^2\ \text{sec}^{-1}$

5. A bar of length 30 cm and uniform cross section 5 cm^2 consists of two halves *AB* of copper and *BC* of iron welded together at *B*. The end *A* is maintained at 200 °C, the end C at 0 °C and the sides are thermally insulated. Find the rate of flow of heat along the bar when the steady state has been reached, thermal conductivity of copper = 0.9 cgs unit and of iron = 0.12 cgs unit.

   Ans. 7.05 cal/sec

6. The hollow space between two very thin concentric copper shells is filled with sand of thermal conductivity 0.13×10^{-3} cgs unit. The radii of the spheres are 6 cm and 4 cm, respectively and the temperature of the hollow space inside the inner sphere is maintained at 100 °C while the outer sphere is kept at 0 °C. Find the quantity of heat passing per minute through the sand when a steady state has been reached.

   Ans. 117.6 cal/minute

7. In the periodic flow method, a rod is heated at one end with a heating cycle of 4 minutes. The temperature maximum travels at the rate of 6 cm per minute. Assuming density of the metal to be 7.8 gm/cc and specific heat 0.11, calculate the thermal conductivity of the metal.

   Ans. 0.164 cgs unit

QUESTIONS

1. Deduce the Fourier equation of one dimensional heat flow. Prove that the length to which the wax melts in the steady state along a wax coated bar is proportional to the square root of the coefficient of thermal conductivity of the material of the bar.
2. Describe Ingen-Hausz's experiment and prove, from mathematical theory, that the conductivities of the different bars vary as the square of the length upto which wax is melted.
3. Describe Forbes' method of determining the thermal conductivity of a metallic bar. Deduce the necessary formula.
4. Work out Despretz's method of comparison of thermal conductivities.
5. Describe Lees' method of determining thermal conductivity of poor conductors.
6. Derive the theory of spherical shell method of determining thermal conductivity of powdered materials.
7. Deduce the theory of cylindrical shell method of determining thermal conductivity of rubber and describe the experiment of measuring it.
8. Describe the experiment of measuring thermal conductivity of glass. Deduce the relevant theory.
9. State the law of Wiedemann and Franz and describe the method to obtain a comparison of thermal conductivities of metal bars.
10. Find an expression for the temperature at any point along a long bar, surrounded by a non-conducting jacket, if one end of the bar has a periodically varying temperature given by $\theta = \theta_0 \cos \omega t$.
11. One end of the long uniform bar is maintained at a temperature θ_1 above its surroundings. Show that when a steady state is attained, the temperature at any point distance x from the hot end exceeds that of the surroundings by an amount $\theta = \theta_1 e^{-bx}$ where b is a constant for specified bar.

12. Describe Angstrom's experiment to measure the thermal conductivities of metal bars.
13. Give an account of the mode of propagation of heat wave into the earth. Give the expression of the velocity of much wave.
14. Prove that a damped heat wave propagates into the interior of earth due to alternate heating and cooling of its surface, and deduce the expression for velocity of propagation of the wave and damping factor.
15. When steam is passed through a circular tube of length l, having internal and external diameters a and b respectively, prove that radial flow of heat outwards is given by

$$Q = \frac{2\pi K l(\theta_1 - \theta_2)}{\log_e \dfrac{b}{a}}$$

16. Describe in detail the method of Forbes and Lees for the determination of conductivity of solids which are good conductors and bad conductors, respectively.
17. Describe suitable methods for measuring conductivities of liquids and gases.
18. A thin rod of uniform cross-sectional area is situated in air at temperature 0 °C. Obtain a differential equation for the flow of heat in the rod, when the steady state is established. Solve it and indicate a problem to which the solution may be applied.

Chapter 12

RADIATION

12.1 INTRODUCTION

In this chapter, we shall study the laws of thermal radiation only. It is the type of radiation the quality and quantity of which depends solely on the temperature of the body emitting radiation. Here, by quality we mean the wavelengths of the radiation emitted and by quantity we mean the energy associated with each wavelength. Thus when a feeble electric current is sent through the wire of an electric heater, we first have a feeling of warmth which gradually increases in intensity as the strength of the current is increased. The wire begins to emit visible light radiation in addition to the invisible heat or infrared radiation, when the temperature of the wire rises to about 550 °C.

At this temperature, the wire appears to be dull red. With rise of temperature, other colours of the visible spectrum are added to the radiation. At the same time, the quantity of visible radiation increases at the expense of heat radiation. At about l200 °C the wire becomes nearly white, that is, almost all the colours of the visible spectrum are emitted by the wire. This is true of all materials of which the heating element may be made. The quality and quantity of radiation, therefore, depends on the temperature of the radiating body and not on the material composing the body.

Thermal radiations are ordinarily emitted by solids and liquids. As such when thermal radiation is dispersed by suitable prism, it shows continuous spectrum.

Radiation emitted by a discharge tube, that resulting from thermal agitation (sodium flame), that caused by bombardment by electrons, photo-electric emission, fluorescence, phosphorescence, gamma radiation from radioactive substances do not come under the category of thermal radiation.

The distribution of energy amongst different wavelengths in the continuous spectrum of thermal radiation emitted by incandescent tungsten wire is shown in Fig.12.1. It is found that there is a region of maximum intensity for each temperature of the radiating body. This region of maximum intensity shifts towards the shorter wave-length as the temperature of the radiating body increases.

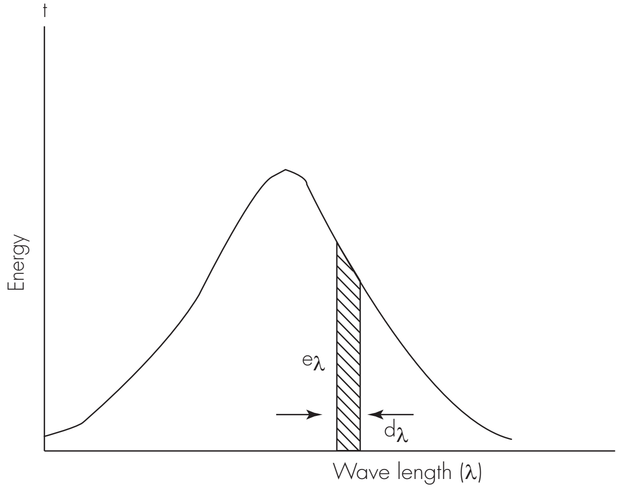


Fig. 12.1 Spectrum of thermal radiation emitted by an incandescent tungsten wire

12.2 SOME FUNDAMENTAL CONCEPTS AND DEFINITIONS

There is much confusion in existing textbooks with regard to the terminology used in connection with emission and absorption of radiation. We shall use, in this chapter, the terminology of the international critica1 tables.

Total emissive power: As already stated, the quality and quantity of radiation emitted by a body depend on the temperature of the body. They also depend on the degree of polish of the radiating surface.

By total emissive power of a body, we shall mean the total energy associated with all the wavelengths in the radiation emitted per unit area of a surface of the body per unit time in all possible directions.

The total emissive power will be represented by E_s and will be expressed in ergs per sq cm per sec.

Monochromatic emissive power: Thermal radiation when dispersed by a prism gives a continuous spectrum. If we select a narrow range of wavelengths λ to $\lambda + d\lambda$, then the total energy associated with waves lying in the range gives the monochromatic emissive power in that range. Thus, monochromatic emissive power at wavelength λ is the radiant energy emitted in the spectral range λ to $\lambda + d\lambda$ per unit area of the radiating surface per unit time in all directions.

Monochromatic emissive power of a body is different for different wavelengths of the spectrum. It is represented by $e_\lambda\, d\lambda$ and is expressed in ergs per sq cm per second. It is evident that the relation between the total emissive power and the monochromatic emissive power is

$$E_s = \int_0^\infty e_\lambda\, d\lambda \tag{12.1}$$

The monochromatic emissive power of the body whose spectral distribution of energy is shown in Fig.12.1 within the range λ to $\lambda + d\lambda$ is represented by the shaded area in the figure.

The total emissive power of the same body is the area bounded by the curve and the portion of the wavelength axis under the curve.

Normal monochromatic emissive power of a surface: In Fig. 12.2, *ds* is an element of the radiating surface. Describe a hemisphere of radius ρ round the centre of the element of surface *ds*. Let us determine the quantity of radiation within unit range of wavelength in the neighbourhood of λ passing through an area *dB* of a belt of thickness $\rho\, d\theta$ on this hemisphere.

The amount of radiation received by an element *dB* on the belt per second would evidently be proportional to (1) the area *ds* of the radiating surface, (2) the area *dB* of the surface receiving the radiation, (3) the cosine of the angle θ which the direction of emission makes with the normal to the surface (by the cosine law to be proved presently), (4) $1/\rho^2$, by the inverse square law.

Hence, if *dQ/dt* is the rate at which the energy is received by the surface *dB* per second from the surface *ds*, then

$$\frac{dQ}{dt}\,\alpha\,\frac{ds\cos\theta\, dB}{\rho^2}$$

or

$$\frac{dQ}{dt} = K_\lambda \frac{ds\cos\theta\, dB}{\rho^2} \tag{12.2}$$

where K_λ is the constant of proportionality, dB/ρ^2 is the solid angle $d\omega$ subtended by *dB* at the centre of the area *ds*. Hence,

$$\frac{dQ}{dt} = K_\lambda ds\cos\theta\, d\omega \tag{12.3}$$

or

$$K_\lambda = \frac{dQ/dt}{ds\cos\theta\, d\omega} \tag{12.4}$$

The constant of proportionality K_λ is called the normal monochromatic emissive power.

In Eq. 12.4, $K_\lambda = dQ/dt$ when $ds = 1$ and $d\omega = 1$, $\theta = 0°$. Hence, the normal monochromatic emissive power of a surface corresponding to unit range of wavelength in the neighbourhood of λ at a given temperature is equal to the amount of heat radiated from unit area of surface of the radiating body per unit solid angle per unit time in the direction of normal to the surface.

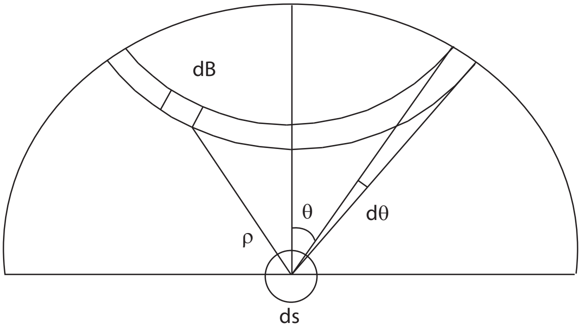


Fig. 12.2 Schematic representation of finding the rate at which the energy is received by surface *dB* per second from surface *ds*

Total normal emissive power is obtained by integrating the normal monochromatic emissive power over all the emitted wavelengths in the direction normal to the emitting surface. Representing this by K,

$$K = \int_0^\infty K_\lambda \, d\lambda \tag{12.5}$$

Relation between emissive power and normal emissive power

We shall first take the case of monochromatic radiation lying within the range of wavelengths λ to $\lambda + d\lambda$

Referring to Fig. 12.2, the area of the belt of thickness $\rho \, d\theta$ is $2\pi\rho$ Sin$\theta \, \rho \, d\theta$. Assuming the distribution of energy to be symmetrical round the normal ON to the emitting surface, the total energy crossing the belt per sec is (by Eq. 12.2)

$$\frac{dQ}{dt} d\lambda = K_\lambda ds \cos\theta \, \frac{2\pi\rho^2 \sin\theta \, d\theta \, d\lambda}{\rho^2}$$

Putting the area of the belt in place of dB in Eq. 12.2,

or
$$\frac{dQ}{dt} d\lambda = \pi K_\lambda ds \sin 2\theta \, d\theta \, d\lambda$$

or
$$\frac{dQ/dt}{ds} d\lambda = \pi K_\lambda \sin 2\theta \, d\theta \, d\lambda$$

This quantity integrated over the whole hemisphere gives the total energy emitted by unit area of surface of the radiating body in unit time. This is the total monochromatic emissive power of the body. Hence,

$$e_\lambda d\lambda = \pi K_\lambda d\lambda \int_0^{\frac{\pi}{2}} \sin 2\theta \, d\theta = -\frac{1}{2}\pi K_\lambda [\cos 2\theta]_0^{\frac{\pi}{2}}$$

or
$$e_\lambda d\lambda = \pi K_\lambda d\lambda \tag{12.6}$$

Total emissive power of the radiating body is

$$E_s = \int_0^\infty e_\lambda \, d\lambda = \pi \int_0^\infty K_\lambda \, d\lambda$$

$$E_s = \pi K \tag{12.7}$$

Absorptivity: When radiation is incident on a surface a part of it is absorbed, a part is reflected from the surface and the remaining portion is transmitted, unless the body is very opaque. By absorptivity we mean the fraction of incident energy which is absorbed. Absorptivity is necessarily a pure numeric, less than unity. It depends largely on the wavelength of the incident radiation and to a lesser extent on the temperature of the absorbing body. We shall represent absorptivity within the range of wavelengths λ to $\lambda + d\lambda$ by a_λ and that for all wavelengths by A.

Reflectivity: This is measured by the fraction of the incident energy which is reflected by the surface. Reflectivity is also pure numeric which is evidently less than unity. We shall represent the reflectivity within the range of wavelengths λ to $\lambda + d\lambda$ by r_λ and that for all wavelengths by R.

Transmissivity: This is measured by the fraction of incident energy which is transmitted. It is represented by the symbol t_λ within the range of wavelengths λ to $\lambda + d\lambda$. Transmissivity for all wavelengths will be represented by T. It is also a numeric less than unity. Bodies considered in this chapter are either very opaque or very thick. Hence for such bodies, transmissivity $t_\lambda = 0$. Evidently for such bodies, $a_\lambda + r_\lambda = 1$.

Black body: A black body is a perfect absorber of radiation of all wavelengths. Hence for such a body, $A = 1$ and $R = T = 0$. No body is perfectly black in the true sense of the term.

Lamp black, black velvet, etc. are only nearest approach to a black body.

For theoretical and experimental purposes, a black body is realized by a cavity inside a material impervious to heat rays and maintained at a uniform temperature. It communicates with the outside through a small hole having a diameter which is very small in comparison with the area of the hollow interior. The inner wall of the cavity is coated with highly absorbing material such as platinum black, bismuth black and the like.

A ray entering the cavity through the hole is diffusedly reflected a large number of times. At each incidence, some amount of energy is absorbed. Evidently, only a very small fraction of energy can come out through the hole. Practically, an approximation sufficient for experimental purposes is obtained by taking a hollow cylindrical tube 20 cm long and 4 to 5 cm in diameter having a hole 1 to 2 cm in diameter.

When such an enclosure is heated, the inner walls of the enclosure radiate. Some of these radiations pass out through the hole. Hence, a black body can radiate as well as absorb energy. The radiation emitted by such a black body is called black body radiation or cavity radiation. We shall represent the total emissive power of a black body by the symbol E_b and its total normal monochromation emissible power by K_b.

Black bodies are usually of two types—absorption type and emission type. The former type was designated by Fery and is called Fery's black body. It consists of a double-walled hollow metallic sphere having a small opening coated inside with lampblack and platinum black and having a conical feature just diametrically opposite to hole to avoid direct reflection of radiation passing through the opening inside the vessel. Its outside is polished with nickel. When heated, it arrives at constant temperature. When a radiation enters into it, it is reflected inside successively and is absorbed. Thus, the body behaves as a perfect absorber.

The emission type of black body was first constructed by Wien and later on modified by Lummer and Pringsheim, Coblentz and others. It consists of a hollow cylindrical brass, platinum or carbon tube which is heated electrically. One end is closed by an airtight plug. In this type, the conditions of emission of ideal black body radiation is taken to be accomplished.

Perfect mirror: A perfect mirror is a surface which reflects all incident rays completely unweakened, while it does not radiate itself. If a mirror which completely reflects all rays could radiate, temperature equilibrium could never be reached inside an enclosure at uniform temperature because such mirror would necessarily cool down.

The density of radiation: The quantity of radiant energy per unit volume in a radiation field is called the density of radiation. We shall represent density of monochromatic radiation by u_λ and the density of total radiation by u.

Homogeneous and isotropic radiation: Radiation in a field is said to be homogeneous and isotropic when the quality and quantity of radiation striking a unit area in unit time is the same for all positions and orientations of the area.
Intensity of radiation at a point in a radiation field is the quantity of radiant energy passing through unit area surrounding the point in one second.

12.3 PREVOST'S THEORY OF EXCHANGES

A body at all temperatures radiates heat and the rate of emission depends on temperatures of the body. Consider an enclosure the walls of which are maintained at a constant temperature. If a body at a lower temperature is placed inside the enclosure, the temperature of the body would rise till it becomes the same as that of the enclosure. In this case, the amount of heat absorbed by the body from the enclosure per second is greater than that emitted by the body in the same time so that there is a net gain of heat by the body. If the body were at a higher temperature than that of the enclosure, the rate of emission of heat by the body would be greater than the rate of absorption of heat from the enclosure. This process of exchange of heat would continue however small the difference of temperature between the body and the enclosure may be. It is natural to conclude that where the body and the enclosure are at the same temperature, the rate of emission of heat must be equal to the rate of absorption. According to the classical notion, there can be no exchange of heat between two bodies at the same temperature. It is difficult to conceive how the exchange of heat between two bodies at different temperatures, which is responsible for their equalization of temperature, could suddenly stop as soon as their temperatures become the same. Thus, a body would continue to radiate heat even when it is in temperature equilibrium with its surroundings. Its temperature does not change because it emits as much heat as it receives in a given time. This idea of exchange of heat under equilibrium condition is called Prevost's theory of exchanges.

The reciprocity theorem: It is a very general theorem applicable to any equilibrium process. It is also known as *the principle of detailed balancing*. It states, "*If one elementary process occurs at equilibrium, exactly the reverse process also occurs and just as frequently*."

Cavity radiation: The laws of thermal radiation can be deduced by studying the characteristics of cavity radiation. We now proceed to study the characteristics of cavity radiation; they are as follows:

1. *The radiation inside an enclosure at uniform temperature must be homogeneous and isotropic.*

To prove this, let a body bounded by surfaces of materials with different emissive powers and absorptivities be introduced inside the enclosure. The body would evidently acquire the temperature of the enclosure. If its temperature in the equilibrium state was different from that of the enclosure, temperature difference could be continuously used to drive a thermodynamic engine for obtaining useful work. This is contrary to the second law of thermodynamics. This is true wherever the body may be placed inside the enclosure and whatever may be its orientation. For temperature equilibrium, the total energy absorbed by the body must he equal to the total energy emitted per second. This must be true for all positions and orientations of the body. Since the absorption of the different surfaces is different and since absorptivity depends on the wavelength, the total absorption can remain constant only when the quality and quantity of radiation remains the same at all points and in all directions.

As a necessary consequence of isotropy, the radiation inside an enclosure at uniform temperature must be unpolarized. This means that the components of vibration in the radiation of a particular frequency in any two perpendicular directions must be equal. If K_λ and K'_λ be the normal emissive powers of vibration in two perpendicular directions, then the total emissive power of a surface would be

$$E_s = \pi \int_0^\infty (K_\lambda + K'_\lambda)\, d\lambda$$

For isotropic radiation, $K_\lambda = K'_\lambda$

$$\therefore \qquad E_s = 2\pi \int_0^\infty K_\lambda d\lambda \tag{12.8}$$

2. *The density of cavity radiation in the range* λ to $\lambda + d\lambda$ *depends only on the temperature of the enclosure and is independent of shape, material and contents of the enclosure.*

Proof: If not, let us suppose we have two enclosures *A* and *B* of different materials both of them being maintained at the same temperature (Fig. 12.3).

Let the density of radiation in the range λ to $\lambda + d\lambda$ be greater in *A* than in *B*. Let the two chambers be separated by a partition which is transparent to radiation in the wavelength range λ to $\lambda + d\lambda$. Since the density in *A* is greater than in *B*, more energy falls on the *A* side than on the *B* side of the screen so that *B* gains a certain amount of energy and *A* loses an equal amount.

Let the transparent partition be replaced by an opaque screen after a certain amount of energy has passed from *A* to *B*. Since the two chambers are at the same constant temperature *T*, the excess energy in *B* must be absorbed by the walls in *B* and, as a result, the temperature of the walls of *B* would rise. For a similar reason, the temperature of walls of *A* would fall to supply the energy transferred from *A* to *B*.

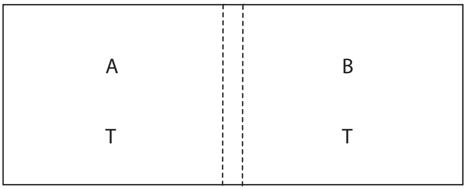


Fig. 12.3 Scheme to study the characteristics of density of cavity radiation

The walls of *B* at higher temperature can thus be used as a source and that of *A* at lower temperature can be used as sink to drive an engine. This can he repeated as often as we please. Thus, useful work can be obtained by utilizing the heat of bodies at the same temperature. This is contrary to experience. Hence, the original assumption must be wrong. The same argument also applies to bodies inside the enclosure. We can easily extend the argument to chambers *A* and *B* of any shape whatsoever.

3. *Radiation emitted by the wall of an enclosure in temperature equilibrium must obey the cosine law.*

Proof of cosine law: Let ds_1 and ds_2 be two elements of surface of the enclosure (Fig. 12.4). Let the line joining the centres of these two surfaces be inclined to their respective normals at angles θ_1 and θ_2.

Let K_λ be the normal monochromatic emission power of the enclosure. Then, the quantity of radiation emitted by ds_1 and passing through ds_2 per second is given by Eq. 12.2.

$$\frac{dQ}{dt} = C_1\, K_\lambda\, ds_1 \frac{ds_2 \cos\theta_2}{r^2} \tag{12.9}$$

Writing $ds_2 \cos\theta_2/r_2$ for dB where the factor C_1 has been introduced to take into account any variation of emission with angle.

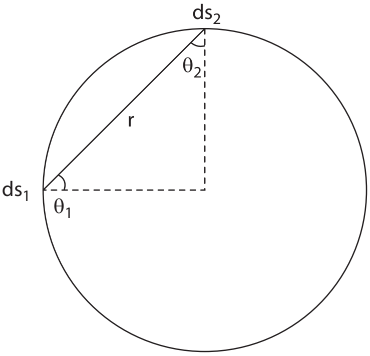


Fig. 12.4 Scheme for proof of cosine law

The fraction of this energy absorbed by ds_2 is

$$C_1 K_\lambda \frac{a_\lambda ds_1 ds_2 \cos\theta_2}{r^2} \tag{12.10}$$

where a_γ is the absorptivity of the surface ds_2 in the wavelength range λ to $\lambda + d\lambda$.

Similarly, the energy emitted by ds_2 and absorbed by ds_1 is

$$C_2 K_\lambda \frac{a_\lambda ds_1 ds_2 \cos\theta_1}{r^2} \tag{12.11}$$

By the reciprocity theorem, the energy emitted by ds_1 in the direction of ds_2 and absorbed by ds_2 must be equal to the energy emitted by ds_2 in the direction of ds_1 and absorbed by ds_1 in a given time. Hence, Eqs 12.10 and 12.11 must be equal. This requires

$$C_1 = \cos\theta_1 \text{ and } C_2 = \cos\theta_2$$

4. *Quantity of radiation crossing unit area per second in a direction inside an enclosure in temperature equilibrium is equal to the emissive power of a black body at the temperature of the enclosure and in the same direction.*

To prove this, let a black body be placed inside the enclosure. In the state of thermal equilibrium, the quantity of radiation absorbed by unit area of the surface of the black body per second must be equal to the quantity of heat emitted by the same area in the same time. Since, by assumption, the absorptivity of a black body is unity, the amount of heat emitted by the unit area per second must be equal to the total quantity of heat energy falling on the area per second. This is true wherever, inside the enclosure, the black body may be placed. In other words, the quantity of radiation crossing unit area per second inside the enclosure must be equal to the emissive power of a black body at the same temperature.

5. *It follows that a hole on the wall of a hollow heated enclosure in temperature equilibrium emits radiation as if the hole were a perfect black body at the temperature of the enclosure and that this rate of emission is quite independent of the nature and shape of the interior surfaces.*

Density of energy inside an enclosure at uniform temperature: Let v be the volume of a small element of space inside the enclosure (Fig. 12.5). Round the centre of the volume v construct a sphere of radius r, the whole surface of the sphere lying inside the enclosure. Then any radiation passing through the volume v must first pass through the surface of the sphere.

Take a small element ds on the surface of the sphere, with the centre P of the area ds as apex, draw a narrow cone intercepting the volume v at A and B. Let the distance AB be 1. Let the mean of the intercepted areas at A and B be f. Then the volume of the space v intercepted by the cone is (f.1). Let c be the velocity of propagation of radiation. Then, the time taken by the radiation to traverse the distance 1 is $dt = 1/c$.

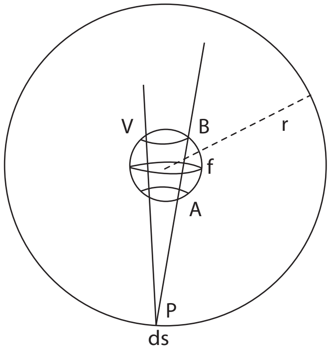


Fig. 12.5 Scheme to study density of energy inside an enclosure at uniform temperature

Let K_λ be the normal monochromatic emissive power of the area *ds* for radiation lying within the range λ to $\lambda + d\lambda$.

The amount of radiation crossing unit area at a point inside the enclosure is equal to the emissive power of a black body at the temperature of the enclosure. The same argument would, therefore, apply if the sphere is replaced by the spherical shell of a black body. Then, the quantity of radiation emitted by the area *ds* in time *dt* in the direction of the cone is

$$dQ = K_\lambda ds\, d\omega\, dt$$

where $d\omega = f/r^2$ is the solid angle subtended by the area *f* at *P*. Substituting for *dt* and *dω*, we get

$$dQ = K_\lambda ds \frac{f}{r^2}\frac{1}{c}$$

Summing over the whole solid angle subtended by *v* at *P*, the total radiation from *ds* passing through *v* in time *dt* is

$$= K_\lambda ds \frac{\sum f\ 1}{cr^2} = K_\lambda ds \frac{v}{cr^2}$$

Summing over the whole surface of the sphere, the total radiation passing through *v* from all directions is

$$= K_\lambda \frac{v}{cr^2}\sum ds = K_\lambda 4\pi r^2 \frac{v}{cr^2} = \frac{4\pi K_\lambda v}{c}$$

Hence, energy density of monochromatic radiation within the range λ to $\lambda + d\lambda$ is

$$u_\lambda = \frac{4\pi K_\lambda}{c} \tag{12.12}$$

Let $u_v dv$ be the energy density in the frequency range v to $v + dv$, corresponding to the energy density in the same special range comprised between λ to $\lambda + d\lambda$ where λ corresponds to frequency v. Thus, we can write

$$u_\lambda d\lambda = -u_v dv$$

The negative sign indicates that the wavelength increases with the decrease in frequency. To find the relation between u_λ and u_v, we have

$$c = v\lambda \text{ or } \lambda = \frac{c}{v} \qquad \therefore d\lambda = -\frac{c}{v^2}dv$$

$$\therefore \qquad -u_\lambda \frac{c}{v^2}dv = -u_v dv \qquad \therefore u_\lambda = \frac{v^2}{c}u_v$$

It can be similarly proved that

$$K_\lambda = \frac{v^2}{c}K_v$$

Substituting the values of U_λ and K_λ in Eq. 12.12,

$$u_v = \frac{4\pi K_v}{c} \tag{12.13}$$

The energy density of full radiation inside the enclosure is

$$u = \int_0^\infty u_\lambda d\lambda = \frac{4\pi}{c}\int_0^\infty K_\lambda d\lambda$$

$$u = \frac{4\pi K}{c} \tag{12.14}$$

It has already been proved that the radiation passing through unit area inside an enclosure in the normal direction in temperature equilibrium is equal to the emissive power of a black body in that direction at the temperature of the enclosure.

Hence, the quantity K in Eq. 12.14 is the total normal emissive power of a black body. Hence, K in Eq. 12.12 is to be replaced by K_b. Thus, the relation between the energy density inside an enclosure and the total normal emissive power of a black body is

$$u_b = \frac{4\pi K_b}{c}$$

But $\pi K_b = E_b \quad \therefore u = \dfrac{4E_b}{c}$ (12.15)

Since the radiation inside an enclosure at uniform temperature is isotropic, the components of vibration in two perpendicular directions are equal. If K_λ and K'_λ are the normal monochromatic emissive powers in two perpendicular directions, then for isotropic radiation $K_\lambda = K'_\lambda$ so that the energy density is

$$u = \frac{4\pi}{c}\int_0^\infty (K_\lambda + K'_\lambda)d\lambda$$

$$u = \frac{8\pi}{c}\int_0^\infty K_\lambda d\lambda \quad = \frac{8\pi K}{c} \tag{12.16}$$

12.4 KIRCHHOFF'S LAW OF RADIATION

Let a body of monochromatic emissive power e_λ and of absorptivity a_λ be placed inside an enclosure at uniform temperature T. It has already been proved that the amount of radiation crossing unit area at any point inside the enclosure is equal to the emissive power of a black body at the temperature of the enclosure. Then, the quantity of radiation falling per second on unit area of the body is $e_{\lambda b} d\lambda$. The amount of energy absorbed by the body is $a_\lambda\, e_{\lambda b}\, d\lambda$. For temperature equilibrium, this must be equal to the quantity of radiation emitted per unit area of the body in one second, that is, $e_\lambda\, d\lambda$. Hence,

$$a_\lambda\, e_{\lambda b}\, d\lambda = e_\lambda\, d\lambda$$

or

$$\frac{e_\lambda}{a_\lambda} = e_{\lambda b} \tag{12.17}$$

Or, the ratio of monochromatic emissive power of a body within the range of wave-length λ to λ + *d*λ to its absorptivity at a given temperature is equal to the monochromatic emissive power of a black body at the same temperature. This is known as Kirchhoff's law of radiation.

A natural conclusion following from Kirchhoff's law of radiation is that "no body can emit more radiation at a given temperature than a black body, for the maximum value of a_λ is equal to unity; the absorptivity of a black body and any smaller value of a_λ would imply a smaller value of e_λ". Hence, *a black body is not only the most efficient absorber, it is the most efficient emitter also.*

Since the emissive power of a black body is independent of material of walls of the enclosure, it must depend on temperature T of the enclosure; in other words,

$$e_b = f(T)$$

We next proceed to find the form of this function.

Pressure of radiation: The fact that radiation exerts pressure on a reflecting or absorbing surface can be proved, independently of any theory of radiation, with the help of the principle of conservation of energy. We shall adopt Larmor's method of proof, for plane waves and normal incidence.

Let a train of plane parallel wave of wave length λ move in the direction of diminishing x with velocity c. Let these waves be incident normally on a mirror M moving in the direction of increasing x with velocity v (Fig. 12.6). Then the displacement due to the incident waves at a point x of the medium at time is

$$y = a\cos\frac{2\pi}{\lambda}(x + ct)$$

where a and λ are the amplitude and wave-length of the incident waves, respectively. The displacement due to the reflected waves moving in the direction of increasing x at the same instant is

$$y' = a'\cos\frac{2\pi}{\lambda'}(x - ct)$$

where a' and λ' are the amplitude and the wave-length of the reflected waves, respectively. Let x be the position occupied by the mirror at the instant t measured from the same origin so that $x = v\,t$. Since the resultant disturbance on the surface of the mirror must be zero,

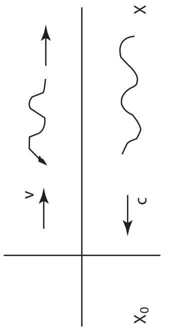


Fig. 12.6 Larmor's proof of pressure of radiation

$$y + y' = 0$$

we have

$$a\cos\frac{2\pi}{\lambda}(vt + ct) = -a'\cos\frac{2\pi}{\lambda'}(vt - ct)$$

$$= -a'\cos\frac{2\pi}{\lambda'}(ct - vt)$$

This can be true for all values of t only when

$$a = -a' \quad \text{and} \quad \frac{2\pi}{\lambda}(c + v) = \frac{2\pi}{\lambda'}(c - v)$$

$$\frac{\lambda'}{\lambda} = \frac{c-v}{c+v} \tag{12.18}$$

Now, energy-density of waves of length λ is inversely proportional to λ^2. Let u and u' be the energy-densities of the incident and reflected waves, respectively; then,

$$\frac{u}{u'} = \frac{\lambda'^2}{\lambda^2} = \frac{(c-v)^2}{(c+v)^2} \tag{12.19}$$

The relative velocities of the incident and reflected waves with respect to the moving mirror are $(c + v)$ and $(c - v)$, respectively. The energy striking unit area of the moving mirror in 1 second is, therefore, $u(c + v)$ and the energy reflected from the same mirror in the same time is $u'(c - v)$. Representing the energy moving away from and that moving up to the mirror in 1 second by E' and E, we get

$$\frac{E'}{E} = \frac{u'(c-v)}{u(c+v)} = \frac{(c+v)^2}{(c-v)^2}\,\frac{c-v}{c+v} = \frac{c+v}{c-v} \tag{12.20}$$

Hence, E' is greater than E. This difference of energy can only be due to the work done by the mirror against the pressure p exerted by the radiation on the mirror .

Hence by the principle of conservation of energy,

$$E' = E + pv$$

$$u'(c-v) = u(c+v) + pv$$

where pv is the amount of work done by the mirror against the pressure p in the second. Thus,

$$pv = E' - E$$

$$= E\frac{c+v}{c-v} - E \quad \text{from Eq. 12.20}$$

or

$$= \frac{2vE}{c-v}$$

or

$$p = \frac{2E}{c-v} \tag{12.21}$$

From Eq. 12.19,

$$\frac{u+u'}{u} = \frac{(c+v)^2 + (c-v)^2}{(c-v)^2} = \frac{2(c^2+v^2)}{(c-v)^2}$$

$$u = \frac{(c-v)^2}{2(c^2+v^2)}(u+u')$$

Substituting the value of u in Eq. 12.21, we get

$$p = \frac{c^2-v^2}{c^2+v^2}(u+u') \tag{12.22}$$

If the mirror is stationary, $v = 0$ and

$$p = u + u' \tag{12.23}$$

If the surface is a perfect mirror, $u = u'$ and $p = 2u$

If the surface is a perfect absorber, $u' = 0$ and $p = u$

Thus, the pressure exerted by radiation on a perfectly absorbing surface is numerically equal to the energy per unit volume in the beam of radiation incident on the surface.

If R is the reflecting power of the mirror, then

$$p = (I + R)u$$

Radiation pressure inside an enclosure at uniform temperature: Since the radiation inside an enclosure at uniform temperature is homogeneous and isotropic, the radiation may be thought of as divided into three equal parallel beams each of density $1/3u$. In this case, the pressure on the walls of a hollow heated enclosure exerted by radiation within the enclosure of any form is

$$p = \frac{1}{3}u$$

This can also be obtained directly as follows:

Consider an element of surface ds of a black body placed inside the heated enclosure (Fig. 12.7). To find the total amount of energy of monochromatic radiation within the spectral interval λ to $\lambda + d\lambda$ coming from open side of the surface ds, construct a hemisphere of radius r round the centre of ds.

Then, any energy falling on the area must have to pass through the surface of the hemisphere. Let the intensity of radiation through an element of surface dB ($= r^2 \sin\theta \, d\theta \, d\phi$)or the normal monochromatic emissive power of a black body at the temperature of the enclosure placed at dB be K_λ.

Then, the quantity of radiation coming from dB and falling on the area $ds \cos\theta$ in one second is given by Eq. 12.2,

$$\frac{dQ}{dt} = \frac{K_\lambda dB ds \cos\theta}{r^2}$$

Quantity of radiation passing per second (dQ/dt) through an area ds is equal to the quantity of energy contained in a cylinder of cross-section ds and of length c. If u be the energy density, then

$$\frac{dQ}{dt} = c\,ds\,u \qquad \therefore u = \frac{\frac{dQ}{dt}}{c\,ds}$$

Evidently, the energy density in the direction θ is

$$\frac{K_\lambda dB ds \cos\theta}{ds\,c\,r^2} = \frac{K_\lambda}{cr^2} \times dB \cos\theta$$

where c is the velocity of propagation of radiation.

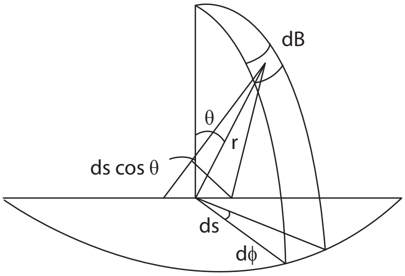


Fig. 12.7 Schematic representation of finding radiation pressure

Now, the density of energy at a point in a radiation field is equal to the force* per unit area placed at the point. Hence, the normal force per unit area on the surface *ds* cosθ is

$$\frac{K_\lambda}{cr^2} dB \cos\theta$$

The component of this force in the direction of normal to the surface *ds* is

$$\frac{K_\lambda}{cr^2} \cos^2\theta \, dB$$

$$= \frac{K_\lambda}{cr^2} r^2 \sin\theta d\theta d\phi \cos^2\theta$$

$$= \frac{K_\lambda}{c} \cos^2\theta \sin\theta \, d\theta \, d\phi$$

Hence, the total normal force per unit area on the surface *ds* due to radiation coming through the hemisphere is

$$\frac{K_\lambda}{c} \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta \, d\theta \, d\phi$$

$$= \frac{2\pi K_\lambda}{c} \int_0^{\frac{\pi}{2}} \cos^2\theta \, d(\cos\theta) \quad = \frac{2\pi}{3} \frac{K_\lambda}{c}$$

For equilibrium of temperature inside the enclosure, the black body must emit the same amount of energy. The reaction of this will produce the same amount of pressure on the surface *ds*. Hence, the total pressure on the surface *ds* is

$$p_\lambda = \frac{4\pi}{3} \frac{K_\lambda}{c}$$

But by Eq. 12.12,

$$u_\lambda = \frac{4\pi}{c} K_\lambda$$

so that

$$p_\lambda = \frac{1}{3} u_\lambda$$

Total pressure due to full radiation is obtained by integration

$$p = \int_0^\infty p_\lambda d\lambda = \frac{1}{3} \int_0^\infty u_\lambda d\lambda \quad \text{or,} \quad p = \frac{1}{3} u \tag{12.24}$$

This relation evidently holds for radiation inside a heated enclosure. The relation $p = u$ holds when the absorber does not emit radiation.

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* Density of energy $= \frac{\text{Energy}}{\text{Volume}} = \frac{(MLT^{-2}L)}{L^3} = (ML^{-1}T^{-2}) = \frac{(MLT^{-2})}{(L^2)} =$ force per unit area so that $p_\lambda = 1/3 \, u_\lambda$

12.5 ANALOGY BETWEEN BLACK BODY RADIATION AND PERFECT GAS

There are some points of fundamental similarity between black body radiation and the so-called perfect gas which makes it possible to apply the methods of thermodynamics to problems of radiation; these are as follows:

1. A gas consists of molecules moving with all possible velocities in all possible directions. By virtue of kinetic energy of these molecules, each unit volume of the contained gas has definite amount of energy which, at the same temperature, is the same everywhere and in all possible directions.

   An evacuated enclosure at a given temperature consists of radiations of all possible wavelengths streaming back and forth in all possible directions. The quality and quantity of this radiation are same at all points and in all directions. Each unit volume of the enclosure contains a definite amount of energy, which is the same at all points at the same temperature.

2. The molecules of the gas exert a pressure on the walls of the container. This pressure is independent of material and shape of the container and depends on the temperature of the container. The density of radiation or the quantity of energy per unit volume is independent of material and shape of the enclosure and depends only on the temperature of the enclosure.

   The density of radiation inside a heated enclosure being a function of temperature only is analogous to internal energy of a perfect gas.

12.6 BOLTZMANN'S ETHER ENGINE

In this engine, radiation is used as the working substance. It consists of a hollow cylinder and a frictionless piston (Fig. 12.8). The walls and base of the cylinder also the piston are impervious to heat. They have vanishingly small heat capacity and are placed in perfect vacuum. In the base of the cylinder, there

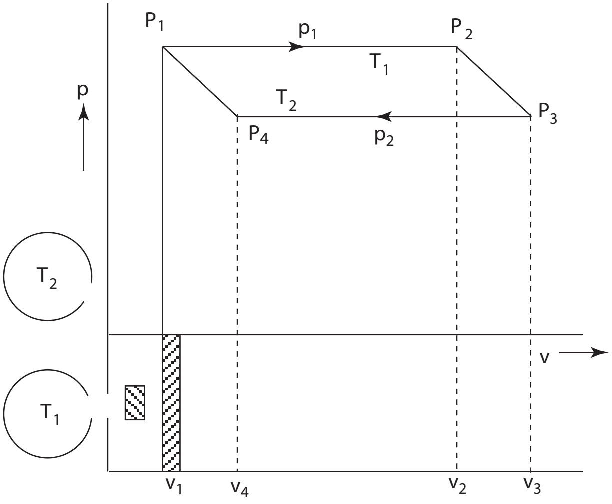

Fig. 12.8 Boltzmann's ether engine

is a small hole through which radiation can pass into or out of the cylinder. This hole may be closed by a disc which is a perfect reflector. The source of heat is a black body at temperature T_1. The sink is another black body at a lower temperature T_2. We shall suppose the temperature T_1 to be only slightly higher than T_2; with this engine, we now perform the following cycle of operations:

Stroke I: Place the piston in the position P_1. Let the initial state of radiation be represented by pressure p_1, volume v_1 and temperature T_1. Uncover the hole and place the black body at temperature T_1 close to the hole. Allow the piston to move forward slowly till the volume increases by an infinitesimally small amount to v_2. The path of this operation is P_1P_2.

In this operation the two chambers, the black body and the cylinder are maintained at uniform temperature T_1. Hence, the energy density and, therefore, pressure of radiation remains constant all throughout the operation. The amount of radiation drawn into the cylinder is due to following two causes:

1. Work done by the piston against external pressure. Since it is an equilibrium process, the work done is

$$W_e = p_1(v_2 - v_1) = \frac{1}{3}u(v_2 - v_1)$$

2. Radiation required to fill up the space $(v_2 - v_1)$. This is $u(v_2 - v_1)$

   Hence, total radiation entering the cylinder is

$$\frac{1}{3}u(v_2 - v_1) + u(v_2 - v_1) = \frac{4}{3}u(v_2 - v_1) = \frac{4}{3}udv \tag{12.25}$$

Stroke II: The hole of the cylinder is now covered by the disc and the piston is allowed to move to the position P_3 so that the new volume is now v_3. This is evidently an adiabatic process. The density of radiation within the cylinder must decrease partly because of external work and partly because of increase of volume. Let the amount of expansion be such that the temperature of the cylinder falls to T_2, the temperature of the sink. Let the change in density of radiation in this operation be *du* so that the change in pressure is

$$dp = \frac{1}{3}du$$

Stroke III: The insulating disc is then removed and the hole is placed opposite the black body at temperature T_2. The piston is then moved slowly to the position P_3 to P_4. The path of operation is P_3P_4.

Stroke IV: The opening of the cylinder is now closed and the radiation is further compressed till the temperature rises to T_1 and it occupies the initial volume at the same initial pressure. The path of this operation is P_4P_1.

The net amount of work done in the cycle is the area of the parallelogram $P_1P_2P_3P_4$.

or

$$dw = dp\, dv = \frac{1}{3}du\, dv$$

Since the cycle is perfectly reversible, the efficiency of the engine is

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{\text{Work done in the cycle}}{\text{Heat drawn from the source}}$$

or $$\frac{dT}{T} = \frac{\frac{1}{3}du\,dv}{\frac{4}{3}u\,dv}$$

or $$\frac{dT}{T} = \frac{1}{4}\frac{du}{u}$$

or $$4\log_e T = \log_e u - \log_e a \text{ where } \log_e a = \text{const. of integration}$$

or $$u = aT^4 \tag{12.26}$$

The constant a is called the total radiation constant. This is because a black body at a given temperature emits full radiation corresponding to that temperature.

By Eq. 12.15,

$$u = \frac{4E_b}{c}$$

or $$E_b = \frac{cu}{4} = \frac{caT^4}{4}$$

or $$E_b = \sigma T^4 \tag{12.27}$$

where $$\sigma = \frac{c\,a}{4} \tag{12.28}$$

The quantity σ is called the Stefan's constant or the Stefan–Boltzmann constant. It is to be noted that E_b is the total quantity of radiation crossing unit area of an opening in the side of a uniformly heated enclosure at temperature T in 1 second.

In all experimental determinations it is the value of σ that is determined. The accepted value of σ is

$$= 5.709 \times 10^{-5} \text{ ergs per sq. cm per sec per (degree)}^4$$

Hence $$a = \frac{4 \times 5.709 \times 10^{-5}\,\text{erg cm}^{-2}\ \text{sec}^{-1}\ \text{deg}^{-4}}{3 \times 10^{10}\,\text{cm sec}^{-1}}$$

or $$a = 7.617 \times 10^{-15}\ \text{erg cm}^{-3}\ \text{deg}^{-4}$$

Stefan's law is based upon Carnot's cycle employing radiation as working substance which obeys the laws of perfect gas. Evidently, temperature measured with the help of Stefan's law is absolute temperature. Temperature above 1400 °C can be accurately determined with the help of Stefan's law.

12.7 THERMODYNAMICS OF RADIATION

We have proved that radiation inside an enclosure at a uniform temperature can be regarded as a perfect gas. Accordingly, radiation should obey the laws of perfect gas.

Let V be the total volume of the enclosure and u the energy density inside the enclosure. Then, total energy in the enclosure is

$$U = V u$$

But,

$$u = aT^4$$

∴

$$U = VaT^4 \tag{12.29}$$

This gives

$$\frac{dU}{dT} = 4aVT^3 \tag{12.30}$$

Again,

$$p = \frac{u}{3} = \frac{1}{3}aT^4$$

This gives

$$\frac{dp}{dT} = \frac{4}{3}aT^3 \tag{12.31}$$

Substituting the value in the most general energy equation,

$$T\,ds = \left(\frac{dU}{dT}\right)_v dT + T\left(\frac{dp}{dT}\right)_v dV$$

We get the energy equation of radiation as

$$dQ = T\,ds = 4aVT^3 dT + \frac{4}{3}aT^4\,dV \tag{12.32}$$

12.7.1 Reversible Isothermal Change of Volume Occupied by Radiation

For isothermal condition, the cylinder containing the radiation must communicate through a hole with a black body maintained at the given temperature as in Boltzmann's ether engine. Since $dT = 0$, we get from Eq. 12.32 for the total quantity of radiation enter the cylinder

$$Q = \frac{4}{3}aT^4(V_f - V_i) = \frac{4}{3}u(V_f - V_i)$$

where V_i and V_f are the initial and final volumes, respectively. This agrees with Eq. 12.25.

We have seen that the fundamental quantity in radiation is energy density and it is a function of temperature only. Hence, energy density does not depend on any process by which the change of temperature is effected. To find the characteristics of radiation at different temperatures, we can adopt any method of production of change of temperature. Here, we adopt the adiabatic process.

12.7.2 Reversible Adiabatic Change of Volume Occupied by Radiation

In this case, there is no exchange of heat between the radiation and the surroundings. As a consequence of the change of volume, the density of radiation in the enclosure would change. Since the density of radiation is a function of temperature only, the temperature of radiation would necessarily change. In order to be able to apply the laws of black body radiation to the radiation undergoing adiabatic change of volume, we have to prove that the radiation, in the process of change, maintains the spectral energy distribution characteristic of a black body, that is, the radiation remains complete black.

To prove this let us take a cylinder with a piston, all the interior surfaces being perfect reflectors. Let the cylinder be filled with black body radiation at temperature T_1. Let the piston move outwards, thus increasing the volume occupied by the radiation. This has the effect of lowering the temperature of radiation. If the radiation at any temperature other than T_1 is not black body radiation, it can be made to have the characteristics of black body radiation by introducing a very small black body of negligible thermal capacity inside the cylinder*. This process being irreversible causes the entropy of the radiation to increase for the radiation still remains black by removing the black body from inside the enclosure.

With the black body still inside the enclosure, move the piston inwards till the radiation occupies its initial volume. The work done during backward drive of the piston $\int pdv$ is the same as that done during the forward drive.

This is because the density of radiation and, therefore, the pressure of radiation is the same at every stage or compression or expansion of volume. The original stage of radiation has thus been reached and in the entire cycle, there has been no gain of work or heat energy though the entropy of radiation has increased. This is violation of the second law of thermodynamics. The original assumption that the irreversible process of the redistribution of energy by the introduction of the black body cannot have occurred. Hence, the energy distribution must have retained the characteristic of black body radiation during the process of adiabatic change.

We are now in a position to apply the Eq. 12.32 to the adiabatic process. In this process, $ds = 0$.

$$\therefore \qquad 4aVT^3 dT = -\frac{4}{3} aT^4 dV$$

or
$$3\frac{dT}{T} + \frac{dV}{V} = 0$$

or
$$VT^3 = \text{constant} \tag{12.33}$$

This gives the relation between temperature of radiation and volume occupied by radiation during an adiabatic change. Thus if the volume of black body radiation was increased 8 times adiabatically, the radiation would be capable of existing in equilibrium with that of a black body at one-half or the original temperature.

Since
$$u = aT^4$$

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* The black body at the temperature under consideration must emit its radiation corresponding to that temperature. For temperature equilibrium, it, therefore, must absorb exactly similar type of radiation.

we get by substitution in Eq. 12.33,

$$u^3V^4 = \text{constant} \tag{12.34}$$

This gives the relation between energy density of black body radiation and the volume of the radiation during an adiabatic change.

12.8 THE WAVELENGTH–TEMPERATURE DISPLACEMENT LAW

For the sake of convenience of proof, we perform an imaginary experiment. Suggested by Larmor to simplify the calculation, we take an enclosure of the shape of a sphere of radius *r* (Fig.12.9). It has got perfectly reflecting interior walls consisting of small segments of perfect mirror oriented at random so as to obtain diffuse reflection and is impervious to heat and is capable of uniform adiabatic expansion in the radial direction. Since the volume of the sphere is proportional to the cube of its radius, Eq. 12.34 takes the following form

$$ur^4 = \text{constant} \tag{12.35}$$

and Eq. 12.33 takes the following form

$$rT = \text{constant} \tag{12.36}$$

When a wave train of length λ moving with velocity c is incident obliquely at an angle θ on a mirror moving with velocity w parallel to itself, the change in wavelength due to Doppler's effect is

$$d\lambda = \frac{2w\lambda\cos\theta}{c} \tag{12.37}$$

w being very small compared to c. A ray incident on the inner wall of the spherical enclosure at an angle θ suffers successive reflection. Length of each chord between two successive reflections is $2r\cos\theta$. Time taken to traverse each chord is thus $2r\cos\theta/c$. The rate at which wavelength changes with time is

$$\frac{d\lambda}{dt} = \frac{2w\lambda\cos\theta}{c} \times \frac{c}{2r\cos\theta} = \frac{w\lambda}{r}$$

Since $$w = \frac{dr}{dt}, \quad \frac{d\lambda}{dt} = \frac{\lambda}{r} \times \frac{dr}{dt}$$

$$\therefore \qquad \frac{d\lambda}{\lambda} = \frac{dr}{r}$$

This gives $\lambda/r = \text{constant}$ (12.38)

Equation 12.36 reduces to

$$\lambda/T = \text{constant} \tag{12.39}$$

Equation 12.39 is called Wien's wavelength temperature displacement law.

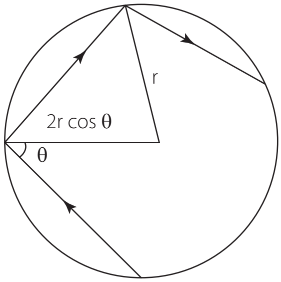

Fig. 12.9 Change in wavelength on reflections

12.8.1 Wien's Energy–Temperature Displacement Law

Instead of filling up the spherical enclosure with full radiation coming from a black body as in the imaginary experiment described earlier, let us now fill up the enclosure with monochromatic radiation within a narrow spectral range λ to $\lambda + d\lambda$ by means of suitable filter. Equation 12.35 would then take the form

$$u_\lambda r^4 d\lambda = u'_\lambda r'^4 d\lambda' \tag{12.40}$$

where r and r' are the radii of the enclosure before and after the adiabatic change, respectively.

For the same reason, Eq. 12.38 changes to

$$\frac{\lambda + d\lambda}{r} = \frac{\lambda' + d\lambda'}{r'} \tag{12.41}$$

for wavelengths $\lambda + d\lambda$ and $\lambda' + d\lambda'$.For wavelengths λ and λ', we get by Eq. 12.38

$$\frac{\lambda}{r} = \frac{\lambda'}{r'} \tag{12.42}$$

Subtracting Eq. 12.42 from Eq. 12.41, we get

$$\frac{d\lambda}{r} = \frac{d\lambda'}{r'}$$

Substituting the value in Eq. 12.40, we get

$$u_\lambda r^5 = u'_\lambda r'^5$$

Using Eq. 12.36, this reduces to

$$\frac{u_\lambda}{T^5} = \frac{u'_\lambda}{T'^5} \tag{12.43}$$

This is Wien's energy–temperature displacement law. Since the monochromatic energy density inside an enclosure at temperature T is proportional to monochromatic emissive power of a black body at that temperature, Eq. 12.43 may also be written as

$$\frac{e_{\lambda b}}{T^5} = \text{constant} \tag{12.44}$$

This constant is evidently independent of both $e_{\lambda b}$ and T.

Equation 12.43 means that "the energy density of radiation in a narrow wavelength range $d\lambda$ when divided by the fifth power of temperature of the enclosure emitting the radiation is equal to the energy density in the corresponding wavelength range after an adiabatic change, when this is divided by the fifth power of the final temperature".

With the help of the Eqs 12.39 and 12.44, we can find the energy distribution curve at temperature T_2 when the curve at T_1 is known.

Thus, let curve I in Fig. 12.10 be the energy distribution curve at temperature 1259 °C. To obtain the distribution curve II at temperature 1449 °C, take a wavelength at $\lambda = 4.1\ \mu$ on curve I. In curve II, this would correspond to wavelength

$$\lambda' = 4.19\left(\frac{1259}{1449}\right) = 3.55\mu$$

The energy associated with wavelength $\lambda = 4.1\mu$ at 1259 °C is $e_{\lambda b} = 20$ by Eq. 12.44; the energy associated with wavelength λ' at 1449 °C is

$$e'_{\lambda b} = 20 \times \left(\frac{1449}{1259}\right)^5 = 40.5$$

For each wavelength λ of curve I, corresponding wavelength λ' and $e_{\lambda'}$ can be thus obtained. Plotting $e_{\lambda'}$ against λ'. the curve II can be plotted.

Equations 12.39 and 12.44 apply to every corresponding point of the wavelength and emissive power curves I and II, accordingly, they also apply to the point of maximum emissive power.

Let λ_m be the wavelength at which the emissive power is the maximum. Then by Eq. 12.39,

$$\lambda_m T = \text{constant} = b \qquad (12.45)$$

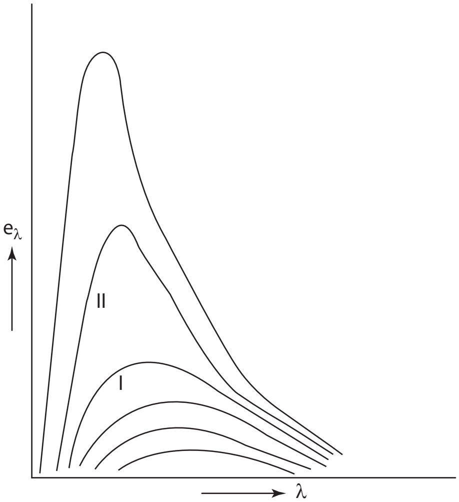

Fig. 12.10 Wien's energy temperature distribution curve

Equation 12.45 is known as Wien's displacement law. Evidently as T increases, λ_m decreases. Hence, Wien's displacement law states that with increase of temperature of the black body emitting radiation the point of maximum intensity in the emitted spectrum shifts towards the shorter wavelength side.

The constant b in Eq. 12.45 has the value

$$b = 0.2885 \text{ cm degree}$$

The corresponding emissive power at the wavelength λ_m is given by

$$\frac{e_m}{T^5} = B \qquad (12.46)$$

Since λT and $e\lambda/r^5$ are constant, there must exist a functional relation between λT and (e_λ/T^5)

Hence instead of plotting $e_{\lambda b}$ against λ at a particular temperature T, we may plot $\lambda\, T\,(= x)$ against $e_{\lambda b}/T^5\ (= y)$. This has the advantage that a single curve thus drawn will describe the dependence of $e_{\lambda b}$ on λ for all temperatures.

Let us represent this functional relation by

$$y = \phi(x)$$

or

$$\frac{e_{\lambda b}}{T^5} = \phi(\lambda\, T) \qquad (12.47)$$

Since $\lambda\, T$ is constant, Eq. 12.47 may also be written as

$$e_{\lambda b}\lambda^5 = f(\lambda\, T) \qquad (12.48)$$

Again,

$$e_{\nu b} d\nu = -e_{\lambda b} d\lambda \qquad (12.49)$$

The negative sign indicates that v diminishes as λ increases.

Now,

$$c = v\lambda \quad \text{or} \quad \lambda = \frac{c}{v}$$

$$d\lambda = -\frac{c}{v^2}dv$$

Substituting the value in Eq. 12.49, we get

$$e_{vb}dv = e_{\lambda b}\frac{c}{v^2}dv$$

or

$$e_{\lambda b} = \frac{v^2}{c}e_{vb}$$

Substituting this value in Eq. 12.48, we get

$$\frac{v^2}{c}e_{vb} = \frac{v^5}{c^5}f\left(\frac{c}{v}T\right) = \frac{v^5}{c^5}\times f'\left(\frac{T}{v}\right)$$

or

$$e_{vb} = \frac{v^3}{c^4}f'\left(\frac{T}{v}\right) \tag{12.50}$$

12.9 FORMS OF THE DISTRIBUTION FUNCTION $f(\lambda)$

From purely thermodynamic reasoning, Wien arrived at the relation

$$e_\lambda = \lambda^{-5}f(\lambda\, T)$$

where e_λ is the monochromatic emissive power of a black body within the wavelength range λ to $\lambda + d\lambda$ and at absolute temperature T.

12.9.1 Wien's Formula

Wien arrived at the following relation

$$f(\lambda\, T) = Ae^{-\frac{\alpha}{\lambda T}}$$

on certain arbitrary assumptions; these assumptions are as follows:

1. The radiation was produced by oscillators of atomic dimensions.
2. The frequency of the emitted waves was proportional to the kinetic energy of the oscillators.
3. The intensity in any particular wavelength range was proportional to the number of oscillators having the requisite energy.

Substituting the value of $f(\lambda\, T)$ in Eq. 12.48, we get

$$e_\lambda = A\lambda^{-5}e^{-\frac{\alpha}{\lambda T}} \tag{12.51}$$

This formula fits with the experimental curve only in the region of short wavelength (1 to 3μ where $\mu = 10^4$ Angstroms)

12.9.2 Rayleigh's Formula

It is based upon two theorems:

1. The theorem of equipartition of energy.
2. The theorem of stationary waves in a closed space.

Jeans and Lorentz proved later on that Rayleigh's formula gives the only law consistent with the principles of classical dynamics. Hence, it is known as Rayleigh–Jeans' formula. This famous Rayleigh–Jeans' formula is usually written in the following form

$$u = \frac{8\pi k}{\lambda^5}(\lambda T) \tag{12.52}$$

where u_λ is the energy density within the range λ to $\lambda + d\lambda$ and k is the Boltzmann constant.

From Eq. 12.12, $u_\lambda = \dfrac{4\pi K_\lambda}{c}$

Substituting the value in Eq. 12.52, we get

$$K_\lambda = \frac{2kc}{\lambda^5}(\lambda\, T)$$

For black body radiation, $K_\lambda = e_{\lambda b}$ so that

$$e_{\lambda b} = \frac{2kc}{\lambda^5}(\lambda\, T) \tag{12.53}$$

Difficulties of Rayleigh–Jeans' formula: Following are the difficulties of this formula:

1. It agrees with the experimental results only in the region of large wavelengths.
2. At any definite temperature, $u_\lambda = 0$ when $\lambda = \infty$.
3. At any definite temperature, $u_\lambda = 0$ when $\lambda = 0$.
4. It does not give any maximum value of u_λ, which is contrary to the experimental results.
5. By Stefan–Boltzmann's law, the total energy density over all wavelengths must be finite for finite values of T but from Rayleigh–Jeans' law, the energy density integrated over all wavelengths at any temperature must be infinite. The only temperature at which the total energy density would be finite is zero. Hence, all energy would pass into smallest wavelengths which the medium is capable of sustaining.

The consequences of (5) are as follows:

(a) A hot body placed inside the enclosure would speedily lose all its energy and fall to the absolute zero of temperature so that temperature equilibrium can never be attained.
(b) A thermometer placed inside an enclosure would not be able to record the temperature of the enclosure.
(c) For the same reason, the earth would not be able to maintain its average temperature.

The state of things predicted by classical mechanics is, therefore, so utterly different from that observed in nature that we are compelled to abandon or at least modify the classical mechanics in so far as the mechanism of interaction between matter and energy is concerned.

12.9.3 Planck's Radiation Formula

In 1901, Planck introduced revolutionary concepts regarding interaction of matter and energy. He assumed that

1. Radiation is not emitted or absorbed in a continuous manner but in discrete finite amounts known as quanta.
2. The energy associated with wave of frequency v is $\in = hv$

where h is a universal constant known as Planck's constant.

Based on these assumptions, Planck deduced the following radiation formula

$$u_\lambda = \frac{8\pi ch}{\lambda^5}\frac{1}{e^{\frac{ch}{\lambda kT}}-1} \tag{12.54}$$

where k is Boltzmann's constant.

This formula can also be expressed in terms of frequency with the help of the following relation $v = \dfrac{c}{\lambda}$

This gives
$$dv = -\left(\frac{c}{\lambda^2}\right)d\lambda \tag{12.55}$$

Let v and $v + dv$ correspond to λ and $\lambda + d\lambda$ and let u_v correspond to u_λ, so that

$$u_v dv = -u_\lambda d\lambda$$

Substituting for $d\lambda$ from Eq. 12.55 , we get

$$u_v dv = -u_\lambda\left(-\frac{\lambda^2}{c}\right)dv$$

or
$$u_\lambda = +\frac{c}{\lambda^2}u_v$$

From Eq. 12.54, we get

$$+\frac{c}{\lambda^2}u_v = \frac{8\pi ch}{\lambda^2\left(\frac{c}{v}\right)^3}\frac{1}{e^{\frac{ch}{\lambda kT}\frac{v}{c}}-1}$$

or
$$u_v = \frac{8\pi h}{c^3}\frac{v^3}{e^{\frac{hv}{\lambda kT}}-1} \tag{12.56}$$

Again by Eq. 12.14,

$$u_\lambda = \frac{4\pi K_\lambda}{c}$$

Substituting the value in Eq. 12.54, we get

$$e_{\lambda b} = \frac{2c^2h}{\lambda^5}\frac{1}{e^{\frac{ch}{\lambda kT}}-1} \tag{12.57}$$

Planck's formula is universal in application and covers the complete range of wavelengths in the field of radiation. Wien's formula and Rayleigh–Jeans' formula can be deduced as special cases of Planck's formula.

Deduction of Wien's formula: For short wavelengths, $-ch/\lambda kT$ is very large so that

$$\left(e^{\frac{ch}{\lambda kT}}-1\right)^{-1} \approx e^{-\frac{ch}{\lambda kT}}$$

Substituting the value in Eq. 12.57, we get

$$e_\lambda = \frac{2c^2 h}{\lambda^5} e^{-\frac{ch}{\lambda kT}}$$

which is of the same form as Wien's formula.

Deduction of Rayleigh–Jeans' formula: For large wavelengths, $(ch/\lambda kT)$ is small. Hence,

$$e^{-\frac{ch}{\lambda kT}} = 1+\frac{ch}{\lambda kT}+\ldots\ldots$$

or
$$e^{-\frac{ch}{\lambda kT}} - 1 = \frac{ch}{\lambda kT}$$

Substituting the value in Eq. 12.57, we get

$$e_\lambda = \frac{2c^2 h}{\lambda^5} \times \frac{\lambda kT}{ch}$$

or
$$e_\lambda = 2ckT\lambda^{-4}$$

which is of the same form as Rayleigh–Jeans' formula.

Deduction of Stefan–Boltzmann's law from Planck's formula: Total energy density is

$$u = \int_0^\infty u_\nu d\nu = \frac{8\pi h}{c^3}\int \frac{\nu^3 d\nu}{e^{\frac{h\nu}{kT}}-1} \tag{12.58}$$

Put
$$x = \frac{h\nu}{kT} \quad \text{so that} \quad dx = \frac{h}{kT}d\nu$$

Substituting for ν and $d\nu$ in Eq. 12.58, we get

$$u = \frac{8\pi h}{c^3}\int_0^\infty \frac{\left(\frac{kTx}{h}\right)^3\left(\frac{kT}{h}\right)dx}{e^x-1}$$

or
$$u=\frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^4\int_0^\infty \frac{x^3dx}{e^x-1}$$

It follows that u is proportional to T^4 which is Stefan–Boltzmann's law, since the integral is definite and, as such, it is a pure number.

The total radiation constant is

$$a=\frac{8\pi k^4}{h^3c^3}\int_0^\infty \frac{x^3dx}{e^x-1}$$

To evaluate the integral, we expand $(e^x-1)^{-1}$

$$(e^x-1)^{-1}=e^{-x}(1-e^{-x})^{-1}=e^{-x}\left(1+e^{-x}+e^{-2x}+e^{-3x}+\ldots\ldots\right)$$

$$=e^{-x}+e^{-2x}+e^{-3x}+\ldots.$$

and integrate the series. Thus,

$$a=\frac{8\pi k^4}{h^3c^3}\int_0^\infty x^3dx\left(e^{-x}+e^{-2x}+e^{-3x}+\ldots.\right)$$

$$=\frac{8\pi k^4}{h^3c^3}\sum_{r=1}^{\infty}\int_0^\infty x^3e^{-rx}dx$$

$$=\frac{8\pi k^4}{h^3c^3}\sum_{r=1}^{r=\infty}\frac{6}{r^4}$$

or
$$a=\frac{48\pi k^4}{h^3c^3}\frac{\pi^4}{90}=\frac{48\pi k^4}{h^3c^3}\times 1.0823 \tag{12.59}$$

Substituting the value of

$$k=1.3808\times 10^{-16}\ \text{erg deg}^{-1}$$

$$h=6.625\times 10^{-27}\ \text{erg}-\text{sec}$$

$$c=2.9986\times 10^{10}\ \text{cm sec}^{-1}$$

in Eq. 12.59, we get

$$a=7.582\times 10^{-15}\ \text{erg cm}^{-3}\ \text{degree}^{-4}$$

This agrees closely with the experimental value.

Determination of Wien's constant from Planck's formula: This is obtained from the following equation

$$\frac{de_{\lambda b}}{d\lambda}=0$$

$$\frac{de_{\lambda b}}{dx}\frac{dx}{d\lambda}=0 \text{ where } x=\frac{ch}{\lambda kT}$$

Substituting this value of x in Eq. 12.57, it reduces to

$$e_{\lambda b}=\frac{2c^2hx^5k^5T^5}{c^5h^5}\times\frac{1}{e^x-1}$$

$$=\frac{2k^5T^5}{c^3h^4}\frac{x^5}{e^x-1} \quad (12.60)$$

Differentiating Eq. 12.60 with respect to x, we get

$$\frac{de_{\lambda b}}{dx}=\frac{2k^5T^5}{c^3h^4}\left(\frac{5x^4}{e^x-1}-\frac{x^5e^x}{(e^x-1)^2}\right)=0$$

or

$$5-\frac{xe^x}{e^x-1}=0$$

or

$$5(e^x-1)-xe^x=0$$

Dividing by $5e^x$, this reduces to

$$1-e^{-x}-\frac{x}{5}=0 \quad (12.61)$$

The solution of the Eq. 12.61 is

$$x=4.9651$$

This gives

$$\frac{ch}{k\lambda_mT}=4.9651 \quad (12.62)$$

By Wien's displacement law, $\lambda_mT=b$.
From Eq. 12.62,

$$b=\frac{ch}{4.9651\,\mathrm{k}}$$

$$b=\frac{2.9986\times10^{10}\times6.554\times10^{-27}}{1.3708\times10^{-16}\times4.9651}$$

$$b=0.2888$$

This agrees clearly with the experimental value.

12.10 THE EQUIPARTITION PRINCIPLE

Degrees of freedom: In the case of a moving body, the separate and independent quantities which need be known to specify the position and configuration of a body completely are called the degrees of freedom of the body.

Examples: A block sliding in a groove has only one degree of freedom. The same block sliding on the surface of a table has two degrees of freedom. A billiard ball rolling on a table has five degrees of freedom, two co-ordinates specifying the position of its centre and three co-ordinates specifying its orientations.

A monatomic gas molecule has only a point mass. It can have motion of translation in any of the three directions, mutually perpendicular to each other. *Hence, a monatomic molecule has three degrees of freedom.*

A rigid diatomic molecule consists of two point masses, a fixed distance apart. In this case, the centre of gravity of the molecule can have free motions in three mutually perpendicular directions. In addition, it can rotate about two axes perpendicular to each other and to the line joining the molecules. The rotation about the axis of symmetry is of no consequence because the mass of the atom is practically concentrated at the nucleus which is very nearly a point. Hence, *a rigid diatomic molecule has five degrees of freedom.*

If the diatomic molecule is not rigid, it can vibrate in the direction of the line joining their centres. This gives the molecule an additional degree of freedom. *Hence, a non-rigid diatomic molecule has six degrees of freedom*.

A triatomic molecule should have nine degrees of freedom, three degrees of translation, three degrees of rotation and three of vibration, if none of the vibrational degrees are frozen up.

Degrees of freedom are additive: Thus, a system may consist of N bodies, each having n degrees of freedom. In this case, the degree of freedom of the system is Nn. If we have a mixture of two gases containing N_1 and N_2 molecules with respective degrees of freedom n_1 and n_2, then the degrees of freedom of the system is $(N_1n_1 + N_2n_2)$.

Corresponding to each degree of freedom, there is a possible motion with associated kinetic energy. Hence, the number of degrees of freedom may also be defined as follows:

"*The number of degrees of freedom of a body is the number of independent terms necessary to express the kinetic energy of the body (both translational and rotational) as a function of its co-ordinates*".

Let V_x, V_y and V_z be the three components of linear velocities of a body along three mutually perpendicular directions OX, OY and OZ, and let W_x, W_y and W_z be the three component angular velocities of the body round these axes. Let I_x, I_y and I_z be the moments of inertia of the body round the axes OX, OY and OZ, respectively. Let E_x, E_y and E_z be the kinetic energy of vibrational motion. Then, the kinetic energy of a monatomic molecule of mass m is

$$W = \frac{1}{2}m(V_x^2 + V_y^2 + V_z^2)$$

That of a rigid diatomic molecule is

$$W = \frac{1}{2}M(V_x^2 + V_y^2 + V_z^2) + \frac{1}{2}I_yW_y^2 + \frac{1}{2}I_zW_z^2$$

where M is the reduced mass of the molecule, that for a non-rigid diatomic molecule, the total energy is

$$W = \frac{1}{2}M(V_x^2 + V_y^2 + V_z^2) + \frac{1}{2}I_yW_y^2 + \frac{1}{2}I_zW_z^2 + E_x$$

The equipartition theorem: The theorem of equipartition of energy developed by Maxwell, Gibbs and Boltzmann states that *the group average of kinetic energy of each component of large group is the same for each degree of freedom*.

Here by group average we mean the sum of the kinetic energies of all the components corresponding to one degree of freedom divided by the total number of components which constitute the group.

The equipartition energy: Consider the case of a monomatic gas with density at temperature T. According to the kinetic theory, the pressure exerted by the gas is

$$p = \frac{1}{3}\rho\overline{c^2} \tag{12.63}$$

where $\overline{c^2}$ is the mean square velocity. If M be the molecular weight of the gas and V its molecular volume, then

$$\rho = \frac{M}{V} = \frac{mN}{V}$$

where m is the mass of the atom and N, the Avogadro number.

Substituting for ρ in Eq. 12.63, we get

$$pV = \frac{1}{3}mN\overline{c^2} = \frac{2}{3}N\frac{1}{2}m\overline{c^2}$$

or $$pV = \frac{2}{3}NE \tag{12.64}$$

where E is the average kinetic energy of an atom.

But, $$pV = RT$$

where R is the universal gas constant.

$$\frac{2}{3}NE = RT \tag{12.65}$$

If E_x, E_y and E_z are the average kinetic energies corresponding to three mutually perpendicular directions OX, OY and OZ, then

$$\frac{2}{3}N(E_x + E_y + E_z) = RT$$

By equipartition theorem, $$E_x = E_y = E_z = \overline{E}$$

or $$\frac{2}{3}N3\overline{E} = RT$$

or
$$\bar{E}=\frac{1}{2}\frac{RT}{N}$$

or
$$\bar{E}=\frac{1}{2}kT \tag{12.66}$$

The constant $k=\dfrac{R}{N}$ is called the Boltzmann's constant.

Its value is

$$k=\frac{8.315\times 10^{7}}{6.023\times 10^{23}}=1.382\times 10^{-16}\text{ ergs per molecule per degree.}$$

In 1905, Einstein developed a theory of motion of Brownian particles. His equation is

$$\frac{\overline{\Delta s^2}}{\tau}=\frac{2}{\alpha}\frac{R}{N}T$$

where $\overline{\Delta s^2}$ is the average square of small distance traversed by the particle in time τ, α is a constant depending on viscosity of the medium and size of the particle. $\overline{\Delta s^2}$ can be determined. From the value thus obtained, the Avogadro number N can be calculated. This value of N agrees with the value of N obtained by dividing the Faraday by the charge on the electron. This proves the validity of the equipartition theorem.

Relation between degrees of freedom and ratio of specific heats: Let each molecule of a gas have n degrees of freedom. Then, the total internal energy of the gas is

$$U=\frac{1}{2}nkT\,N=\frac{1}{2}nRT$$

where N is the Avogadro number. The molecular heat at constant volume is

$$C_v=\left(\frac{dU}{dT}\right)_v=\frac{1}{2}nR$$

For a perfect gas, $C_p-C_v=R$

$$\therefore \qquad C_p=C_v+R=R\left(1+\frac{n}{2}\right)$$

$$\therefore \qquad \gamma=\frac{C_p}{C_v}=\frac{\frac{R}{2}(2+n)}{\frac{R}{2}n} \quad \text{or} \quad \gamma=1+\frac{2}{n}$$

Hence, the degrees of freedom of a molecule can be calculated knowing the value of γ.

12.11 THE RAYLEIGH–JEANS' RADIATION FORMULA

The law of equipartition of energy was applied by Lord Rayleigh and Jeans to derive a formula for distribution of energy in the black body radiation. Every vibrating system has, in general, different modes of vibration. Each of these modes corresponds to one degree of freedom*.

According to Rayleigh and Jeans, an amount of energy 1/2 kT may be assigned to each degree of freedom. To develop the idea, we shall for simplicity consider a cubical box of side a containing a medium capable of sustaining vibrations. One corner of the cube will be taken as the origin of co-ordinates and its three sides meeting at that corner as the axes OX, OY and OZ. Since the boundary walls of the cube are supposed to be fixed, in the steady state, the medium can only sustain stationary oscillations. The essential condition for formation of stationary waves is that the two opposite boundaries must be two nodes. For this to occur, the distance between any two opposite walls of the cubical box must be equal to integral multiples of half wavelengths of the component waves.

Let the direction cosines of the normal to the nodal planes be l, m and n (Fig. 12.11). Let the intercepts between two consecutive nodal planes on the three axes OX, OY and OZ be p_1, p_2 and p_3, respectively. Then by the condition of formation of stationary waves,

$p_1 = \lambda/2l$, $p_2 = \lambda/2m$ and $p_3 = \lambda/2n$ where λ is the wavelength of the component waves. Let n_1, n_2 and n_3 be the number of intercepts on the three axes; then $a = n_1p_1 = n_2p_2 = n_3p_3$ where n_1, n_2 and n_3 can only assume integral values.

Then,

$$n_1 = \frac{a}{p_1} = \frac{2al}{\lambda} \qquad n_2 = \frac{a}{p_2} = \frac{2am}{\lambda} \qquad n_3 = \frac{a}{p_3} = \frac{2an}{\lambda}$$

Squaring and adding we get

$$n_1^2 + n_2^2 + n_3^2 = \left(\frac{2a}{\lambda}\right)^2 (l^2 + m^2 + n^2)$$

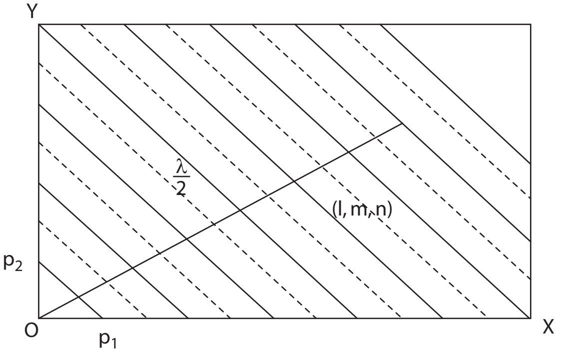

Fig. 12.11 Scheme to study equipartition of energy of vibrating system

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* This is because the expression for energy of the vibrating system is the sum of energies associated with each mode.

or $$n_1^2 + n_2^2 + n_3^2 = \frac{4a^2}{\lambda^2} \text{ since } l^2 + m^2 + n^2 = 1$$

Since $c = \lambda\nu$ where ν is the frequency,

$$n_1^2 + n_2^2 + n_3^2 = \frac{4a^2\nu^2}{c^2} \tag{12.67}$$

From Eq. 12.67, the possible modes of vibration for a given value is given by the possible combination of the integers n_1, n_2, n_3, the sum of whose squares is equal to $4a^2\nu^2/c^2$. Evidently, it is given by points on the surface of a sphere of radius $(2a\nu/c)$ the coordinates of the point being only integers. Since n_1, n_2 and n_3 are necessarily positive, only the points lying on the positive octant of the sphere are to be considered to compute the possible modes of vibration (N) for frequencies *0* to ν and is one eighth of the volume of the sphere of radius $(2a\nu/c)$

or $$N' = \frac{1}{8}\frac{4\pi}{3}\left(\frac{2a\nu}{c}\right)^3 = \frac{4\pi}{3}\frac{a^3\nu^3}{c^3}$$

Again since each possible mode of vibration may be polarized in two perpendicular planes, we have two waves for each mode.

Hence, the total number of modes within the frequency range 0 to ν is

$$2N' = \frac{8\pi}{3}\frac{a^3\nu^3}{c^3}$$

Since a^3 is the volume of the cube, the total number of modes and, therefore, total number of degrees of freedom per unit volume is

$$N = \frac{2N'}{a^3} = \frac{8\pi}{3}\frac{\nu^3}{c^3}$$

Number of degree of freedom within the frequency range ν to $\nu + d\nu$ is

$$dN = \frac{8\pi\nu^2 d\nu}{c^3} \tag{12.68}$$

Now, the time-average of kinetic energy of a vibrating system is the same as the time-average of its potential energy and the total energy of the system is partly kinetic and partly potential.

Hence, the time-average of total energy = 2 × time average of kinetic energy

$$= 2 \times \frac{1}{2}kT = kT,$$

In the case of an enclosure in temperature equilibrium, whatever the nature of radiating or absorbing mechanism with each vibratory degree of freedom, an amount of energy equal to kT is associated. Hence by Eq. 12.58, energy associated with frequencies within the range of ν to $\nu + d\nu$ per unit volume is

$$u_\nu d\nu = \frac{8\pi\nu^2 kT}{c^3} d\nu \tag{12.69}$$

or since
$$c = \nu\lambda \text{ or } \nu = \frac{c}{\lambda},\ d\nu = -\frac{c}{\lambda^2} d\lambda$$

$$-u_\lambda \frac{c}{\lambda^2} d\lambda = -\frac{8\pi\nu^2}{\nu^3\lambda^3} kT \frac{c}{\lambda^2} d\lambda = -\frac{8\pi\nu^2}{\nu^3\lambda^3} kT \frac{\nu\lambda}{\lambda^2} d\lambda$$

$$u_\lambda d\lambda = \frac{8\pi k(\lambda\, T)}{\lambda^5} d\lambda \ldots\ldots \tag{12.70}$$

This is the Rayleigh–Jeans' formula. We have seen that this formula does not agree with experimental results.

The problem of energy distribution was attacked by numerous investigations during the first decade of the twentieth century on the basis of classical statistical mechanics, all leading to the same result—the Rayleigh–Jeans' formula. We are led to conclude that the equipartition principle is not applicable to the partition of energy between matter and ether.

In the meantime, numerous evidences accumulated in support of the atomic nature of energy. These atoms of energy are called photons. We reproduce below some of the facts which have led to the idea of atomicity of energy:

1. The experimental curve of distribution of energy of radiation emitted by a black body amongst the different wavelengths resembles the Maxwell's distribution curve of velocity amongst different molecules.
2. Radiation, like a gas, exerts pressure. In fact, pressure of radiation can be calculated from the impacts of photons on the walls of the vessel enclosing the radiation.
3. In the process of ionization by *X*-rays or other ionizing radiations, only a few of the molecules of the gas are ionized. By doubling the intensity of radiation, the number of molecules ionized is not doubled. If the radiation were propagated as waves, all the molecules lying in the path of waves would be ionized.
4. Light falling on some metals ejects electrons known as photoelectrons. The capacity of radiation to eject photoelectrons depends on the frequency of the incident radiation and not on the intensity of the radiation. Further, there is no time lag between emission of photoelectrons and incidence of radiation. It is impossible to understand this phenomenon except by supposing that light is in some way tied up in very concentrated packets, where strength depends on frequency.
5. By Einstein's law of equivalence of mass and energy, we can associate mass with every photon. Every photon moves with the velocity of light. Hence, a photon possesses momentum.
6. Professor Compton has obtained direct evidence of the existence of mass of photon from the recoil of a photon on striking an atom. This produces a change in energy of the photon with consequent change in frequency. The photon can also spin about an axis. This has been recently detected and measured by Raman and Bhagavantam.

12.12 THE DYNAMICAL AND THERMODYNAMICAL STATE OF A SYSTEM

The dynamical state of a system consisting of a large number of components is determined by the total number of degrees of freedom specifying the positional and momentum co-ordinates of all the components. The thermodynamical state of a system is defined by its average property taken in bulk. It is defined by lesser number of co-ordinates such as pressure, volume and temperature.

A dynamical state with a particular distribution of velocities amongst the component parts of the system is called a macro state or a thermodynamic state. Now, one macro state can be realized in a large number of ways each of which is called a complexion. Thus suppose we have a system consisting of N parts, each part being different from the other so that they can be identified. Let us name the different parts a, b and c, etc.

Consider a velocity space with co-ordinates U, V and W. Let the velocity space be divided into n number of elementary cells. Let these cells be numbered I, II, III ----- λ.

Table 12.1 shows only two ways of filing up the cells I, II, III ----- λ with N_1 parts in the first cell, N_2 parts in the second cell ------ N_λ parts in the λ^{th} cell. This gives only two comp1exions of one macro state in which N_1 parts are placed in the first cell, N_2 parts in the second cell and N_λ parts in the λ^{th} cell. In a macro state, we are not concerned with the possible number of arrangement of given number of parts in a cell, but only with the number of parts in each cell.

Hence, the total number of complexions by which the particular macro state can be realized is the number of ways in which N_1, N_2, N_3 ....N_λ members can be selected out of the total number of members equal to N

$$W = \frac{N!}{N_1!, N_2!, N_3!\ldots\ldots N_\lambda!}$$

Now, the more often a condition occurs the more probable it is. Hence, the probability of a particular distribution or a macro state must be proportional to the number of complexions by which the state can be realized. In a spontaneous process, a system passes from a state of lower to a state of higher probability. Hence, the most stable state of the system will be the state of highest thermodynamic probability* consistent with the given energy content of the system. Hence, the statement that in a spontaneous

Table 12.1 Characteristics of a dynamical state

Number of cell / Complexion	I	II	III	
1.	a, e, f	b, g	h, r,	
2.	c, d, g	p, q	a, f	
3.	N_1	N_2	N_3	N

---

* A material system composed of large number of parts left to itself tends to move from an orderly to a chaotic state. With progress of time, the state of chaos or confusion increases and it continues till no further confusion is possible. This state of maximum confusion is called the *kinetic equilibrium*.

process the entropy of a system tends to increase is equivalent to the statement that a system left to itself tends to pass from a state of lower to a state of higher thermodynamic probability or from an orderly to a disorderly state.

The ratio of occurrence of a macro state (w) to the probability of occurrence of standard state of ordered arrangement (W_o) is called the thermodynamic probability of that state, or thermodynamic probability $W = w/W_o$

Since the probability of occurrence of an ordered state is vanishingly small, W is always greater than unity.

If a particular event happens in a ways and fails in b ways, then the algebraic probability of happening of the event is $a/(a + b)$ and probability of failing is $b/(a + b)$. Hence, algebraic probability is always less than unity.

This parallelism suggests a functional relationship between entropy and thermodynamic probability. Representing the thermodynamical probability of a state by W, we assume that the entropy of the state is connected by the relation

$$S = f(W) \tag{12.71}$$

To evaluate the function, let us consider two independent systems with different states for which the entropy and corresponding probability are S_1 and S_2, W_1 and W_2, respectively; then,

$$S_1 = f(W_1) \quad \text{and} \quad S_2 = f(W_2)$$

Then, the total entropy of the combined system is

$$S = S_1 + S_2 = f(W_1) + f(W_2) \tag{12.72}$$

Now, the actual state we are considering for the first system can be realized by selecting any one of the W_1 complexions of that particular state, and similarly for any one of the W_2 complexions of the second system. Then for the combined system, the state can be realized by selecting any one of the W_1 complexions of the first system and any one of the W_2 complexions of the second system and combining these two. Hence, the total number of combinations or complexions by which the state of the combined system can be realized is given by

$$W = W_1 \times W_2 \tag{12.73}$$

Hence by Eq. 12.71, $S = f(W) = f(W_1 \times W_2)$

Thus, $$f(W_1W_2) = f(W_1) + f(W_2) \tag{12.74}$$

This is true only if the function is a logarithmic one, that is

$$\log_e W_1W_2 = \log_e W_1 + \log_e W_2 \tag{12.75}$$

It follows that $S \, \alpha \log_e W$

or $$S = \mathrm{k} \log_e W \tag{12.76}$$

or writing it in the most general form,

$$S = k \log_e W + \text{constant} \tag{12.77}$$

It can be easily shown thermodynamically that the value of constant k is

$$k = \frac{R}{N}$$

where N is the number of molecules in one gm-molecule, that is, k is the gas constant per molecule.

12.13 PLANCK'S RADIATION FORMULA

To deduce an equation for the law of distribution of energy amongst different wavelengths, we require a known mechanism of emission and absorption of radiant energy by matter. At the time when Planck deduced his radiation formula, the mechanism of emission and absorption of radiant energy (as later developed by Bohr) was not known. But, the idea of Hertzian oscillators was fully developed. They are electromagnetic oscillators consisting of two poles with equal and opposite charges. Radiation being of electromagnetic nature, such an oscillator placed in a radiation field will be caused to execute forced oscillations. The damping force on these oscillators being very small, the oscillators are only sensitive to radiations whose frequency differs only slightly from their natural frequency. Hence, these oscillators behave like resonators. They absorb energy from the radiation and transfer their energy partly or wholly to the surrounding molecules by collision.

We now imagine an enclosure with perfectly reflecting walls containing resonators, molecules at a given temperature in radiation equilibrium. Let the number of resonators inside the enclosure be N and let $\bar{U}$ be the mean energy of these oscillators. Then, the total energy of the resonators is

$$U_N = N\bar{U}$$

Here Planck makes an assumption that in the process of interaction between matter and radiation, the energy is not emitted or absorbed in continuous stream but in integral multiples of a smallest element or quantum. So, we divide the total energy U_N into P elements each of magnitude $\in$, so that

$$U_N = N\bar{U} = P\in$$

so that the number of elements of energy is

$$P = \frac{N\bar{U}}{\in}$$

The number of ways of distributing P energy elements among N resonators is

$$\frac{(N+P-1)!}{(N-1)!P!} = \frac{\left(N + \frac{N\bar{U}}{\in} - 1\right)!}{(N-1)!\left(\frac{N\bar{U}}{\in}!\right)}$$

This gives the number of complexions determining the thermodynamic probability of the energy state of the system of resonators. From Boltzmann's entropy–probability relation (Eq. 12.76), the entropy of the resonators is

$$S_N = k \log_e W$$

or $$S_N = k\log_e \frac{\left(N+\dfrac{N\bar{U}}{\in}-1\right)!}{(N-1)!\left(\dfrac{N\bar{U}}{\in}\right)!}$$

or $$S_N = k\log_e \frac{[N(1+\bar{U}/\in)]!}{N!(N\bar{U}/\in)!}$$

Neglecting 1 in comparison with N which is very large

or $$S_N = k[\log_e[N(1+\bar{U}/\in)]! - \log_e N! - \log_e(N\bar{U}/\in)!] \tag{12.78}$$

To evaluate the expression on the right hand side of Eq. 12.78, we use Stirling's theorem*

$$\log_e p! = p\log_e p - p \tag{12.79}$$

for large value of p. Applying in Eq. 12.78, we get

$$S_N = k[N(1+\bar{U}/\in)\log_e[N(1+\bar{U}/\in)] - N(1+\bar{U}/\in) - N\log_e N + N - (N\bar{U}/\in)\log_e(N\bar{U}/\in) + (N\bar{U}/\in)]$$

$$= k\left[N(1+\bar{U}/\in)\log_e N(1+\bar{U}/\in) - (N\bar{U}/\in)\log_e(N\bar{U}/\in) - N\log_e N\right]$$

$$S_N = kN\left[\left(1+\frac{\bar{U}}{\in}\right)\log_e N + \left(1+\frac{\bar{U}}{\in}\right)\log_e\left(1+\frac{\bar{U}}{\in}\right) - \frac{\bar{U}}{\in}\log_e N - \frac{\bar{U}}{\in}\log_e\frac{\bar{U}}{\in} - \log_e N\right]$$

$$= kN\left[\left(1+\frac{\bar{U}}{\in}\right)\log_e\left(1+\frac{\bar{U}}{\in}\right) - \frac{\bar{U}}{\in}\log_e\frac{\bar{U}}{\in}\right]$$

The entropy of one resonator is

$$S = \frac{S_N}{N} = k\left[\left(1+\frac{\bar{U}}{\in}\right)\log_e\left(1+\frac{\bar{U}}{\in}\right) - \frac{\bar{U}}{\in}\log_e\frac{\bar{U}}{\in}\right]$$

By the second law of thermodynamics,

$$\frac{dS}{dU} = \frac{1}{T}$$

or $$\frac{1}{T} = k\left[\frac{1}{\in}\log_e\left(1+\frac{\bar{U}}{\in}\right) + \frac{1}{\in} - \frac{1}{\in}\log_e\frac{\bar{U}}{\in} - \frac{1}{\in}\right]$$

---

* This is $\text{Lim}_{p\to\infty} p! = \sqrt{2p\pi}\left(\frac{p}{e}\right)^p = \frac{1}{2}\log_e 2\pi + \left(p+\frac{1}{2}\right)\log_e p - p = p\log_e p - p$

$$= \frac{k}{\in} \log_e \frac{1 + \frac{\bar{U}}{\in}}{\frac{\bar{U}}{\in}} = \frac{k}{\in} \log_e \left(1 + \frac{\in}{\bar{U}}\right)$$

or

$$\log_e \left(1 + \frac{\in}{\bar{U}}\right) = \frac{\in}{kT}$$

or

$$\bar{U} = \frac{\in}{e^{\frac{\in}{kT}} - 1} \tag{12.80}$$

From the laws of electromagnetism, Planck deduced the relation

$$e_\nu = \frac{\nu^2}{c^2} \bar{U} \tag{12.81}$$

or

$$\bar{U} = \frac{c^2}{\nu^2} e_\nu$$

or

$$\bar{U} = \frac{c^2}{\nu^2} \frac{\nu^3}{c^4} f'\left(\frac{T}{\nu}\right) \quad \text{from Eq. 12.50}$$

or

$$\bar{U} = \frac{\nu}{c^2} f'\left(\frac{T}{\nu}\right)$$

or

$$\bar{U} = \nu F\left(\frac{\nu}{T}\right) \tag{12.82}$$

From Eqs 12.80 and 12.82,

$$\frac{\in}{e^{\frac{\in}{kT}} - 1} = \nu F\left(\frac{\nu}{T}\right)$$

This can be true only if

$$\in \alpha \ \nu$$

or

$$\in = h\nu \tag{12.83}$$

This constant of proportionality h is called Planck's constant.
Substituting $\in = h\nu$ in Eq. 12.80, the average energy of the resonator becomes

$$\bar{U} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \tag{12.84}$$

Substituting this value in Eq. 12.81, we get

$$e_v = \frac{v^2}{c^2}\frac{hv}{e^{\frac{hv}{kT}}-1}$$

From Eq. 12.13, if the radiation is unpolarized

$$U_v = \frac{8\pi}{c}e_v = \frac{8\pi hv^3}{c^3}\frac{1}{e^{\frac{hv}{kT}}-1} \quad \text{Eq. (12.56)}$$

Equation 12.56 is the famous Planck's radiation formula.

Equation 12.84 may be written as

$$\bar{U} = \frac{hv}{\left[1+\frac{hv}{kT}+\frac{1}{2!}\left(\frac{hv}{kT}\right)^2+\frac{1}{3!}\left(\frac{hv}{kT}\right)^3+\ldots\ldots\right]-1}$$

$$= \frac{hv}{\frac{hv}{kT}+\frac{1}{2!}\left(\frac{hv}{kT}\right)^2+\frac{1}{3!}\left(\frac{hv}{kT}\right)^3+\ldots\ldots} \tag{12.85}$$

For large value of T and small values of $v, \bar{U}$ becomes equal to kT, which is the classical equipartition law for energy distribution amongst waves.

12.14 JEAN'S METHOD OF DEDUCTION OF PLANCK'S RADIATION FORMULA

According to Planck, a member of a system in temperature equilibrium can emit or absorb energy in integral multiples of a definite smallest amount called the quantum of energy. Hence, the total energy of a system of oscillators in temperature equilibrium can only be distributed amongst themselves in integral multiples of this quantum.

Let us call the quantum of energy $\in$. Now from the laws of classical statistics, the number of oscillators having energy between $\in$ and $\in + d\in$ is

$$Be^{-\frac{\in}{kT}}\, d\in \tag{12.86}$$

where B is a constant. To apply this result to the case of oscillators, $\in$ can assume values 0, $\in$, $2\in$, $3\in$ …… etc. Number of oscillators having energy $r\in$ is

$$n_r = Be^{-\frac{r\in}{kT}} \tag{12.87}$$

Let n_0 be the number of molecules having zero energy; then, putting r = 0 in Eq. 12.87

$$n_0 = B$$

so that Eq. 12.87 takes the form

$$n_r = n_0 e^{-\frac{r\in}{kT}} \tag{12.88}$$

If N be the total number of oscillators, then

$$N = n_0 + n_1 + n_2 + n_3 + \ldots\ldots$$

$$= n_0\left(1 + e^{-\frac{\in}{kT}} + e^{-\frac{2\in}{kT}} + e^{-\frac{3\in}{kT}} + \ldots\ldots\right)$$

or $$N = \frac{n_0}{1 - e^{-\frac{\in}{kT}}} \tag{12.89}$$

The total energy of all the oscillators is

$$U = n_0 e^{-\frac{\in}{kT}} \in + n_0 e^{-\frac{2\in}{kT}}\, 2\in + n_0 e^{-\frac{3\in}{kT}}\, 3\in + \ldots\ldots$$

$$= n_0 \in e^{-\frac{\in}{kT}}\left(1 + 2e^{-\frac{\in}{kT}} + 3e^{-\frac{\in}{kT}} + \ldots\ldots\right)$$

or $$U = \frac{n_0 \in e^{-\frac{\in}{kT}}}{\left(1 - e^{-\frac{\in}{kT}}\right)^2} \tag{12.90}$$

Substituting for n_0 from Eq.12.89, we get

$$U = \frac{N \in e^{-\frac{\in}{kT}}}{1 - e^{-\frac{\in}{kT}}} = \frac{N\in}{e^{\frac{\in}{kT}} - 1}$$

Hence, the mean energy of an oscillator is

$$\bar{U} = \frac{U}{N} = \frac{\in}{e^{\frac{\in}{kT}} - 1} \tag{12.91}$$

If T is large, $$\bar{U} = \frac{\in}{1 + \frac{\in}{kT} - 1} = \frac{\in}{\frac{\in}{kT}} = kT$$

which agrees with the classical equipartition principle.

Inside an enclosure containing radiation and oscillators in temperature equilibrium, the average energy of the oscillators must be the same as the average energy of each mode of vibration of waves of frequency constituting the radiation.

Now, the number of degrees of freedom per unit volume associated with frequency ν is given by Eq. 12.68

$$\frac{8\pi\nu^2}{c^3}$$

Energy associated with frequency ν per unit volume is

$$u_\nu = \frac{8\pi\nu^2}{c^3}\bar{U}$$

or $$u_\nu = \frac{8\pi\nu^2}{c^3}\frac{\in}{e^{\frac{\in}{kT}}-1} \tag{12.92}$$

Wien's displacement law gives us the relation

$$e_{\lambda b} = f(\lambda T)\,\lambda^{-5}$$

Now, $$e_{\nu b}d\nu = -e_{\lambda b}d\lambda$$

Since $$\lambda = \frac{c}{\nu},\quad d\lambda = -\frac{c}{\nu^2}d\nu$$

Hence, $$e_{\nu b}d\nu = e_{\lambda b}\frac{c}{\nu^2}d\nu$$

or $$e_{\lambda b} = \frac{\nu^2}{c}e_{\nu b}$$

This gives $$\frac{\nu^2}{c}e_{\nu b} = f\left(\frac{cT}{\nu}\right)\times\left(\frac{c}{\nu}\right)^{-5}$$

$$e_{\nu b} = f\left(\frac{cT}{\nu}\right)\times\frac{c}{\nu^2}\times\frac{\nu^5}{c^5} = f'\left(\frac{T}{\nu}\right)\times\frac{\nu^3}{c^4}$$

From the laws of electrodynamics, Planck deduced the relation

$$e_{\nu b} = \frac{\nu^2}{c^2}\bar{U}$$

so that $$\bar{U} = e_{\nu b}\frac{c^2}{\nu^2} = \frac{\nu^3}{c^4}\frac{c^2}{\nu^2}f'\left(\frac{T}{\nu}\right)$$

or $$\bar{U} = \frac{\nu}{c^2}f'\left(\frac{T}{\nu}\right)$$

or
$$\bar{U} = \nu F\left(\frac{\nu}{T}\right)$$

Comparing Eq. 12.91 with the electromagnetic equation of Planck (Eq. 12.82)

$$\bar{U} = \nu F\left(\frac{\nu}{T}\right)$$

We find that these equations can be satisfied only if

$$\in \alpha\, \nu$$

$$\in = h\nu \tag{12.93}$$

where *h* is the constant of proportionality, called the Planck's constant.

Substituting $\in = h\nu$ in Eq. 12.92, we get Planck's radiation formula

$$u_\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

12.15 SPECIFIC HEATS OF SUBSTANCES

The simplest law of specific heat of monatomic solids was given by Dulong and Petit. It runs as follows:

The product of atomic weight and specific heat is the same for all elementary monatomic solid substances and is called atomic heat.

Regnault's experiments on a large number of substances give a mean value of 6.38 calories per gram per degree for specific heats of the substances investigated.

This law can be readily explained on the basis of equipartition principle. An atom of a monatomic solid has three degrees of freedom of vibrational motion; with each degree of kinetic energy, an amount of energy 1/2 *kT* is associated. Since the average energy of vibrational motion is equally divided between the kinetic and potential forms, the total amount of energy per degree of freedom is *kT.* Hence, the energy of each atom is *3kT*. If *N* be the Avogadro number, the total energy of the solid per gram atom is

$$U = 3NkT = 3RT$$

Now,
$$C_v = \left(\frac{dU}{dT}\right)_\upsilon = 3R$$

or
$$C_v = 3 \times 1.988 = 5.1965 \text{ cal per gm atom per degree}$$

Thus according to Dulong and Petit, the specific heat of substance would be the same at all temperatures.

12.16 DEVIATIONS FROM DULONG AND PETIT'S LAWS

Extensive researches by Magnus, Nernst and Lindemann, and Lewis conclusively prove that specific heats of substances actually vary with temperature. The curves in Fig. 12.12 show the nature of variation of C_v with temperature.

The atomic heat of diamond rises from a low value of 0.03 at 86.5 K to 5.077 at 1100 K. All light substances such as boron, beryllium and silicon behave in a similar manner.

At room temperature, atomic heat of lead approximates the value required by Dulong and Petit.

But below 100 K, it drops rapidly to zero value.

Some general conclusions:

1. The general form of the specific heat and temperature curve is the same for all substances.
2. At high temperature, the curves approach asymptotically to the value required by Dulong and Petit's law.
3. The substances differ in temperature above which they obey Dulong and Petit's law.
4. At low temperature, the specific heat rapidly falls and in the case of some substances (such as diamond) acquires zero value long before the zero of temperature is reached.
5. From 0 K up to a certain specified temperature, the atomic heat at constant volume varies as the cube of the absolute temperature. This is true for all substances and the law is known as Debye's T^3-law.
6. The curves showing the relation between C_v and T for all substances can be brought nearly into coincidence by suitably altering the temperature scale of each substance. Thus if the abscissae of the curve for aluminium are multiplied by a factor 4.6, the specific heat curve for aluminium will coincide with that for diamond. In fact if instead of plotting C_v against T, C_v is plotted against T/θ where θ is a quantity characteristic of the substance then the specific heat curves for all substances would coincide. This temperature θ is called the characteristic temperature of the substance. Under these circumstances, C_v can be represented as a function of T/θ where T is the absolute temperature at which the specific heat is determined.

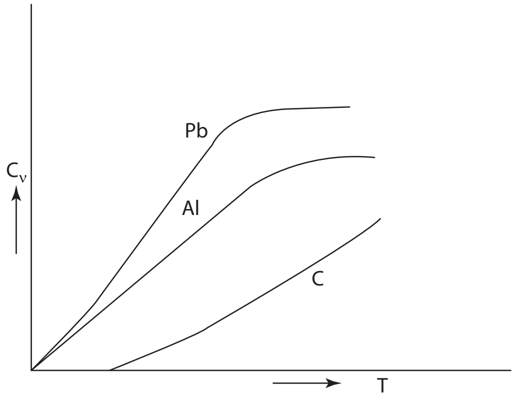

Fig. 12.12 Variation of specific heat of some substances with temperature

It appears that the departure from the Dulong and Pelit's value of specific heat at different temperature is much larger than the experimental error. This is another case of failure of the equipartition principle which is based on classical mechanics. We shall prove that in the field of specific heat also, the quantum theory has acquired astonishing success.

12.17 EINSTEIN'S THEORY OF SPECIFIC HEAT

Einstein's derivation of specific heat formula is based upon the following assumptions:

1. All atoms of a monatomic solid vibrate with the same frequency v.
2. The frequency depends on the mass of the atom and the restoring force.
3. These atoms, like Planck's oscillators, are in equilibrium with ether vibrations of the same frequency.
4. Instead of classical law of equipartition, that is ½ KT for each degree of freedom, Einstein uses the mean energy of Planck's oscillator for each degree of freedom, that is,

$$\bar{U} = \frac{hv}{e^{\frac{hv}{kT}} - 1}$$

For one gram-atom of a monatomic solid, consisting of N atoms each with 3 degrees of freedom, the total internal energy per gm-atom is

$$U = 3N\bar{U} = \frac{3Nhv}{e^{\frac{hv}{kT}} - 1}$$

This can be written as

$$U = 3Nk\frac{\frac{hv}{k}}{e^{\frac{hv}{kT}} - 1} = 3R\frac{\frac{hv}{k}}{e^{\frac{hv}{kT}} - 1}$$

Now

$$C_v = \left(\frac{dU}{dT}\right)_v$$

$$= -3R\left(\frac{hv}{k}\right)\frac{e^{\frac{hv}{kT}}}{\left(e^{\frac{hv}{kT}} - 1\right)^2}\frac{hv}{k}\left(-\frac{1}{T^2}\right)$$

$$C_v = 3R\left(\frac{hv}{kT}\right)^2 \frac{e^{\frac{hv}{kT}}}{\left(e^{\frac{hv}{kT}} - 1\right)^2} \qquad (12.94)$$

writing $\theta = h\nu/k$, Eq. 12.94 takes the form

$$C_v = 3R\left(\frac{\theta}{T}\right)^2 \frac{e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}} - 1\right)^2} = 3RF\left(\frac{\theta}{T}\right) \tag{12.95}$$

The function F is called Einstein's function.
Putting $x = \theta/T$, Eq. 12.95 reduces to

$$C_v = 3R\frac{x^2 e^x}{(e^x - 1)^2}$$

Now,

$$\frac{e^x}{(e^x-1)^2} = \frac{e^x}{e^{2x}\left(1-\frac{1}{e^x}\right)^2} = \frac{1}{e^x\left(1-\frac{2}{e^x}+\frac{1}{e^{2x}}\right)}$$

$$= \frac{1}{e^x - 2 + e^{-x}}$$

$$= \frac{1}{\left(1+x+\frac{x^2}{2}+\ldots\ldots\right) - 2 + \left(1-x+\frac{x^2}{2}-\ldots\ldots\right)}$$

If T is large, x is small. Hence neglecting terms higher than the second power,

$$\frac{e^x}{(e^x-1)^2} \approx \frac{1}{x^2}$$

or

$$\frac{x^2 e^x}{(e^x-1)^2} \approx 1$$

so that $C_v \approx 3R$ for high values of T. This agrees with the experimental result.

If T is very small, x is very large. In this case,

$$\frac{x^2 e^x}{(e^x-1)^2} = \frac{x^2}{e^{-x}e^{2x}(1-e^{-x})^2} = \frac{x^2}{e^x\left(1-\frac{1}{e^x}\right)^2}$$

If x is large, $1/e^x = 0$, so that

$$\frac{x^2e^x}{(e^x-1)^2}\approx\frac{x^2}{e^x}=\frac{x^2}{1+x+\dfrac{x^2}{2!}+\dfrac{x^3}{3!}+\ldots\ldots}=0$$

Thus at the absolute zero of temperature, the atomic heat reduces to zero value. This is in accord with experiment.

12.17.1 The Characteristic Temperature

We have defined the characteristic temperature by

$$\theta=\frac{h\nu}{k}$$

It is evidently a temperature T for which

$$h\nu=kT\quad\text{or}\quad\frac{h\nu}{kT}=1$$

Substituting $h\nu/kT=1$ in Eq. 12.94, it reduces to

$$C_v=\frac{3\text{Re}}{(e-1)^2}=3R\times0.921=5.96\times0.92=5.49$$

Hence, the characteristic temperature of a substance is that temperature at which the specific heat at constant volume becomes 5.49. Hence from the experimental (C_v - T) curve of a substance, its characteristic temperature can be determined.

12.17.2 Characteristic Frequency

Knowing the characteristic temperature θ, the characteristic frequency ν can be calculated from the relation

$$\nu=\frac{k\theta}{h}$$

where k is Boltzmann's constant and h is Planck's constant.

Other methods of determining characteristic frequency: The characteristic frequency of a solid can also be determined in other ways; they are as follows:

1. *The residual rays method:* A substance which exhibits selective reflection at a particular region of the spectrum must consist of resonators which respond to vibration of frequencies corresponding to that region. Rubens and his collaborators succeeded in isolating these frequencies by successive reflections from the surfaces of a number of substances.
2. *From compressibility:* This is determined with the help of the relation

$$\nu=2.8\times10^7\left(\frac{V_A}{K^3A^3}\right)^6 \tag{12.96}$$

where K is the compressibility, A is the atomic weight and V_A is the volume of the gram-atom.

3. *From melting point:* This is obtained from the relation

$$\nu = C\sqrt{\frac{T_m}{AV_A^{2/3}}} \tag{12.97}$$

where T_m is the temperature of the melting point, A is the atomic weight and V_A is the volume of the gram-atom. The constant C has the order of magnitude 2.8×10^{12}.

Knowing the characteristic frequencies by any of the above methods, the specific heat of a substance at any temperature can be calculated with the help of Einstein's equation.

We have seen that the values of C_v calculated from Einstein's equation agrees with experimental values at very high and very low temperatures. In the case of diamond, the experimental values of C_v down to 30 K agree remarkably with values calculated from Einstein's formula. In the case of other substances, the atomic heats at low temperatures fall off much more slowly than those demanded by Einstein's equation. Thus for silver at 14 K, the value of C_v calculated from Einstein's formula is 28 times lower than the experimental value and at lower temperatures the discrepancy is still greater.

The weak point in Einstein's theory is that in the ideal solid postulated by him, all atoms are supposed to vibrate with the same frequency at all temperatures.

12.18 DEBYE'S THEORY OF SPECIFIC HEAT

According to Debye, the actual vibration of an atom in an elastic solid must be necessarily complex owing to collisions and mutual action of the neighbouring atoms. This complex vibration of an atom can be analysed into a large number of simple components. The number of such components must be finite, though large because the total number of degrees of freedom cannot exceed $3N$ where N is the number of atoms constituting the monatomic solid. Hence, the possible frequencies must have an upper limit. Let us call this limiting frequency ν_m.

Now, a solid can transmit both longitudinal and transverse waves represented by c_L and c_T, respectively. We have already proved in Eq. 12.68 that the number of degrees of freedom per unit volume of longitudinal waves in the frequency range ν to $\nu + d\nu$ is

$$dN_L = 4\pi \frac{\nu^2}{c_L^3} d\nu$$

and those of transverse waves in the same frequency range is

$$dN_T = 8\pi \frac{\nu^2}{c_T^3} d\nu$$

Hence, the total number of degrees of freedom within the frequency range ν to $\nu + d\nu$ is

$$dN = dN_L + dN_T = 4\pi\left(\frac{1}{c_L^3} + \frac{2}{c_T^3}\right)\nu^2 d\nu$$

Let V be the volume of gram-atom of the solid. Then, the total number of degrees of freedom in this volume is

$$dNV = 4\pi V\left(\frac{1}{c_L^3} + \frac{2}{c_T^3}\right)\nu^2 d\nu$$

or
$$dNV = A\nu^2 d\nu \quad \text{where} \quad A = 4\pi V\left(\frac{1}{c_L^3}+\frac{2}{c_T^3}\right)$$

Since the total number of degrees of freedom must be equal to 3N where N is the number of atoms in gm-atom, we must have

$$3N = A\int_0^{\nu_m}\nu^2 d\nu = \frac{A}{3}\nu_m{}^3$$

so that
$$A = \frac{9N}{\nu_m^3} \tag{12.98}$$

$$dNV = \frac{9N}{\nu_m^3}\nu^2 d\nu$$

With each degree of freedom, we associate the mean energy

$$\bar{U} = \frac{h\nu}{e^{\frac{h\nu}{kT}}-1}$$

Then, the total internal energy of the solid is

$$U = \frac{9N}{\nu_m^3}\int_0^{\nu_m}\frac{h\nu^3 d\nu}{e^{\frac{h\nu}{kT}}-1}$$

Now,
$$C_v = \left(\frac{dU}{dT}\right)_v$$

or
$$C_v = -\frac{9N}{\nu_m^3}\int_0^{\nu_m} h\nu^3 d\nu\left(e^{\frac{h\nu}{kT}}-1\right)^{-2} e^{\frac{h\nu}{kT}}\left(-\frac{h\nu}{kT^2}\right)$$

$$= \frac{9N}{\nu_m^3}\int_0^{\nu_m}\frac{h^2\nu^4}{kT^2}\frac{e^{\frac{h\nu}{kT}}d\nu}{\left(e^{\frac{h\nu}{kT}}-1\right)^2}$$

or
$$C_v = \frac{9Nh^2}{kT^2\nu_m^3}\int_0^{\nu_m}\frac{e^{\frac{h\nu}{kT}}\nu^4 d\nu}{\left(e^{\frac{h\nu}{kT}}-1\right)^2} \tag{12.99}$$

Put
$$\frac{h\nu}{kT} = x, \quad x_m = \frac{h\nu_m}{kT}$$

Then,
$$dv = \frac{kT}{h}\,dx$$

Substituting for v in Eq. 12.99, we get

$$C_v = \frac{9Nh^2}{\left(\frac{kT}{h}\right)^3 x_m^3 kT^2} \int_0^{x_m} \frac{e^x \left(\frac{kT}{h}\right)^4 x^4 \left(\frac{kT}{h}\right) dx}{(e^x - 1)^2}$$

or
$$C_v = \frac{9Nk}{x_m^3} \int_0^{x_m} \frac{x^4 e^x\,dx}{(e^x - 1)^2}$$

or
$$C_v = \frac{9R}{x_m^3} \int_0^{x_m} \frac{x^4 e^x\,dx}{(e^x - 1)^2} \qquad (12.100)$$

Equation 12.100 is known as Debye's specific heat equation.

For high temperature, x is small and it has already been proved that for small values of x

$$\frac{e^x}{(e^x - 1)^2} \approx \frac{1}{x^2}$$

Hence for high temperature, Eq. 12.100 reduces to

$$C_v = \frac{9R}{x_m^3} \int_0^{x_m} x^2\,dx$$

or
$$C_v = \frac{9R}{x_m^3} \times \frac{x_m^3}{3} = 3R$$

This agrees with Dulong and Petit's result. At low temperature, x is large and the upper limit of the integral can be made equal to infinity. Equation 12.100 can then be put into the following form

$$C_v = \frac{9R}{x_m^3} B \quad \text{where} \quad B = \int_0^{\infty} \frac{x^4 e^x\,dx}{(e^x - 1)^2}$$

or
$$C_v = 9BR\frac{k^3 T^3}{h^3 v_m^3}$$

or
$$C_v = \text{Const} \times T^3 \qquad (12.101)$$

This is Debye's T^3-law.

The value of v_m can be calculated from Eq. 12.98.

$$v_m^3 = \frac{9N}{A}$$

or
$$\nu_m^3 = \frac{9N}{4\pi V}\frac{1}{\left(\frac{1}{c_L^3}+\frac{2}{c_T^3}\right)}$$

The values of c_L and c_T can be calculated from the elastic constants of the solid. Therefore, ν_m depends on the nature of material of the solid. From Eq. 12.100, C_v is necessarily a function of x_m where

$$x_m = \frac{h\nu_m}{kT} = \frac{\theta_m}{T} \quad \text{where} \quad \theta_m = \frac{h\nu_m}{k}$$

Thus,
$$C_v = F\left(\frac{\theta_m}{T}\right) \tag{12.102}$$

Evidently instead of plotting C_V against T, if we plot C_V against T/θ_m we shall get a curve which will represent the variation of specific heat with temperature for all substances. The value of θ_m ranges from 88 to 846. For diamond, it is as high as 1860.

Experiments of Blackmann and Kellermann prove that there is actually a region of temperature in which the T^3-law holds, but that is a region of very low temperature. At this region, only long waves contribute to the energy and the wavelengths are large compared to interatomic distances. Accordingly, the idea of a continuum is more fully realized at this temperature. But we must not expect too much of the Debye law. Schaefer concludes there is for each substance a very low temperature below which Debye T^3-law does not hold. At helium temperatures, the specific heats of metals are represented by the formula

$$C_v = a\left(\frac{T}{\theta}\right)^3 + bT \tag{12.103}$$

the first term is due to contribution from the lattice vibration, the second gives the contribution from the conduction electrons which can be treated like perfect gas molecules. For copper, the value of a and b are

$$a = 464.5 \qquad \text{and} \qquad b = 0.000177$$

In addition to all these, some amount of energy is absorbed by atoms to raise them from a state of lower to that of higher energy at the absolute zero temperature, the atoms occupy the lowest or the ground state; with rise of temperature, the higher states begin to be populated. If ΔE is the energy associated with the higher state, then the contribution to specific heat due to this cause is

$$\Delta C = \frac{k\left(\frac{\Delta E}{kT}\right)^2 e^{\frac{\Delta E}{kT}}}{\left(1+e^{\frac{\Delta E}{kT}}\right)^2} \tag{12.104}$$

12.19 SPECIFIC HEAT OF GASES

The atoms of a solid have only vibrational degrees of freedom. The gas molecules can have three types of motion—translational, rational and vibrational. Hence, the total energy of atoms of a mass M is

$$U_M = U_T + U_R + U_V \tag{12.105}$$

where U_T, U_R and U_V are the energies associated with translational, rotational and vibrational degrees of freedom, respectively.

12.19.1 Calculation of Specific Heat Due to Translational Motion

With each degree of freedom of translational motion, an amount of energy 1/2 kT is associated. Hence if N be the number of molecule per gm-molecule, then the energy per gm-molecule due to translational motion is

$$U_T = 3N \times \frac{1}{2}kT = \frac{3}{2}RT$$

Since the centre of gravity of the molecule can have only three degrees of freedom of translation, contribution to specific heat due to this cause is

$$C_T = \left(\frac{dU_R}{dT}\right)_V = \frac{3}{2}R = 2.98$$

12.19.2 Calculation of Specific Heat Due to Rotational Motion

The energy of rotational motion per degree of freedom can be calculated from the classical quantum theory. According to this theory,

$$\int pdq = nh \tag{12.106}$$

where p is the momentum co-ordinate and q is the positional co-ordinate. In the case of rotational motion, p is the angular momentum ($I\omega$) and q is the angular displacement (θ). Substituting the values of p and θ in Eq. 12.105 and integrating from 0 to 2π , we get

$$\int_0^{2\pi} I\omega d\theta = nh \qquad (n = 0, 1, 2, 3\ldots\ldots)$$

or $$2\pi I\omega = nh$$

so that $$\omega = \frac{nh}{2\pi I}$$

In other words, angular momentum is quantized. The kinetic energy of rotational motion is

$$\frac{1}{2}I\omega^2 = \frac{n^2h^2}{8\pi^2 I}$$

According to the new quantum theory, this is equal to

$$\frac{1}{2}I\omega^2 = n(n+1)\frac{h^2}{8\pi^2 I}$$

12.19.3 Calculation of Specific Heat Due to Vibrational Motion

According to Planck, the mean energy of an oscillator is

$$U_V = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

If *N* be the number of molecule per gm-molecule, then the mean energy per gm-molecule is

$$U_V = N\bar{U}_V = \frac{Nh\nu}{e^{\frac{h\nu}{kT}} - 1}$$

Now

$$C_V = \left(\frac{dU_V}{dT}\right) = -Nh\nu \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}\left(-\frac{h\nu}{kT^2}\right)$$

or

$$C_V = Nk\left(\frac{h\nu}{kT}\right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2} \qquad (12.107)$$

or

$$C_V = R\frac{x^2 e^x}{(e^x - 1)^2} \quad \text{where} \quad x = \frac{h\nu}{kT}$$

12.19.4 Specific Heat of Hydrogen

The variation of specific heat of hydrogen with fall of temperature is given in Table 12.2.

It follows that below 60 K, hydrogen behaves like a monatomic gas having only three degrees of freedom. At higher temperatures, rotational degrees of freedom appear. It can be proved that the contribution to specific heat due to rotational motion of a diatomic molecule is

Table 12.2 Variation of specific heat of hydrogen with fall of temperature

TK	196.5	100	80	60	45	35
C_V	48.39	3.42	3.14	2.99	3.00	2.98

$$U_R = R\sigma^2 \frac{d^2}{d\sigma^2}(\log_e Q) \tag{12.108}$$

where $$\sigma = \frac{h^2}{8\pi^2 IkT} \quad \text{and} \quad Q = \sum_{n=0,1,2,3,4,\ldots} (2n+1)e^{-n(n+1)\sigma}$$

Subtracting $U_T = 2.98$ for hydrogen at 60 K from the observed value of U_M in Eq. 12.105, we can find the value of U_R. This value of U_R does not agree with the value of U_R calculated from Eq. 12.108.

Now, analysis of band spectra of hydrogen led to the discovery of two types of hydrogen molecules—(1) orthohydrogen in which the molecules can assume rotational quantum states specified by odd values of *n;* (2) parahydrogen in which the molecules can assume rotational quantum states specified by even values of *n*.

Wave mechanics indicated that in the orthohydrogen, the magnetic moments of the two nuclei are parallel and in the parahydrogen, they are antiparallel.

Hence for parahydrogen,

$$Q_P = \sum_{n=0,2,4,6,\ldots\ldots} (2n+1)\, e^{-n(n+1)\sigma}$$

and for orthohydrogen,

$$Q_O = \sum_{n=1,3,5,\ldots\ldots} (2n+1)\, e^{-n(n+1)\sigma}$$

Hence, a mass of hydrogen gas consists of a mixture of ortho- and parahydrogen whose proportion depends upon temperature. Assuming that

$$\frac{\text{mass of ortho-hydrogen}}{\text{mass of para-hydrogen}} = \frac{1}{\rho}$$

in a mass of hydrogen and representing the specific heat of orthohydrogen by $U_R(O)$ and that of parahydrogen by $U_R(P)$, the specific heat of a mass of hydrogen due to rotational motion is

$$U_R = \frac{\rho U_R(P) + U_R(O)}{1+\rho} \tag{12.109}$$

Eucken and Hiller produced various proportions of ortho- and parahydrogen by leaving hydrogen in contact with activated charcoal which serves as catalyst for transformation and verifies the truth of Eq. 12.108.

12.20 EXPERIMENTAL DETERMINATION OF STEFAN'S CONSTANT

The principle of the method is as follows: The instrument consists of three essential parts (Fig. 12.13):

1. A source of radiation (a black body) (FG).
2. A screen with a shutter (CD).
3. A receiver (AB).

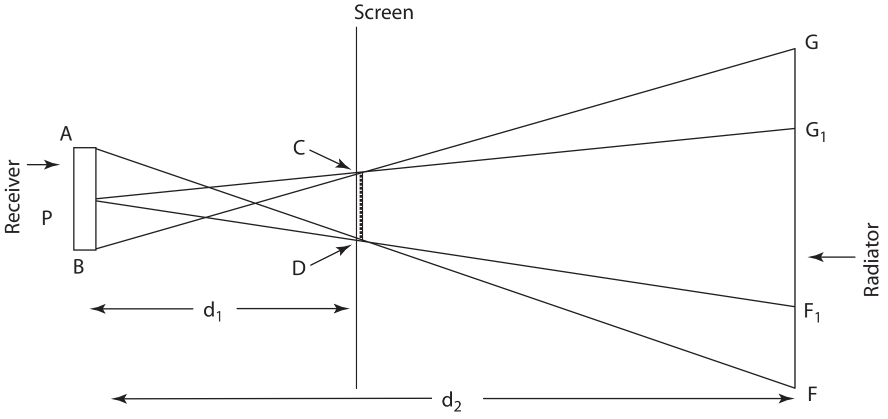

Fig. 12.13 Apparatus' arrangement for determination of stefan's constant

The first important adjustment is that the centres of the receiver, the shutter and the radiator must lie in the same straight line. The second adjustment is that the surfaces of the receiver, the shutter and the radiator must be perpendicular to the central line. The third important adjustment in setting of the instrument is that the line joining the points *A*, *D* and *B*, *C* must intersect the radiating surfaces at two points *F* and *G* (say). In that case, every point of the receiver must receive the same amount of radiation per second; this can be seen as follows:

To find the radiation received by the point *p* of the receiver, join *P*, *C* and *P*, *D* and produce them to intersect the screen at G_1 and F_1. Then, *p* will receive radiation contained only within the cone F_1PG_1. Let *E* be the radiation emitted per unit area of the radiator within the cone F_1PG_1 and let the area of *CD* be a_1 and that of F_1G_1, a_2; the distance between receiver and screen be d_1 and that between receiver and radiator be d_2. Then,

$$\frac{a_1}{a_2} = \frac{d_1^2}{d_2^2}$$

By the law of inverse squares, the radiation received by unit area around *p* when the radiator is placed at *FG* is

$$I_2 = E\frac{a_2}{d_2^2}$$

If the same radiation be placed in the position of the screen *CD*, the radiation received by unit area around *P* would be

$$I_1 = E\frac{a_1}{d_1^2} = E\frac{a_2 d_1^2}{d_1^2 d_2^2} = E\frac{a_2}{d_2^2} = I_2$$

Hence under the condition of adjustment, the radiation falling on the receiver per unit area around *P* would be independent of the position of the radiator.

Now, let A_1 = the area of the receiver
A_2 = the area of the shutter
d = distance of the receiver from shutter
T_1 = the temperature of the radiator
T_2 = the temperature of the shutter

The solid angle subtended by the radiator at the centre of the receiver = that subtended by the shutter at the same point = $d\Omega = A_2/d_1^2$, since $\cos\theta = 1$. The energy falling on unit area of the receiver per second is obtained from the relation

$$K\,dt\,d\sigma\,d\Omega\cos\theta$$

Now by Stefan–Boltzmann law,

$$H = \pi K = \sigma T_1^4$$

so that
$$K = \frac{\sigma T_1^4}{\pi}$$

Hence, the energy falling on unit area of the receiver per second

$$= \sigma T_1^4 dtd\,\sigma d\Omega \frac{\cos\theta}{\pi}$$

In this particular case, $\theta = 0$ so that $\cos\theta = 1$, $d\sigma = A_1$, the area of the receiver, $dt = 1$ second and $d\Omega = A_2/d_1^2$

Hence, energy falling on the receiver per second from the radiator is

$$Q_1 = \frac{\sigma T_1^4 A_1 A_2}{\pi d_1^2}$$

Similarly, the energy falling on the receiver per second from the shutter at temperature T_2 is

$$Q_2 = \frac{\sigma T_2^4 A_1 A_2}{\pi d_1^2}$$

(This holds on the assumption that the shutter is also a black body.)

Hence, the difference of energy falling on the receiver per second with the shutter open and closed is

$$Q_1 - Q_2 = \sigma A_1 A_2 \frac{(T_1^4 - T_2^4)}{\pi d^2}$$

This is the working formula for the determination of σ.

The apparatus: In Lummer Pringsheim's method, the receiver was the surface bolometer made up of exceedingly thin strip of platinum (1 to 2 × 10^{-3} mm thick) coated with platinum black and joined together in series so as to form a grating (Fig. 12.14).

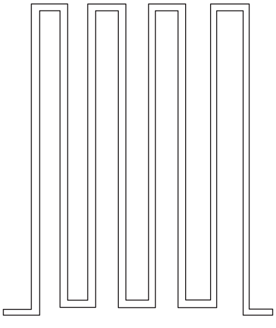

Fig. 12.14 Sketch of receiver

Resistance of each grating is about 60 ohms. For experimental purposes, four exactly similar gratings are taken and placed in the four arms of the Wheatstone's bridge as shown in the figure (Fig. 12.15). The gratings in arms 3 and 1 are placed one back to the other with edges overlapping so as to form a continuous surface. The gratings 1 and 3 are exposed to the radiation while those in arms 2 and 4 are shielded from the radiation. Usual battery and galvanometer connections being made, the bridge is balanced with all the gratings shielded from the radiation. When radiation falls on the gratings 1 and 3 the temperatures of these gratings rises, the balance is disturbed and the galvanometer shows a deflection.

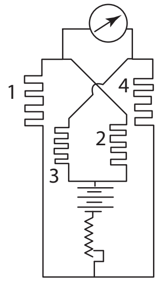

Fig. 12.15 Sketch of wheatstone's bridge

The radiator: For measurement of temperature of radiation within the range 200 ° to 600 °C, a copper sphere coated on the inside with platinum black is used (Fig. 12.16).

It is enclosed in an iron vessel filled with a mixture of sodium and potassium nitrates which melts at 219 °C. It is heated by a burner supplied with regulated amounts of gas and air. The temperature of the bath is measured by high pressure gas thermometer and by a thermoelement. The bath is also provided with an efficient stirring arrangement. The opening of the copper vessel is surrounded by a diaphragm *vv* through which water at atmospheric temperature flows. In front of the copper vessel, there is a double walled cylinder whose opening can be closed by a double walled shutter. Through each of these, water at atmospheric temperature is made to flow. The water-filled vessels protect the bolometer from radiations coming from the heated chamber.

For measurements in the temperature range 600 °C to 1300 °C, an iron cylinder is substituted for the copper sphere. The inner surface is coated with platinum black. The cylinder is enclosed in a double-walled gas furnace. The temperature measured by this thermometer is reduced to the scale of nitrogen thermometer from the results of Holborn and Day's comparison.

The bolometer is placed on a bench in front of the radiator so that its distance from the radiator can be varied. The radiation reaches the bolometer through a number of stops in a cylindrical casing, the narrowest one being just in front of the grating. The inner wall of the casing and the surfaces of the stops are covered partly with black velvet and partly with felt.

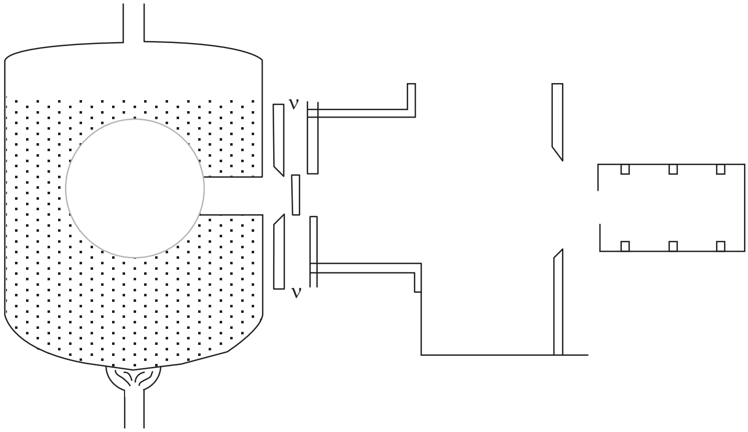

Fig. 12.16 Experimental arrangement to determine stefan's constant

In making an observation, the shutter is raised allowing the radiation to fall on the surface of the bolometer and the maximum deflection of the spot of light is noted. The shutter is then lowered and the maximum deflection due to radiation from the shutter is again noted.

In actual experiments, the deflection of each temperature should be about 300 mm either by altering the distance of the bolometer from the radiator or by regulating the current through the battery connected to the Wheatstone bridge.

12.21 MEASUREMENT OF HIGH TEMPERATURES BY RADIATION

At high temperatures above the melting point of gold (1063 °C), the difficulties of gas thermometers are too high. Hence, they are of no use in establishing the thermodynamical scale of temperature. Thermometers based on laws of radiation are wonderfully suited for the measurement of high temperatures beyond the limit of gas thermometer.

We have seen that the radiation inside an enclosure whose walls are maintained at a constant temperature is unique in character and is independent of the nature of walls of the enclosure. Further, the radiation inside such an enclosure behaves as a perfect gas. Hence, radiation inside the enclosure can be used as the thermometric substance for defining a scale of temperature which is absolute in the same sense that Kelvin's scale is absolute.

The only serious objection in using the laws of radiation for the measurement of temperature is that these laws are only applicable to the case of black bodies like the Bessemer converter or any other chamber at a fairly uniform temperature with a small aperture.

For measuring temperature, any of the following laws of radiation may be used:

$$U = \sigma T^4$$

$$\lambda_m T = \text{constant}$$

$$E_\lambda = \frac{C_1}{\lambda^5}\left(e^{\frac{c_2}{\lambda T}} - 1\right)$$

Of these formulae the second one is not generally used, for it requires elaborate apparatus like infrared spectrometer.

The measurement of temperature by Stefan's laws has led to the so-called total radiation pyrometers while the method based on Planck's formula is used in the optical pyrometers.

12.21.1 The Optical Pyrometer

If we put $T = 4000$ K as the upper limit of temperature, $c_2 = 1.432$ (from experiment) and $\lambda = 6.58 \times 10^{-5}$ cm for wavelength of red light, then

$$e^{\frac{c_2}{\lambda T}} = 230$$

With these values of c_2, λ and T,

$$e^{\frac{c_2}{\lambda T}} - 1 \approx e^{\frac{c_2}{\lambda T}}$$

and Planck's formula reduces to Wien' s formula

$$E_\lambda = C_1\lambda^{-5}e^{-\frac{c_2}{\lambda T}}$$

If E_1 and E_2 are the energies at two temperatures T_1 and T_2 respectively, then

$$E_1 = C_1\lambda^{-5}e^{-\frac{c_2}{\lambda T_1}}$$

and
$$E_2 = C_1\lambda^{-5}e^{-\frac{c_2}{\lambda T_2}}$$

so that
$$\frac{E_2}{E_1} = e^{\frac{c_2}{\lambda}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

or
$$\log_e\left(\frac{E_2}{E_1}\right) = \frac{c_2}{\lambda}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{1.432}{\lambda}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

If T_1 and E_1 be known at a known wavelength, then from measured value of E_2, T_2 can be calculated; T_1 is taken to be the temperature at the gold point and the scale thus obtained has been legalized by international conference.

12.21.2 The Disappearing Filament Pyrometer

The instrument is really a telescope consisting of the object glass *L* with a diaphragm placed in front of the eyepiece *E* (Fig. 12.17). *C* is a red filter which transmits only a narrow band of wavelength in the red part of the visible spectrum. The image of the source *S* is projected on the filament.

Calibration of the pyrometer: The pyrometer is sighted on a black body *S* which can be kept at various temperatures upto the melting point of gold, the temperature of the black body being measured by a standardized thermocouple. At each temperature, the current through the filament is adjusted till the filament becomes invisible against the image of the source *S* which is formed in the plane of the filament. The temperature is plotted against the current and from the calibration curve, any unknown temperature can be determined if the corresponding current required to match the radiation is known.

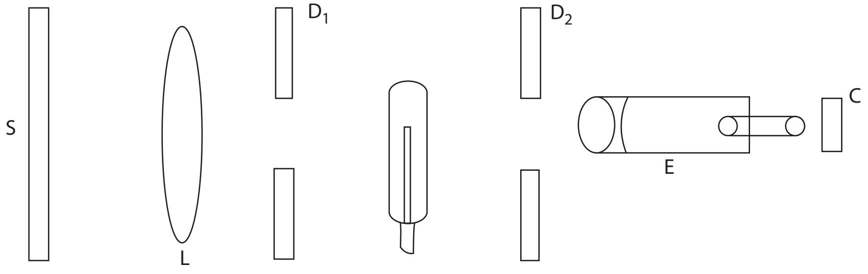

Fig. 12.17 Disappearing filament pyrometer

For measurement of temperature above the gold point, a rotating sector is placed between S and L. The number of rotation of the sector is adjusted at 30 to 40 revolutions per second. This sector cuts down the intensity of radiation from S in the ratio $\theta/2\pi$ where θ is the angular width of the opening of the sector. By this means, the observed intensity is allowed to fall within the limits of the calibration curve.

Let T_1 be the apparent temperature corresponding to the observed reducing intensity E_1. Then if the actual intensity is E_2, we must have

$$\frac{E_2}{E_1} = \frac{2\pi}{\theta}$$

Hence,
$$\log_e\left(\frac{2\pi}{\theta}\right) = \frac{1.432}{\lambda}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12.110}$$

From Eq. 12.110, the temperature T_2 corresponding to actual intensity E_2 can be calculated.

In the polarizing type of optical pyrometer, the intensity of standard light is maintained constant and the intensity of light from the source is varied by means of a polarizing and analyzing Nicol.

12.21.3 The Total Radiation Pyrometer

This instrument measures the total energy of radiation of all wavelengths from the body whose temperature is to be measured. Figure 12.18 shows the design of Fery's radiation pyrometer.

In this figure, M is a concave mirror which is silvered on the front. D is a diaphragm with a central hole. The blackened surfaces of the receiver T is placed just behind the diaphragm. One junction of the thermocouple called the hot junction is soldered to the back of the receiver. The cold junction is shielded from the direct radiation by means of a tongue and a box. The leads of the thermocouple are joined to a millivoltmeter. The concave mirror can be moved backwards and forwards by means of a rack and pinion arrangement. The diaphragm is sighted by means of an eyepiece E fitted to a hole in the centre of the concave mirror.

The principle of working of the instrument is based on the fact that the intensity of the image of a distant object formed on a fixed plane by a mirror (or lens) is independent of distance of the object

Fig. 12.18 Fery's radiation pyrometer

from the mirror or the lens. This is because with the increase of distance, the amount of radiation falling on the aperture of the mirror falls off inversely as the square of the distance. If the object distance u is large, the mirror requires only small displacement to focus the image on the same plane so that the image distance v remains practically unaltered. Now, magnification of the image is

$$m = \frac{v}{u} = \frac{I}{O}$$

so that the linear dimension of the image is inversely proportional to the object distance. Hence, the area of the image is inversely proportional to the square of the distance. Hence, intensity of image at every point of the plane is the same and is independent of the object distance.

The essential conditions of using the instrument, therefore, are as follows:

1. The image of aperture of the black body should always be accurately focussed in the plane of the diaphragm.
2. The size of the heat image formed by the concave mirror should be larger than the hole in the diaphragm.

In that case, the thermocouple would measure the intensity of total radiation and not the total radiation.

The first condition was realized by Fery by the following optical device. Two semicircular skew mirrors each with a semicircular opening of 15 mm radius were placed in the plane of the diaphragm. Through this opening, the radiation passed on to the hot junction. The inclination of the skew diameters of the mirror was about 5° to 10°. It is evident that unless the heat image is formed in the plane of the diaphragm, the two images of the hot object formed by two semicircular mirrors would be displaced relatively to each other. Hence to focus the image on the diaphragm, the concave mirror is moved backward or forward till the two semicircular images of the mirror lie on the same circle.

The second condition requires that the distance of the pyrometer from the hot object can not be too large so that the image may not be smaller than the opening in the semicircular mirrors.

Let T_o be the temperature of the receiving surface and let T be the temperature of the source. In actual practice, the electromotive force of the thermocouple is

$$v = a(T^b - T_o^b)$$

where b varies from 3.8 to 4.2. This departure from the index value of 4 is due to the following causes:

1. The emf of the thermocouple is not exactly proportional to the difference of temperature between the junctions.
2. Stray reflections cause error.
3. Conduction along the wire raises the temperature of the junctions.
4. The loss of heat from the hot junction is not proportional to the temperature excess.

For this reason, the instrument is calibrated directly at number of points by sighting a furnace and comparing its readings with a standard thermometer or an optical pyrometer at temperatures higher than the gold point.

The range of the instrument can be extended beyond the calibration limit by using a rotating sector. In this case if T_1 is the apparent temperature as read on the calibrated instrument and θ is the sector opening, then the true temperature T is given by

$$T_1^4 = \frac{\theta}{2\pi} T^4$$

12.21.4 Methods of Determination of High Temperature Melting Points

1. The metal whose melting point is to be determined is welded between two thermocouple wires. The junction is placed inside a furnace whose temperature is gradually raised. At the melting point, the deflection of the galvanometer remains steady for a short time; the circuit then breaks and the emf falls to zero.
2. A small sight tube is immersed in the molten metal. The tube thus behaves like a black body whose temperature is determined by the optical pyrometer as described above.
3. The temperature of molten iron is determined by inserting a tube in the molten metal and blowing a bubble at its end. This bubble forms a black body whose temperature is determined by the optical pyrometer.
4. A strip of metal whose melting point is to be determined is folded into the shape of a wedge of small angle and electrically heated. The inside of the wedge forms a black body and is sighted by an optical pyrometer. The strength of the current is gradually increased and its temperature is determined when it begins to melt.

12.22 DETERMINATION OF SOLAR CONSTANT

Dominating our little corner of the universe is the mighty glowing orb of the Sun which is the ultimate source of all terrestrial energy. The warmth and light of the Sun are the most important things to us on the Earth; without them there would be no life of any type, the sky would be black and the temperature would be deadly cold. The blazing Sun is a sphere remarkable in magnitude of hot glowing gas, the diameter of the main ball of the Sun is nearly 13,90,000 km which is 109 times the diameter of the Earth. The Sun is 150 million km distant from us. Astronomers considers this distance as a convenient unit of distance in solar system called astronomical unit. It is highly dangerous to see the Sun by any means, even through smoked glass or photograph negative. The safest way of looking at it is looking at the image formed by suitable means. It is one of the many stars in the Milky Way. Present evaluation considers the Sun's distance from galactic centre to be about 32,000 light years. The Sun and other such stars usually rotate with the mean speed of 250 km per second about the galactic centre. The Sun takes 250 million years to complete one such revolution and this time is now called a cosmic year. The visible portion of the Sun seen as a bright disc called photosphere is not bright throughout. Powerful telescope shows tiny bright specks called granules against a less bright background, these are considered to be currents of hot gases emerging out of the Sun's atmosphere. Prominent characteristics of the photosphere are dark markings called sunspots. These are areas of madly whirling gases, areas varying from a few hundred kilometers to tens of thousands kilometers in diameter. These sunspots are about 2,000 degree Celsius lower than the rest of the photosphere which is about 6,000 degree Celsius. This sunspot activity rises and falls in intensity in a cyclic period of 11 years, namely sunspot cycle. At times of maximum intensity, sunspot outbursts, in the form of hot ionized gas rolling out as enormous cloud known as solar wind, called solar flares are seen which affect electrical, magnetic instruments and radio disturbances on the Earth. This stream of electrified particles become confined in great belts by Earth's magnetism giving rise to luminous shimmering arcs and streamers in northern region called aurora boreales (northern lights) and aurora australis (southern lights). Surrounding the photosphere, there is a region of thinner gas which normally remains unseen because of the dazzlingness of the photosphere. It is only seen during an eclipse for a short time when the moon covers the photosphere. At that time, narrow rose-red fringe around the dark body of the Moon is seen. This lower part of the Sun's atmosphere is called chromosphere (coloursphere) extending to several thousand kilometers. Sometimes exalted flame like streamers of hot gas shoot up hundreds of thousands of kilometers through the chromosphere which are known as solar prominences. The outer atmosphere is called corona which can be seen as a pearly white halo during total solar eclipse.

Sun is the ultimate source of energy which is formed by nuclear fusion occurring at the core of the Sun where the temperature is believed to be several million degrees Celsius. Like all other stars Sun is composed of hydrogen, simplest of all elements. There, four atoms of hydrogen combine together to form one atom of next simplest element helium. In doing so, a small amount of matter is lost which is converted into unbelievable amount of energy because the mass of one helium atom is less than the combined mass of four hydrogen atoms. Thus, the temperature of the Sun is different at different regions.

Usually we mean by the Sun's effective temperature the temperature of the photosphere which can be calculated by applying Stefan's law of total radiation after determining solar constant.

12.22.1 Solar Constant and its Determination

The amount of solar energy received normally per minute per unit area of a black body kept on the Earth's surface without intermediate absorption in the space is known as solar constant. By determining this value, temperature of Sun can be estimated.

Solar constant can be determined by various methods such as water-stir pyrheliometer, water-flow pyrheliometer and Angstrom's pyrheliometer. However, we shall describe the simplest method as suggested by Angstrom (Fig. 12.19).

Two similarly blackened platinum strips *A* and *B* are exposed normally to the Sun's rays. Strip *A* is covered with source *C* so that no sunrays fall on it. Two thermocouple junctions are attached to *A* and *B* with a galvanometer *G* for measuring the thermocurrent generated. The ends of the unexposed strip *A* is connected with a current providing arrangement with cells *E*, ammeter *M* and a rheostat *R*. When Sun's rays fall on *B*, it will be heated and a thermocurrent will flow; as a result, the galvanometer will be deflected. When the deflection becomes constant, strip *A* is heated by passing a current through it. By adjusting current in *A*, galvanometer deflection is annulled which indicates that the two strips *A* and *B* are receiving some heat. Then if *E* be the voltage of cell in volts and *I* be the current in amperes shown in ammeter, then the heat received per minute by $A = EI \times 60/4.2$ calories. If *S* be the solar constant, *A* be the area of *B* or *A*, α be the absorption coefficient of the strip then the heat energy received is $S\,\alpha\,A$ per minute.

Then, $S \propto A = \dfrac{EI \times 60}{4.2}$

$$\therefore \qquad S = \frac{EI \times 60}{\propto A\,4.2} \text{ cal per cm}^2 \text{ per minute.}$$

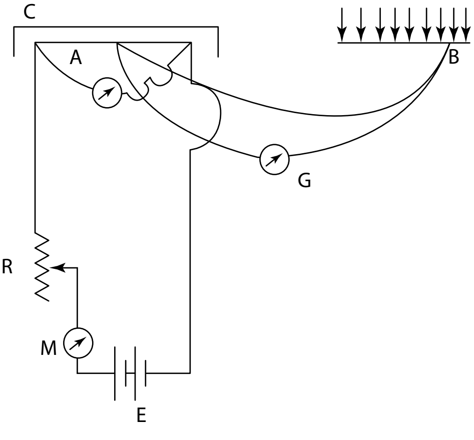

Fig. 12.19 Angstrom's pyrheliometer

The experiment is repeated and a proper correction for absorption of Sun's rays in space is done; thus S is determined. It comes out to be 1.34×10^6 ergs per cm^2 per second or 1.94 calories per cm^2 per minute.

12.22.2 Temperature of the Sun

Considering that the photosphere is emitting black body radiation, we can determine the temperature of the Sun from the measurement of solar constant.

Let T be the temperature of the Sun, r be its radius and R being the distance of earth from Sun, σ be the Stefan's constant then applying Stefan's radiation law, energy emitted by the Sun per minute $= \sigma T^4 4\pi r^2 \times 60$.

The energy received per unit area of the Earth's surface per minute is

$$\frac{\sigma T^4 4\pi r^2 \times 60}{4\pi R^2}$$

$$\therefore \qquad S = \sigma T^4 \left(\frac{r}{R}\right)^2 \times 60$$

$$\text{or} \qquad T = \sqrt[4]{\left(\frac{R}{r}\right)^2 \frac{S}{60\sigma}}$$

Putting the values, T comes out to be 5723 K which corroborates the value calculated from Wien's displacement law.

12.22.3 Some Everyday Applications

Radiations from the Sun mostly consists of long wavelength electromagnetic radiation. It ranges from ultraviolet to infrared through visible region. Visible region has seven colours—violet, indigo, blue, green, yellow, orange and red. Infrared region gives heating effect which decreases with the decrease in wavelength. For the study of different regions, different types of instruments are needed. Solar spectrum consists of a large number of dark lines called Fraunhofer lines. Fraunhofer measured the wavelengths of these lines and found that they occupy the same position as the bright lines emitted by different elements which are present in the Earth's and the Sun's outer atmosphere. Infrared radiations are not sucked up by atmosphere; so, infrared photograph can be derived through fog and mist which visible light can not penetrate. In World War II, these photographs played a serviceable role in detecting objects in dark through mist, fog and clouds. Infrared radiations play a magnificent role in medicine, industry, etc. It penetrates deep into the human body and by their heating effect can dilate blood vessels at the part of the body exposed to such radiation thereby enabling increased flow of blood causing comfort. Ultraviolet (UV) radiations also have variety of applications. Rooms where blood plasma, drug, vaccines are prepared and sealed in containers are sterilized by UV radiation. Resolving power of microscopes is increased when UV light is used. Fluorescent tubes are based on the principle of fluorescence caused by UV radiation. Skin disease specialists use UV radiation for treatment of skin disease by phototherapy with UV B (311 nanometer) or photochemotherapy where UV A (365 nanometer) are used.

Recently, exploration of the unlimited worldwide available solar energy has drawn the attention of all to overcome electrical energy crisis and to operate electrical equipments in secluded areas and islands.

Profusely available solar energy can be used directly as heat which is used to make pure drinking water from saline water using plate collector methods. In addition to solar distillation, solar drying, solar water heating, absorption type solar refrigeration, solar energy may be stored by suitable methods.

Solar energy is converted into electrical power using photovoltaic cells. The photovoltaic cells are constructed of semiconductor materials mainly silicon with little amount of gallium arsenide or cadmium sulfide so as to be more effective in producing electrical energy.

In India as the fossil fuel is limited and profuse sunshine is available throughout the year, utilization of solar energy should be explored as the best possible alternative.

SOLVED PROBLEMS

Q 1. Two substances P and Q are kept in evacuated vessels maintained at temperatures of 27 °C. Temperatures of P and Q are 627 °C and 227 °C, respectively. Find the ratio of the rates at which heat is lost from the two substances.

Ans. We know that the rate of loss of heat $= \sigma(T^4 - T_o^4)$

where $\sigma =$ Stefan's constant, $T =$ temperature of hot body, $T_o =$ temperature of surroundings.

$$\frac{\text{Rate of loss of heat by } P}{\text{Rate of loss of heat by } Q} = \frac{\sigma[(627+273)^4 - (27+273)^4]}{\sigma[(227+273)^4 - (27+273)^4]} = \frac{11.9}{1}$$

Q 2. A black body of 300 °C is allowed to cool inside an evacuated enclosure surrounded by melting ice at the rate of 0.35 °C/s. lf the mass, specific heat and surface area of the body are 82 gm, 0.01 and 8 sq cm, respectively, calculate Stefan's constant.

Ans. We know that $m\ s\ dT/dt = \sigma A(T^4 - T_o^{\,4})$

$$\sigma = \frac{msdT/dt}{A(T^4 - T_o^{\,4})} = \frac{82\times 0.1\times 0.35}{8[(573)^4 - (273)^4]} = 0.35\times 10^{-11}\ \text{cal/sq cm/s/degree}^4$$

Q 3. Compare the intensity of radiation at a distance of 60 cm from a black body at 600 °C with that from the same source at 30 cm when the temperature is 300 °C.

Ans. We know that energy emitted by a black body $E = \sigma\ T^4$ and the intensity of radiation varies inversely as the square of the distance; so, we can write

$$\frac{I_2}{I_1} = \frac{T_2^4}{T_1^4}\frac{r_1^2}{r_2^2} = \left(\frac{573}{873}\right)^4 2^2 = 0.74$$

Q 4. A black body at 10 °C radiates heat at the rate of 4.17×10^5 ergs/sq cm/s. Find the heat in calories radiated per second by a sphere of 6 cm radius at 1100 °C, assuming it to behave as a black body.

Ans. If E_1 be the heat radiated in ergs/sq cm/s from a black body at T_1 and E_2 be that the heat radiated at T_2, then we have

$$\frac{E_2}{E_1} = \frac{\sigma T_2^4}{\sigma T_1^4} = \frac{(1100+273)^4}{(10+273)^4}$$

$$E_2 = E_1 \times \left(\frac{1373}{283}\right)^4$$

Surface area of the sphere $= 4\pi\, 6^2 = 452.16$ sq cm

Total heat radiated $= 4.17 \times 10^5 \left(\frac{1373}{283}\right)^4 \times 452.16$ erg/s

$= 2496.67$ cal/s

Q 5. Rays from the sun are allowed to fall on a lens of diameter 20 cm. They are then brought to a focus on a calorimeter containing 25 gm of ice. If the absorption due to the passage through the lens is ignored, how long will it be before all the ice is melted (amount of heat from the sun received on one sq cm of earth's surface = 2 cal/min, latent heat of ice = 80 cal/gm)?

Ans. Amount of heat received by the lens per second $= \frac{2}{60} \times \pi \times 10^2$ calories

If t be the total time for which the sun' s rays are allowed to fall, then we have

$$\frac{2}{60} \times 3.14 \times 10^2 t = 80 \times 25 \qquad \therefore t = 3.184 \text{ min}$$

Q 6. The sun's rays are reflected from a concave mirror 35 cm in diameter and are brought to a focus on a copper calorimeter of mass 30 gm containing 60 gm of water. The temperature of water is found to rise to 16 °C in 5 minutes. Obtain an estimate of the amount of heat received by the earth per sq m per min. The specific heat of copper is 0.1 cal/gm/degree.

Ans. Let the amount of heat received by the earth per sq m per min be Q, then

$$Q \frac{0.35^2 \pi}{4} \times 5 = (60 + 30 \times 0.1)16$$

$\therefore$ $Q = 2096$ calories

Q 7. Compare (a) the rate of loss of heat and (b) the rate of cooling of two blackened copper spheres of radius 5 cm and 10 cm at temperatures of 427 °C and 227 °C by radiation in an evacuated enclosure at 27 °C.

Ans. Rate of loss of heat $= \sigma A(T^4 - T_o^4)$

Rate of cooling is the rate of decrease of temperature per second.

Then for the first sphere,

$$\frac{4}{3}\pi 5^3 \rho S c_1 = \sigma 4\pi 5^2 [(427 + 273)^4 - (27 + 273)^4]$$

where ρ = density of copper, S = specific heat of copper, c_1 = rate of cooling of first sphere. Similarly, for the second sphere

$$\frac{4}{3}\pi 10^3\,\rho S c_2 = \sigma 4\pi 10^2[(227+273)^4-(27+273)^4]$$

Dividing these two equations,

$$\frac{c_1}{c_2} = 8.52$$

Rate of loss of heat $= \dfrac{\frac{4}{3}\pi 5^3\,\rho S c_1}{\frac{4}{3}\pi 10^3\,\rho S c_2} = \dfrac{8.52}{8} = 1.066$

Q 8. When a Fery total radiation pyrometer in a room with surroundings at 300 K is sighted on black body at 600 K, the deflection observed in the galvanometer is 6 divisions. When sighted on another black body, the deflection is found to be 400 divisions. Calculate the temperature of the latter.

Ans. Using the formula $d = A(T^4 - T_o^4)$ where d is deflection, A is constant, T_1 is temperature of the black body, T_0 that of the surroundings, then we can write

$$6 = A[(600)^4-(300)^4] \text{ and } 400 = A[T^4-300^4]$$

or $$6(T^4-300^4) = 400(600^4-300^4)$$

$$T^4-300^4 = \frac{400}{6}(600^4-300^4) = 162\times 10^{11}$$

$$T^4 = 162\times 10^{11} + 81\times 10^8 = 162.081\times 10^{11}$$

$$T = 2006\text{ K}$$

Q 9. Luminosity of the star Regel in Orion constellation is 17000 times that of our sun. If the surface temperature of the sun is 6000 K, calculate that of Regel.

Ans. Supposing the sun and Regel as black bodies and that luminosity is proportional to σT^4

Then, $$\sigma T^4 = 17000\,\sigma(6000)^4$$

$$T = 68510\text{ K}$$

Q10. Show how Newton's law of cooling can be deduced from Stefan's law.

Ans. Rate of cooling α Rate of loss of heat $\alpha\ \sigma(T^4 - T_o^4)$ where σ is Stefan's constant, T is temperature of the hot body *and* T_o is the temperature of the surroundings.

Rate of cooling $\alpha\ \ \sigma(T^4 - T_o^4)\ \ \alpha\ \ \sigma(T-T_o)(T^3 + T^2T_0 + T\,T_0^2 + T_0^3)$

If temperature difference is small, $T \approx T_0$

Rate of cooling $\alpha\ \ \sigma(T-T_o)4T_0^3\ \ \alpha\ \ K(T-T_o)$

Q 11. If the degree to which a given material absorbs radiation depends upon the wavelength of radiation, show that the intensity of radiation falls in geometric progression as the thickness of the material increases in arithmetic progression.

Ans. Let the amount of monochromatic radiant energy conveyed per second (that is, initial intensity) be I and let it travel through a thickness x of some material. Due to absorption, let the intensity be reduced from I to KI (say, where K is a constant). If this energy (KI) passes through another layer of thickness x, then this energy is reduced by K of its value, that is, K^2I after travelling a total distance of $2x$. Similarly after travelling through a total distance of $3x$, it is further reduced to K^3I or if it passes through thickness nx the intensity is reduced to K^nI.

PROBLEMS

1. Calculate the maximum net rate of loss of heat by radiation from a sphere of 10 cm radius at a temperature of 200 °C when the surroundings are at a temperature of 20 °C, if Stefan's constant is 5.7×10^{-5} ergs/sq cm/s/deg^4.

Ans. 3.659×10^9 ergs/s

2. Calculate the radiation loss per sq cm per second from a black cylinder of emissivity 0.95 at 327 °C when surrounded by an enclosure at 27 °C.

Ans. 6579×10^3 ergs

3. A hot black body of mass 64 gm, area 16 sq cm and specific heat 0.1 cal/gm/ °C is allowed to cool inside an evacuated enclosure surrounded by melting ice. It is found that at 300 °C, the body cools at the rate of 21 °C per minute; calculate Stefan's constant.

Ans. 1.37×10^{-12} cal/sq cm/s/deg^{4}C

4. A solid copper sphere cools at the rate of 2.8 degree per minute when its temperature is 127 °C. At what rate will a solid copper sphere of twice the radius cool when its temperature is 227 °C, if in both cases the surroundings are maintained at 27 °C and the conditions are such that Stefan's law may be applied.

Ans. 4.35 °C per minute

5. The distances of Venus, Earth and Mars from the Sun are, approximately, in the ratio of 0.72:1.00:1.52, respectively. Assume that all radiate as black bodies, calculate approximate mean temperatures of Venus and Mars (taking that of the Earth to be 15 °C).

Ans. 66.4 °C , −39.4 °C

QUESTIONS

1. Discuss Prevost's theory of heat exchanges. Define emissive power and absorptive power of a body and deduce the relationship between them.

2. Explain the terms emissive power and absorptive power. Deduce that at any temperature, the ratio of the emissive power to the absorptive power of a substance is constant and is equal to the emissive power of a perfectly black body.

3. What is meant by a black body? What are the characteristics of a black body radiation? How has it been realized in practice? Discuss Stefan–Boltzmann's law for black body radiation. What is the value of Stefan's constant?
4. Discuss Kirchhoff's law of black body radiation. How will you verify the law experimentally?
5. State and explain the laws relating to the radiation and temperature of a radiating body. What do you mean by (a) perfectly black body, (b) co-efficient of absorption and (c) co-efficient of emission?
6. Describe suitable method for verifying experimentally the Stefan–Boltzmann's law. In what circumstances may it be applied?
7. Discuss the principles underlying the measurement of temperature by radiation pyrometer and describe any one method of measuring a high temperature from such consideration.

Chapter 13

INTRODUCTION TO STATISTICAL THERMODYNAMICS

13.1 Significance of Statistics

The scientific study of all physical phenomena began through dynamical principle which is evident from the writing of a Dutch scientist Christian Huygens "In true philosophy we should conceive the cause of all natural phenomena in terms of mechanics". This notion was so deep rooted in the beginning of scientific study that he wrote "We must do or for ever renounce the hope of understanding anything of physics."

In kinetic theory of gases while finding the pressure and temperature of a gas enclosed in a vessel by general approach, we refer to the macroscopic or bulk state of the gas. Each individual molecule of the gas belongs to the microscopic state whose individual information is difficult to attain. So to study the general behaviour of a system, whether it is a gas, liquid or solid, consisting of large number of individual particles we should employ statistical methods. Thus, we see the system consisting of a large number of individual particles producing together common single effects. This system as a whole is called an ensemble whose concept was introduced by Josiah Willard Gibbs, an American scientist. Again, the behaviour of individual particle in a system is different and is a characteristic of the system. For example in a gas, the molecules are always in motion at a particular temperature without any interacting force or intermolecular force, individuality and indistinguishability are maintained. There is an interaction only when they collide with another individual molecule or wall of the container; so, these particles are weakly interacting or quasi-independent. They are indistinguishable as they are not located in space. But, the situation is different in liquids and solids where the particles are distinguishable because they are constrained to move or oscillate about fixed positions; so, one particle can be distinguished from its neighbour by its position. The particles are distinguishable quasi-independent. This necessitates another kind of statistical approach.

Before the arrival of quantum theory, scientists like James Clerk Maxwell, Ludwig Boltzmann and Josiah Willard Gibbs applied statistical methods for studying classical physics which is known as Maxwell–Boltzmann statistics or classical statistics. This approach explains satisfactorily physical properties such as temperature, pressure and energy, but could not explain other observed properties such as black body radiation, photoelectric effect and specific heat at low temperature. In order to explain these effects, a new approach was devised by scientists like Satyendranath Bose, Albert Einstein, Enrico Fermi and Paul Adrien Maurice Dirac whereby the Planck's quantum concept of discrete exchange of energy between particles in a system was used instead of continuous energy available for the systems.

So till now, there are three statistics depending upon three different kinds of particle and energy exchange processes; they are as follows:

1. Maxwell–Boltzmann statistics applicable to identical, distinguishable particles of any spin possessing continuous energy exchange nature.
2. Bose–Einstein statistics applicable to identical, indistinguishable particles of zero or integral spin called bosons such as helium atoms at low temperature, hydrogen molecules and photons having the nature of discrete energy exchange.
3. Fermi–Dirac statistics applicable to identical, indistinguishable particles of odd half integral spin obeying Pauli exclusion principle called fermions such as electrons, positrons, protons and neutrons possessing the nature of discrete energy exchange.

Classical Maxwell–Boltzmann statistics is the limiting case of the later two quantum statistics.

13.2 SOME BASIC CONCEPTS

We shall develop these statistical methods after discussing related basic concepts.

13.2.1 Probability

The notion of probability is the key note of statistical physics. Its concept was thought to represent the capability of visualization of the behaviour of electrons and protons in wave mechanics. There are two kinds of probability: (i) mathematical probability and (ii) thermodynamical probability.

Mathematical probability: Let us suppose that we play tossing of a coin like the captains of two teams doing before the beginning of the play. If we take a coin and toss it, two events may occur with either tail falling uppermost or head falling uppermost; the total number of events being two, experience shows that if the number of toss is very large the chances of head or tail falling uppermost will be equal in number. Thus, the probability of each event or the ratio of the number of toss in which each event occurs to the total number of toss is 1/2. In the same way if we throw a six-faced cubical dice, it is evident that the dice will fall with any one of its six faces upwards.

Thermodynamic probability: Thermodynamic probability is defined as the number of equally likely states in which a substance may exist and is obviously a whole number. It is proportional to mathematical probability and is not exactly equal to its numerical value.

13.2.2 Complexion and Statistical State

A happening is often referred to as a complexion or a combination and the happening is specified as statistical state. Thus in tossing a coin, head or tail falling uppermost is a happening or event or complexion or combination.

13.2.3 Statistical Weight

The number of happenings or events or complexions or combinations of any assigned statistical state is called its statistical weight.

13.2.4 Probability of a Composite Event

If two or more events are mutually independent of each other, then the probability or possibility of all events happening simultaneously is the product of individual events.

13.2.5 The Postulate of Equal a Priori Probability

The doctrine of assuming equal probability for events which are equally likely to occur is known as the principle of equal a priori probability. A priori means something derived by reasoning from self-evident propositions, presupposed by experience.

Let us suppose that we take two coins for tossing, denoted by 1 and 2, and toss them a large number of times and consider the following events:

1. Heads of the two coins falling uppermost a_1a_2
2. Tails of the two coins falling uppermost b_1b_2
3. Head of 1 and tail of 2 falling uppermost a_1b_2
4. Tail of 1 and head of 2 falling uppermost b_1a_2

where a_1 means head of coin 1 and a_2 means head of coin 2, b_1 means tail of coin 1 and b_2 means tail of coin 2. The possible events are the product of $(a_1 + b_1)(a_2 + b_2)$.

It is evident that probability of each event is 1/4 as all four events are of equal likelihood. This can be thought in the following way—if we toss the first coin, the probability of getting head uppermost is 1/2 and if we toss the second coin, the probability of getting head uppermost is also 1/2. Thus, the probability of getting of heads uppermost in a simultaneous toss of both the coins is $1/2 \times 1/2 = 1/4$. In other words, the probability of a composite event is the product of the probabilities of the individual and independent component events.

But if we toss two identical silver coins, events (3) and (4) as mentioned earlier can not be differentiated because $a_1 = a_2 = a$, $b_1 = b_2 = b$, $a_1b_2 = a_2b_1 = ab$, possible combinations are now given by a^2, b^2, $2ab$ the terms of a binomial expression $(a + b)^2$. The probability of getting a^2 or b^2 is 1/4 while that of getting ab is 1/2. It is, thus, found that the relative happenings are in the ratio of the coefficients of the corresponding terms in binomial expansion.

Extending this for n identical coins and tossing them a large number of times, we get choosing r coins with heads uppermost and s coins with tail uppermost happening in ${}^nC_r$ ways which is the coefficient of a^rb^s in the binomial expansion $(a + b)^n$.

The mathematical probability of such combination a^rb^s is

$$W = \frac{{}^nC_r}{\sum {}^nC_r} = \frac{\dfrac{n!}{r!(n-r)!}}{2^n} = \frac{n!}{r!s!}2^{-n} \tag{13.1}$$

Since $$\sum {}^nC_r = (1+1)^n = 2^n$$

Let us now determine which of the $(n + 1)$ events $a^r b^s$ has maximum probability. This necessitates the finding of maximum value of ${}^nC_r$. Elementary algebra shows that ${}^nC_r$ is maximum when $r = n/2$. This corresponds to most probable state known as equilibrium state. This is called *statistical equilibrium*.

Hence, we have

$$W_{max} = \frac{n!}{\left(\frac{n}{2}!\right)^2} 2^{-n} \tag{13.2}$$

We now compare W_{max} with W_x where W_x is a combination in which $r = n/2 + x$ and $s = n/2 - x$, x being a small number. Thus, we have

$$W_x = W_{max} \frac{\left(\frac{n}{2}!\right)^2}{\left(\frac{n}{2}+x\right)!\left(\frac{n}{2}-x\right)!} \tag{13.3}$$

where x is a very large number; the expression can be reduced to a very simple form by applying a well-known theorem in the theory of numbers called Stirling's theorem.

13.3 STIRLING'S THEOREM

The value of $n!$ increases very quickly with n. 30! produces a member requiring 33 figures to write. Stirling gave an approximate formula for $n!$

$$n! = \left(\frac{n}{e}\right)^n \sqrt{2\pi n}\left(1 + \frac{1}{12n} + \frac{1}{228n^2} - \frac{139}{51840n^3} + \cdots\right)$$

$$= \left(\frac{n}{e}\right)^n \sqrt{2\pi n} \text{ approximately.}$$

Taking log of both sides, $$\ln n! = n \ln n - n \ln e + \frac{1}{2}\ln 2\pi n \ (\ln = \log_e)$$

$$= n\,(\ln n - 1) \text{ roughly} \tag{13.4}$$

It can be proved in the following way

$$\ln n! = \ln 1 + \ln 2 + \ln 3 + \ldots + \ln x + \ldots + \ln n$$

$$\ln n^n = \ln n + \ln n + \ln n + \ldots + \ln n + \ldots + \ln n$$

or $$\ln\left(\frac{n!}{n^n}\right) = \ln\frac{1}{n} + \ln\frac{2}{n} + \ln\frac{3}{n} + \cdots + \ln\frac{x}{n} + \cdots + \ln\frac{n}{n}$$

$$= \sum(\ln x - \ln n)$$

The summation can be approximately replaced by the integration

$$\int_1^n (\ln x - \ln n)dx = (x \ln x - x)_1^n - (x \ln n)_0^1$$

$$= -(n-1) + \ln n$$

or

$$\ln\left(\frac{n!}{n^n}\right) = -(n-1) + \ln n$$

or

$$\ln n! = n \ln n - (n - 1) + \ln n$$

$$= n (\ln n - 1) + \ln n + 1$$

the last two terms can be neglected in comparison to others when n is very large leading to

$$\ln n! = n (\ln n - 1)$$

This is known as Stirling's theorem or Stirling's approximation.

13.4 MATHEMATICAL PROBABILITY

We have considered earlier mathematical probability by notations W, W_{max} and W_x. We shall now exemplify. Let us first express W, W_{max} and W_x using Stirling's theorem.

Equation 13.3 yields

$$\ln W_x = \ln W_{max} + 2\frac{n}{2}\left(\ln\frac{n}{2} - 1\right)$$

$$-\left(\frac{n}{2} + x\right)\left[\ln\left(\frac{n}{2} + x\right) - 1\right]$$

$$-\left(\frac{n}{2} - x\right)\left[\ln\left(\frac{n}{2} - x\right) - 1\right]$$

Assuming $\frac{x}{n} << 1$ and using $\ln\left(1 + \frac{2x}{n}\right) = \frac{2x}{n} - \frac{2x^2}{n^2}$

we get

$$\ln W_x = \ln W_{max} - 2\frac{x^2}{n}$$

Hence,

$$W_x = W_{max} e^{-2\frac{x^2}{n}}$$

$$= \frac{n!}{\left(\frac{n}{2}!\right)^2} e^{\frac{-2x^2}{n}} 2^{-n} \tag{13.5}$$

This shows the probability of large deviations x from most probable value is vanishingly small.

Equation 13.1 was presented by Newton. Later, Laplace presented a convenient form through approximation of factorials. In this, Stirling's theorem is used giving Laplace's formula

$$W_x = \sqrt{\frac{2}{\pi n}}\, e^{\frac{-2x^2}{n}} \tag{13.6}$$

when $x << n$.

We want to extend the consideration further taking the game of dice each of which has 6 faces denoted by a, b, c, d, e and f. If we throw n dice for a large number of times giving complexion represented by

$$a^{n_1}\, b^{n_2}\, c^{n_3}\, d^{n_4}\, e^{n_5} f^{n_6}$$

which means that n_1 dice fall with face a uppermost, n_2 dice fall with face b uppermost etc. where $n = n_1 + n_2 + n_3 + n_4 + n_5 + n_6$. Probability that n_1 dice will fall with a uppermost $= {}^nC_{n_1} = \dfrac{n!}{n_1!(n-n_1)!}$.

Probability that n_2 of $n - n_1$ dice will fall with b uppermost $= {}^{n-n_1}C_{n_2} = \dfrac{(n-n_1)!}{n_2\,!(n-n_1-n_2)!}$ and so on.

The probability number of the above complexion

$$P_x = a^{n_1}\, b^{n_2}\, c^{n_3}\, d^{n_4}\, e^{n_5} f^{n_6}$$

$$= \frac{n!}{n_1!\, n_2!\, n_3!\, n_4!\, n_5!\, n_6!}$$

Since each aspect of a dice has a priori probability 1/6 on account of six faces, the probability of the complexion is

$$W = \frac{n!}{n_1!\, n_2!\, n_3!\, n_4!\, n_5!\, n_6!} 6^{-n} \tag{13.7}$$

In general case, let us take a board with p square cells arranged side by side and let us throw into these cells n number of balls from a long distance, and let us suppose that n_1 balls are found within cell a_1, n_2 balls are found within cell a_2 and so on.

Each cell-wise distribution of particles is known as a microstate, total number of microstates for n particles is $(n + 1)$. The probable number of such combination is given by

$$\frac{n!}{n_1!\, n_2!\, n_3!\, n_4!\, n_5!\, n_6!} = \frac{n!}{\pi n_r!} \tag{13.8}$$

where π denotes the product of the factorial $n_1!\ n_2!\ n_3!\ n_4$ ……

Again in this case, a priori probability of each combination is $1/p$; the probability of the above combination is

$$W = \frac{n!}{\pi n_r!} p^{-n} \tag{13.9}$$

When n is very large, Stirling's theorem is used; then,

$$\ln W = \ln\left(\frac{n!}{\pi n_r!} p^{-n}\right) \tag{13.10}$$

13.5 STATISTICAL METHODS OF A MOLECULAR SYSTEM

We now consider the case of dealing with the statistics of the motion of an assembly of weakly interacting like particles such as molecules of a perfect gas. The argument holds good for any dynamical system may it be the oscillators in a black body radiation, velocity distribution of the molecules of a gas. There are various ways of attacking the problem, but we shall adopt the method of statistical distribution due to Maxwell and Boltzmann which is the simplest and historically the oldest.

The dynamical situation of a particle is decided by its positional coordinates x, y, z, and velocity coordinates or better momenta $p_x = mv_x$, $p_y = mv_y$, $p_z = mv_z$ where it seems ν_x, ν_y, ν_z are the velocity coordinates of a particle of mass m. The precise presentation of these values for all the particles defines the microscopic state of the system. The question is now to determine how many particles occupy very nearly the same position and have nearly the same velocity components. It is evident that two particles can not occupy the same position in space. We, therefore, take into account the particles having their positional coordinates lying between x and $x + dx$, y and $y + dy$, z and $z + dz$. They may have velocity components lying between 0 and ∞, but we are interested with those having their momenta components lying between p_x, $p_x + dp_x$, p_y, $p_y + dp_y$, p_z and $p_z + dp_z$. Thus, we define an element of volume in *phase space* given by $dxdp_x\ dydp_y\ dzdp_z$ (this is called an elementary phase cell) to which we fix n_x particles. In case of linear harmonic oscillators as well, we can assign n_x to a similar element of *hyper space* which will be two dimensional in this case. The three-dimensional space in which the location of a particle is completely given by three position coordinates is known as *position space*. Similarly, three mutually perpendicular momentum coordinates $p_x p_y p_z$ in three-dimensional space is known as *momentum space* and the small volume element in momentum space is given by $dp_x dp_y dp_z$. A combination of position space and momentum space is known as phase space. For a monatomic gas, this hyperspace called *molecular phase space or* μ *space* is six dimensional. We can indicate the dynamical state of the gas completely by imagining a number of small cells p of equal size extending throughout the complete phase space and, thus, embracing the whole volume and the whole range of momenta between 0 and ∞. Let the cells be denoted by a_0, a_1, a_2, … a_r, the cell a_r containing molecules each having a definite amount of energy $\in_r$ and let us allot n indistinguishable molecules among these cells. Let us consider the distribution of the molecules with respect to their energy so that n_0 molecules are found in a_0, n_1 in a_1, n_2 in a_2 … n_r in a_r and so on. The cells now correspond to the sides of the dice.

The probability number of realizing this distribution which may be characterized by suffix x

$$P_x = \frac{n!}{\pi n_r!} \tag{13.11}$$

and

$$W_x = \frac{P_x}{\sum P_x} = P_x p^{-n} \tag{13.12}$$

In deducing Eq. 13.10, we assumed that a molecule was as likely to be in one cell as in the other. This is because the cells are of equal size. This result is obvious if the cells were like boxes in the ordinary three-dimensional space. The same result can, however, be proved for cells in the six-dimensional phase space. Hence, the probability of distribution is proportional to P_x. We have

$$n = n_0 + n_1 + n_2 + \cdots + n_r + \cdots \tag{13.13}$$

and the total kinetic energy

$$U = n_0\in_0 + n_1\in_1 + n_2\in_2 + \cdots + n_r\in_r + \cdots \tag{13.14}$$

13.6 LIOUVILLE'S THEOREM

We shall now study the variation of density with time. The density of distribution ρ of representative points in phase space can describe the condition of an ensemble at any instant. We consider now the motion of points in phase space according to the principle of mechanics and study the changes of density with time. Let us consider any point $q_1, q_2, \ldots q_m, p_1, p_2 \ldots p_m$ in phase space, the differential element of extension that may be defined at that point by $\delta q_1, \ldots \delta q_m, \delta p_1, \ldots \delta p_m$. The number of representative points within the element at any instant

$$n = \rho \delta q_1 \ldots \delta q_m \, \delta p_1 \ldots \delta p_m \tag{13.15}$$

This number will change with time as the number of representative points entering the volume in phase space through any face will, in general, be different from the number leaving through the opposite face. Let us consider the two faces perpendicular to q_1 axis at q_1 and $q_1 + \delta q_1$, then the number of representative points entering the surface at q_1 per second is

$$\rho \dot{q}_1 \, \delta q_2 \ldots \delta q_m \, \delta p_1 \ldots \delta p_m \tag{13.16}$$

where ρ is the density and $\dot{q}_1$ is the component of velocity for points at $q_1 \ldots q_m, p_1 \ldots p_m$

The corresponding expression for the number of representative points leaving the opposite face at $q_1 + \delta q_1$ is

$$\left(\rho + \frac{\partial \rho}{\partial q_1} \delta q_1\right)\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1\right) \delta q_2 \cdots \delta q_m \delta p_1 \cdots \delta p_m \tag{13.17}$$

In expressions represented by Eqs 13.16 and 13.17, higher order differentials have been neglected.

Combining these two expressions again, neglecting higher order differentials and summing up over all such resulting terms i for m coordinates and m momenta we have

$$\frac{dn}{dt} = -\sum_{i=1}^{i=m} \left[\rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i\right)\right] \times$$
$$dq_1 \ldots dq_m \, dp_1 \ldots dp_m \tag{13.18}$$

as an expression for the rate of change of representative points n within the specified volume element of phase space with time.

In order to simplify this, we consider the equation of motion in canonical form; we may now write

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{13.19}$$

as expressions for rate of change of coordinates and momenta with time of a system as considered above.

H is the Hamiltonian for the system as a function of coordinates and momenta; since the order of differentiation is immaterial, we get

$$\frac{\partial \dot{q}_i}{\partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$$

or
$$\sum_{i=1}^{i=m}\left(\frac{\partial \dot{q}_i}{\partial q_i}+-\frac{\partial \dot{p}_i}{\partial p_i}\right)=0 \tag{13.20}$$

Equation 13.18 can now be written as

$$\frac{dn}{dt}\frac{1}{\delta q_1\delta q_2\cdots\delta q_m\delta p_1\delta p_2\cdots\delta p_m}=\left(\frac{\partial \rho}{\partial t}\right)_{p,q}$$

$$=-\sum_{i=1}^{i=m}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i+\frac{\partial \rho}{\partial p_i}\dot{p}_i\right) \tag{13.21}$$

or
$$\left(\frac{\partial \rho}{\partial t}\right)_{p,q}+\sum_{i=1}^{i=m}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i+\frac{\partial \rho}{\partial p_i}\dot{p}_i\right)=0$$

This gives the rate of change of density at the considered point in the phase space. This is of fundamental importance for statistical mechanics known as Liouville's theorem.

Noting the full form of the density ρ (p, q, t) on coordinates, momenta and time $\dot{q}_i$ and $\dot{p}_i$ are the expressions for the components of velocity with which a representative point moves through phase space; we get the simple result $\partial\rho/\partial t = 0$ when we consider the rate of change of density in the proximity of any selected moving representative point in substitute of the neighbourhood of a fixed point in phase space. Gibbs called it the principle of conservation of density in phase space.

13.7 BOLTZMANN'S RELATION BETWEEN ENTROPY AND PROBABILITY

Before deducing the relation, let us consider the actual situation. We know from kinetic theory that the gas as a whole has a particular pressure and temperature as a macroscopic state. But, the constituent molecules of the gas behaving as a microscopic state are in incessant motion colliding with each other and the wall has negligible volume and intermolecular force in actual gas. But, all such characteristics make the microscopic state constant. At a particular instant, the gas as a whole has a constant temperature and pressure as macroscopic state. This process involves, naturally, an increase in the number of possible microscopic states. It is, thus, evident that an equilibrium macroscopic state is one for which the number of microscopic states is maximum.

We know from the second law of thermodynamics that the entropy of a system tends towards a maximum which corresponds to maximum disorder leading to the condition of maximum probability.

Judging all these facts, Boltzmann inferred that there must be a relation between the thermodynamic entropy which has a maximum value in equilibrium state and the maximum probability of the dynamical equilibrium state. Supposing S as the entropy of an isolated system and W the number of possible microscopic states by means of which the system arrives at a given macroscopic state, here the thermodynamic probability of the state of the system, then the duo S and W tend to increase to maximum value and Boltzmann concluded that S is a function of W

$$S=f(W) \tag{13.22}$$

More explicitly, considering two separate systems possessing entropies S_1 and S_2 and thermodynamic probabilities W_1 and W_2, we may write

$$S_1 = f(W_1) \text{ and } S_2 = f(W_2)$$

Total entropy of the two systems

$$S = S_1 + S_2 = f(W_1) + f(W_2)$$

Again, the thermodynamic probability of the two systems taken together is W_1W_2. We may write

$$f(W_1W_2) = f(W_1) + f(W_2) = S_1 + S_2 \tag{13.23}$$

To solve Eq. 13.23, let us differentiate it with respect to W_1 keeping W_2 constant and vice versa giving

$$f'(W_1) = W_2 f'(W_1W_2)$$

and $$f'(W_2) = W_1 f'(W_1W_2)$$

Hence, $$W_1 f'(W_1) = W_2 f'(W_2)$$

$$= W_1W_2 f'(W_1W_2) = \text{constant}$$

or $$W_1 \frac{df(W_1)}{dW_1} = \text{constant} = k$$

$$df(W_1) = k\frac{dW_1}{W_1}$$

Integrating $$f(W_1) = k \ln W_1 + c$$

where c is a constant

or $$S = k \ln W + c \tag{13.24}$$

In classical thermodynamics, entropy is generally taken as the difference between the entropy in the actual state and the entropy in an arbitrarily chosen standard state. If the thermodynamic probability in the standard state is W_o, then

$$S = k \ln W - k \ln W_0 = k \ln \frac{W}{W_0} = k \ln P \tag{13.25}$$

where $P = W/W_0$ represents the number of probable ways in which a particular state (other than that of absolute zero) can be realized.

13.8 CALCULATION OF STATISTICAL PROBABILITY AND NUMBER OF CELLS ACCORDING TO QUANTUM STATISTICS

The most satisfactory way to calculate statistical probability is from wave mechanics. But, a simpler avenue first given by Einstein which arose out of the work by S. N. Bose on the statistics of photon is followed here. This treatment applies only for the translational motion of structureless spherical particles when the interaction amongst the particles is disregarded.

Let us consider particles which have energies $\in$ lying between $\in_t$ and $\in_t + d\in_t$ where t denotes translational energy. The available phase volume G_t of the particles between the above mentioned energy limits is given by

$$G_t = \iiint dx\,dy\,dz \iiint dp_x dp_y dp_z \tag{13.26}$$

the integration is done within energy limits $\in_t$ and $\in_t + d\in_t$.

The first integral is v the volume occupied by the particles and the second integral represents the volume of the spherical shell between p and $p + dp$ where p is given by

$$p^2 = p_x^2 + p_y^2 + p_z^2 = 2m\in_t$$

$$\iiint dp_x dp_y dp_z = 4\pi p^2 dp$$

$$= 4\pi(2m\in_t)\frac{md\in_t}{\sqrt{2m\in_t}}$$

$$= 2\pi(2m)^{3/2} \in_t^{\frac{1}{2}} d\in_t$$

$$\therefore \qquad G_t = 2\pi V(2m)^{3/2} \in_t^{\frac{1}{2}} d\in_t \tag{13.27}$$

From quantum theory, $\iint dp\,dq = h$ for each degree of freedom. For three degrees of freedom of the monatomic gas particles,

$$\iiint dx\,dy\,dz \iiint dp_x dp_y dp_z = h^3$$

is the volume of phase space occupied by each particle which may be taken to be the volume of an elementary cell of phase space. Hence, the number of cells a_t availed by the particles of energy between $\in_t$ and $\in_t + d\in_t$ is given by

$$a_t = \frac{G_t}{h^3} = \frac{2\pi v}{h^3}(2m)^{3/2} \in_t^{\frac{1}{2}} d\in_t \tag{13.28}$$

13.9 BOSE–EINSTEIN, FERMI–DIRAC AND CLASSICAL STATISTICS

There are three ways of calculating the probability P_t depending upon the statistics the particles obey—(1) Bose–Einstein, (2) Fermi–Dirac and (3) classical. Let us study the three methods considering the particles to be indistinguishable from each other.

13.9.1 Calculation of P_t According to Bose–Einstein Method

We have a_t cells to place n_t particles in them, the problem is whether we can place in each cell one particle or more than one. In the first case, we assume as Einstein did, that there is no limit to the number of particles which a cell can contain; it can have any number from 0, 1, 2, … to n_t. The number of ways of accommodating n_t particles in a_t cells according to this conception is the old algebraic problem of combination with repetition and can be done in P_t ways where

$$P_t = \frac{(a_t + n_t - 1)!}{(a_t - 1)! n_t!} \simeq \frac{(a_t + n_t)!}{a_t! n_t!} \tag{13.29}$$

We have, therefore, the total probability P for all energy states

$$P = \pi P_t = \pi \frac{(a_t + n_t)!}{a_t! n_t!} \tag{13.30}$$

where the product π extends over all the states.

Let the cells be designated by $x_1, x_2, \ldots x_{a_t}$. An individual distribution may be represented by

$$x_1^{\alpha}, x_2^{\beta}, \ldots x_{a_t}^{\upsilon} \tag{13.31}$$

where $\alpha, \beta \ldots \upsilon$ are the number of particles in the cells $x_1, x_2 \ldots x_{a_t}$, respectively and

$$\alpha + \beta + \ldots + \upsilon = n_t \tag{13.32}$$

We consider the product

$$(x_1^0 + x_1^1 + x_1^2 + \cdots + x_1^r + \cdots)(x_2^0 + x_2^1 + \cdots + x_2^r + \cdots)(x_{a_t}^0 + x_{a_t}^1 + \cdots + x_{a_t}^r + \cdots)$$

where each factor of the product consists of an infinite number of terms. In this product, we have all possible combinations of the powers of $x_1, x_2 \ldots x_{a_t}$. Hence, the number of ways of distributing n_t particles in the a_t cells is equal to the number of those terms of the Eq. 13.31 for which the condition by Eq. 13.32 is satisfied.

Now let $x_1 = x_2 = \ldots = x_{a_t} = x$, then the number of combinations is equal to the coefficient of x^{n_t} in the expression

$$(x^0 + x^1 + x^2 + \cdots + x^r + \cdots)^{a_t} = \left(\frac{1}{1-x}\right)^{a_t} = (1-x)^{-a_t}$$

$$= 1 + a_t x + a_t \frac{(a_t + 1)}{2!} x^2 + \cdots + \frac{a_t(a_t+1)\cdots(a_t + r - 1)}{r!} x^r$$

Hence, the required number is (that is the coefficient of x^{n_t})

$$\frac{a_t(a_t+1)\cdots(a_t+n_t-1)}{n_t!} = \frac{(a_t-1)!\, a_t(a_t+1)\cdots(a_t+n_t-1)}{(a_t-1)! n_t!}$$

$$= \frac{(a_t+n_t-1)!}{(a_t-1)! n_t!} = \frac{(a_t+n_t)!}{a_t! n_t!} \tag{13.33}$$

Hence, the number of ways of distributing n_t particles in a_t cells such that any number of particles can be accommodated in a cell is

$$P_t = \frac{(a_t + n_t)!}{a_t! n_t!} \tag{13.34}$$

$$W = \pi_t \frac{(a_t + n_t)!}{a_t! n_t!} \tag{13.35}$$

13.9.2 Calculation of P_t According to Fermi–Dirac Method

In this approach, it is supposed that an individual cell can not contain more than one particle. The question, now, is the distribution of n_t particles amongst a_t cells so that a cell contains not more than one particle. The number of ways P_t of doing so is by ordinary algebra to be the expression for combination without repetition, that is

$$P_t = \frac{a_t\,!}{(a_t - n_t)!n_t!} \tag{13.36}$$

and

$$P = \pi P_t = \pi_t \frac{a_t!}{(a_t - n_t)!n_t!} \tag{13.37}$$

13.9.3 Calculation of P_t According to Maxwell and Boltzmann Method

When $a_t >> n_t$ as is usually the case, it can be easily verified that both Bose–Einstein and Fermi–Dirac expressions represented by Eqs 13.34 and 13.36 reduce to

$$P_t = \frac{a_t^{n_t}}{n_t!} \tag{13.38}$$

and

$$P = \pi_t \frac{a_t^{n_t}}{n_t!}$$

This is the classical situation which can be deduced in the following way. First, we have N distinct particles and we have to choose groups of $n_0, n_1, n_2, \ldots n_t$ from the whole. This can be done in

$$\frac{N!}{\pi n_t} \text{ ways}$$

Then we have to distribute n_t particles in the midst of a_t cells, each cell being capable of accommodating 0, 1, 2 … up to n_t particles. The first particle can be adapted in a_t ways either in the 1st, 2nd or a_t^{th} cell, the second particle can also be adapted in either the 1st , 2nd or a_t^{th} cell, the third particle can also be adapted in a_t ways and so on as it has no bar to be in the same cell as the first particle. Going on in the same way, we find that the n_t particles can be placed in a_t cells in a_t^{th} ways. Thus, we can effect the desired distribution in W_t different ways given by

$$W_t = N!\pi \frac{a_t^{n_t}}{n_t!}$$

This may be said to be thermodynamic probability for the intended distribution. To get P_t, we have to divide it by W_0 which is the number of ways in which the particle can be distributed within themselves when at rest. This is $N!$. P_t is obtained by dividing W_t by W_0 and is given by

$$P_t = \pi \frac{a_t^{n_t}}{n_t!}$$

13.10 DISTRIBUTION LAW ACCORDING TO THE THREE STATISTICS

We shall now work out the equilibrium conditions from the three statistics and deduce expression for distribution functions.

13.10.1 Maxwell–Boltzmann Distribution Law

Let us now calculate S from the relation $S = k \ln P$ using Stirling's theorem.

$$\ln P = \ln W = \frac{S}{k} = \sum \left[n_t \ln a_t - n_t(\ln n_t - 1)\right]$$

$$= \sum n_t \ln\left(\frac{a_t}{n_t}\right) + \sum n_t$$

$$= \sum n_t \ln\left(\frac{a_t}{n_t}\right) + N \tag{13.39}$$

13.10.2 Bose–Einstein Distribution Law

$$\ln W = \frac{S}{k} = \sum (a_t + n_t)[\ln (a_t + n_t) - 1]$$

$$-a_t(\ln a_t - 1) - n_t(\ln n_t - 1)]$$

$$= \sum \left[a_t \ln\left(\frac{(a_t + n_t)}{a_t}\right) + n_t \ln\left(\frac{(a_t + n_t)}{n_t}\right) - a_t - n_t + a_t + n_t\right]$$

$$= \sum \left[a_t \ln\left(\frac{(a_t + n_t)}{a_t}\right) + n_t \ln\left(\frac{(a_t + n_t)}{n_t}\right)\right] \tag{13.40}$$

13.10.3 Fermi–Dirac Distribution Law

$$\ln W = \sum a_t(\ln a_t - 1) - (a_t - n_t)[\ln(a_t - n_t) - 1]$$

$$-n_t(\ln n_t - 1)]$$

$$= \sum \left[n_t \ln\left(\frac{(a_t - n_t)}{n_t}\right) - a_t \ln\left(\frac{(a_t - n_t)}{a_t}\right) - a_t + a_t - n_t + n_t\right]$$

$$= \sum \left[n_t \ln\left(\frac{(a_t - n_t)}{n_t}\right) - a_t \ln\left(\frac{(a_t - n_t)}{a_t}\right)\right] \tag{13.41}$$

Equations 13.40 and 13.41 can be combined under the single form

$$\ln W = \frac{S}{k} = \sum\left[n_t \ln\left(\frac{(a_t+\gamma)n_t}{n_t}\right)\right.$$

$$\left. +\gamma a_t \ln\left(\frac{(a_t+\gamma n_t)}{a_t}\right)\right] \tag{13.42}$$

If we put $\gamma = 1$, we get Bose–Einstein statistics and if we put $\gamma = -1$, we get Fermi–Dirac statistics. Putting $\gamma = 0$ we get classical or Maxwell–Boltzmann statistics, neglecting *N*.

13.11 EQUILIBRIUM STATE ACCORDING TO THE THREE STATISTICS

The equilibrium state is obtained from the conditions

$$\delta S = 0, \delta N = \Sigma \delta n_t = 0, \delta U = \Sigma \in_t \delta n_t = 0 \tag{13.43}$$

Using $\delta S = 0$ and remembering that a_t does not vary, we deduce from Eqs 13.39 to 13.42 that

$$\sum \delta n_t \left[\ln\left(\frac{a_t}{n_t}\right)\right] = 0 \tag{13.44}$$

and

$$\sum \delta n_t \ln\left[\frac{(a_t+\gamma n_t)}{n_t}\right] = 0 \tag{13.45}$$

Using the method of undetermined multipliers, we get from Eqs 13.43 and 13.44

$$\ln\left(\frac{a_t}{n_t}\right) - \alpha - \beta \in_t = 0$$

or

$$n_t = \frac{1}{f} a_t e^{-\beta \in_t} \tag{13.46}$$

Equation 13.46 represents the distribution law in Maxwell–Boltzmann statistics.
From Eqs 13.43 and 13.45, we get

$$\ln\left(\frac{(a_t+\gamma n_t)}{n_t}\right) - \alpha - \beta \in_t = 0$$

or

$$\frac{a_t}{n_t} = e^{\alpha + \beta \in_t} - \gamma$$

or

$$n_t = \frac{a_t}{e^{\alpha+\beta\in_t} - \gamma} = \frac{a_t}{f e^{\beta \in_t} - \gamma} \tag{13.47}$$

where $f = e^{\alpha}$ is an unknown parameter to be called the degeneracy parameter whose value is to be inferred from the conditions of the case.

From Eq. 13.47 putting $\gamma = 1$, we get the distribution function in Bose–Einstein statistics and putting $\gamma = -1$, we get the distribution function in Fermi–Dirac statistics.

We see that if $f >> 1$ (weakly degenerate case), the distribution laws according to both Bose–Einstein and Fermi–Dirac statistics transform to classical or Maxwell–Boltzmann statistics.

This is found to be the case with all ordinary gases at N.T.P which behave as ideal gases. So in the region in which kinetic theory of gases is valid, there is practically no difference among the three statistics.

When f is very small $f << 1$, the distribution will not be according to Maxwell–Boltzmann but according to Bose–Einstein and Fermi–Dirac statistics. Here, the particles are said to be in a state of degeneracy when nearly all the cells are filled up since $n_t = a_t$.

13.11.1 Value of β

From Eqs 13.42, 13.46 and 13.47, we have

$$\frac{\delta S}{k} = \sum \delta n_t \ln\left(\frac{(a_t + \gamma n_{\mathrm{t}}}{n_t}\right) = \sum \delta n_t (\alpha + \beta \in_t)$$

$$= \sum \beta \delta n_t \in_t = \beta \delta U \tag{13.48}$$

Hence, using the relation $\dfrac{\partial S}{\partial U} = \dfrac{1}{T}$

we have $\beta = 1/kT$ for all statistics.

13.12 LAW OF DISTRIBUTION OF MOLECULAR VELOCITIES ACCORDING TO CLASSICAL OR MAXWELL–BOLTZMANN STATISTICS

The number of cells a_t at the disposal of the number of particles of energy lying between $\in_t$ and $\in_t + d\in_t$

$$a_t = \frac{2\pi V (2m)^{3/2} \in_t^{\frac{1}{2}} d\in_t}{h^3}$$

Let us put $$\frac{2\pi V (2m)^{3/2}}{h^3} = C \tag{13.49}$$

We have $$N = \sum n_t \text{ and } U = \sum n_t \in_t$$

From Eq. 13.46, $$n_t = \frac{1}{f} a_t e^{-\beta \in_t}$$

$$\sum n_t f = \sum a_t e^{-\beta \in_t}$$

or $$Nf = \sum C \in_t^{\frac{1}{2}} e^{-\beta \in_t} d\in_t \tag{13.50}$$

Putting

$$\beta\in_t = u,\ \in_t^{\frac{1}{2}} = u^{\frac{1}{2}}\beta^{-\frac{1}{2}}$$

$$\beta\, d\in_t = du$$

in Eq. 13.50, we have

$$Nf = C\beta^{-3/2}\int_0^{\infty} u^{\frac{1}{2}} e^{-u}\,du = C\beta^{-3/2}\Gamma\left(\frac{3}{2}\right) \tag{13.51}$$

and

$$\sum n_t f\in_t = \sum a_t\in_t e^{-\beta\in_t}$$

or

$$Uf = C\beta^{-5/2}\int_0^{\infty} e^{-u}u^{3/2}\,du$$

$$= C\beta^{-5/2}\Gamma\left(\frac{5}{2}\right) \tag{13.52}$$

where $\Gamma(n)$ is the Euler's gamma function.

From Eqs 13.51 and 13.52,

$$\frac{U}{N} = \frac{3/2}{\beta} = \frac{3}{2}kT$$

From Eq. 13.51,

$$f = \frac{C\beta^{-3/2}\Gamma\left(\frac{3}{2}\right)}{N} = \frac{(2\pi mkT)^{3/2}}{nh^3} \tag{13.53}$$

where $n = N/V$ = number of particles per unit volume.

From

$$n_t = \frac{1}{f}a_t e^{-\beta\in_t}$$

$$= 2\pi N(\pi kT)^{-3/2}\in_t^{\frac{1}{2}} e^{-\frac{\in_t}{kT}} d\in_t \tag{13.54}$$

$$= 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mc^2}{kT}} c^2\,dc \tag{13.55}$$

since

$$\in_t = \frac{1}{2}mc^2$$

c being molecular velocity. This agrees with the corresponding expression derived in kinetic theory. Thus, we see that the Maxwell–Boltzmann statistics explain the behaviour of ideal gas molecules.

13.13 APPLICATION OF BOSE–EINSTEIN DISTRIBUTION LAW TO PHOTON GAS

We have seen earlier that the three statistics evolved to explain the experimental facts in different fields in order to explain black body radiation and more such phenomena.

Professor S. N. Bose considered the radiation from a black body as photon and Einstein generalized it to describe the energy distribution among physical entity light quanta or photon. The particles have energy distribution not in a continuous manner but in the form of quanta $nh\nu$ where n is an integer, h is Planck's constant and ν is the frequency of radiation. These particles have integral spin having spin angular momenta $n\hbar$ where $\hbar = h/2\pi$.

These particles are generally called bosons, examples of which are α - particles, photons, deuterons, π- mesons and the like.

Considering a black body chamber to be full of photons in thermal equilibrium having energy $h\nu$ moving with constant velocity c thus having momenta $h\nu/c$, we are now going to study the spectral distribution of energy in finding the number of photons which are like particles having momenta p_x, p_y, p_z, $(h\nu_x/c, h\nu_y/c, h\nu_z/c)$ where $\nu_x\nu_y\nu_z = \nu(\alpha, \beta, \gamma)$; α, β and γ are the direction cosines of the direction of motion of photon. The phase volume described by the photons within energy ranges $h\nu_r$ and $h(\nu_r + d\nu_r)$ where ν_r denotes any arbitrary frequency of radiation is given by

$$G_r = \iiint dx\,dy\,dz \iiint dp_x dp_y dp_z$$

$$= V \frac{4\pi\nu_r^2\, d\nu_r}{c^3} h^3$$

Since $$\iiint dx\,dy\,dz = V \text{ and } \quad p_x^2 + p_y^2 + p_z^2 = \frac{h\nu_r^2}{c^2}$$

and the integration is within the limits ν_r and $\nu_r + d\nu_r$, hence the number of cells per unit volume

$$A_r d\nu_r = \frac{G_r}{h^3} = \frac{4\pi\nu_r^2\, d\nu_r}{c^3}$$

The number is to be multiplied by 2 as there are two photons differentiated by their polarization state to a particular frequency and direction. So, the total number of cells are

$$A_r d\nu_r = \frac{8\pi\nu_r^2\, d\nu_r}{c^3} \tag{13.56}$$

Let the number of photons having frequency lying between ν_r and $\nu_r + d\nu_r$ be denoted by $N_r d\nu_r$, we are to find out the number of ways in which $N_r d\nu_r$ can be distributed amongst $A_r d\nu_r$ cells. We assume that each cell may contain 1, 2, 3, … up to $N_r d\nu_r$ photons, then

$$P = \pi \frac{(A_r + N_r)\, d\nu_r\,!}{A_r\, d\nu_r\,!\; N_r d\nu_r\,!}$$

Using Stirling's formula,

$$S = k \ln\, P = k \sum d\nu_r\, \ln \frac{(A_r + N_r)!}{A_r!N_r!}$$

In the equilibrium case, $\delta S = 0$, that is, $\delta(\ln P) = 0$ for the condition

$$E = \sum (N_r d\nu_r)\, h\nu_r = \text{constant.}$$

This leads

$$\delta \sum [(A_r + N_r) \ln (A_r + N_r) - N_r \ln N_r - A_r \ln A_r] = 0$$

subject to the condition $$\sum \nu_r\, \delta N_r = 0$$

Using undetermined multiplier α, the condition gives

$$\ln(A_r + N_r) - \ln N_r - \alpha\nu_r = 0$$

or

$$\frac{(A_r + N_r)}{N_r} = e^{\alpha\nu_r}$$

or

$$N_r = \frac{A_r}{e^{\alpha\upsilon_r} - 1} \tag{13.57}$$

From the condition

$$\frac{\partial S}{\partial E} = \frac{1}{T},$$

we get

$$\alpha = \frac{h}{kT}$$

So, we can write

$$N_r = \frac{A_r}{e^{\frac{h\nu_r}{kT}} - 1}$$

The energy density

$$\rho_{\nu_r} d\nu_r = N_r\, h\nu_r d\nu_r$$

Hence, we have

$$\rho_{\nu_r} d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \frac{h\nu}{\left(e^{\frac{h\nu}{kT}} - 1\right)} \tag{13.58}$$

which represents the density of radiation between frequencies ν and $\nu + d\nu$ as has already been deduced in Chapter 12.

13.14 APPLICATION OF FERMI–DIRAC DISTRIBUTION LAW TO ELECTRON GAS

Fermi–Dirac statistics has many applications in studying electrical and thermal conductivities, thermoelectricity, thermionic and photoelectric effects, specific heat of metals, etc. on the assumption that metals contain free electrons constituting like a perfect gas known as electron gas. Though many scientists like Drude, Lorentz and others worked on this, but Sommerfeld in 1928 revived quantum electron theory of metals. The conductivity of metals is due to the presence of free electrons inside a metallic conductor moving freely inside them colliding with fixed atoms behaving like an electron gas. These are called fermions because electrons obey Pauli's exclusion principle is the electrons have odd half integral spin angular momenta $(n + 1/2)\hbar$ where $n = 0, 1, 2 \ldots$ Though the electrons are not bound to any particular atom in a metal but to the metal as a whole, the interior of which is considered as a region of uniform potential positive relative to free space, so that work is required to be done to extract an electron from the metal. For this reason, the electrons inside metals can not be compared to the free molecules of a gas. The electrons, being of very light mass and dense packing, are considered as degenerate gases.

Further since the electrons are assumed to be governed by Pauli's exclusion principle, they should obey Fermi–Dirac statistics.

To obtain the law of distribution for the electron gas according to Fermi–Dirac statistics, we should note that

$$n_t = \frac{a_t}{f\,e^{\beta \in_t} + 1} \tag{13.59}$$

where n_t is the number of electrons in the energy interval between $\in_t$ and $\in_t + d\in_t$, a_t is the number of phase cells at the disposal of each of these electrons and $\beta = 1/kT$, a_t the number of phase cells at the disposal of particles of energy interval between $\in_t$ and $\in_t + \, d\in_t$ is

$$a_t = \frac{2\pi V(2m)^{3/2} \in_t^{\frac{1}{2}} d\in_t}{h^3} = C\in_t^{\frac{1}{2}}\, d\in_t \tag{13.60}$$

Owing to the special property of the electron known as spin, each cell of momentum space can contain not one electron alone but two corresponding to two directions of spin. This means that a_t must be multiplied by 2,

$$\therefore \qquad a_t = \frac{4\pi V(2m)^{3/2} \in_t^{\frac{1}{2}} d\in_t}{h^3} \tag{13.61}$$

Writing Eq. 13.59 in a differential mode,

$$dn_t = \frac{4\pi V}{h^3}(2m)^{3/2} \frac{\in_t^{\frac{1}{2}} d\in_t}{fe^{\beta\in_t} + 1}$$

Integrating over all possible energy value,

$$N = \frac{4\pi V}{h^3}(2m)^{3/2} \int_0^\infty \frac{\in_t^{\frac{1}{2}} d\in_t}{fe^{\beta\in_t} + 1}$$

Introducing the variable $u = \beta\in_t$,

$$N = \frac{4\pi V}{h^3}(2m)^{3/2} \frac{(kT)^{3/2}}{f} \int_0^\infty \frac{u^{\frac{1}{2}} du}{e^u + \frac{1}{f}}$$

Introducing the integral I_n defined by

$$I_n = \frac{1}{\Gamma(n+1)} \int\limits_0^\infty \frac{u^n du}{e^u + \frac{1}{f}} \tag{13.62}$$

$$N = \frac{4\pi V}{h^3 f}(2mkt)^{3/2}\, \Gamma\left(\frac{3}{2}\right) I_{\frac{1}{2}}$$

$$= \frac{2V}{f h^3}(2\pi mkt)^{3/2} I_{\frac{1}{2}} \tag{13.63}$$

as $$\Gamma\left(\frac{3}{2}\right)=\frac{\sqrt{\pi}}{2}$$

Similarly, the total internal energy

$$U=\int \in_t dn_t = \frac{4\pi V}{h^3}(2m)^{3/2}\int_0^{\infty}\frac{\in_t^{3/2}\in_t}{fe^{\beta\in_t}+1}$$

$$=\frac{4\pi V}{h^3}(2m)^{3/2}\frac{(kT)^{5/2}}{f}\Gamma\left(\frac{5}{2}\right)I_{\frac{3}{2}}$$

$$=\frac{4\pi V}{h^3}(2m)^{3/2}\frac{(kT)^{5/2}}{f}\frac{3\sqrt{\pi}}{4}I_{\frac{3}{2}}$$

$$=\frac{3V}{fh^3}(2\pi mkT)^{3/2}\,kTI_{\frac{3}{2}} \tag{13.64}$$

or $$\frac{U}{N}=\frac{3}{2}kT\frac{I_{3/2}}{I_{1/2}} \tag{13.65}$$

or $$U=\frac{3}{2}NkT\frac{I_{3/2}}{I_{1/2}}=\frac{3}{2}RT\frac{I_{3/2}}{I_{1/2}}$$

Case (1):
When $f >> 1$, $I_{1/2}$, and $I_{3/2}$ may be taken to be equal to unity, so $U/N = 3/2\, kT$ as in classical statistics.

We get from Eq. 13.53,

$$f_0=\frac{2V}{N h^3}(2\pi mkt)^{3/2} \tag{13.66}$$

Supposing that number of free electrons in metals is equal to the number of atoms per cc, that is, of the order of 10^{22} we find that even at ordinary temperature, $T = 300$ K, $f_0 = 10^{-3}$, that is, $f_0 << 1$. Hence, the electron gas will be almost completely degenerate even at ordinary temperature $T = 300$ K, $f_0 = 10^{-3}$, that is, $f_0 << 1$. Hence, the electron gas will be almost completely degenerate even at ordinary temperature which justifies the assumptions of Sommerfeld.

Case (2):
When f << 1, we have the integrals

$$\left.\begin{aligned} I_{3/2}&=\frac{8}{15\sqrt{\pi}}f\alpha^{5/2}\left(1+\frac{5\pi^2}{8\alpha^2}+\cdots\right)\\ I_{1/2}&=\frac{4}{3\sqrt{\pi}}f\alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right)\end{aligned}\right\} \tag{13.67}$$

Putting $\ln f = \alpha = s/kT$ where s is the Fermi energy, the energy value up to which all the energy states are completely filled by electrons at 0 K and above which all the energy states are completely empty, we get

$$N = \frac{2V}{h^3}(2\pi mkt)^{3/2}\frac{4}{3\sqrt{\pi}}\alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right) \tag{13.68}$$

or
$$N = \frac{2V}{h^3}(2mkt)^{3/2}\ \pi\sqrt{\pi}\ \frac{4}{3\sqrt{\pi}}\alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right)$$

or
$$\alpha^{3/2} = \left(\frac{3Nh^3}{V8\pi}\right)\frac{1}{(2mkt)^{3/2}}\ \frac{1}{\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right)}$$

or
$$\alpha = \left(\frac{3n}{8\pi}\right)^{2/3}\ \frac{h^2}{2mkt}\left(\frac{1}{1+\frac{\pi^2}{8\alpha^2}+\cdots}\right)^{2/3}$$

Let the first approximation value of α be α_0. Then, we get

$$\alpha_0 = \frac{h^2}{2mkt}\left(\frac{3n}{8\pi}\right)^{2/3} \tag{13.69}$$

Equation 13.68 assumes the form

$$\alpha_0^{\ 3/2} = \alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right)$$

$$\alpha_0 = \alpha\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right)^{2/3}$$

from which we deduce that to a second approximation,

$$\alpha = \alpha_0\left(1-\frac{\pi^2}{12\alpha_0^{\ 2}}+\cdots\right)$$

From Eq. 13.65, we can write

$$\frac{U}{RT} = \frac{3}{2}\frac{I_{3/2}}{I_{1/2}}$$

or
$$U = \frac{3}{2}RT\frac{8}{15\sqrt{\pi}}f\alpha^{5/2}\left(1+\frac{5\pi^2}{8\alpha^2}+\cdots\right)\frac{3\sqrt{\pi}}{4f\alpha^{3/2}\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right)}$$

$$= \frac{3}{5}RT\alpha\left(1+\frac{5\pi^2}{8\alpha^2}+\cdots\right)\left(1+\frac{\pi^2}{8\alpha^2}+\cdots\right)^{-1}$$

$$= \frac{3}{5} RT\alpha\left(1+\frac{\pi^2}{2\alpha^2}+\cdots\right)$$

$$= \frac{3}{5} RT\alpha_0\left(1-\frac{\pi^2}{12\alpha_0^2}\right)\left(1+\frac{\pi^2}{2\alpha^2}+\cdots\right)$$

$$= \frac{3}{5} RT\alpha_0\left(1+\frac{5\pi^2}{12\alpha_0{}^2}\right) \text{ approximately.}$$

On simplification, we get

$$U = \frac{3}{40}\frac{Nh^2}{m}\left(\frac{3n}{\pi}\right)^{2/3} + \frac{1}{2}\frac{Nm}{h^2}(2\pi k)^2\left(\frac{\pi}{3n}\right)^{2/3} T^2 \tag{13.70}$$

This shows that at absolute zero, the energy of Fermi–Dirac gas for which f << 1 is not zero but possesses a value

$$U_0 = \frac{3}{40}\frac{Nh^2}{m}\left(\frac{3n}{\pi}\right)^{2/3}$$

This may be called null point energy. The energy *U* adds a term to the specific heat given by

$$C_v = \frac{dU}{dT} = \frac{Nm}{h^2}(2\pi k)^2\left(\frac{\pi}{3n}\right)^{2/3} T \tag{13.71}$$

which can be utilized to calculate the heat capacity due to free electrons in a metal like silver.

Putting the known values, $C_v = 0.767 \times 10^{-4}\, RT$ per gram atom = 0.046 cal per gram atom at 300 K. Thus, C_v forms only 0.7 per cent of the ordinary specific heat of silver and hardly adds anything to it. This removes one of the difficulties of the electron theory of metals.

At low temperature, the specific heat is due to lattice vibration diminishing according to T^3 law. This becomes small compared to the electronic specific heat of silver from the temperature range 3 K downwards. Keesom and Kok measured specific heat of silver in this region and found that it varies according to Eq. 13.71 from 1.5 K to 3 K but above 3 K, T^3 term becomes prominent. So, we may say that free electrons contribute chiefly at specific heat.

The entropy is given by

$$S = \int \frac{C_v}{T} dT = \frac{Nm}{h^2}(2\pi k)^2\left(\frac{\pi}{3n}\right)^{2/3} T$$

which gives that as *T* tends to zero, entropy tends to zero.

All physical and thermodynamic properties of three states can be studied with the help of these three statistics, that is, Maxwell–Boltzmann, Bose–Einstein and Fermi– Dirac such as pressure, temperature, entropy, enthalpy, free energy, Gibb's potential, partition functions, vapour pressure, chemical constants, emission of electrons, Nernst heat theorem and equipartition of energy.

Table 13.1 Characteristics of three statistics

Maxwell–Boltzmann	Bose–Einstein	Fermi–Dirac
The idea was developed by James Clerk Maxwell in 1859 and by Ludwig Boltzmann in 1872.	The idea was set forth by Satyendranath Bose and Albert Einstein in 1924.	The idea was evolved by Enrico Fermi and Paul Adrien Maurice Dirac in 1926.
The particles are identical, distinguishable and of any spin.	The particles are identical, indistinguishable having zero or integral spin.	The particles are identical, indistinguishable and of odd half integral spin.
Particles are minute, like gas molecules without intermolecular force.	Particles are called bosons; examples are α particles, photons, deuterons and π-mesons.	Particles are called fermions; examples are electrons, positrons, protons, neutrons and µ-mesons.
It is based on classical mechanics acting on particles.	It is based on quantum mechanics where quantum states are considered.	It is based on quantum mechanics where quantum states are considered.
Pauli's exclusion principle is not applicable, that is, there is no restriction on the number of particles in a given state.	Pauli's exclusion principle is not applicable, that is, there is no restriction on the number of particles in a given quantum state.	Pauli's exclusion principle is applicable, that is, only one particle can be there in a given quantum state.
Particles are of very minute volume, which is neglected.	Volume occupied by each particle in phase space is h^3.	Volume occupied by each particle in phase space is h^3.
The number of ways of accommodating n_t particles in a_t cells $= \pi \frac{a_t^{n_t}}{n_t!}$	The number of ways of accommodating n_t particles in a_t cells $= \pi \frac{(a_t + n_t - 1)!}{a_t! n_t!}$	The number of ways of accommodating n_t particles in a_t cells $= \pi \frac{a_t!}{a_t!(a_t - n_t)!}$
Distribution law is represented by $n_t = \frac{1}{f} a_t e^{-\beta\epsilon_t}$	Distribution laws is represented by $n_t = \frac{1}{f} \frac{a_t}{e^{\beta\epsilon_t} - 1}$	Distribution law is represented by $n_t = \frac{1}{f} \frac{a_t}{e^{\beta\epsilon_t} + 1}$
Nature of distribution is independent of temperature.	Bose–Einstein distribution approaches Maxwell–Boltzmann distribution at high temperature.	Fermi–Dirac distribution approaches Maxwell–Boltzmann distribution at high temperature.
Internal energy of an ideal monatomic gas depends on its temperature. At absolute zero, energy is zero.	The energy at absolute zero is taken to be zero.	Even at absolute zero temperature, the energy is not zero.
The number of cells available in a phase space is very large compared to the number of particles.	The number of cells available is approximately equal to the number of particles.	The number of cells available is approximately equal to the number of particles.

13.15 COMPARISON OF THE THREE STATISTICS

The three statistics—Maxwell–Boltzmann, Bose–Einstein and Fermi–Dirac may be scrutinized by indicating their main characteristics in Table 13.1.

13.16 CRITICISM OF THE THREE STATISTICS

Classical statistics manifested by Maxwell–Boltzmann interprets energy and velocity distribution of the molecules of an ideal gas assuming that all the energy levels are accessible to all the particles of the system. Actually, certain energy levels are prohibited to a certain group of particles for which it could not expound some experimental phenomena such as black body radiation, photoelectric effect, specific heat at low temperature, etc. Here comes quantum statistics with the idea of discrete energy exchange to explain them introducing photons and electrons as the elementary particles. Bosons and fermions are very much helpful in the study of nuclear physics. But everything is not perfect with this new statistics. It has some limitations; firstly, it assumes absolute freedom of the particles making theoretical results very approximate in thermionic and photoelectric emissions, and paramagnetic susceptibilities of alkali metals. Secondly, it supposes constant potential for the electrons hindering full fledged explanation of thermal and electrical conductivities of metals. This necessitates the refinement of constant potential by space periodic potential which was well introduced by Kronig and Penney.

SOLVED PROBLEMS

Q 1. Two six faced dice each marked 1 to 6 are thrown. Calculate the probability that one of the dice shows 6 and the other shows 5.

Ans. The probability that the first throw gives a 6 is 1/6. The probability that the first throw gives 5 is 1/6. These two events are independent; hence, the probability $= 1/6 \times 1/6 = 1/36$ and as there are two dice the required probability will be $= 2 \times 1/36 = 1/18$.

Q 2. What is the probability of drawing four aces in succession from a pack of 52 cards?

Ans. The number of ways in which the first ace can be drawn is 52. As there are 4 aces, the number of ways in which the first ace may be drawn is 4. Probability of getting an ace in the first draw is $P_1 = 4/52 = 1/13$. The number of ways in which the second card can be drawn is 51 because one ace has been drawn already; now, number of cards left is 51 and the number of aces are 3. Therefore, the number of ways for the second incident, that is, the second card drawn may be an ace is 3.

Probability of getting an ace in the second draw is $P_2 = 3/51 = 1/17$.

Similarly, probability of getting an ace in the third draw is $P_3 = 2/50 = 1/25\cdot$

Similarly, probability of getting an ace in the fourth draw is $P_4 = 1/49$.

Since the incidents are independent, the total probability $P = P_1 \times P_2 \times P_3 \times P_4$

$$= \frac{1}{13} \times \frac{1}{17} \times \frac{1}{25} \times \frac{1}{49} = \frac{1}{270725}$$

Q 3. If 12 particles are distributed among two boxes of equal size, find the probability of distribution (8, 4).

Ans. Probability of distribution (8, 4) corresponding to the distribution of 12 particles into two boxes of equal size is given by

$$P = \frac{12!}{8!4!} \times \frac{1}{2^{12}} = \frac{12.11.10.9.8!}{8!4.3.2} \times \frac{1}{2^{12}} = \frac{495}{4096}$$

Q 4. Calculate the probability that the speed of oxygen molecule lies between 100 and 101 m/s at 200 K.

Ans. The probability of a molecule with its speed between *c* and *c* + *dc* is given by

$$P(c)dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2\, e^{\frac{-mc^2}{2kT}}\, dc$$

$$= 4 \times 3.14\left(\frac{32 \times 1.67 \times 10^{-27}}{2 \times 3.14 \times 1.38 \times 10^{-23} \times 200}\right)^{3/2} (100.5)^2$$

$$e^{-\frac{32 \times 1.67 \times 10^{-27}}{2 \times 1.38 \times 10^{-23} \times 200}} \times 1$$

$$= 659169 \times 10^{-9}$$

PROBLEMS

1. A dice has six numbers depicted on its six faces. By throwing it twice, what is the probability of getting 6 and 4?

Ans. 1/36

2. A container has 5 red and 4 green balls. What are the probabilities that on two successive draws (a) both will be red and (b) both will be green?

Ans. (a) 5/18, (b) 1/6

3. Calculate the probability of getting 1 head and 5 tails in tossing a coin 6 times.

Ans. 3/32

4. Four similar dice *P*, *Q*, *R*, *S* each having 6 equally likely faces marked as 1, 2, 3, 4, 5 and 6 are thrown simultaneously; and in a toss, all the faces have equal probability of appearing up. Calculate the probability of getting the faces of all the dice up marked with 2.

Ans. 1/1296

5. Calculate the probability of drawing 3 jacks in succession from a pack of 52 cards.

Ans. 1/5525

6. Identical n coins are tossed simultaneously for a large number of times. Calculate the probability of falling γ heads uppermost.

Ans. $\dfrac{n!}{r!(n-r)!}2^{-n}$

7. In a system of 14 distinguishable particles distributed in two equally probable halves of a box, find out the probability distribution (10, 4), (14, 0) and (7, 7).

Ans. $\dfrac{1001}{16384}, \dfrac{1}{16384}, \dfrac{3432}{16384}$

QUESTIONS

1. Define
   i. Ensemble
   ii. Microscopic and macroscopic states
   iii. Phase space
   iv. Probability
   v. Mathematical probability
   vi. Thermodynamic probability
   vii. Postulate of equal a priori probability
   viii. Statistical equilibrium
   ix. Most probable state

2. Discuss the importance of statistical approach in Physics.

3. What do you mean by probability? When will it be zero and one?

4. What is the postulate of equal probability? Does the microstate of the system change continuously? What is the most probable microstate?

5. Show the difference among the three statistics. Calculate thermodynamic probability of microstate for all these three statistics.

6. Define and explain macrostate and microstate citing examples.

7. What are the advantages of statistical methods?

8. Show that the probability of large deviation from most probable state is very small.

9. Derive Boltzmann relation between entropy and probability.

10. Derive Maxwell–Boltzmann distribution law of molecular velocities.

11. Derive Maxwell–Boltzmann distribution law and, hence, show that

$$n_t(E) = \frac{2\pi N}{(\pi kT)^{3/2}} E^{\frac{1}{2}} \exp\left(-\frac{E}{kT}\right) dE$$

where $n_t(E)$ is the number of molecules with energies lying between E and $E + dE$.

12. Derive Bose–Einstein distribution law of energy among different frequencies. What are bosons? Which statistics is used to study them? What is the speciality of this statistics?

13. How does Fermi–Dirac statistics differ from Bose–Einstein statistics?
14. What is the method of Lagrange's undetermined multiplier and when is it used? Evaluate this.
15. Show that Bose–Einstein and Fermi–Dirac statistics reduce to Maxwell–Boltzmann statistics in the limiting case.
16. What are fermions? Derive an expression for the probability distribution of particles governed by Fermi–Dirac statistics.
17. Deduce Fermi–Dirac distribution law as applied to electron gas.
18. Calculate the value of total internal energy.
19. Find out the value of Fermi energy at absolute zero temperature.
20. Deduce expression for null point energy as applied to electron gas according to Fermi–Dirac statistics.
21. Do electrons have zero energy at 0 K? If not, why? Explain.
22. Derive expression for specific heat for metals and entropy according to Fermi–Dirac statistics.
23. Show how specific heats of metals at low temperature are explained by Fermi–Dirac statistics.
24. Describe a comparative picture of the three statistics.
25. What are the merits and demerits of the three statistics?

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