



# ADVANCED HEAT AND THERMODYNAMICS

K. D. KRORI

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## PREFACE

The study of physics, as one knows, calls for *good mathematical foundation* and *sound conceptual clarity*. This philosophy has guided me all through the pleasant journey of writing this book on "Heat and Thermodynamics" so that the fundamental ideas and principles of the subject can at once be picked up and assimilated by the student.

Besides, a number of topics have perhaps been treated in a book of this kind for the first time such as—(a) a direct derivation of Avogadro number, (b) Clausius' virial theory for real gases, (c) thermo-chemical phenomena, (d) why a hollow chamber at a temperature is filled with black radiation, (e) Born's quantum theory of specific heats of solids, (f) Raman's quantum theory of specific heats of solids, (g) quantum theory of specific heats of diatomic gases, (h) classical statistics as developed by Boltzmann, (i) Pauli's theory of paramagnetism of alkali metals, (j) Sackur-Tetrode equation, (k) Saha's theory of ionisation, etc., etc.

Now I proceed to recount some highlights of different chapters. Temperature is the basic concept in heat and thermodynamics. Chapter 0 deals with this concept and its measurement. This concept follows from the zeroth law of thermodynamics. The first law of thermodynamics is introduced in Chapter 1. Experimental methods of the determination of the specific heats of a gas are explained. The kinetic theory of gases is the subject-matter of Chapter 2. Clausius' treatment of the pressure of a perfect gas has been presented and a theoretical derivation of Avogadro number is given. Besides the usual topics, particular mention should be made of the electric and thermal conductivities of metals, vapour pressure over a curved surface and formation of raindrops and Perrin's camera lucida arrangement to study Brownian motion. Both Einstein's and Langevin's derivations of Brownian motion have been given in a lucid language.

Chapter 3 is devoted to the study of real gases. Experimental studies have been described in fair detail leading to the formulation of van der Waals' equation of state. Clausius' virial theory has been developed for a rigorous derivation of van der Waals' equation.

Chapter 4 deals with thermal conduction. Experimental methods for determination of conductivities of good and bad conductors, crystals, liquids, and gases have been described. This chapter also discusses periodic flow of heat, conductivity of earth's crust and age of the earth. The second law of thermodynamics is the subject-matter of Chapter 5. The concept of entropy has been developed and discussed in minute detail. Kelvin's absolute thermodynamic scale of temperature and its realisation are also given due weightage.

Chapter 6 deals with the applications of thermodynamical principles to latent heat phenomena, thermionic emission, surface tension and reversible electric cells. Thermodynamic functions and Maxwell's thermodynamic relations and their wide applications including thermoelectric effect, magneto-caloric effect, Joule-Thomson effect, saturated vapour pressure, etc., have been derived. Certain aspects of thermo-chemistry have also been treated including Hess's law, law of mass action and principle of Le Chatelier.

Chapter 7 considers the thermodynamics of radiation in fair detail ending up with an impasse involving distribution of energy in black-body radiation. Radiation pyrometry has also been discussed. Chapter 8 opens with Planck's derivation of the law of radiation introducing a novel idea, namely, quantum hypothesis. Quantum theories of specific heats of solids due to Einstein, Debye, Born and finally Raman are treated at length.

Classical statistics as it was developed by Boltzmann before the advent of the idea of phase cells has been treated in Chapter 9. This pre-quantum theory of statistics has not been accorded its due importance in the present-day literature. In this chapter, Maxwell-Boltzmann laws of a single gas and a mixture of gases have been derived. It ends with a generalised treatment of the principle of equipartition of energy.

Quantum statistics is the subject-matter of Chapter 10. This chapter presents how Bose gave the most elegant deduction of Planck's law. The Bose-Einstein statistics and Fermi-Dirac statistics have been derived by a simple, concise method. Bose-Einstein statistics has been applied to hydrogen and helium. It has been shown that the Bose-Einstein condensation is a consequence of this statistics at low temperature. The Fermi-Dirac statistics has been applied to electron gas in metals, paramagnetism of alkali metals, thermionic emission, etc. It has been shown that the Fermi-Dirac repulsion is a consequence of this statistics at low temperatures.

Statistical thermodynamics has been treated in Chapter 11. It opens with a complete deduction of the Boltzmann law :  $S = k \log G$ . The highlights of this chapter are Sackur-Tetrode equation, Saha's theory of ionisation, and Nernst's theorem.

This treatise closes with eight appendices, viz., (1) some useful integrals, (2) equivalence of different statements of the second law of thermodynamics, (3) Liouville's theorem, (4) quantum-mechanical basis of B-E and F-D statistics, (5) liquefaction of air, hydrogen and helium, (6) a rigorous deduction of gaseous viscosity and conductivity, (7) heat engines and (8) superfluidity.

I express my heartiest thanks to Mr Amitabha Sen, Director, New Central Book Agency (P) Ltd, for undertaking the publication of this treatise. I also extend my sincere appreciation to the editorial staff for their unstinted cooperation at all stages. Finally, I put on record my boundless gratitude to my wife, Rina Krori, for inspiration and encouragement she gives me in all my academic activity.

K D Krori

# Chapter 0

## Zeroth Law of Thermodynamics—Concept of Temperature

### 0.1 Mechanics and Thermodynamics

It would be appropriate to clarify, at the outset, the scopes of mechanics and thermodynamics. Mechanics deals with the *external state* of a body in terms of its position, velocity, momentum, kinetic energy, potential energy, etc. On the other hand, thermodynamics deals with the *internal state* of a system in terms of its pressure, volume and temperature called its *thermodynamic coordinates*. We are familiar with the pressure and volume of a system, but not so with its temperature in the *thermodynamic sense*. We, therefore, proceed to develop the concept of temperature in the following section.

### 0.2 Thermal Equilibrium : Zeroth Law of Thermodynamics—Concept of Temperature

When two systems, *A* and *B*, are put in diathermic contact (i.e., separated by a heat conducting thin wall), heat flows from one to the other till the *macroscopic properties* like the pressure and volume acquire constant, though in general different, values in the two systems [Fig. 0.1(a)]. In such a condition, we say that *A* and *B* are in *thermal equilibrium* with each other. In other words, both the systems are *thermally* in the same state.

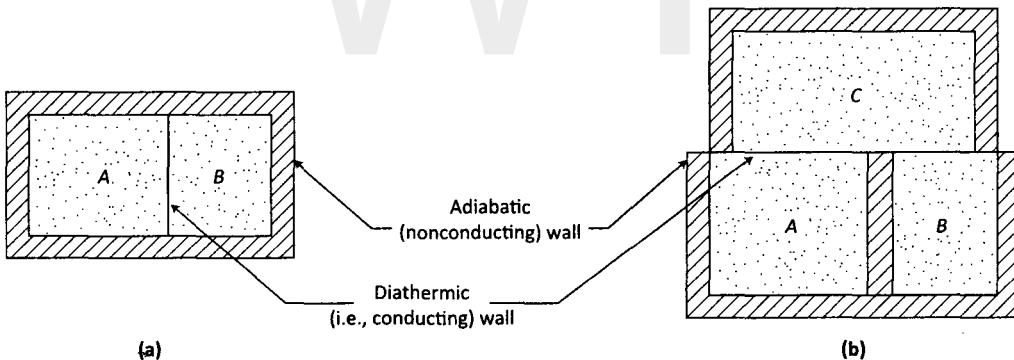


Fig. 0.1: Thermal equilibrium

Now, it may so happen that *A* and *B* are not in diathermic contact but both of them are in diathermic contact with a third *handy* system, *C* [Fig. 0.1(b)]. Then, in due course, *A* and *C* are in the same thermal state and also *B* and *C* are in the same thermal state. Then, obviously *A* and *B* would be in the same thermal state. This is stated in the form of a law, called the *zeroth law of thermodynamics* :

*If two systems, A and B, are each in thermal equilibrium with a third system, C, then A and B are in thermal equilibrium with each other.*

Now we gain two ideas from this law :

(1) If some systems (*A*, *B* and *C*) are in thermal equilibrium with one another, i.e., if they are in the same thermal state, then a *certain property* must have the same value for all of them. We call this property *temperature*. In other words, all systems in thermal equilibrium with one another have the same temperature. It, therefore, follows that they have different temperatures if they are not in thermal equilibrium with one another.

(2) The third *handy* system, *C*, that we have used to study the thermal state of *A* and *B* represents an instrument, called a *thermometer*, to measure temperature.

The zeroth law of thermodynamics was formulated during 1930s by R. H. Fowler whereas the first and second laws were developed during the nineteenth century. But since temperature, which is basic to both the first and second laws, follows from the zeroth law, this law has been allotted a lower number, zero.

### 0.3 Measurement of Temperature

In order to set up a scale for measurement of temperature, we choose a substance that has a property which varies with temperature. Such a substance is called the *thermometric substance* and its property that varies with temperature is called the *thermometric property*. Some common examples are : the volume of a liquid (as in mercury thermometer), the pressure of a gas maintained at constant volume (as in a constant-volume gas thermometer), the electrical resistance of a wire (as in a platinum resistance thermometer), etc. However, different thermometric substances define temperature scales which do not necessarily agree with one another. This is an anomalous situation. The way out of this difficulty is to find a universally accepted temperature scale and to calibrate the temperature scales with different thermometric substances against this universal scale.

If the thermometric property of a (thermometric) substance is denoted by *x*, then the temperature, *T*, will be a function of *x*. Let us assume the simplest relationship between *T* and *x*, viz., a linear relationship as follows :

$$T(x) = ax + b, \quad (0.1)$$

where *a* and *b* are constants. In order to find these constants, we choose two calibration points such that *T* is *T*<sub>1</sub> and *T*<sub>2</sub> and *x* has values *x*<sub>1</sub> and *x*<sub>2</sub> at these points. Thus, from (0.1) we have

$$T_1 = ax_1 + b \quad (0.2)$$

$$T_2 = ax_2 + b. \quad (0.3)$$

From these equations, we obtain

$$a = \frac{T_2 - T_1}{x_2 - x_1} \quad \text{and} \quad b = \frac{T_1 x_2 - T_2 x_1}{x_2 - x_1}. \quad (0.4)$$

Using (0.4) in (0.1),

$$T = \frac{1}{x_2 - x_1} [(T_2 - T_1)x + (T_1 x_2 - T_2 x_1)] \quad (0.5)$$

so that subtracting (0.2) from (0.5), we have

$$T - T_1 = \left( \frac{T_2 - T_1}{x_2 - x_1} \right) (x - x_1). \quad (0.6)$$

### Celsius and Fahrenheit Scales

The Celsius scale was devised by Anders Celsius (1701–1744), a Swedish astronomer. In this scale, the normal freezing point of water, defined as 0 °C, and the normal boiling point of water, defined as 100 °C, were adopted as the calibration points. A temperature in this scale is, therefore, from (0.6),

$$\begin{aligned} t &= T - T_1 = \left( \frac{T_2 - T_1}{x_2 - x_1} \right) (x - x_1) \\ &= \left( \frac{100 \text{ } ^\circ\text{C}}{x_2 - x_1} \right) (x - x_1). \end{aligned} \quad (0.7)$$

It is easy to verify that  $t = 0 \text{ } ^\circ\text{C}$  for  $T = T_1$  and  $x = x_1$  and also that  $t = 100 \text{ } ^\circ\text{C}$  for  $T = T_2$  and  $x = x_2$ .

The Fahrenheit scale was devised by Daniel Fahrenheit (1686–1736), a German physicist. In this scale, the normal freezing point of water, defined as 32 °F, and the normal boiling point of water, defined as 212 °F, were adopted as the calibration points. A temperature in this scale is, therefore, from (0.6),

$$\begin{aligned} t &= (T - T_1) + 32 \text{ } ^\circ\text{F} = \left( \frac{T_2 - T_1}{x_2 - x_1} \right) (x - x_1) + 32 \text{ } ^\circ\text{F} \\ &= \left( \frac{180 \text{ } ^\circ\text{F}}{x_2 - x_1} \right) (x - x_1) + 32 \text{ } ^\circ\text{F} \end{aligned} \quad (0.8)$$

It is easy to verify in this case also that

$$t = 32 \text{ } ^\circ\text{F} \quad \text{for } T = T_1 \quad \text{and} \quad x = x_1$$

and that  $t = 212 \text{ } ^\circ\text{F}$  for  $T = T_2$  and  $x = x_2$ .

Again one can see that

$$\begin{aligned} t &= \left( \frac{180 \text{ } ^\circ\text{F}}{x_2 - x_1} \right) (x - x_1) + 32 \text{ } ^\circ\text{F}, \text{ from (0.8),} \\ &= \frac{9}{5} \left( \frac{100 \text{ } ^\circ\text{C}}{x_2 - x_1} \right) (x - x_1) + 32 \text{ } ^\circ\text{F} \\ &= \frac{9}{5} t \text{ } ^\circ\text{C} + 32 \text{ } ^\circ\text{F}, \text{ from (0.7).} \end{aligned} \quad (0.9)$$

It is evident from (0.7) and (0.8) that

$$\left. \begin{aligned} 100 \text{ } ^\circ\text{C} &= T_2 - T_1 = 180 \text{ } ^\circ\text{F} \\ \text{i.e., } 5 \text{ } ^\circ\text{C} &= 9 \text{ } ^\circ\text{F} \end{aligned} \right\} \quad (0.10)$$

In (0.10), we have written C° and F° instead of °C and °F, because in this case we get *not readings* on the temperature scales but *differences in readings* on these scales.

### Kelvin Scale

We have already mentioned above the disadvantage that different temperature scales based on the thermometric properties of different thermometric substances do not necessarily agree

with one another. Hence, it is necessary to have a universal temperature scale which does not depend on the nature of the thermometric substance. Lord Kelvin (William Thomson, 1824–1907), a Scottish physicist, devised such a temperature scale on thermodynamic considerations. This temperature scale is known as the *Kelvin thermodynamic or absolute scale of temperature*. The unit of temperature in this scale is Kelvin (symbolically K, and not °K).

In the Kelvin scale, a temperature of zero is defined to be a point at which the thermometric property has a value of zero. This temperature, called *absolute zero*, is taken as one of the two calibration points. Then  $b$  has to be set to zero in (0.1) so that we have

$$T(x) = ax. \quad (0.11)$$

The *triple point* of water, i.e., the temperature at which ice, liquid water and water vapour coexist in equilibrium, has been adopted as the other calibration point. By international agreement, the triple point of water has been assigned a value of 273.16 K. Unit Kelvin is, therefore, defined as 1/273.16 of the difference between absolute zero and the triple point of water. Then, according to (0.11), we have

$$T_{tp} = 273.16 \text{ K} = ax_{tp}, \quad (0.12)$$

where  $x_{tp}$  is the value of the thermometric property at the triple point (tp). Hence,

$$a = \frac{273.16 \text{ K}}{x_{tp}}. \quad (0.13)$$

Using (0.13) in (0.11),

$$T(x) = (273.16 \text{ K}) \frac{x}{x_{tp}}. \quad (0.14)$$

The size of the degree is the same in the Celsius and the Kelvin scale. The relationship between the Celsius temperature,  $t$  °C, and the Kelvin temperature is set as

$$t \text{ } ^\circ\text{C} = T \text{ K} - 273.16 \text{ K}, \quad (0.15)$$

where 273.16 K is the freezing point of water. The freezing and boiling points of water measured in the Kelvin scale and then converted to the Celsius scale have the values 0.00 °C and 99.975 °C respectively.

## 0.4 Standard Constant-volume Hydrogen Thermometer

The Kelvin absolute thermodynamic scale (See section 5.7) has been internationally adopted as the standard scale of temperature. We shall see that this scale and the perfect gas scale are identical. It has been shown in section 5.8 that the readings of a constant-volume gas thermometer or a constant-pressure gas thermometer may be directly reduced to readings on the absolute scale. For this reason, the gas thermometers are called *primary thermometers*. In 1887, the International Committee of Weights and Measures decided to adopt as a practical standard the constant-volume hydrogen thermometer. This thermometer is filled with hydrogen gas at a pressure of 1 metre of mercury at 0 °C. One important consideration in the choice of the constant-volume hydrogen thermometer as a standard is the ease with which it may be constructed. The materials of this thermometer are easily obtainable and the instrument can be made to standard specifications. The second consideration is that there is only small disagreement between the constant-volume hydrogen thermometer and the absolute

thermodynamic scale. The third consideration is that this thermometer may be used over a wide range of temperature from  $-200^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ .

A constant-volume gas thermometer is, however, most inconvenient to use. So mercury thermometers, resistance thermometers, thermocouples, etc., are the instruments actually used. These instruments are calibrated in comparison with the constant-volume hydrogen thermometer scale. For this reason they are called *secondary thermometers*.

The standard constant-volume hydrogen thermometer consists essentially of a bulb  $B$  and a manometer  $AG$  containing mercury (Fig. 0.2). The bulb is a cylinder of platinum-iridium. It is of length 1 metre, volume 1 litre and diameter 3.6 cm. It is filled with hydrogen gas at a pressure of 1 metre of mercury at the temperature of melting ice ( $0^{\circ}\text{C}$ ).  $B$  communicates with the manometer by a narrow platinum tube  $C$ . There is a fine platinum point  $P_1$  inside  $G$ . The volume of the gas is kept constant by adjusting the height of the mercury column in  $G$  until its top just touches  $P_1$ . This is done by raising or lowering the mercury reservoir  $E$  connected to the manometer by a long rubber tube  $R$ . Above  $G$ , there is a column of mercury in  $D$  separated from that in  $G$  by a steel-piece  $S$ .

The stem of barometer  $F$  dips into  $A$ . This stem is so bent that the mercury level in  $F$  stands vertically above that in  $D$ . The barometer can be raised or lowered so that the mercury in  $F$  touches a fine platinum point  $P_2$ . Evidently, the pressure of the gas in  $B$  is given by the difference in the levels of mercury in  $F$  and  $G$ . This difference in levels of mercury is, in fact, measured with a cathetometer from the height difference between the points  $P_1$  and  $P_2$  (after necessary adjustments of mercury levels in  $F$  and  $G$  as already stated).

We shall now show how from the pressure of the gas in  $B$  its temperature can be found out. Let  $P_0$ ,  $P_{100}$  be the pressures of the gas at the ice-point and the steam-point respectively and let  $T_0$  be the ice-point on the absolute scale.

Then, since the volume of the gas is constant,

$$\frac{P_{100}}{P_0} = \frac{T_0 + 100}{T_0}$$

$$\text{i.e., } \frac{1}{T_0} = \frac{P_{100} - P_0}{100P_0} = \alpha. \quad (0.16)$$

where  $\alpha$  is evidently the pressure co-efficient at constant volume and can be determined from a knowledge of  $P_0$  and  $P_{100}$ . If, now,  $P$  be the pressure of the gas at temperature  $T$  K, then,

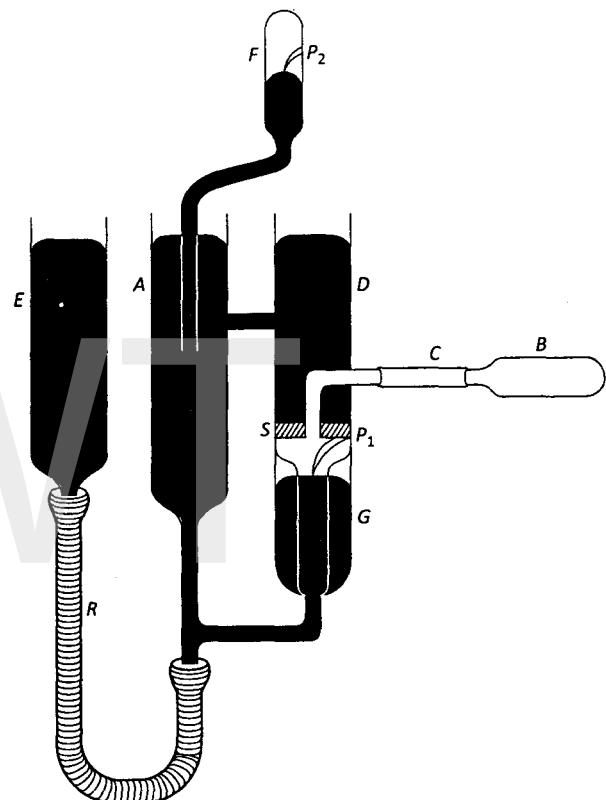


Fig. 0.2: Constant-volume Hydrogen Thermometer

as before,

$$\frac{P}{P_0} = \frac{T}{T_0} \quad \text{or, } T = \frac{PT_0}{P_0} = \frac{P}{\alpha P_0}. \quad [\text{from (0.16)}] \quad (0.17)$$

As stated earlier, the constant-volume hydrogen thermometer can be used over a wide range of temperature from  $-200^\circ\text{C}$  to  $500^\circ\text{C}$ . Above  $500^\circ\text{C}$ , hydrogen diffuses through platinum because heated platinum is permeable to hydrogen. So for higher temperatures above  $500^\circ\text{C}$  up to  $1500^\circ\text{C}$ , nitrogen is used. On the other hand, below  $-200^\circ\text{C}$  helium is often used.

This constant-volume hydrogen thermometer suffers from the following drawbacks for which corrections must be made :

- (1) The volumes of the bulb  $B$ , capillary  $C$ , etc., change with the change of temperature and internal pressure.
- (2) The walls of the bulb and capillary adsorb some gas. This adsorption increases with the fall of temperature.
- (3) If the diameter of the capillary is of the order of the mean free path of the molecules of the gas, a gradient of pressure occurs in the capillary. This is called *Knudsen effect*.
- (4) The gas present in the space (called *dead space*) below the steel-piece  $S$ , has a temperature different from that in the bulb.
- (5) There is gradient of temperature in the gas inside the capillary.
- (6) The temperature and compressibility of the mercury in the manometer have also effects which call for correction.

## 0.5 An Improved Constant-volume Gas Thermometer

Fig. 0.3 shows an improved form of a constant-volume gas thermometer in use at the US National Bureau of Standards.  $B_1$  is a bulb containing thermometric gas. It is surrounded by another bulb,  $B_2$ , containing manometric gas (also called *equalising gas*).  $C$  is a connecting tube.  $D_1$  is a diaphragm separating the thermometric gas from the manometric gas. It acts as a capacitor plate,  $D_2$  being the other capacitor plate. The capacitor is connected to an *AC* bridge.  $D_1$  and  $D_2$  are normally parallel to each other when the pressure is the same on either face of  $D_1$ . Any distortion occurring due to even a slight difference in pressure between the two faces of  $D_1$  is at once detected by the *AC* bridge. The manometric gas is connected to a mercury manometer.

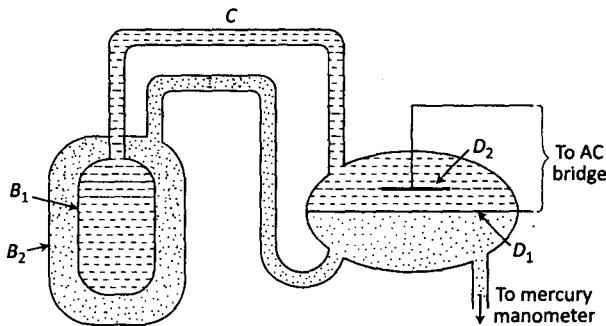


Fig. 0.3: An Improved Constant-volume Gas-thermometer

This gas thermometer possesses two improvements over the thermometer described in the preceding section.

The drawback mentioned in (1) in the preceding section is eliminated since the volume of the bulb  $B_1$  does not alter on account of equal pressures acting on both the sides of the bulb due to the thermometric gas in  $B_1$  and the manometric gas in  $B_2$ .

Secondly, no dead space occurs in this thermometer. So the drawback mentioned in (4) in the preceding section does not occur here.

## 0.6 Ideal-gas Temperature

We start with a certain amount of a thermometric gas in the bulb of a constant-volume gas thermometer and find the pressure,  $P_{tp}$ , of the gas at the triple point of water as well as the pressure,  $P_s$ , of the gas at the condensing point of steam at 1 atm pressure. Finally, we calculate the quantity

$$\theta(P_s) = 273.16 \text{ K} \left( \frac{P_s}{P_{tp}} \right). \quad (0.18)$$

Next, we remove some gas from the bulb and again find  $P_{tp}$  and  $P_s$  for the remaining gas. Finally, we calculate  $\theta(P_s)$  as above in this case.

Again, we further remove some gas from the bulb and calculate  $\theta(P_s)$  in this case also.

We continue this operation a number of times and obtain the straight lines  $AB$  and  $CD$ , shown in Fig. 0.4 for  $O_2$  and  $H_2$ .

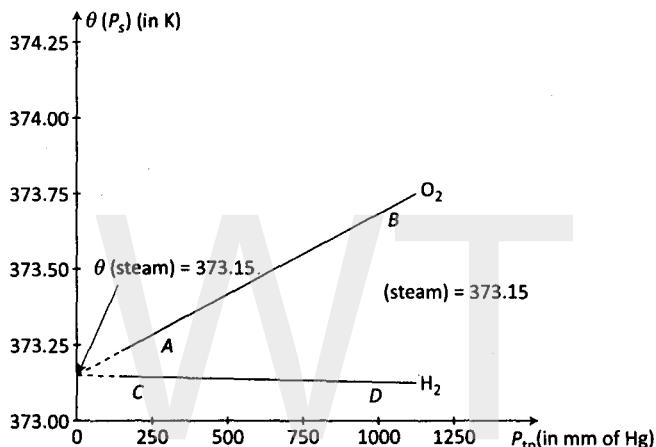


Fig. 0.4: Extrapolation to temperature corresponding to  $P_{tp} \rightarrow 0$ .

Next we repeat the same sequence of operations with the condensing point of sulphur instead of the condensing point of steam and obtain the straight lines  $EF$  and  $GH$ , shown in Fig. 0.5 for  $O_2$  and  $H_2$ .

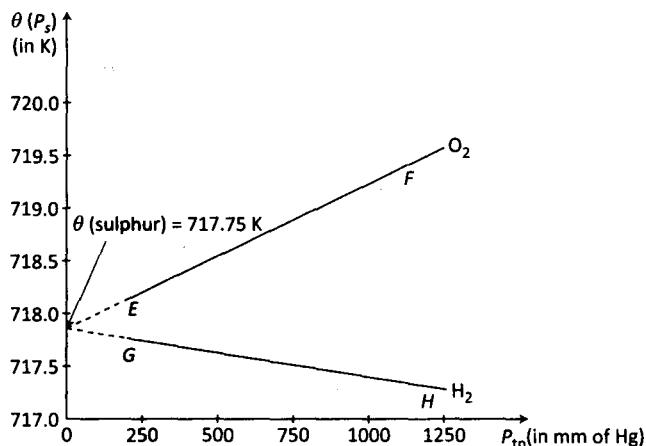


Fig. 0.5: Extrapolation to temperature corresponding to  $P_{tp} \rightarrow 0$

It is interesting to note that on extrapolation to  $P_{tp} \rightarrow 0$  in Fig. 0.4,

$$\theta(P_s) = 273.16 \text{ K} \underset{P_{tp} \rightarrow 0}{\text{Lt}} \left( \frac{P_s}{P_{tp}} \right) = 373.15 \text{ K} \quad (0.19)$$

is the same for O<sub>2</sub>, H<sub>2</sub> or any other thermometric gas.  $\theta(P_s)$  gives the condensing point of steam.

Also, on extrapolation to  $P_{tp} \rightarrow 0$  in Fig. 0.5,

$$\theta(P_s) = 273.16 \text{ K} \underset{P_{tp} \rightarrow 0}{\text{Lt}} \left( \frac{P_s}{P_{tp}} \right) = 717.75 \text{ K} \quad (0.20)$$

is the same for O<sub>2</sub>, H<sub>2</sub> or any other thermometric gas.  $\theta(P_s)$  is the condensing point of sulphur.

We now define the ideal-gas temperature (i.e., temperature irrespective of any thermometric gas)  $\theta$  by the expression :

$$\theta(P) = 273.16 \text{ K} \underset{P_{tp} \rightarrow 0}{\text{Lt}} \left( \frac{P_s}{P_{tp}} \right) \text{ at constant } V, \quad (0.21)$$

where  $P$  represents the pressure of the thermometric gas (corresponding to  $P_{tp} \rightarrow 0$ ) which is to be measured by the thermometer following the sequence of operations carried out to determine the condensing point of steam or sulphur.

It may be mentioned that helium has two distinct advantages as a thermometric gas. (1) At high temperatures helium does not diffuse through platinum. (2) As helium condenses at a temperature lower than any other gas, it can be used as a thermometric gas at temperatures lower than all other gases.

It will be seen in Chapter 5 that the ideal-gas scale is identical with the Kelvin scale.

### Exercise

Study the following chart for air and nitrogen and find  $\theta(P_s)$  for  $P_{tp} \rightarrow 0$  in each case :

$P_{tp}$ (in mm of Hg)	$\theta(P_s)$ in K
750	718.07
500	717.93
250	
750	717.90
500	717.85
250	
	717.80

## 0.7 Secondary Thermometers

### 0.7.1 Platinum Resistance Thermometer

The electrical resistance of pure metals increases as the temperature rises. Callendar and Griffiths showed that over a range of temperature from 0 °C to 500 °C, the resistance of a piece of pure platinum varies with  $t$  °C (measured on the standard gas thermometer) according to the formula :

$$R_t = R_0(1 + \alpha t + \beta t^2), \quad (0.22)$$

where  $R_t$ ,  $R_0$  are the resistances at  $t$  °C and 0 °C respectively, and  $\alpha$ ,  $\beta$  are constants for the particular specimen used. For pure platinum  $\alpha = 3.94 \times 10^{-3}$  and  $\beta = -5.8 \times 10^{-7}$

For practical purposes, however, Callendar defined a temperature  $t_p$  on the platinum thermometer by the relation [using the approximate formula  $R_t = R_0(1 + \gamma t_p)$ ]\*

$$t_p = \frac{R_t - R_0}{R_{100} - R_0} \times 100, \quad (0.23)$$

where  $t$  °C is the temperature measured on the standard gas thermometer corresponding to  $t_p$  on the platinum thermometer. Here  $R_t$ ,  $R_{100}$ ,  $R_0$  are the resistances at  $t$  °C, 100 °C, and 0 °C respectively (measured on the standard gas thermometer). Callendar also calculated the difference between the true temperature  $t$  °C (measured on the standard gas thermometer) and the temperature  $t_p$  [measured on the platinum thermometer according to (0.23)]. We have from (0.22) and (0.23)

$$\begin{aligned} t - t_p &= t - \frac{\alpha t + \beta t^2}{100\alpha \times (100)^2\beta} \times 100 = t - \frac{\alpha t + \beta t^2}{\alpha + 100\beta} \\ &= \frac{\beta(100t - t^2)}{\alpha + 100\beta} = -\frac{(100)^2\beta}{\alpha + 100\beta} \left\{ \left( \frac{t}{100} \right)^2 - \frac{t}{100} \right\} \\ &= \delta \left\{ \left( \frac{t}{100} \right)^2 - \frac{t}{100} \right\} \quad (\text{say}). \end{aligned} \quad (0.24)$$

The value of  $\delta$  is about 1.5 for pure platinum. In fact, it lies between 1.488 and 1.498 for the specimens of platinum usually used.

The platinum resistance thermometer consists essentially of a coil of platinum wire Pt (Fig. 0.6) wound non-inductively on a mica frame  $M$  (also shown separately). The two ends of the coil are connected to the terminals  $P$ ,  $P$  at the top of the thermometer by means of two thick leads  $P_1$ ,  $P_2$  of copper, silver or platinum.  $C_1$ ,  $C_2$  are two other leads identical with  $P_1$ ,  $P_2$  and connected to the terminals  $C$ ,  $C$ . These leads ( $C_1$ ,  $C_2$ ) are called *compensating leads*, because they compensate the resistances of  $P_1$ ,  $P_2$ . All the four leads are separated from one another by some mica sheets ( $S$ ). These mica sheets also prevent the convection currents of air up and down the porcelain tube  $T$  in which the whole thing is enclosed.

A modified form of Wheatstone's bridge, called *Callendar and Griffiths' bridge*, is used to measure the resistance of the platinum wire Pt of the thermometer at any temperature (Fig. 0.7).

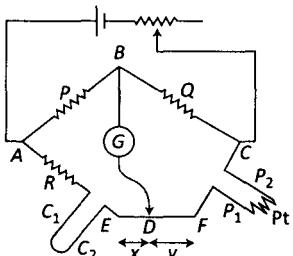


Fig. 0.7: Callendar and Griffiths' Bridge

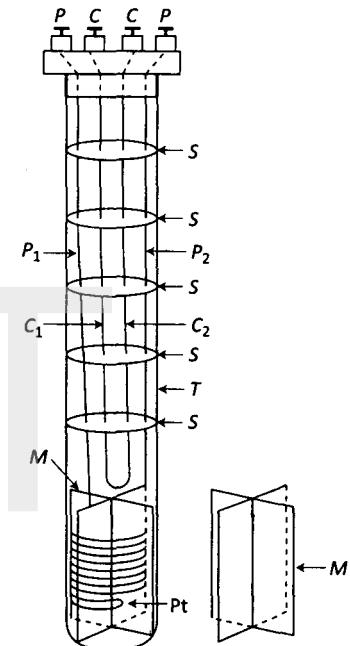


Fig. 0.6: Platinum Resistance Thermometer

$P$ ,  $Q$  are the ratio arms and  $R$  is the third arm. The compensating leads  $C_1$ ,  $C_2$  are connected in series with  $R$ . Pt with its leads  $P_1$ ,  $P_2$  is connected to the fourth arm of the bridge. Between the third and the fourth arms a uniform wire  $EF$  is included.

Now, if  $P$ ,  $Q$  are equal and if the bridge is balanced, then we obtain

$$\begin{aligned} R + r + x\rho &= y\rho + r + R_t \\ \text{i.e., } R_t &= R + (x - y)\rho. \end{aligned} \quad (0.25)$$

\*  $\gamma$  is slightly different from  $\alpha$ . In fact, we may see easily with the help of (0.24) that  $\alpha = \gamma \left( 1 + \frac{\delta}{100} \right)$ .

Here  $r$  = resistance of  $C_1$ ,  $C_2$  = resistance of  $P_1$ ,  $P_2$ ,  $\rho$  = resistance per unit length of the wire  $EF$  and  $R_t$  = resistance of platinum wire Pt at  $t$  °C (measured on the standard gas thermometer).

With the platinum thermometer at ice-point (0 °C)\*, at steampoint (100°C)\* and at the unknown temperature  $t$  °C,  $R_0$ ,  $R_{100}$  and Pt can be found out using (0.25). Then, putting their values in (0.23)  $t_p$  may be obtained. From  $t_p$ ,  $t$  (the true unknown temperature) is evaluated from (0.24).

It is evident from (0.24) that in order to obtain  $t$  from  $t_p$ ,  $\delta$  must be known. How is  $\delta$  obtained? With the platinum thermometer at ice-point (0 °C)\*, at steam point (100 °C)\* and at boiling point of sulphur (444.60 °C)\*,  $R_0$ ,  $R_{100}$  and  $R_{444.60}$  can be found out using (0.25). Now, putting these values in (0.22), we obtain

$$R_{100} = R_0 \{1 + \alpha \cdot 100 + \beta \cdot (100)^2\} \quad (0.26)$$

$$R_{444.60} = R_0 \{1 + \alpha \cdot 444.60 + \beta \cdot (444.60)^2\} \quad (0.27)$$

Solving (0.26) and (0.27) for  $\alpha$  and  $\beta, \delta$  can be determined from the formula [See (0.24)] :

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

In practice, however, all calculations are avoided by providing each platinum thermometer with a temperature-resistance calibration curve drawn from actual comparison with a standard gas thermometer. From this curve any unknown temperature  $t$  °C can be directly read when the corresponding resistance  $R_t$  is measured using (0.25).

The quantity  $(R_{100} - R_0)$  occurring in (0.23) is called the *fundamental interval* of platinum thermometer. It is usually about 1 ohm.

The platinum thermometer has the great *advantage* that it can be used over a very wide range from -200 °C to 1200 °C. If carefully prepared, it can read correct to 0.02 °C in the range 0 °C to 630 °C and to 0.1 °C upto 1200 °C. Its chief *drawback* is that due to the large thermal capacity and the low thermal conductivity of the porcelain tube, it cannot quickly attain the temperature of the bath in which it is immersed. Also it takes some time to balance the bridge. Thus, this thermometer is not used to measure rapidly varying temperatures.

### 0.7.2 Thermocouple (Thermoelectric Thermometer)

When a closed circuit composed of two dissimilar metals, say copper and iron, has the

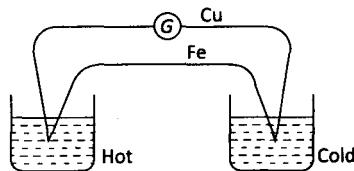


Fig. 0.8: Thermocouple

two junctions maintained at two different temperatures, a current flows through the circuit (Fig. 0.8). This arrangement is called a *thermocouple*. It is evident that when the two junctions of a thermocouple are at different temperatures, an e.m.f. is developed in the circuit. The magnitude and direction of this e.m.f., called *thermo-e.m.f.*, depend on the nature of the two metals and the temperatures of the junctions.

Now we shall describe by a simple arrangement the principle to measure the e.m.f. developed in a thermocouple (Fig. 0.9). Suppose  $M$  is a 2.2-volt battery,  $AB$  a resistance of 999 ohms and  $BC$  a potentiometer wire of resistance 1 ohm. It is evident that the potential difference between  $A$  and  $B$  will be  $\frac{2.2 \times 999}{1000}$  volts = 2.198 volts and the potential difference between  $B$  and

\*These points correspond to standard atmospheric pressure.

$D$  will be  $\frac{2.2 \times 1}{1000}$  volt = 0.002 volt. If the length of the potentiometer wire is 100 cm, then the potential drop per cm of the wire will be 0.00002 volt/cm. One terminal of the thermocouple is connected to  $B$  and the other terminal is connected to a sliding key  $D$  through a sensitive galvanometer  $G$ . Now, the position of  $D$  is so adjusted that no current flows through  $G$ . In this condition, the potential difference between  $B$  and  $D$  balances the e.m.f. of the thermocouple. If  $l$  cm is the distance between  $B$  and  $D$ , then evidently the e.m.f. of the thermocouple is ( $l \times 0.00002$ ) volt.

From the above example, it must be clear that the e.m.f. developed in a thermocouple is extremely small. To measure this extremely small e.m.f. the resistance between  $A$  and  $B$  must be sufficiently high so that the potential drop per cm of the potentiometer wire may be very small.

In actual practice, the cold junction of a thermocouple is always maintained at 0 °C.

Keeping the cold junction of a thermocouple in melting ice (0 °C), and heating the hot junction to different temperatures determined by a constant-volume gas thermometer, the e.m.f. at each temperature is measured. A calibration curve is drawn with e.m.f. against temperature. Then, the temperature of a body can be immediately found from the curve when the e.m.f. of the thermocouple with the hot junction in contact with the body and the cold junction at 0 °C is measured.

A shorter method of calibration may also be applied sometimes. For example, a thermocouple composed of platinum and an alloy of platinum-rhodium (90% platinum and 10% rhodium) follows the following e.m.f.-temperature formula

$$E = a_1 t + b_1 (1 - e^{c_1 t}) \quad (0.28)$$

when the temperature of its cold junction is 0 °C and the temperature  $t$  of its hot junction may have any value between 0 °C and 400 °C. Now  $E$  may be measured with the hot junction at three fixed points\*, say, freezing points of tin (231.9 °C), cadmium (320.9 °C) and lead (327.3 °C). Putting these values of  $E$  and  $t$  in (0.28), three equations will be obtained. Solving these equations,  $a_1$ ,  $b_1$  and  $c_1$  will be found. Then a complete  $E-t$  calibration curve may at once be drawn over the range 0 °C to 400 °C from (0.28).

Following the same technique, calibration curves for the same Pt-Pt-Rh thermocouple may be drawn also

(a) over the range 300 °C to 1200 °C using the formula :

$$E = a_2 + b_2 t + c_2 t^2 \quad (0.29)$$

and three fixed points, say, melting point of antimony (630.5 °C), melting point of silver (960.8 °C) and melting point of gold (1063 °C),

and

(b) over the range 1100 °C to 1750 °C using the formula

$$E = a_3 + b_3 t + c_3 t^2 \quad (0.30)$$

and three standard fixed points.

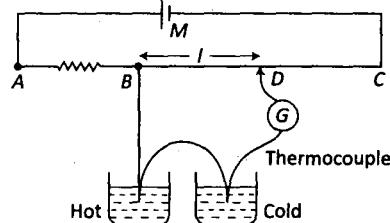


Fig. 0.9: Thermoelectric Thermometer

\*These and other fixed points correspond to standard atmospheric pressure.

Thermocouples have got certain *advantages* for which they are very often used in laboratory work.

- (i) They can measure rapidly-varying temperatures, because the thermal capacity of the hot junction is small so that the junction readily attains the temperature of the body with which it is put in contact.
- (ii) Thermocouples can measure the temperature at a point, because the hot junction has a negligible size.
- (iii) They are very cheap and may be very easily constructed in the laboratory.
- (iv) They have a wide range from  $-200^{\circ}\text{C}$  to  $1600^{\circ}\text{C}$ .

Thermocouples have also got some *disadvantages*.

- (i) There is no theoretical formula which can be applied over a wide range. So every thermocouple requires calibration.
- (ii) A thermocouple is not capable of such accurate measurements as the platinum resistance thermometer over similar ranges of temperature.

There are three main *sources of error* in work with thermocouples :

- (i) Stray e.m.f.s are developed in the circuit. These are (a) the Peltier e.m.f. developed due to heating of junctions of dissimilar metals at points of the circuit other than the hot and the cold junction, and (b) the Becquerel e.m.f. developed due to inhomogeneities in thermocouple wires.
- (ii) If the cold junction is not maintained at  $0^{\circ}\text{C}$ , some correction is required on this account.
- (iii) Leakage currents from the light mains or the furnace circuit may flow through the potentiometer. These currents may be detected by observing if the galvanometer continues to show deflection even after short-circuiting the thermocouple.

We close this discussion with a description of a *thermoelectric thermometer*. The hot junction  $J$  is formed by welding together electrically (or in an oxyhydrogen flame) the ends of two wires

chosen as the elements of the thermocouple (Fig. 0.10). The portions of the wires near  $J$  are insulated from each other with capillary tubes  $C_1$ ,  $C_2$  of fireclay (for use at higher temperatures) or hard glass (for use at lower temperatures). Then the wires pass through mica sheets ( $S$ ) and end up at the terminals  $T_1$ ,  $T_2$ . The whole thing is put inside a tube  $A$  of porcelain, quartz or hard glass depending on the temperature for which the thermometer is to be used. To the terminals  $T_1$ ,  $T_2$ , long leads, usually of the same materials as the two thermocouple elements, are connected. These leads form the cold junction at  $0^{\circ}\text{C}$  at a fairly distant place [Fig. 0.11(i)]. But for the Pt-Pt-Rh couple, leads of copper and an alloy of nickel-copper are used since the elements of the thermocouple are very costly. Copper lead is connected to Pt-Rh and nickel-copper lead is joined to Pt [Fig. 0.11(ii)]. At the cold junction (maintained at  $0^{\circ}\text{C}$ ), copper wires are connected to the leads for inclusion of the galvanometer in the circuit.

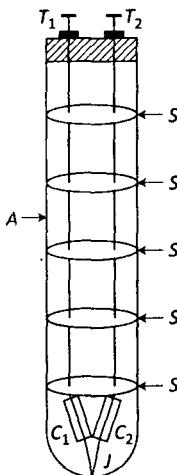


Fig. 0.10: Thermoelectric Thermometer

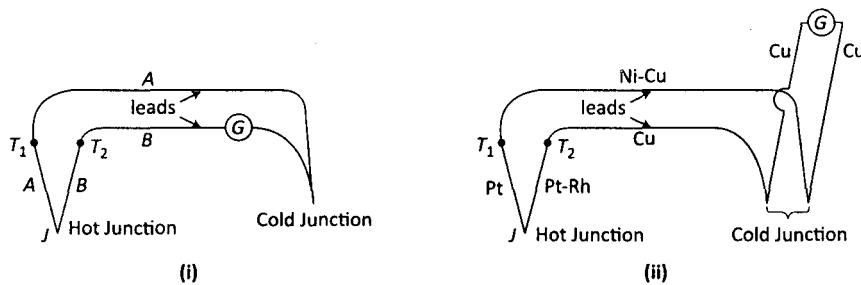


Fig. 0.11: Thermocouples

## 0.8 Radiation Pyrometer

We have seen above that while the platinum resistance thermometers can measure temperatures up to  $1200\text{ }^{\circ}\text{C}$ , the thermocouples may be used up to  $1600\text{ }^{\circ}\text{C}$ . Then, how to measure temperatures beyond  $1600\text{ }^{\circ}\text{C}$ ? This question is answered by radiation pyrometers. We shall discuss radiation pyrometry in detail in section 7.14. So we shall not repeat the discussion here. But we only mention here the fact that there is no upper limit to temperatures that may be measured by radiation pyrometers.

## 0.9 Vapour Pressure Thermometer

Vapour pressure thermometers are based on the fact that the pressure exerted by a saturated vapour depends *only* on its temperature (See sections 6.14 and 11.8). A particular vapour pressure corresponds to a definite temperature. Vapour pressure thermometers are very convenient and sensitive for low-temperature work. The liquids used in these thermometers are oxygen, neon, hydrogen, helium, etc. Oxygen is useful in the range  $123\text{ K}$  to  $63\text{ K}$ , neon in the range  $27\text{ K}$  to  $24\text{ K}$ , hydrogen in the range  $20\text{ K}$  to  $11\text{ K}$  and helium in the range  $5\text{ K}$  to  $0.75\text{ K}$ . In the case of each of these liquids, the pressure is too high for convenient measurement above the upper limit of temperature (say,  $123\text{ K}$  for oxygen,  $27\text{ K}$  for neon,  $20\text{ K}$  for hydrogen and  $5\text{ K}$  for helium) while the pressure is too small for accurate measurement below the lower limit of temperature (say,  $63\text{ K}$  for oxygen,  $24\text{ K}$  for neon,  $11\text{ K}$  for hydrogen and  $0.75\text{ K}$  for helium).

We now proceed to explain the principle of construction of a vapour pressure thermometer.  $V$  is the vessel containing the liquid (Fig. 0.12). From  $V$  extends a capillary tube  $T$  up to the mercury manometer  $AB$  which measures pressure of vapour.  $R$  is a reservoir of mercury. Part of the capillary tube  $T$  is surrounded by a glass tube  $G$  to prevent radiation from and to the tube. Again,  $V$  and part of  $G$  are surrounded by a copper tube  $C$  to produce uniformity of temperature. In order to set up the apparatus, the level of mercury in  $A$  is lowered by lowering  $R$ . Then,  $V$  is evacuated through  $E$  and finally the desired gas is introduced into  $V$  through  $E$ . Now, the level of mercury in  $A$  is raised by raising  $R$  so that the gas becomes compressed and partly liquefied in  $V$ . There is vacuum above the mercury level in  $B$  so that the difference in the levels of mercury in  $A$  and  $B$  directly gives the vapour

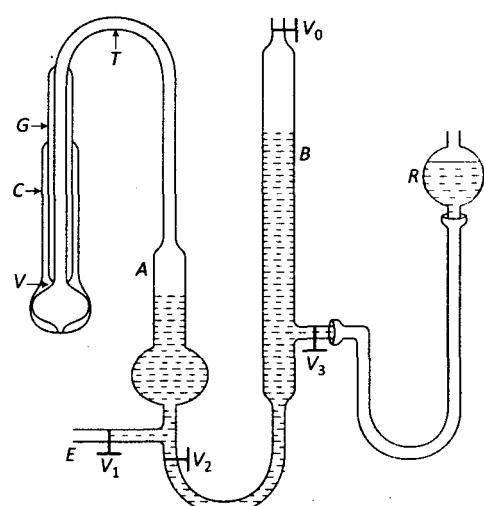


Fig. 0.12: Vapour Pressure Thermometer

pressure. The temperature corresponding to any vapour pressure can be read readily from tables which are usually available.

In the helium vapour pressure thermometer which is used down to 0.75 K, the manometer  $AB$  is replaced by a McLeod gauge or a hot-wire manometer. For this thermometer, the following formulae are used to measure temperature :

Between 5.2 K and 4.3 K :

$$T = 2.967 + 1.905 \times 10^{-2}P - 3.521 \times 10^{-5}P^2. \quad (0.31)$$

Between 4.3 K and 2.19 K :

$$\log_{10} P = -\frac{4.7921}{T} + 0.00783T + 0.017601T^2 + 2.6730. \quad (0.32)$$

Between 2.19 K and 1.6 K :

$$\log_{10} P = -\frac{3.1189}{T} + 2.5 \log_{10} T - 5.981 \times 10^{-5}T^8 + 1.1958. \quad (0.33)$$

[In (0.32) and (0.33),  $P$  is expressed in cm of mercury at 0 °C.]

Between 1.6 K and 0.75 K :

$$\log_{10} P = -\frac{3.117}{T} + 2.5 \log_{10} T + 1.196 + \Delta. \quad (0.34)$$

where  $\Delta$  is a small correction term which is obtained by a graphical analysis.

## 0.10 Magnetic Thermometer

It has been explained in section 2.25 (also see section 6.11) that adiabatic demagnetisation of a paramagnetic substance produces temperatures very close to the absolute zero. These temperatures can be measured, not by the helium vapour pressure thermometer but by magnetic thermometry. The magnetic susceptibility  $\chi$  of a paramagnetic substance obeys Curie's law

$$\chi = \frac{C}{T}, \quad (0.35)$$

where  $C$  is a constant and  $T$  the absolute temperature. At very low temperatures,  $\chi$  becomes very large according to (0.35) and can, therefore, be accurately measured. Hence, by use of (0.35) low temperatures can be determined accurately. But unfortunately, Curie's law is known to fail very near the absolute zero. However, what is done in practice is to assume the validity of (0.35) near absolute zero and to calculate from the measurement of  $\chi$  a temperature (called *Curie temperature*)

$$T^* = \frac{C}{\chi}. \quad (0.36)$$

There are methods<sup>†</sup> to determine the thermodynamic temperature  $T$  from the Curie temperature  $T^*$ . But often readings are simply expressed on the Curie scale ( $T^*$ ).

## 0.11 International Temperature Scale

We have stated at the beginning of this chapter that the Kelvin absolute thermodynamic scale (See section 5.7) has been internationally adopted as the standard scale of temperature. In 1927, the International Committee of Weights and Measures agreed upon a scale which is close

<sup>†</sup>For these methods see for example, Saha and Srivastava, *A Treatise on Heat*, Pp. 536-8 (1958).

to the absolute centigrade scale as our present measurements may permit. This scale is known as the *International Temperature Scale*. This scale deals with only temperatures above the oxygen point ( $-182.97^{\circ}\text{C}$ ) and is based on seven fixed points. These seven points are ice-point ( $0^{\circ}\text{C}$ ), steam point ( $100^{\circ}\text{C}$ ), oxygen point ( $-182.97^{\circ}\text{C}$ ), sulphur point ( $444.60^{\circ}\text{C}$ ), antimony point ( $630.5^{\circ}\text{C}$ ), silver point ( $960.8^{\circ}\text{C}$ ) and gold point ( $1063^{\circ}\text{C}$ ). The third and fourth are boiling points while the last three are freezing points. All these seven points correspond to standard atmospheric pressure.

The thermometers specified by the International Temperature Scale for the different ranges of temperature are :

- (a) *From ice point to  $660^{\circ}\text{C}$*  : The platinum resistance thermometer using the formula  $R_t = R_0(1 + at + bt^2)$ , the constants  $R_0$ ,  $a$ ,  $b$  being determined from observations at the ice, steam and sulphur points.
- (b) *From  $-190^{\circ}\text{C}$  to  $0^{\circ}\text{C}$*  : The platinum resistance thermometer using the formula  $R_t = R_0\{1 + at + bt^2 + c(t - 100)t^3\}$ , the constants  $a$ ,  $b$ ,  $c$  being determined from observations at ice, steam, sulphur and oxygen points.
- (c) *From  $660^{\circ}\text{C}$  to  $1063^{\circ}\text{C}$*  : The Pt-Pt-Rh thermometer with the cold junction at  $0^{\circ}\text{C}$ , while the temperature of the hot junction is defined by the e.m.f. equation  $E = a + bt + ct^2$ , the constants  $a$ ,  $b$ ,  $c$  being determined from observations at freezing point of antimony and at the silver and gold points.
- (d) *Above  $1063^{\circ}\text{C}$*  : An optical pyrometer (See section 7.14) calibrated at the gold point.

## PROBLEM

Study different thermometers in terms of their ranges and their relative advantages and disadvantages.

# Chapter 1

## First Law of Thermodynamics

### 1.1 First Law of Thermodynamics

Prior to the discovery of the first law of thermodynamics, it was only known that the mechanical energy was conserved in bulk motion (i.e., in motion of finite masses) in the absence of dissipative forces such as friction. At that time, heat was not known as a form of energy. But, later from intensive experiments conducted by Joule, Mayer, Rowland, Hirn and a host of other workers, it was established beyond doubt that *when mechanical energy is converted into heat, or vice versa, for each unit of mechanical energy converted into heat a definite amount of heat is generated and for each unit of heat converted into mechanical energy a definite amount of mechanical energy is produced.* This clearly shows that heat must be accepted as a form of energy, and so energy is conserved when mechanical energy in bulk motion is lost due to friction, etc. and appears in the form of heat. Quantitatively, the newly discovered truth may be stated thus: if  $W$  units of mechanical energy are converted into  $H$  units of heat, or *vice versa*, then

$$W = JH$$

or,  $W = H$ ,  $H$  being expressed in work unit here.

$J$  is a conversion constant known as Joule's mechanical equivalent of heat. Its value is about 4.2 joules/cal. This means that from 4.2 joules of mechanical energy, 1 cal of heat is obtained and vice versa. The above equation gives the mathematical formulation of the first law of thermodynamics. In the following sections of this chapter we shall make use of this fundamental law of nature.

### 1.2 Specific Heats of a Gas

Let us consider unit mass (or a gram-molecule\*) of a gas, contained in a cylinder with a very light, frictionless, movable piston on which weights may be put to change the pressure of

the gas (Fig. 1.1). Now heat is supplied through the conducting bottom to raise the temperature of the gas by  $1\text{ }^{\circ}\text{C}$ , keeping all the time the volume fixed by adding weights. The heat thus added in this case is known as the *specific heat (or gram-molecular specific heat, if a gm-molecule is taken) at constant volume*,  $C_v$ . Next, the experiment is repeated starting from the same initial condition. But now heat is added to raise the temperature by  $1\text{ }^{\circ}\text{C}$  without altering weights on the piston. The amount of heat added in this case is called the *specific heat (or gram-molecular specific heat, if a gm-molecule is taken) at constant pressure*,  $C_p$ . In this case, the gas expands doing work against gravity in raising the weights. Thus, evidently  $C_p$  is larger than  $C_v$ , because

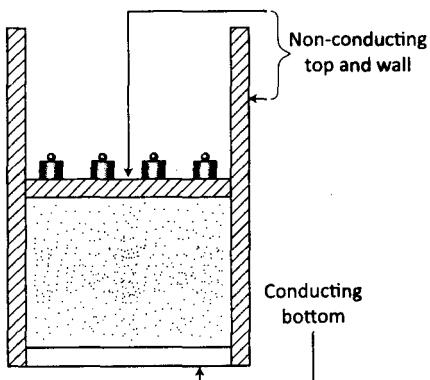


Fig. 1.1: Cylinder with piston

\*A gram-molecule of a gas is equal to its molecular weight expressed in grammes.

in addition to raising the temperature of the gas by  $1\text{ }^{\circ}\text{C}$ , heat required to do the work must also be supplied.

From above, it is clear that the specific heat of a gas depends upon the condition under which the heat is supplied. Constant volume and constant pressure are just two of innumerable possible sets of conditions. In fact, the specific heat of a gas may have any value from 0 to  $\infty$ . It becomes 0 where the temperature of the gas is raised by  $1\text{ }^{\circ}\text{C}$ , not by addition of heat but by compressing the gas by adding weights. The specific heat becomes  $\infty$  when the gas is allowed to expand (by removing weights) so that all the heat added is used up in doing work in expansion. In this case, there will be hardly any rise of temperature even by the addition of an infinite amount of heat.

Now, we proceed to find a relationship between  $C_v$  and  $C_p$ . Let us take a gram-molecule of a gas at pressure  $P$ , volume  $V$  and temperature  $T$ . Keeping the volume constant, the temperature is raised from  $T$  to  $T + dT$ . For this purpose, the heat supplied is

$$dU_1 = C_v dT \text{ (work unit implied).}$$

Next, we consider the rise of temperature from  $T$  to  $T + dT$ , keeping pressure constant. In this case, the volume  $V$  goes up to  $V + dV$  and an amount of work

$$dW = PdV$$

is done. Thus, we have the equation for the heat added:

$$dQ = C_p dT = dU_2 + dW.$$

Here  $dU_2$  is the heat required to raise the temperature by  $dT$  without any work done, and so must be same as  $dU_1$ . Thus  $dU$  represents the increase of *internal energy* of the gas. Then (in work units),

$$dQ = C_p dT = dU + PdV = C_v dT + PdV. \quad (1.1)$$

For a constant-pressure expansion, from  $PV = RT$ , we have

$$PdV = RdT. \quad (1.2)$$

From (1.1) and (1.2),

$$C_p - C_v = R. \quad (1.3)$$

If  $C_p$  and  $C_v$  are expressed in heat unit and  $R$  in work unit, then

$$C_p - C_v = \frac{R}{J^*} \quad (1.4)$$

In the above calculation, it has been assumed that no work has been done by the gas against molecular attraction during expansion at constant pressure.

### 1.3 Experimental Determination of $C_v$ : Joly's Method

The arrangement devised by Joly is known as a differential steam calorimeter. It consists of two hollow identical copper spheres ( $S, S$ ) (Fig. 1.2) suspended, by very fine wires ( $W, W$ ) from the arms of a highly sensitive balance, in a chamber into which steam can be introduced. The wires pass through two plugs of plaster of paris in the roof of the chamber. Just above the plugs

\*This relation was first derived by J.R.M. Mayer in 1842.

are two electrically heating wires to prevent any condensation of moisture in the openings so that the wires may move through them without obstruction. Small light trays are hung under both spheres in order to catch any drops of condensed water which may fall off them. Also shields are attached to the top of the chamber to prevent water condensed on the roof from falling on the spheres.

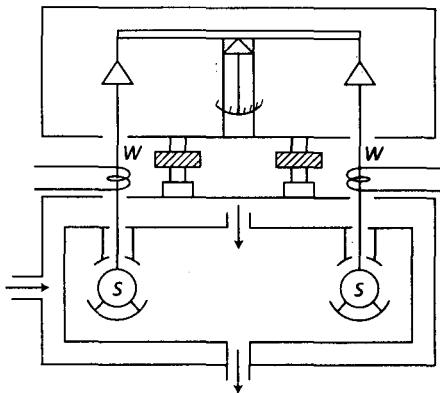


Fig. 1.2: Joly's calorimeter

Now, if the beam of the balance is brought into equilibrium by placing weights on one of the pans, the equilibrium will be preserved when the chamber is filled with steam, since equal masses of steam will be condensed on the two identical spheres.

One of the spheres is now filled with the experimental gas at a pressure of about 22 atmospheres, and the mass of this gas is determined by adding weights. Next,

steam is passed into the chamber. Now, a larger amount of steam will be condensed on the sphere containing the gas, because the gas will also require a certain quantity of heat to be raised to the temperature of steam, i.e., the final steady temperature.

Now, we take:

$m$  = mass of gas taken,  $c_v$  = specific heat of gas at constant volume,  $\theta_1$  = initial temperature of gas,  $\theta_2$  = final steady temperature (equal to steam temperature),  $\omega$  = mass of excess of steam condensed on the sphere containing the gas and  $L$  = latent heat of steam. Then, we have

$$mc_v(\theta_2 - \theta_1) = \omega L$$

giving

$$c_v = \frac{\omega L}{m(\theta_2 - \theta_1)}.$$

Corrections are made for a number of errors :

- (a) Expansion of the sphere containing the gas, both because of its own rise of temperature and because of the increase in pressure of the gas. Thus, the gas has actually expanded and hence done work so that the value of  $c_v$  obtained is slightly higher.
- (b) Unequal thermal capacities of the spheres. Thus, the spheres will absorb different amounts of heat from steam. This effect can be compensated by repeating the experiment with the spheres exchanging their roles.
- (c) The weight of condensed water must be reduced to vacuum condition.

**Exercise :** Given that  $c_v$  (per gram) = 2.402 cal for  $H_2$ ,

$$= 0.1721 \text{ cal for air,}$$

$$= 0.1684 \text{ cal for } CO_2,$$

find the corresponding values of  $c_p$  (per gram) for these gases. Take  $R = 4.28 \text{ joules/K}$ .

#### 1.4 Experimental Determination of $C_p$ : Regnault's Method

Regnault made an elaborate arrangement (Fig. 1.3) to find  $c_p$  of a gas. Pure and dry gas is stored in a reservoir  $R$  which is kept immersed in a constant-temperature water-bath  $W$ . The pressure of the gas in the reservoir is known at any instant from the mercury manometer  $M_1$ . By opening the stop-cock  $T_2$  and adjusting the screw valve  $V$ , gas can be allowed to flow at

a constant pressure which can be read from the manometer  $M_2$ . The gas then passes through a coiled tube  $C_1$  dipped in a hot oil-bath and then into the coiled tube  $C_2$  immersed in a calorimeter. Finally, the gas escapes into the atmosphere.

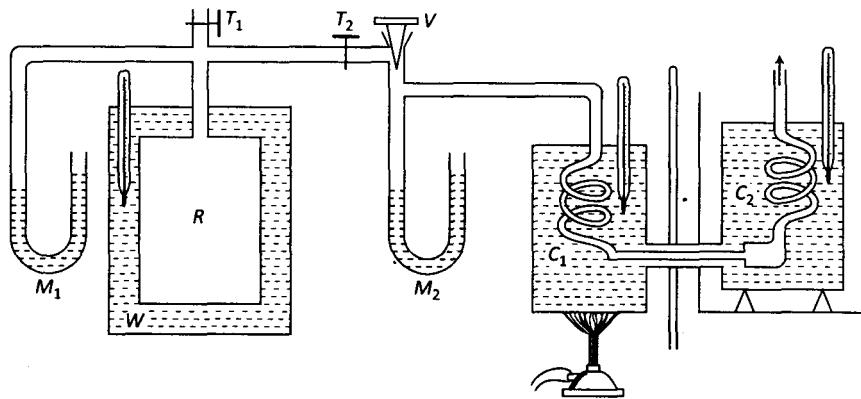


Fig. 1.3: Regnault's Apparatus

Let the temperature acquired by the gas in the oil bath be  $\theta$ . Let the temperature of the calorimeter be raised by the flow of the gas during the experiment from  $\theta_1$  to  $\theta_2$  so that for the flowing gas the final temperature may be taken =  $(\theta_1 + \theta_2)/2$ .

Now, if  $m$  be the mass of the gas that passes through the calorimeter during the experiment, then

$$mc_p \left( \theta - \frac{\theta_1 + \theta_2}{2} \right) = \omega(\theta_2 - \theta_1),$$

where  $\omega$  is the thermal capacity of the calorimeter and its contents.

$m$  can be found in the following way\* by assuming the gas to follow the law:  $PV = RT$ ,

$$\text{i.e., } \frac{P}{\rho} = CT, \quad (1.5)$$

where  $P$ ,  $\rho$ ,  $T$  are respectively pressure, density and temperature, and  $C$  is a constant equal to  $R/M$  ( $M$  = gm-mol mass). Let  $V$  and  $\theta$  be the volume and temperature (in centigrade scale) of the reservoir, and  $P_1$ ,  $P_2$  be the initial and final pressures of the reservoir. Also, we take  $\rho_1$ ,  $\rho_2$  as the initial and final densities. Then, from (1.5),

$$\frac{P_1}{\rho_1} = CT = C(273 + \theta) \quad \text{and} \quad \frac{P_2}{\rho_2} = C(273 + \theta).$$

From these equations, we obtain

$$\rho_1 - \rho_2 = \frac{(P_1 - P_2)}{C(273 + \theta)}. \quad (1.6)$$

If  $\rho_0$ ,  $P_0$ ,  $T_0$  (= 273 K) are the density, pressure and temperature respectively at N.T.P., then from (1.5),

$$\frac{P_0}{\rho_0} = CT_0 \quad (1.7)$$

\*In fact, Regnault found  $m$  by assuming that the weight  $W$  of the gas contained at pressure  $P$  and temperature  $\theta$  °C in the reservoir are given by

$$W(1 + \alpha\theta) = AP + BP^2 + CP^3,$$

where  $A$ ,  $B$ ,  $C$  are determined from a series of preliminary experiments. For details, see Searle's discussion in *Proc. Camb. Phil. Soc.*, 13, Pp. 106, 321.

Then, eliminating  $C$  between (1.6) and (1.7), we find

$$m = (\rho_1 - \rho_2)V = V \cdot \frac{273}{273 + \theta} \cdot \frac{P_1 - P_2}{P_0} \cdot \rho_0 \quad (1.8)$$

## 1.5 Isothermal and Adiabatic Changes

Let the cylinder of Fig. 1.1 be made of a perfect conductor of heat. Then, if the gas is allowed to expand by gradual removal of weights (or compressed by gradual addition of weights) such that the temperature of the gas remains constant by flow of heat from outside (or by outflow of heat from inside), then such a change of the gas is called an *isothermal change*. In this case, any work done by the gas in expansion is at the cost of heat coming from outside. Also, any heat generated by work done on the gas during compression flows out.

Next, let us suppose, the cylinder is made of a non-conductor of heat. In this case, there can be no communication of heat between inside and outside. Now, any work done by the gas during expansion is at the cost of its internal energy so that its temperature falls. On the other hand, any heat generated by work done on the gas during compression remains in the gas and the temperature rises. These changes where there is no communication of heat between inside and outside are called *adiabatic changes*.

Now, let us take a gram-molecule of a gas contained in a non-conducting cylinder (Fig. 1.1). If the gas is allowed to expand from volume  $V$  to volume  $V + dV$  by removal of weights, there will be a fall of temperature from  $T$  to  $T - dT$  (say), because the change here is evidently adiabatic. Then,

$$\text{loss of internal heat energy} = \frac{(\text{work done})}{J} \quad \text{or,} \quad -C_v dT = \frac{PdV}{J},$$

where  $P$  is the pressure of the gas initially\*. If  $C_v$  is expressed in work unit,

$$C_v dT + PdV = 0. \quad (1.9)$$

Let us suppose, the gas obeys the equation

$$PV = RT. \quad (1.10)$$

Then, from (1.10) by differentiation,

$$dPV + PdV = RdT. \quad (1.11)$$

From (1.9) and (1.11), eliminating  $dT$ ,

$$\frac{C_v}{R}(dPV + PdV) + PdV = 0.$$

Substituting  $C_p - C_v$  for  $R$ ,

$$C_v VdP + C_p PdV = 0.$$

If we write  $C_p/C_v = \gamma$ ,

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0.$$

\*If  $A$  is the area of the piston, the force exerted by the gas on it =  $PA$ . Then, if it is raised by the gas through a distance  $dx$ , work done by the gas =  $PA \times dx = P(dxA) = PdV$ .

On integration,

$$\log_e P + \gamma \log_e V = \log_e C \text{ (a constant)}$$

or,  $PV^\gamma = C$ .

(1.12)

This is the adiabatic equation for a gas which obeys (1.10). Such a gas is usually called a perfect gas. (The reason for this nomenclature will be clear in Chapters 2 and 3.)

Now, from (1.10) and (1.12), eliminating  $P$ , we get

$$TV^{\gamma-1} = \text{const} \quad (1.13)$$

and eliminating  $V$ , we get

$$TP^{(1-\gamma)/\gamma} = \text{const.} \quad (1.14)$$

**Exercise 1.** Find expressions for the work done by a gas undergoing (a) isothermal change, (b) adiabatic change.

*Hints:* Take  $PdV$  as the work done for an elementary change in volume by  $dV$ . (For (a), integrate it using  $PV = \text{const}$ . For (b), integrate it using  $PV^\gamma = \text{const}$ .)

**Exercise 2.** A football is pumped to a pressure of one and a half atmospheres at 30 °C. Calculate the change in temperature, if any, (a) when it leaks slowly, (b) when it suddenly bursts.

## 1.6 Determination of $\gamma$

We shall discuss an adiabatic expansion method to find  $\gamma$ , the ratio of specific heats of a gas. In fact, Clément and Désormes\* were the first to find  $\gamma$  by such a method. We shall, however take up a method due to Lummer and Pringsheim\*\* and later improved by Partington†.

If  $P_1, T_1$  are the pressure and temperature of a gas before adiabatic expansion and if  $P_2, T_2$  are their values after the expansion, then from (1.14),

$$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}.$$

Taking logarithm of both sides and rearranging,

$$(1 - \gamma) \log_e \left( \frac{P_1}{P_2} \right) = \gamma \log_e \left( \frac{T_2}{T_1} \right)$$

or,  $\gamma \left\{ \log_e \left( \frac{T_2}{T_1} \right) + \log_e \left( \frac{P_1}{P_2} \right) \right\} = \log_e \left( \frac{P_1}{P_2} \right)$

Hence,  $\gamma = \frac{\log_e \left( \frac{P_1}{P_2} \right)}{\log_e \left( \frac{P_1}{P_2} \right) + \log_e \left( \frac{T_2}{T_1} \right)}$ . (1.15)

So, a knowledge of the values of pressure and temperature before and after adiabatic expansion will give us  $\gamma$ .

Partington's apparatus is shown in Fig. 1.4. The experimental gas is passed through the drying tubes  $F$  and stored at a high pressure (denoted by the manometer,  $m$ ) in a large spherical vessel  $A$  of 130 litres capacity. The vessel is immersed in a water-bath which is well stirred

\* *Observations sur la Physique*, Vol. 89, Pp. 321, 428 (1889).

\*\* *B. A. Reports*, P. 565 (1894).

† *Proc. Roy. Soc.*, A, Vol. 100, P.27 (1921).

by  $S$ . A carefully standardised mercury thermometer  $T$  reads the temperature of the bath up to  $0.01\text{ }^{\circ}\text{C}$ .

At the centre of  $A$  is a bolometer,  $X$ , of a very fine platinum wire (0.001 to 0.002 mm in diameter) connected to one arm of a Wheatstone bridge. The vessel is provided with an expansion valve  $V$  operated by a spring  $N$  such that the size of the aperture may be suitably adjusted\*.

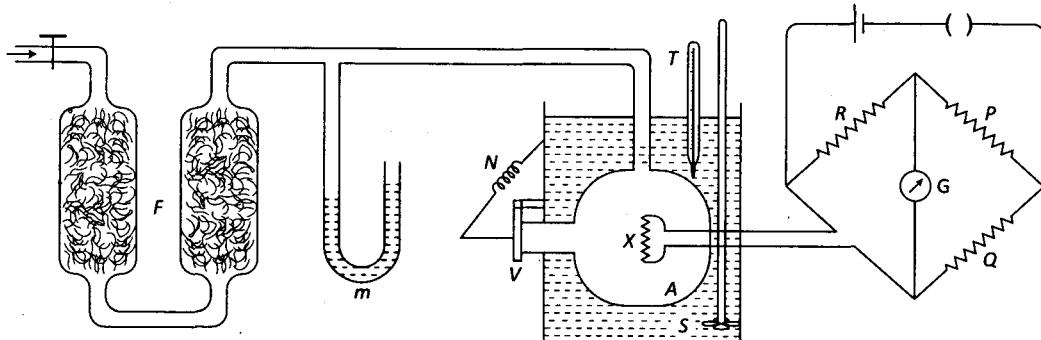


Fig. 1.4: Partington's apparatus

After the gas is stored in the vessel  $A$ , the initial temperature,  $T_1$  and pressure  $P_1$  are noted. Then, the valve is suddenly opened and the pressure immediately falls to a steady value  $P_2$  equal to the atmospheric pressure provided the aperture has been suitably adjusted to a proper size (See footnote). The final temperature,  $T_2$ , is found in the following way. The resistance in one arm of the Wheatstone bridge is altered to give some deflection in the galvanometer before the actual expansion takes place. This is so arranged by trials that immediately after expansion the deflection becomes zero. So immediately after opening the valve, bits of ice are added to the water bath to keep its temperature constant and equal to that attained immediately after expansion. This can be ascertained by keeping the galvanometer deflection steadily at zero. The temperature of the bath under these conditions read from  $T$  gives the final temperature  $T_2$ .

**Exercise :** From the above experiment, Partington found for air a value of  $\gamma$  equal to 1.403. Check up the correctness of this result by calculating the velocity of sound in air at N.T.P. Take density of air at N.T.P. = 0.001293 gm/cc.

## 1.7 Specific Heats of Solids at Low Temperatures

We close this chapter with a discussion of the specific heats of solids at low temperatures, because this has immense theoretical importance. It will be found in section 2.12 that this is inexplicable on the basis of classical physics. In chapter 8, attempts will be made to explain the anomaly on the basis of quantum theory.

Here we shall present the method developed by Nernst and Lindemann\*\* for measuring the specific heat at low temperatures. The arrangement for good conducting solids is shown in Fig. 1.5(a). The calorimeter  $B$  is the substance itself shaped into a thick cylinder with a circular rod  $P$  along the axis.  $P$  is wound over with pure platinum wire  $C$  which is insulated from it with paraffin paper. Finally, the inter-space is filled with liquid paraffin for good thermal

\*If the aperture is too large, oscillations of the gas take place (gas once goes out and then comes into the vessel) and the galvanometer deflection is not steady. If the aperture is too narrow, expansion of gas becomes slow, and so not adiabatic. Hence, the aperture is so adjusted that it is of the proper size and the galvanometer deflection is steady.

\*\* *Journal de Physique* (4) 1910, Vol. 9; *Ann. d. Phys.*, Vol. 36, P. 395 (1911).

communication. The calorimeter is suspended by connecting leads (i.e., wires) in a pear-shaped glass bulb  $A$  with an outlet  $O$ .  $A$  can be filled with any gas or evacuated through  $O$ . The whole system is kept in a low-temperature bath of liquid air or liquid hydrogen. In order to bring the calorimeter to the temperature of the bath, hydrogen (a good conductor of heat) is introduced into  $A$  and after some time the gas is completely removed so that heat losses due to conduction and radiation are minimised.

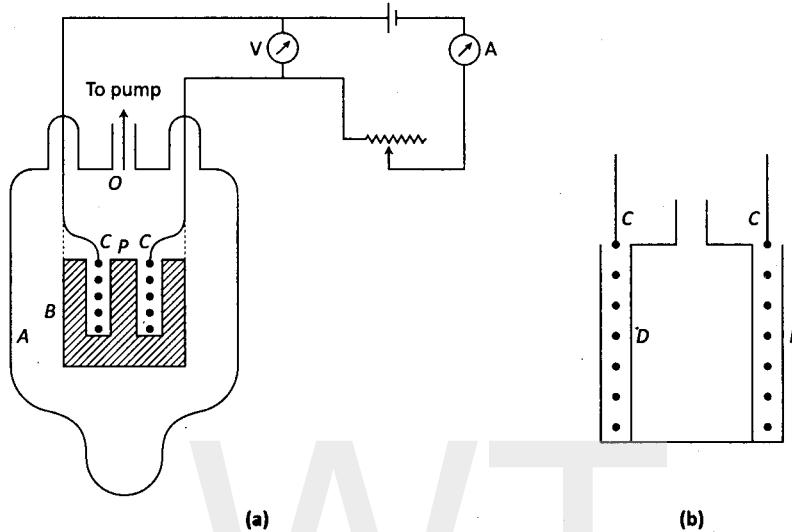


Fig. 1.5: Nernst-Lindemann experiments

The mass  $m$  of the substance (i.e., the calorimeter) is obtained. Then, a current is passed through the platinum wire for time  $t$  during which the potential difference  $V$  across the wire is maintained constant by adjusting the rheostat. Let  $I_1$  and  $I_2$  be the currents at the beginning and at the end of the experiment. Then, by Ohm's law, the resistances of the platinum wire at the beginning and at the end are respectively  $R_1 = V/I_1$  and  $R_2 = V/I_2$ . From the change in resistance ( $R_2 - R_1$ ), the small rise in temperature  $\delta\theta$  can be found out. Finally, from the average current  $I [= (I_1 + I_2)/2]$ , the heat developed,  $VIt/J$  cal\*, is calculated. If  $c$  is the specific heat, then

$$\frac{VIt}{J} = mc\delta\theta + h.$$

where  $h$  is a small correction for any heat lost due to radiation. In this experiment, the rise of temperature being very small, the value of specific heat is practically obtained at a particular temperature.

Now, for non-conducting solids, the calorimeter is a cylindrical silver vessel  $D$  (Fig. 1.5(b)) over which the platinum wire  $C$  is wound with necessary insulation as explained above. The whole system is covered with silver foil  $F$  to minimise heat loss. The solid (or liquid or gas) whose specific heat is to be found is put in the silver vessel which maintains a uniform temperature throughout because of its high conductivity. The silver calorimeter is suspended inside the pear-shaped glass bulb during the experiment.

\*The current in a wire is due to the electric field inside it pushing forward the electrons. Thus, the electric field does work (here it is  $VI$ ) which converts the electrical energy into the mechanical (i.e., kinetic) energy of electrons. Finally, this mechanical energy is converted into heat in the wire due to collisions between electrons and atoms (ions) (See section 2.1).

## 1.8 Break-down of Dulong-Petit Law at Low Temperatures

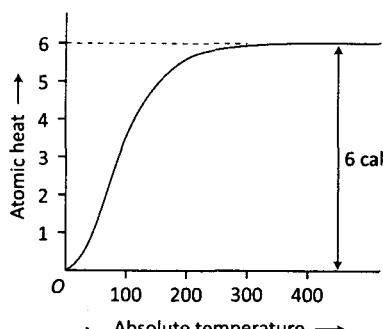


Fig. 1.6: Break-down of Dulong-Petit law

Dulong and Petit carried out investigations on the specific heats of elements in the solid state and enunciated in 1819 a law (called Dulong-Petit law): The atomic heat (i.e., the heat required by a gram-atom\* of a solid element for unit rise of temperature) is the same for all elements in the solid state and is equal to about 6 cal.

But, now, measurements of specific heats by Nernst and his co-workers show that below a certain temperature characteristic of each solid element, the atomic heat falls rapidly with temperature and tends to zero value at absolute zero for all elements (Fig. 1.6). This is explained by quantum theory (See Chapter 8).

## PROBLEMS

1. Point out the significance of the first law of thermodynamics.
2. A gas at 27 °C and 76 cm of mercury is allowed to expand adiabatically until its volume is doubled, and then isothermally until it is redoubled. Calculate the final pressure and temperature. ( $\gamma = 1.40$ ).
3. A gram-molecule of a perfect diatomic gas under atmospheric pressure and at temperature 30 °C is adiabatically compressed to a pressure of 100 atmospheres. Find the rise in temperature of the gas.
4. A volume of helium gas at 27 °C and at a pressure of 20 atmospheres is compressed adiabatically to a pressure of 200 atmospheres. Calculate the final temperature.
5. A quantity of heat  $dQ$  is added to a gas. Then, in general, its internal energy is increased by  $dU$  and an amount of work  $PdV$  is done:  $dQ = dU + PdV$ . From this expression show that

$$C_v = \left( \frac{dU}{dT} \right)_v, \quad C_p = \left( \frac{dU}{dT} \right)_p + P \left( \frac{dV}{dT} \right)_p.$$

6. Calculate the work done by a gram-molecule of a gas during a quasi-static, isothermal expansion from an initial volume  $V_1$  to a final volume  $V_2$ , the equation of state being given by

$$PV = RT - \frac{a}{V} + bP.$$

7. Calculate  $C_p$  and  $C_v$  for a gram-molecule of a gas whose equation of state is given above and whose internal energy is given by

$$U = CT - \frac{a}{V}.$$

8. Rüchardt's Experiment\*\* (*Phys. Zeits.*, 30, 57, 1929)—A large glass-bottle of volume  $V$  is fitted airtight with a vertical glass-tube at the top. If a steel ball of mass  $m$  which fits accurately in the tube, is dropped into the tube, it begins to oscillate up and down and comes to rest after a few oscillations. Show that

$$T = 2\pi \sqrt{\frac{mV}{\gamma PA^2}}.$$

where  $T$  is the period of oscillation,  $P$  is the pressure in the bottle when the ball is in position of equilibrium inside the tube, and  $A$  is the cross section of the tube. [Assume adiabatic conditions to obtain in the bottle during oscillation and use the relation  $PV^\gamma = \text{const.}$ ]

\*A gram-atom of an element is equal to its atomic weight expressed in grammes.

\*\*See also Saha and Srivastava, *A Treatise on Heat*, Pp. 97–8, (1958).

## Chapter 2

# Kinetic Theory of Gases

### 2.1 Fundamental Postulates of Kinetic Theory

The philosophy of theoretical physics in the nineteenth century was to explain physical phenomena on Newtonian mechanics, i.e., in terms of Newton's laws of motion. The kinetic theory of matter—in particular, of gases—developed exactly on this idea. Bernoulli explained Boyle's law on the basis of kinetic theory in the eighteenth century (1730), about a hundred years before the theory itself was formally accepted by the scientific world and was placed on a firm mathematical foundation by Clausius, Maxwell and Boltzmann. So Bernoulli may be considered as the founder of this theory.

The kinetic theory of matter is based on two fundamental postulates :

- (a) The first postulate is the chemical hypothesis that matter consists of tiny particles, called molecules, and that molecules of the same substance are all identical in size, shape, mass, etc. This is exactly Dalton's theory of matter.
- (b) The second postulate is that the molecules of a substance are in constant motion which is closely related to temperature. This postulate comes directly from the experiments of Rumford, Joule, Mayer and Colding. They established the fact that heat is a form of energy (See section 1.1) so that heat added to a system may appear only as the increase in molecular kinetic energy. Then, if the temperature is constant, the total kinetic energy of molecules (or average kinetic energy of a molecule) is also constant. [In fact, Bernoulli pointed out that the average kinetic energy of a gas molecule is directly proportional to the temperature\* ( $T$ ).]

The truth of these postulates is supported by a large number of physical phenomena such as (i) the bursting of a balloon when heated in the sun, (ii) the unlimited expansibility of a gas, (iii) diffusion of gases, liquids and solids (e.g., gold is found to diffuse into lead), (iv) Brownian motion (see section 2.23), etc. Also the kinetic theory of gases stands on a solid basis due to the fact that various gas laws can be deduced from it.

We can also qualitatively understand from kinetic theory how, by heating, a solid is converted into a liquid and a liquid into a gas. When a solid is gradually heated and the molecules gain more and more kinetic energy, a stage arrives when the cohesive forces can no longer keep the molecules rigidly in their respective positions. At this stage, however, these forces are still strong enough to prevent the molecules from flying apart. The body is no longer rigid now, but yet maintains a finite volume. It is now a liquid. On further heating, the molecules move so fast that they tear apart from one another and fly off in all directions. We have now a gas with a tendency towards unlimited expansion. The fact that some substances melt and evaporate at much lower temperatures is due to the differences in the strength of cohesive forces among their respective molecules.

\*See J. De Boer's article in *Physics*, edited by R. Kronig, (English Translation), Pp. 540–41, (1959), Pergamon Press.

## 2.2 Some General Assumptions for Gases

In order to simplify the calculations carried out on the basis of the above postulates, in this chapter, we make the following general assumptions. They may be reinforced by other assumptions to solve some particular problems.

- The molecules of a gas behave like hard, elastic spheres so that when they collide among themselves or with the wall of the containing vessel, there is no loss of kinetic energy.
- The gas is in a state of molecular chaos. This means that the molecules are moving in all directions with all possible velocities.
- The time during which a collision lasts is very small compared with the time required to travel the distance between two consecutive collisions.
- The molecules exert no forces on one another except when they actually collide. This means that they move in straight lines between two consecutive collisions. In other words, there is no intermolecular attraction.

## 2.3 Pressure of a Perfect Gas : Clausius' Treatment\*

In addition to the above assumptions, we adopt here the further assumption that the molecules are infinitely small, i.e., just like point-particles. A gas having all these properties is called a perfect or an ideal gas. We now proceed to calculate the pressure exerted by such a gas when the molecules bombard the wall of the containing vessel.

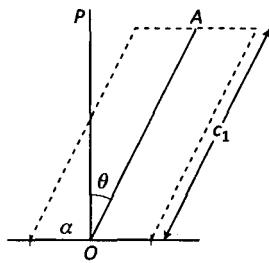


Fig. 2.1: Wall area

Let  $n$  be the number of molecules per unit volume. We divide these molecules into a number of classes such that all the molecules of any one class possess about the same velocity. Let  $n_{c_1}, n_{c_2}, n_{c_3}, \dots$  be the numbers per unit volume in these classes ( $c_1, c_2, c_3, \dots$  being their respective velocities) so that

$$n_{c_1} + n_{c_2} + n_{c_3} + \dots = n.$$

We calculate first the pressure due to  $c_1$ -molecules (i.e., molecules having velocity  $c_1$ ) only. We take an area  $\alpha$  at  $O$  on the wall [Fig. 2.1].  $PO$  is perpendicular to  $\alpha$ . We first start with those  $c_1$ -molecules which are coming in the  $(\theta, \phi)$ -direction (i.e., at angle  $\theta$  with  $PO$ ) [See Fig. 2.2.(a)] and hitting the area  $\alpha$  per second. For this purpose, on  $\alpha$  we draw an inclined cylinder  $AO$  of length  $c_1$  so that all the  $c_1$ -molecules existing in the cylinder at any instant and coming in  $(\theta, \phi)$ -direction will strike  $\alpha$  in one second. The total number of  $c_1$ -molecules at any instant in the cylinder is  $n_{c_1} \times c_1 \cos \theta \times \alpha$ , but they are travelling in all directions. It should be noted that the probability of a  $c_1$ -molecule moving exactly in the  $(\theta, \phi)$ -direction is almost nil. So we find the number of  $c_1$ -molecules moving in directions between  $\theta & \theta + d\theta$  and  $\phi & \phi + d\phi$  [Fig. 2.2 (a)]. The directions of these molecules may be represented as passing normally into a cone,  $M$ , through the area  $ds = r^2 \sin \theta d\theta d\phi$  ( $r$  may have any value), the cone denoting here a bundle of directions between  $\theta & \theta + d\theta$  and  $\phi & \phi + d\phi$ . On the other hand, the directions of all the  $n_{c_1} c_1 \alpha \cos \theta$  molecules may be represented as passing into a sphere  $S$  through the area  $= 4\pi r^2$  [Fig. 2.2 (b)]. Hence, the number of  $c_1$ -molecules coming in directions between  $\theta & \theta + d\theta$  and  $\phi & \phi + d\phi$  and hitting the area  $\alpha$  per sec is

$$dn_{c_1 \theta \phi} = \frac{r^2 \sin \theta d\theta d\phi}{4\pi r^2} (n_{c_1} c_1 \alpha \cos \theta) = \frac{\sin \theta d\theta d\phi}{4\pi} \times (n_{c_1} c_1 \alpha \cos \theta). \quad (2.1)$$

\*See W. Wilson, *Theoretical Physics*, Vol. I, P. 218 (1931).

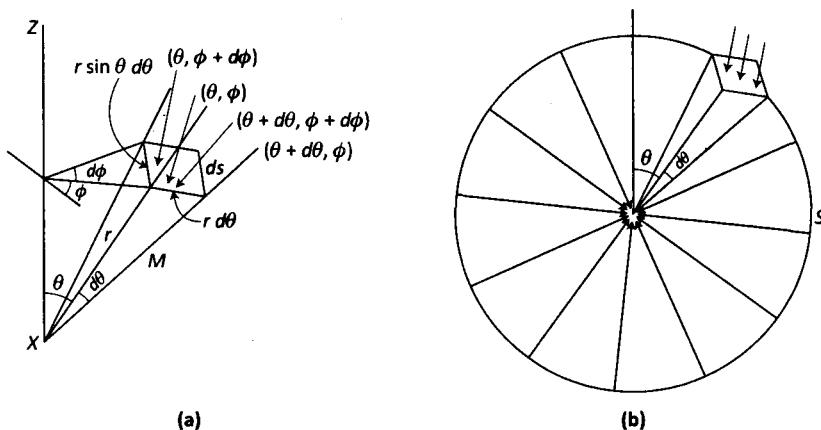


Fig. 2.2: Spherical coordinates

Now, each such molecule has, normal to  $\alpha$ , a component of velocity  $c_1 \cos \theta$  which will be reversed on impact, giving to the wall an impulse (by Newton's third law)  $2mc_1 \cos \theta$  ( $m$  being the molecular mass), whereas the component  $c_1 \sin \theta$  parallel to  $\alpha$  will remain unaffected.

Then, force on  $\alpha$  = momentum imparted to  $\alpha$  per sec

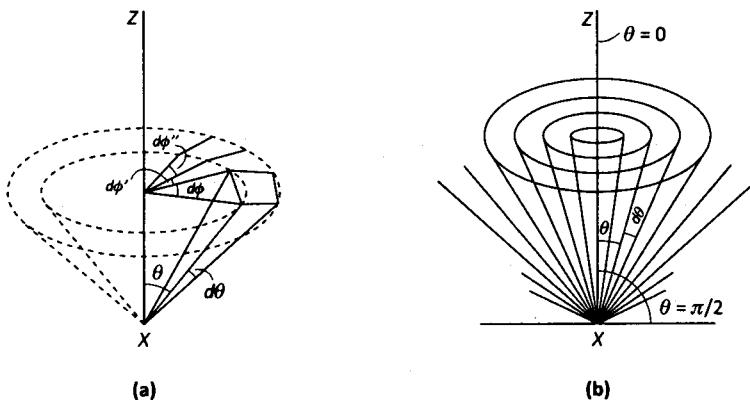
$$= 2mc_1 \cos \theta \times \frac{\alpha}{4\pi} n_{c_1} c_1 \cos \theta \sin \theta d\theta d\phi.$$

Thus, we have for the pressure exerted by these molecules

$$dP_{c_1\theta\phi} = \frac{1}{2\pi} n_{c_1} mc_1^2 \cos^2 \theta \sin \theta d\theta d\phi. \quad (2.2)$$

Then, the total pressure exerted by  $c_1$ -molecules is obtained by integrating over  $\theta$  and  $\phi$  [visualise these integrations from Figs. 2.3 (a) and (b)] :

$$\begin{aligned} P_{c_1} &= \int dP_{c_1\theta\phi} = \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi/2} \frac{1}{2\pi} n_{c_1} mc_1^2 \cos^2 \theta \sin \theta d\theta d\phi. \\ &= \frac{1}{3} n_{c_1} mc_1^2. \end{aligned} \quad (2.3)$$

Fig. 2.3: (a)  $\sum d\phi = 2\pi$  ( $\phi$ -integration) (b) ( $\theta$ -integration) From cone of  $\theta = 0$  to cone of  $\theta = \pi/2$

Thus, the pressure on the wall due to all kinds of molecules,

$$\begin{aligned} P = P_{c_1} + P_{c_2} + \dots &= \frac{1}{3}m(n_{c_1}c_1^2 + n_{c_2}c_2^2 + \dots) = \frac{1}{3}nm\frac{(n_{c_1}c_1^2 + n_{c_2}c_2^2 + \dots)}{n}, \\ &= \frac{1}{3}nm\bar{c^2}, \end{aligned} \quad (2.4)^*$$

where  $\bar{c^2}$  is the mean square velocity (i.e., the mean of the squares of the molecular velocities). (2.4) may also be written as

$$P = \frac{1}{3}\rho\bar{c^2} = \frac{1}{3}\rho C^2 \quad (2.5)$$

( $\rho = nm$  and  $C^2 = \bar{c^2}$ ,  $C = \sqrt{\bar{c^2}}$  being called root mean square (RMS) speed)

$$= \frac{2}{3}\left(\frac{1}{2}\rho C^2\right) = \frac{2}{3} \times (\text{kinetic energy/vol}). \quad (2.6)$$

So we find that the pressure of a perfect gas is numerically equal to two-third of the kinetic energy of translation per unit volume.

#### Note :

- (1) In the above calculation, we have not considered the probability that a molecule may be prevented by collision from reaching the wall. But it should be remembered that at the beginning of this section it has been assumed that molecules are just like point-particles. In that case, collisions become highly improbable\*\*.
- (2) One may wonder if such a perfect or an ideal gas is at all realised in practice. A real gas at a high temperature and at an extremely low pressure approaches such a perfect gas. Because, (i) on account of high kinetic energy at a high temperature intermolecular attraction becomes quite ineffective, and, (ii) at extremely low pressure, molecules hardly meet one another and therefore behave just like point-particles which hardly collide with one another†.

## 2.4 Deduction of Gas Laws

(a) **Boyle's Law** : For a gram-molecule of a gas of mass  $M$  and volume  $V$ , we obtain from (2.5)

$$P = \frac{1}{3} \frac{M}{V} C^2$$

$$\text{or, } PV = \frac{1}{3}MC^2 = \frac{2}{3}\left(\frac{1}{2}MC^2\right). \quad (2.7)$$

Here we find that the pressure is inversely proportional to volume at constant temperature, because  $\frac{1}{2}MC^2$  is constant at constant temperature by second postulate of kinetic theory.

(b) **Avogadro's Law** : For two gases at the same pressure, we have from (2.4),

$$P = \frac{1}{2}n_1m_1C_1^2 = \frac{1}{3}n_2m_2C_2^2. \quad (2.8)$$

\*This expression of pressure was first given by Bernoulli in 1730. However, the calculation presented here is due to Clausius (given probably about 1857).

\*\*See, for example, G. Joos, *Theoretical Physics*, P. 555 (1956).

†If we consider molecular size and intermolecular attraction, (2.4) [or (2.5) or (2.6)] gets modified into an equation for real gases. This is van der Waals equation (See Chapter 3)

Further, if they are at the same temperature, the mean kinetic energy per molecule in one gas will be equal to that per molecule in the other gas according to the second postulate of kinetic theory (section 2.1), i.e.,

$$\frac{1}{2}m_1C_1^2 = \frac{1}{2}m_2C_2^2. \quad (2.9)$$

From (2.8) and (2.9),

$$n_1 = n_2. \quad (2.10)$$

Thus, two gases at the same temperature and pressure possess the same number of molecules per unit volume. This is Avogadro's law.

**N.B. :** We give here a simple deduction of *Avogadro number*,  $N$ . Suppose, a gram-molecule of a gas  $X$  has  $N$  molecules, each of molecular weight  $M$ . Then, the mass of a gram-molecule of the gas is  $M$  gm. Then,

$$M \text{ gm} = [1.66 \times 10^{-24} \text{ gm (atomic mass unit)} \times M] \times N$$

$$\therefore N = (1.66 \times 10^{-24})^{-1} = 6.02 \times 10^{23} \text{ (Avogadro number).}$$

**(c) Dalton's Law :** If a number of gases having densities  $\rho_1, \rho_2, \dots$  and mean square velocities  $C_1^2, C_2^2, \dots$  are mixed in the same volume, then the total pressure is, from (2.6),

$$\begin{aligned} P &= \frac{2}{3} \times (\text{total kinetic energy/volume}) \\ &= \frac{2}{3} \left\{ \frac{1}{2}\rho_1C_1^2 + \frac{1}{2}\rho_2C_2^2 + \dots \right\} = \frac{1}{3}\rho_1C_1^2 + \frac{1}{3}\rho_2C_2^2 + \dots \\ &= P_1 + P_2 + \dots \end{aligned} \quad (2.12)$$

This is Dalton's law of partial pressures. We obtain the law here because of the fact that the pressure is proportional to kinetic energy per unit volume and that the kinetic energy is a physical quantity of additive character\*.

Thus, we have been able to deduce, on the basis of kinetic theory, a number of gas laws which were much earlier discovered from experiments. It is, however, evident that these laws are true only within the limits imposed by the assumptions adopted in the above calculations.

## 2.5 Relation between $C$ and $T$

For a gram-molecule of a gas at a very low pressure and at a high temperature, we have the experimentally observed law

$$PV = RT. \quad (2.13)$$

Comparing (2.13) with the theoretically obtained law (2.7),

$$\begin{aligned} \frac{1}{3}MC^2 &= RT \\ \text{or, } \frac{1}{2}mC^2 &= \frac{3}{2}\frac{R}{N}T = \frac{3}{2}kT, \end{aligned} \quad (2.14)$$

where  $m$  is the mass of a molecule,  $N$  the number of molecules in a gram-molecule (called Avogadro Number  $= 6.023 \times 10^{23}$ ) and  $k$  the Boltzmann constant. The relation expressed in

\*See Loeb, *Kinetic Theory of Gases*, Pp. 24–25 (1927); Roberts and Miller, *Heat and Thermodynamics*, P. 73 (1962).

(2.14) is a very important relation connecting quantitatively the average kinetic energy of a molecule and the temperature.

From (2.14) one may readily infer that at  $T = 0$ , the molecules will be at complete rest. But this inference is not at all tenable for the following reasons : (a) (2.14) deduced for a gas at low pressure and at high temperature cannot be expected to hold down to  $T = 0$  where it is definitely in the solid state. (b) The interpretation of  $T = 0$  given by classical thermodynamics (See Chapter 5) is quite different and more reasonable also. (c) Finally, according to modern quantum theory, molecules may have even at  $T = 0$  some energy, called the null-point or zero-point energy (*Nullpunktssenergie*)\*

**Exercise 1.** Show that the mean square velocities of the molecules of different gases passing through a porous wall under the same pressure are inversely proportional to the densities of the respective gases. (Graham's experiment)

**Exercise 2.** Calculate the root mean square velocity of an air molecule at N.T.P. Take  $\rho = 0.001293 \text{ gm/cc}$  at N.T.P.

**Exercise 3.** Find the average kinetic energy of a chlorine molecule at the boiling point of water. Take  $R \approx 2 \text{ cal}$ .

## 2.6 Maxwell's Law\*\* of Speed Distribution

Before proceeding to discuss the distribution of velocities among the molecules of a gas, let us first acquaint ourselves with some realities of the problem : (a) Molecules are too small to be visible even in an ultramicroscope. (b) The number of molecules per unit volume (about  $2.7 \times 10^{19}/\text{cc}$  at N.T.P.) is very large. (c) No particular molecule possesses the same speed all the time, because, at each collision, its velocity will be changed. Under such circumstances, Maxwell did not at all consider it worthwhile to study the behaviour of individual molecules. On the other hand, he proceeded to find the number of molecules possessing in a steady state (i.e., at constant temperature and pressure), velocities in a certain range, say, between  $c$  and  $c + dc$ . For this purpose, he assumed that in the steady state, this number remains constant and is not altered by collisions. He applied the laws of probability† to tackle this problem.

Let us suppose that the components of a molecular velocity  $c$  are denoted by  $u, v, w$  along

\*See Saha and Srivastava, *A Treatise on Heat*, P. 129 (1958).

\*\*J. C. Maxwell, Collected Works, 1, 380.

†The concept of probability may be briefly introduced in the following manner to a pedestrian. Let us suppose, a certain society *A* desires to distribute 30 prizes by lottery among 40 equally qualified students. Then, the probability of a student getting a prize is given by

$$P_A = \frac{30 \text{ actual prize-winners}}{40 \text{ students}} = \frac{3}{4}.$$

Hence, the no. of actual prize-winners = probability of getting a prize  $\times$  total no. of students.

This is called simple probability. The maximum value of probability is unity, when it becomes a certainty, i.e., when, say, 40 prizes are to be distributed among 40 students. Next, let us suppose, another entirely independent society *B* also desires to distribute 20 prizes by lottery to the same 40 equally qualified students. Then, in this case, (as already stated) the probability is

$$P_B = \frac{20 \text{ actual prize-winners}}{40 \text{ students}} = \frac{1}{2}.$$

This is also simple probability. Now, if we ask, "What is the probability of a student getting a prize both from *A* and *B*? ", then this probability is called compound probability and is given by the product of independent probabilities. Thus, it is

$$P = P_A \times P_B = \frac{3}{4} \times \frac{2}{4} = \frac{3}{8}.$$

Evidently,  $P$  is less than  $P_A$  or  $P_B$ , as one may easily guess.

$x, y, z$  axes respectively. Now the probability of a molecule having a particular value for component  $u$  exactly is evidently zero, because  $u$  can have any value between  $+\infty$  and  $-\infty$ . But the probability of its having a component between  $u$  and  $u + du$  will have some finite value. It will depend, in general, upon both  $u$  and  $du$ . Let us denote it by  $f(u)du$ , where  $f(u)$  is a function of  $u$  (called *probability density function* in statistics). In the same fashion, the probability of the  $y$ -component lying between  $v$  and  $v + dv$  is  $f(v)dv$  and that for the  $z$ -component lying between  $w$  and  $w + dw$  is  $f(w)dw$ . Then the compound probability of a molecule having its velocity components lying between  $u$  and  $u + du$ ,  $v$  and  $v + dv$ , and  $w$  and  $w + dw$  is

$$P_{uvw} = f(u)f(v)f(w)dudvdw. \quad (2.15)$$

Now,  $f(u)f(v)f(w)$  is evidently a function of  $u, v, w$  which constitute the resultant velocity  $c$ . Then, we may write

$$f(u)f(v)f(w) = F(c^2). \quad (2.16)$$

Also we have

$$u^2 + v^2 + w^2 = c^2. \quad (2.17)$$

Taking logarithm of both sides of (2.16) and differentiating (with  $c$  constant),

$$\frac{\frac{df(u)}{du}}{f(u)}du + \frac{\frac{df(v)}{dv}}{f(v)}dv + \frac{\frac{df(w)}{dw}}{f(w)}dw = 0. \quad (2.18)$$

Also differentiating (2.17) (with  $c$  constant)

$$udu + vdv + wdw = 0. \quad (2.19)$$

It is possible to combine (2.18) and (2.19) by multiplying (2.19) by an *arbitrary* parameter  $\beta$  and adding to (2.18) :

$$\left( \frac{\frac{df(u)}{du}}{f(u)} + \beta u \right) du + \left( \frac{\frac{df(v)}{dv}}{f(v)} + \beta v \right) dv + \left( \frac{\frac{df(w)}{dw}}{f(w)} + \beta w \right) dw = 0. \quad (2.20)$$

Since  $du$ , etc. are *arbitrary* variations, the coefficient of each of them should independently vanish. Then, we have

$$\frac{\frac{df(u)}{du}}{f(u)} + \beta u = 0, \quad \frac{\frac{df(v)}{dv}}{f(v)} + \beta v = 0, \quad \frac{\frac{df(w)}{dw}}{f(w)} + \beta w = 0 \quad (2.21)$$

Integrating the first of these equations first,

$$\log_e f(u) = -\frac{1}{2}\beta u^2 + \log_e a$$

$$\text{or, } f(u) = ae^{-\frac{1}{2}\beta u^2}, \quad (2.22)$$

where  $a$  is a constant of integration. In the same manner, we obtain

$$f(v) = ae^{-\frac{1}{2}\beta v^2}, \quad f(w) = ae^{-\frac{1}{2}\beta w^2}. \quad (2.23)$$

It should be noted that we have retained the same constant of integration,  $a$ , in all the integrations. Because, evidently  $f(u), f(v), f(w)$  should have the same mathematical form so that for  $u \rightarrow 0, v \rightarrow 0, w \rightarrow 0$ , we should obtain

$$f(u)|_{u \rightarrow 0} = f(v)|_{v \rightarrow 0} = f(w)|_{w \rightarrow 0} = a. \quad (2.24)$$

Hence,

$$f(u)f(v)f(w) = a^3 e^{-\frac{1}{2}\beta(u^2+v^2+w^2)} \quad (2.25)$$

so that from (2.15),

$$\begin{aligned} P_{uvw} &= a^3 e^{-b(u^2+v^2+w^2)} dudvdw, \text{ where } b = \frac{1}{2}\beta, \\ &= a^3 e^{-bc^2} dudvdw. \end{aligned} \quad (2.26)$$

This gives us the probability of a molecule having velocity components lying between  $u$  and  $u + du$ ,  $v$  and  $v + dv$ , and  $w$  and  $w + dw$ . In other words, we may say that (2.26) gives the probability of a molecule having the tip of its velocity lying within the elementary box of volume  $dudvdw$ , according to Fig. 2.4(a). The corresponding elementary box at the head of  $c$  in the spherical coordinate system is shown in Fig. 2.4(b) and has the volume  $cd\theta \times dc \times c \sin \theta d\phi = c^2 dc \sin \theta d\theta d\phi$ . Then, in this coordinate system, (2.26) takes the form :

$$P_{c\theta\phi} = a^3 e^{-bc^2} c^2 dc \sin \theta d\theta d\phi. \quad (2.27)$$

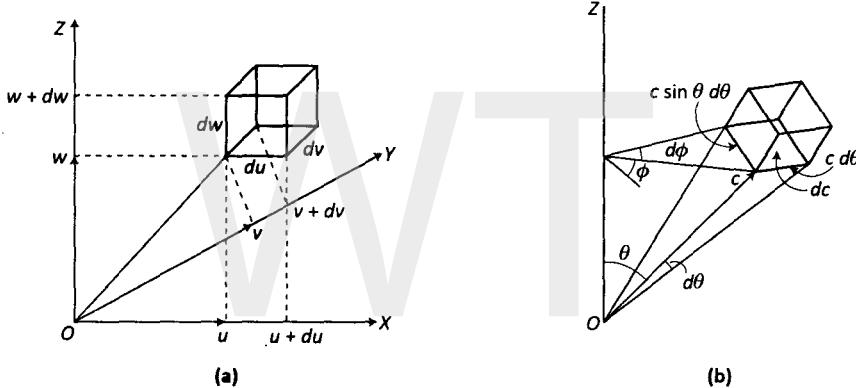


Fig. 2.4: (a) Cartesian system and (b) Spherical coordinate system

Interpreted in the new coordinate system, (2.27) gives us the probability of a molecule moving with a velocity lying between  $c$  and  $c + dc$  and in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$ . Then, the probability of a molecule moving with a velocity between  $c$  and  $c + dc$  in any direction in space is

$$\begin{aligned} P_c &= \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} a^3 e^{-bc^2} c^2 dc \sin \theta d\theta d\phi \\ &= 4\pi a^3 e^{-bc^2} c^2 dc. \end{aligned} \quad (2.28)$$

Then, of  $n$  molecules per cc, the number  $dn_c$  moving with velocity between  $c$  and  $c + dc$  is (See foot-note on P. 30)

$$dn_c = P_c \times n = 4\pi n a^3 e^{-bc^2} c^2 dc. \quad (2.29)$$

It may, however, be noted for future use that of  $n$  molecules/cc, the number  $dn_{c\theta\phi}$  moving with velocities between  $c$  and  $c + dc$  and in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$  is

$$P_{c\theta\phi} \times n = a^3 n e^{-bc^2} c^2 dc \sin \theta d\theta d\phi. \quad [\text{from (2.27)}] \quad (2.29')$$

The mean square velocity is [see (2.4)]

$$\begin{aligned} C^2 = \bar{c}^2 &= \frac{1}{n} \int_0^\infty dn_c \times c^2 = \frac{1}{n} \int_0^\infty 4\pi n a^3 e^{-bc^2} c^2 dc \times c^2 \\ &= 4\pi a^3 \int_0^\infty e^{-bc^2} c^4 dc = \frac{3}{2}\pi a^3 \sqrt{\frac{\pi}{b^5}}. \quad [\text{See Appendix 1}] \end{aligned} \quad (2.30)$$

Similarly, the mean velocity is

$$\bar{c} = \frac{1}{n} \int_0^\infty dn_c \times c = 4\pi a^3 \int_0^\infty e^{-bc^2} c^3 dc = \frac{2\pi a^3}{b^2}. \quad [\text{See Appendix 1}] \quad (2.31)$$

Now,  $a$  and  $b$  are inter-related. This can be seen from the fact that the probability of a molecule having, say, its  $x$ -component of velocity lying between  $-\infty$  and  $+\infty$  is a certainty, i.e.,

$$1 = \int_{-\infty}^{+\infty} f(u) du = \int_{-\infty}^{+\infty} ae^{-bu^2} du = a \sqrt{\frac{\pi}{b}}. \quad [\text{See Appendix 1}] \quad (2.32)$$

Therefore,  $a = \sqrt{\frac{b}{\pi}}$ . (2.33)

Then, from (2.14), (2.30) and (2.33)

$$C^2 = \frac{3kT}{m} = \frac{3}{2}\pi \sqrt{\frac{b^3}{\pi^3}} \times \sqrt{\frac{\pi}{b^5}} = \frac{3}{2b}$$

or,  $b = \frac{m}{2kT}$  (2.34)

and  $a = \sqrt{\frac{m}{2\pi kT}}$ . [from (2.33) and (2.34)] (2.35)

Hence, from (2.31), (2.34) and (2.35),

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}. \quad (2.36)$$

Now, since  $a$  and  $b$  are known from (2.34) and (2.35), plotting  $4\pi n a^3 e^{-bc^2} c^2$  against  $c$ , we obtain a graph of the form shown in Fig. 2.5. Now, the shaded area between  $c$  and  $c + dc = 4\pi n a^3 e^{-bc^2} c^2 \times dc = dn_c = \text{number of molecules/cc}$ , with velocities between  $c$  and  $c + dc$ . Then, since the graph shows a maximum at  $c = c_0$ , the largest number of molecules in any unit volume (= shaded area at  $c = c_0$ ) have got velocities between  $c_0$  and  $c_0 + dc$ .  $c_0$  is, therefore, called the most probable velocity. It is evident, therefore, that the number of molecules having very small velocity is very small and also that the number of molecules having very high velocities is very small (See the shaded areas at very small and at very high velocities).

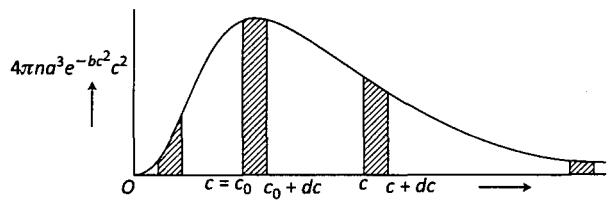


Fig. 2.5: Speed distribution

Now, in order to find  $c_0$ , we put

$$0 = \frac{d}{dc} \left\{ 4\pi n a^3 e^{-bc^2} c^2 \right\} \Big|_{c=c_0} = 4\pi n a^3 \left\{ e^{-bc^2} 2c(1 - bc^2) \right\} \Big|_{c=c_0}$$

It is clear from the graph that since the maximum is neither at  $c \rightarrow \infty$  nor at  $c \rightarrow 0$ ,

$$(1 - bc^2) \Big|_{c=c_0} = 0 \quad \text{or, } c_0 = \frac{1}{\sqrt{b}} = \sqrt{\frac{2kT}{m}}. \quad [\text{from (2.34)}] \quad (2.37)$$

**Exercise 1.** Find an expression for the number of gas molecules hitting unit area of the wall of the containing vessel per second.

**Solution :** Let us suppose, the  $x$ -axis is normal to the wall. Then, it is the  $x$ -component of velocity that will be effective in carrying the molecules towards the wall. Now, the number of molecules/cc, having  $x$ -components of velocity between  $u$  and  $u + du$  is

$$dn_u = P_u \times n = n \times f(u)du = nae^{-bu^2}du. \quad (2.38)$$

Then, the number of such molecules hitting unit area of the wall per second is  $dn_u \times u$  so that the total number of molecules hitting unit area of the wall per second is, from (2.38),

$$\begin{aligned} &= \int_0^\infty dn_u \times u = an \int_0^\infty e^{-bu^2} u du = an \times \frac{1}{2b} \quad [\text{from Appendix 1}] \\ &= \frac{1}{4} n \bar{c} \quad [\text{from (2.34), (2.35) and (2.36)}] \end{aligned} \quad (2.39)$$

**Exercise 2.** Exploit the idea of the above solution to show that the pressure exerted by a gas on the wall of the containing vessel is  $\frac{1}{3} mnc^2$ .

**Exercise 3.** Prove that the average kinetic energy of molecules in a vessel is equal to  $\frac{3}{4}$  times the average kinetic energy of molecules hitting the wall of the vessel for any length of time.

**Solution :** The kinetic energy of molecules hitting per second unit area of the wall in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$  is, from (2.1),  $= (dn_{c\theta\phi} \times c \cos \theta) \times \frac{1}{2} mc^2$ . The total kinetic energy of all molecules hitting unit area of the wall per sec is, from (2.29'),

$$\begin{aligned} &= \frac{1}{2} ma^3 n \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi/2} \int_0^\infty e^{-bc^2} c^5 dc \sin \theta \cos \theta d\theta d\phi \\ &= \frac{1}{4} n \bar{c} (2kT) \end{aligned}$$

so that the average kinetic energy of a hitting molecule is, from Ex. 1,

$$= \left\{ \frac{1}{4} n \bar{c} (2kT) \right\} / \frac{1}{4} n \bar{c} = 2kT.$$

$$\text{Now, } \frac{1}{2} \frac{mc^2}{2kT} = \frac{3}{2} \frac{kT}{2kT} = \frac{3}{4}. \quad (\text{QED})$$

## 2.7 Criticism of Maxwell's Deduction\*

Maxwell's derivation of his law is not very satisfactory owing to the fact that he considered the velocity-components to be independent (See how  $P_{uvw}$  has been set up). This is not

\*See, for detailed discussion, Saha & Srivastava, loc. cit, Pp. 137-39 (1958).

rigorously correct. Later, he put forward another proof\*, but it is doubtful if this is better than the original proof. However, the proof of the law developed by Boltzmann from statistics is very elegant (See Chapter 9).

## 2.8 Verification of Maxwell's Law

Maxwell's law has been verified by a number of workers in indirect (spectroscopic and electronic emission) experiments\*\* till about 1920 and thereafter in direct experiments. Here, however, we shall first discuss a direct experiment carried out by a skilful German physicist, Otto Stern†.

Stern's arrangement is shown in Fig. 2.6(a).  $C$  is a large chamber evacuated completely with a pump. At one end of the chamber is a vessel  $L$ , in which the experimental substance (say,  $Na$ ) is put. This is electrically heated and the substance is vaporized. The molecules of the vapour move about in all directions and some of them escape through the hole  $O$  in the form of a fine molecular spray. With two diaphragms,  $D_1$ ,  $D_2$ , a thin parallel beam of molecules is obtained, all moving in the same direction with their original velocities.

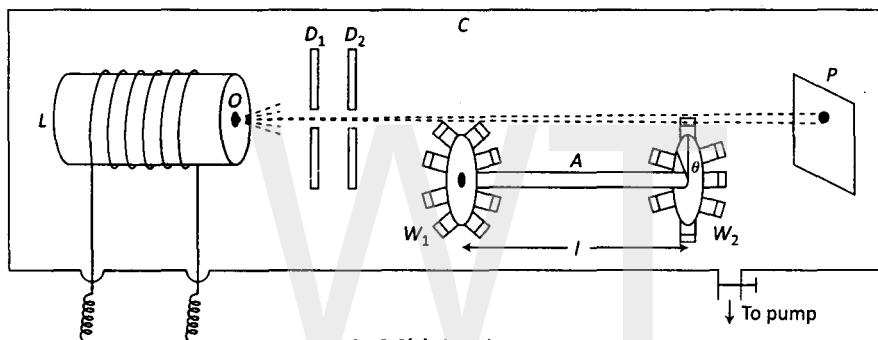


Fig. 2.6(a): Stern's apparatus

Now, in order to measure the velocities of the molecules in the beam, a stop-and-go system is used. In the path of the molecules two toothed wheels  $W_1$ ,  $W_2$ , attached to the opposite ends of a rapidly rotating axle  $A$  are so adjusted that the teeth of one wheel are just opposite the openings of the other wheel. Then, when the axle is stationary, no molecule can pass through. But if the wheels are rotated at such a speed,  $\omega$ , that the time in which a tooth turns just by half its angular breadth  $\theta$ , is exactly the time required for molecules of a particular velocity  $c$  to cover the distance  $l$  between the wheels, then all the molecules of this velocity would pass through both the wheels and would be registered on the plate  $P$  at the other end of the evacuated chamber. In this case, we have

$$\frac{l}{c} = \frac{\theta}{2\omega}$$

or,  $c = \frac{2l\omega}{\theta}$ . (2.40)

$l$  and  $\theta$  are constants of the apparatus so that by changing  $\omega$ , molecules of different velocities (i.e., of different values of  $c$ ) are obtained on the plate. For comparison between molecular deposits of different velocities on the plate, molecules of each particular velocity  $c$  were allowed to be registered on the plate for the same interval of time. From an analysis of the deposits for

\*Maxwell, *Collected Works*, 2, 43.

\*\*See, for detailed discussion, Saha & Srivastava, *loc. cit*, Pp. 137-39 (1958).

†For a lucid discussion, see, for example, G. Gamow, *The Birth and Death of the Sun*, Pp. 24-28, (1953).

different molecular velocities, it is actually found (See the discussion at the end of the following experiment) that the graph of Fig. 2.5 exactly represents the distribution.

Now we describe a later experiment carried out in 1955 by Miller and Kusch of Columbia University.

$C$  is an evacuated chamber in which thallium vapour is produced in an oven  $O$  by electrical heating (Fig. 2.6(b)). A parallel beam of the vapour enters into a cylinder  $R$  (velocity selector) of length  $l$ . There are curved grooves in the interior wall of the cylinder. If a groove happens to be just opposite to the outlet of the oven, the vapour will pass direct into it, but will not be able to emerge at the other end if the cylinder is at rest, because the groove is not straight. If

the angular displacement of one end of a groove relative to the other is  $\phi$ , then those thallium atoms will be able to pass out of the rotating cylinder whose speed is  $c$  satisfying the following relation :

$$\frac{\phi}{\omega} = \frac{l}{c}$$

$$\text{or, } c = \frac{l}{\phi} \omega. \quad (2.41)$$

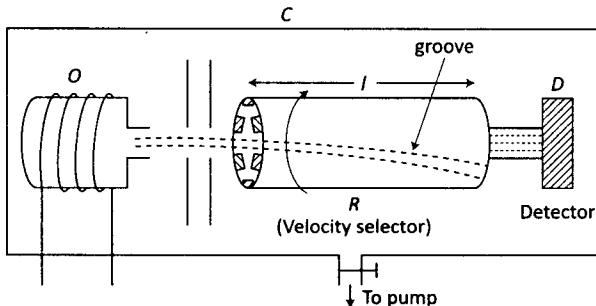


Fig. 2.6(b): Miller-Kusch apparatus

(2.41) shows that corresponding to a particular value of  $\omega$  thallium atoms of a particular speed  $c$  will be recorded on the detector  $D$ .

Let us suppose that the law of speed distribution in the thallium vapour inside the oven is given by

$$dn_c = f(c)dc, \quad (2.42)$$

where  $f(c)$  is a function of  $c$ . Now,  $\nu_c dc$ , the number of thallium atoms having speed between  $c$  and  $c + dc$  per unit volume of the vapour stream issuing from the oven will be given by

$$\nu_c dc \propto dn_c \\ \propto c$$

That is,  $\nu_c dc = \text{constant}$ .  $dn_c c = \text{constant } f(c)cdc$

$$\therefore \frac{\nu_c}{c} = \text{constant } f(c). \quad (2.43)$$

It is obvious from (2.43) that  $\nu_c/c$  would behave like  $f(c)$ . Now, Miller and Kusch observed from the deposits on  $D$  that  $\nu_c/c$  varies with  $c$  in the following manner :

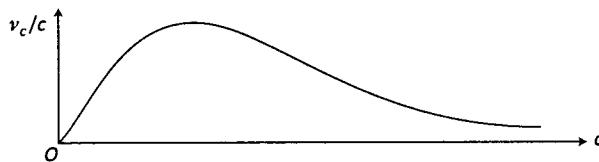


Fig. 2.6(c): Speed distribution

This fairly agrees with the Maxwell speed distribution curve. Here  $f(c)$  must have, therefore, the following expression according to Maxwell's law :

$$f(c) = 4\pi a^3 n e^{-bc^2} c^2. \quad (2.44)$$

## 2.9 Rarefaction of Moon's Atmosphere\*

It is observed that the moon has hardly got any atmosphere, although it once had a fairly thick atmosphere. This can be easily explained on the basis of Maxwell's law. It appears from Fig. 2.5 that there will be always some molecules having very high velocities. Now, these molecules, owing to the moon's gravitational pull being not very strong, escape into outer space. Then, again applying Maxwell's law to the remaining molecules of the atmosphere, we find according to Fig. 2.5 that there will be again a group of molecules having very high velocities. These fast molecules will also escape into space due to the weakness of the moon's gravitational pull. This process continues and ultimately results in a highly rarefied atmosphere on the moon.

**Exercise 1.** Comment on the fact that the sun\* and other stars, although completely gaseous, continue to exist whereas the solid moon has almost lost all the atmosphere in a short period.

**Exercise 2.** Compare the atmosphere on the earth with those on the jupiter\* and the saturn\*.

## 2.10 Importance of Maxwell's Law

This law applies not only to gas molecules but also to the stars forming a galaxy. It also plays an important role in questions concerning the liberation of nuclear energy from substances brought to very high temperatures.

## 2.11 Degrees of Freedom

The energy of a single particle is usually a homogeneous function of the squares of a number of position and/or momentum co-ordinates. The total number  $\nu$  of independent squared terms occurring in the expression for the energy of the system is called the *number of degrees of freedom of the system*\*\*. This idea will be clarified with a number of examples here.

**(a) A Monatomic Gas :** Let us consider a system of  $N$  identical monatomic molecules. Each molecule is a particle of mass  $m$  and is capable of translation only, but not of rotation<sup>†</sup>. The kinetic energy of such a molecule is given by

$$\frac{1}{2}mc^2 = \frac{1}{2m}(mc)^2 = \frac{1}{2m}\{(mu)^2 + (mv)^2 + (mw)^2\}.$$

Here, there are three independent squared momentum terms in the expression for energy. So each monatomic molecule has got three degrees of freedom and hence,  $N$  molecules have got  $3N$  degrees of freedom<sup>†</sup>.

**(b) A Diatomic Gas :** We assume a diatomic molecule to consist of two atoms at a fixed distance apart (Fig. 2.7). Such a system can easily be excited into rotation about an axis  $OP$

\*See James Jeans, *Dynamical Theory of Gases*, (1904), Pp. 323–25.

\*\*G. Joos, *Ibid*, P. 587; J. K. Roberts & A. R. Miller, *Heat and Thermodynamics*, P. 202 (1962)

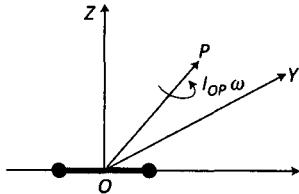
<sup>†</sup>According to Quantum Mechanics (See, for example, N. F. Mott & I. N. Sneddon, *Wave Mechanics and Its Application*, Pp. 60–1, (1948), the energy of a rigid rotator is

$$E_l = \frac{\hbar^2 l(l+1)}{8\pi^2 I}, \quad l = 1, 2, 3, \dots,$$

where  $\hbar$  is Planck's constant and  $I$  the moment of inertia about the axis of rotation. Now, for an atom,  $I$  is extremely small so that  $E_l$  is very high. This means that to excite rotation, a very large amount of energy is required but is not generally available. Hence, a monatomic molecule is not usually capable of rotation. This also makes it clear that it is very difficult to excite rotation of a diatomic molecule about its axis of symmetry. (See also Roberts and Miller, *Ibid*, Pp. 206–7).

<sup>†</sup>The number of degrees of freedom is additive, because the energy which is involved in this case, is a physical quantity of additive character.

perpendicular to  $OX$ , the axis of symmetry, but cannot rotate about  $OX$ , as has been explained in the footnote on p. 37. Then, the kinetic energy of rotation of a diatomic molecule can be written as



$$\frac{1}{2}I_{OP}\omega^2 = \frac{1}{2I_{OP}}(I_{OP}\omega)^2 = \frac{1}{2I_{OP}}\{(I_y\omega_y)^2 + (I_z\omega_z)^2\},$$

since the angular momentum  $I_{OP}\omega$  is a vector (with  $OP$  as its direction), it can be resolved like a vector. Thus, due to rotation, a diatomic molecule has got two degrees of freedom. The number of degrees of freedom on account of translational kinetic energy is, as usual, three so that the total number of degrees of freedom is five. Hence,  $N$  such molecules in a system possess  $5N$  degrees of freedom.

**(c) A Polyatomic Gas :** For such a gas molecule (triatomic, quadratomic or pentatomic, etc.), it is not difficult to excite rotation about any axis passing through its centre of mass. Because, here,  $I$  for any such axis is sufficiently large so that the energy required (See footnote on p. 37) to excite rotation about that axis is not large. Thus, for such a molecule, the rotational kinetic energy for any axis is

$$\frac{1}{2}I\omega^2 = \frac{1}{2I}\{(I_x\omega_x)^2 + (I_y\omega_y)^2 + (I_z\omega_z)^2\}.$$

So there are three degrees of freedom for rotation. These, added to 3 degrees of freedom for translational kinetic energy, make 6 degrees of freedom of a polyatomic molecule.  $N$  such molecules in a system can, thus, have  $6N$  degrees of freedom.

It may be pointed out here that for some polyatomic gases, the number of degrees of freedom for a molecule may be larger than 6. Because, due to vibrations set up among the atoms inside such molecules, there will be some more independent squared terms appearing in the expression for energy (See the following paragraph).

**(d) An Elementary Solid\* :** An atom of an elementary solid executes vibration about its equilibrium (i.e., mean) position under the action of some quasi-elastic restoring force. During vibration, the atom possesses, on the whole, not only kinetic energy, but also potential energy due to its displacement from the mean position against the restoring force. The expression for this potential energy is of the form :

$$\frac{1}{2}kr^2 = \frac{1}{2}k(x^2 + y^2 + z^2),$$

where  $k$  is a constant of the solid and  $r$  is the displacement of the atom at any instant from the mean position which has been taken as the origin of the coordinate system. Thus, an atom will have 6 degrees\*\* of freedom, 3 due to kinetic energy and 3 due to potential energy. For a solid containing  $N$  such atoms, the total number of degrees of freedom is  $6N$ .

## 2.12 Law of Equipartition of Energy

Maxwell showed that if in their motion the molecules obey the ordinary laws of mechanics, then the total translational energy of a system is equally divided among the different degrees of freedom. This is called the *principle of equipartition of energy*. Boltzmann extended it to

\*An elementary solid is a chemical element in the solid state.

\*\*See, for example, G. Joos, *loc. cit.* Pp. 589–90.

the energy of rotation and vibration also\*. It can be shown that the average energy associated with each degree of freedom for a molecule is  $\frac{1}{2}kT$ .

Here we give a simple proof of this theorem for a monatomic gas containing, say,  $N$  molecules. The average kinetic energy of a monatomic molecule for  $x$ -component of momentum, i.e.,  $x$ -momentum, is :

$$\begin{aligned}
 \bar{E}_x &= \frac{\text{Total energy in the system due to } x\text{-momemtum}}{\text{Total no. of molecules in the system}} \\
 &= \frac{1}{N} \int_{-\infty}^{+\infty} \left( \frac{1}{2}mu^2 \right) \times Nae^{-bu^2} du \quad [\text{from (2.26)}] \\
 &= \frac{1}{2}ma \int_{-\infty}^{+\infty} e^{-bu^2} u^2 du \\
 &= \frac{1}{2}ma \times \frac{1}{2} \sqrt{\frac{\pi}{b^3}} \quad [\text{See Appendix 1}] \\
 &= \frac{1}{2}m \cdot \frac{1}{2b} \quad [\text{from (2.32)}] \\
 &= \frac{1}{2}kT. \quad [\text{from (2.34)}]
 \end{aligned} \tag{2.45}$$

The same value will also be obtained for  $\bar{E}_y$  and  $\bar{E}_z$ . Thus, the law of equipartition of energy is established for monatomic molecules from Maxwell's law.

Let us consider a gram-molecule of a gas of which each molecule has, say,  $n$  degrees of freedom. Then, from the law of equipartition of energy, we have for the total internal energy  $U$  of the system at  $T$  K,

$$U = N \times n \times \left( \frac{1}{2}kT \right) = \frac{n}{2}RT, \tag{2.46}$$

where  $N$  is the Avogadro number. Now, the gram-molecular specific heat at constant volume is, from (2.46),

$$C_v = \left( \frac{dU}{dT} \right)_v = \frac{n}{2}R. \tag{2.47}$$

For a perfect gas,  $C_p - C_v = R$  so that

$$C_p = C_v + R = \frac{1}{2}(n+2)R. \tag{2.48}$$

$$\text{Hence, } \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{n}. \tag{2.49}$$

Let us now take up some special cases :

- (a) A monatomic gas—For this case,  $n = 3$ . So  $\gamma = 1 + 2/3 = 1.66$ .
- (b) A diatomic gas—For this case,  $n = 5$ . So  $\gamma = 1 + 2/5 = 1.40$ .
- (c) A polyatomic gas—Here  $n = 6$ . So  $\gamma = 1 + 2/6 = 1.33$ . But, as explained in the above section, for some polyatomic gases,  $n$  may be  $> 6$  due to vibrations set up among the atoms inside the molecules so that  $\gamma$  becomes  $< 1.33$  and approaches unity.

Thus, a knowledge of  $\gamma$  gives us an idea of the molecular structure of a gas.

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\*For proof for rotational and vibrational motions, see section 9.7.

Finally, we consider a gram-atom of an elementary solid. In this case, from (2.47),

$$C_v = 6 \cdot \frac{R}{2} = 3R \approx 6 \text{ cal} \quad (\because R \approx 2 \text{ cal}). \quad (2.50)$$

This is exactly the Dulong-Petit law of atomic heats briefly discussed in section 1.8. Thus, the law has been successfully derived on the kinetic theory. But unfortunately, the kinetic theory cannot explain why the law breaks down at low temperatures, the atomic heat tending to zero at absolute zero. Attempts to explain this anomaly on quantum theory will be presented in Chapter 8.

## 2.13 Mean Free Path

In deducing the expression for pressure and from it the gas laws (sections 2.3 and 2.4), Clausius assumed that molecules of a gas are just like point-particles. But this assumption created a difficulty. It is highly improbable for point-particles to collide with one another so that they would move all the time in rectilinear paths. Such a gas, if kept in a vessel with an opening, would disappear in no time. But this is contrary to observation. In order to get over this difficulty, Clausius assumed for the molecules a finite, though small, size. Now, collisions between molecules may be considered to take place frequently so that it now becomes quite easy to explain many observed phenomena. The path of a molecule between two collisions is a straight line described with constant velocity (see assumption (d) of section 2.2), because no attraction is assumed to exist between two molecules.

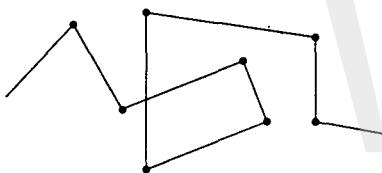


Fig. 2.8: Molecular path in a gas

Taking collisions into consideration, the path of a molecule consists of a series of short zig-zag paths as shown in Fig. 2.8. The distance travelled between any two consecutive collisions is called a *free* (i.e., unobstructed) path,  $\lambda$ . Adding up a large number of such free paths and dividing the same by the total number, we obtain the mean free path,  $\bar{\lambda}$ . We now proceed to calculate rigorously an expression for  $\bar{\lambda}$ .

*Preliminary Calculation of  $\bar{\lambda}$*  : In this calculation, we shall first start with assuming unreal situations and then, we shall move step by step into the real, physical situation.

Let us consider a molecule  $X$ , moving with a velocity  $c$ , very high compared with that of the vast majority of the remaining molecules. Then, we may suppose the remaining molecules to be at rest. The moving molecule will collide with all those molecules whose centres lie within a distance  $\sigma$  (= diameter of a molecule) from its centre (Fig. 2.9). In one second, it will collide with all the molecules whose centres lie in a cylinder (its axis being along the direction of molecule,  $X$ ) of radius  $\sigma$  and of length  $c$ . Since the number of molecules in this cylindrical volume ( $= \pi\sigma^2 c$ ) is  $\pi\sigma^2 cn$  ( $n$  = number of molecules/cc), the number of collisions also suffered by the moving molecule  $X$  per sec is also  $\pi\sigma^2 cn$ . Since each collision means the end of a free path,  $\pi\sigma^2 cn$  is the number of free paths of the molecule in one second. Now, because the sum of these free paths is equal to  $c$ , the total distance traversed in one second, the mean free path is

$$\bar{\lambda} = \frac{c}{\pi\sigma^2 cn} = \frac{1}{\pi\sigma^2 n}. \quad (2.51)$$

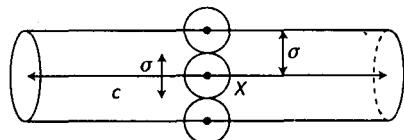


Fig. 2.9

\*See W. Wilson *Theoretical Physics*, Vol. I. (1931), Pp. 232–35. See, for Maxwell's theory, J. Jeans, *Kinetic Theory of Gases*, Pp. 131–35 (1940).

Next we go one step forward. We now suppose, the molecule,  $X$ , has velocity  $c$  and all the remaining molecules have velocity  $c'$ , and all the molecules of the system are going in the same direction. First, we take  $c > c'$ . Then, (See Fig. 2.9(a)) as the molecule  $X$  goes in one second from  $A$  to  $C$ , it collides with the molecules in the length  $AB (= c - c')$ . Because, as the molecule  $X$  will reach  $C$ , the molecules just on the right side of  $B$  will pass out of  $C$ . If, however, we suppose  $c' > c$ , then (See Fig. 2.9(b)) as the molecules  $X$  goes in one second from  $B$  to  $C$ , there will be collisions between it and all the molecules between  $A$  and  $B$  ( $AB = c' - c$ ). Because, as the molecule  $X$  will proceed toward  $C$ , the molecules just on the right side of  $B$  will move faster ( $c' > c$ ) and will not collide with  $X$ . In both cases the sum of the free paths of the molecule  $X$  in one second is equal to  $c$ , and the number of free paths in one second is equal to the number of collisions taking place in the volume  $\pi\sigma^2 \times (c \sim c')^*$ . This number is the same as the number of molecules in this volume ( $= \pi\sigma^2(c \sim c')n$ ). Then, the mean free path is

$$\bar{\lambda} = \frac{c}{\pi\sigma^2(c \sim c')} \quad (2.52)$$

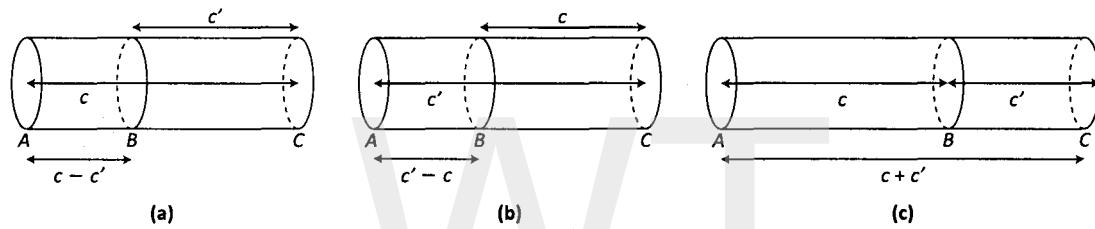


Fig. 2.9

If, however, the molecule  $X$  with velocity  $c$  and the remaining molecules with velocity  $c'$  move in opposite directions (Fig. 2.9(c)), then it is evident that as the molecule  $X$  will go towards  $B$  in one second, it will collide with all the molecules contained in the volume  $\pi\sigma^2(c + c')$ . At the beginning of one second, it will collide with the molecules at  $A$  and at the end of one second when it will arrive at  $B$ , it will collide with the molecules which have arrived there (i.e., at  $B$ ) from  $C$  by that time. For this case, the mean free path is

$$\bar{\lambda} = \frac{c}{\pi\sigma^2(c + c')n} \quad (2.53)$$

Now we are in a position to take the final step.

*Detailed Calculation :* It is evident that in order to find the number of collisions taking place in one second between a molecule  $X$  and other molecules, we must take a cylinder (its axis being along the direction of molecule  $X$ ) of radius  $\sigma$  and of length = relative velocity between the molecule  $X$  and other molecules. If we now suppose that the molecule  $X$  is moving with velocity  $c$ , but all other molecules are moving at an angle  $\theta$  (Fig. 2.10) with velocity  $c'$ , then the mean free path will be

$$\bar{\lambda} = \frac{c}{\pi\sigma^2 r n} \quad (2.54)$$

where  $r$  (= relative velocity) =  $|c^2 + c'^2 - 2cc' \cos \theta|^{1/2}$ . (2.55)

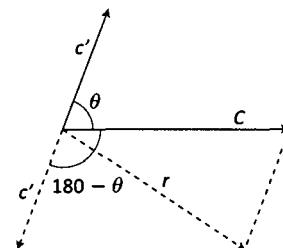


Fig. 2.10

\*We have taken  $(c \sim c')$ , because this means that we shall adopt  $c - c'$ , if  $c > c'$ , or  $c' - c$ , if  $c' > c$ .

[See (p. 41) foot-note for the reason why here the bars have been adopted\*. The usefulness of this will be seen in (2.58).]

Now, the molecule  $X$  may have any velocity from 0 to  $\infty$  so that we must take  $\bar{c}$ , the average velocity, as the velocity of the molecule in (2.54). Also, (2.55) shows that  $r$  depends upon  $c, c'$  and direction ( $\theta$ ). So  $r$  must also be averaged for all values of  $c$  and  $c'$  and for all directions ( $\theta, \phi$ ). Then (2.54) is reduced to

$$\bar{r} = \frac{\bar{c}}{\pi\sigma^2\bar{r}n}. \quad (2.56)$$

Now  $\bar{c}$  has already been calculated in (2.36) from Maxwell's law. Following Clausius, we now proceed, step by step, to calculate  $\bar{r}^{\theta\phi}$

According to statistics, the average value of a quantity  $Q$  is given by\*\*

$$\bar{Q} = \int_Q \{( \text{Probability of occurrence of } Q \text{ between } Q \text{ and } Q + dQ ) \times Q\}. \quad (2.57)$$

Hence, following (2.57),

$$\begin{aligned} \bar{r}^{\theta\phi} &= \int_r (\text{Probability of occurrence of } r \text{ in directions between } \theta \text{ and } \theta + d\theta \\ &\quad \text{and } \phi \text{ and } \phi + d\phi) \times r \\ &= \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} \left( \frac{1}{4\pi} \sin \theta d\theta d\phi \right) \times r [\text{look at Figs. 2.2(a) and (b) and (2.1)}] \end{aligned}$$

( $\because$  probability of  $r$  for any direction = probability of a  $c'$ -molecule moving in that direction relative to a  $c$ -molecule)

$$\begin{aligned} &= \frac{1}{2} \int_{0(\theta)}^{\pi} \left| (c^2 + c'^2 - 2cc' \cos \theta)^{\frac{1}{2}} \right| \sin \theta d\theta \\ &= \frac{1}{6cc'} [(c + c')^3 - (c - c')^3]. \end{aligned} \quad (2.58)$$

$$\text{Therefore, for } c > c', \bar{r}^{\theta\phi} = \frac{3c^2 + c'^2}{3c} \quad (2.59)$$

$$\text{and for } c' > c, \bar{r}^{\theta\phi} = \frac{3c'^2 + c^2}{3c'}. \quad (2.60)$$

Now, from Maxwell's law, the probability that there occur molecules of velocity  $c'$  (i.e., of velocities between  $c'$  and  $c' + dc'$ ) is, from (2.29),

$$\frac{dn_{c'}}{n} = 4\pi a^3 e^{-bc^2} c'^2 dc'. \quad (2.61)$$

\* $|x|$  means that we are interested in the magnitude of  $x$  only, and not in its sign.

\*\*Look at equations (2.30) and (2.31) :

$C^2 = \bar{c}^2 = \int_0^\infty \frac{dn_c}{n} \times c^2$ , where  $\frac{dn_c}{n}$  is the probability of occurrence of  $c^2$

and  $\bar{c} = \int_0^\infty \frac{dn_c}{n} \times c$ , where  $\frac{dn_c}{n}$  is the probability of occurrence of  $c$ .

Here, the probability of occurrence of  $c^2$  (or  $c$ ) is the same as the probability of occurrence of a molecule having velocity  $c$ .

This is also the probability of occurrence of  $r$  for velocity  $c'$  (i.e., for velocities between  $c'$  and  $c' + dc'$ ). Then,

$$\bar{r}^{\theta\phi} = \int_0^{c'} (4\pi a^3 e^{-bc'^2} c'^2 dc') \times \bar{r}^{\theta\phi}. \quad (2.62)$$

Taking into account the fact that  $\bar{r}^{\theta\phi}$  has two different values depending upon whether  $c$  is  $>$  or  $< c'$ , we write (2.62) as

$$\bar{r}^{\theta\phi} = \int_0^{c'} \frac{3c^2 + c'^2}{3c} 4\pi a^3 e^{-bc'^2} c'^2 dc' + \int_{c'}^{\infty} \frac{3c' + c^2}{3c'} 4\pi a^3 e^{-bc'^2} c'^2 dc'. \quad (2.63)$$

Here, in the first integral  $c' < c$ , so (2.59) has been used and in the second integral  $c' > c$ , so (2.60) has been used.

As in (2.62), in order to obtain the average value of  $\bar{r}^{\theta\phi}$  for all values of  $c$ , we write :

$$\begin{aligned} \bar{r} = \bar{r}^{\theta\phi} &= \int_0^{\infty} (4\pi a^3 e^{-bc^2} c^2 dc) \times \bar{r}^{\theta\phi} \\ &= \int_0^{\infty} 4\pi a^3 e^{-bc^2} c^2 dc \int_0^{c'} \frac{3c^2 + c'^2}{3c} 4\pi a^3 e^{-bc'^2} c'^2 dc' \\ &\quad + \int_0^{\infty} 4\pi a^3 e^{-bc^2} c^2 dc \int_{c'}^{\infty} \frac{3c'^2 + c^2}{3c'} 4\pi a^3 e^{-bc'^2} c'^2 dc' \quad [\text{from (2.63)}] \\ &= 16\pi^2 a^6 \left[ \int_0^{\infty} c^2 e^{-bc^2} dc \int_0^{c'} \frac{3c^2 + c'^2}{3c} c'^2 e^{-bc'^2} dc' \right. \\ &\quad \left. + \int_0^{\infty} c^2 e^{-bc^2} dc \int_{c'}^{\infty} \frac{3c'^2 + c^2}{3c'} c'^2 e^{-bc'^2} dc' \right] \\ &= 16\pi^2 a^6 [C + D] \quad (\text{say}). \end{aligned} \quad (2.64)$$

Now, the spirit of the integrals in  $C$  is that  $c$  shall vary from 0 to  $\infty$  and  $c'$  shall remain always less than  $c$ . Keeping this spirit in tact, we can write  $C$  as below :

$$C = \int_0^{\infty} c'^2 e^{-bc'^2} c'^2 dc' \int_{c'}^{\infty} \frac{3c^2 + c'^2}{3c} c^2 e^{-bc^2} dc, \quad (2.65)$$

where  $c'$ , remaining  $< c$ , varies from 0 to  $\infty$ , so that the order of integration has been reversed\*. The result of integration in (2.65) will not change, if we replace in (2.65)  $c$  by  $c'$  and  $c'$  by  $c$ . Then we obtain

$$C = \int_0^{\infty} c^2 e^{-bc^2} dc \int_c^{\infty} \frac{3c'^2 + c^2}{3c'} c'^2 e^{-bc'^2} dc'. \quad (2.66)$$

Now, comparing (2.64) and (2.66), we find that

$$\begin{aligned} D \quad [\text{as in (2.64)}] &= C \quad [\text{as in (2.66)}] \\ &= \frac{1}{8\sqrt{2}} \sqrt{\left(\frac{\pi}{b^7}\right)}, \quad \text{on integration.} \end{aligned} \quad (2.67)$$

\* Keeping the spirit of integration in tact, one can reverse the order of integration without any harm. Take, for example,  $\int_0^r x^3 dx \int_0^x y^2 dy = r^7/21$ . Here  $x$  varies from 0 to  $r$ , but  $y$  is less than  $x$ . Next, keeping this spirit in tact, we reverse the order of integration and obtain  $\int_0^r y^2 dy \int_y^r x^3 dx = r^7/21$ . Here  $y$ , remaining  $< x$ , varies from 0 to  $r$ .

Then, from (2.64) and (2.67),

$$\begin{aligned}\bar{r} &= 16\pi^2 a^6 \times \left( 2 \times \frac{1}{8\sqrt{2}} \sqrt{\frac{\pi}{b^7}} \right) \\ &= \sqrt{2c} \text{ [from (2.34), (2.35) and (2.36)].}\end{aligned}\quad (2.68)$$

Then, from (2.56) and (2.68),

$$\bar{\lambda} = \frac{\bar{c}}{\pi\sigma^2\bar{c}\sqrt{2n}} = \frac{1}{\sqrt{2}\pi\sigma^2 n}. \quad (2.69)$$

This expression for mean free path is known as Maxwell's mean free path.

**Exercise 1.** Take  $n = 2.705 \times 10^{19}$  molecules/cc at N.T.P. and compute the diameter of an oxygen molecule assuming  $\bar{\lambda} = 6.3 \times 10^{-6}$  cm under this condition.

**Exercise 2.** Take  $n = 2.687 \times 10^{19}$  molecules/cc at N.T.P. and calculate the mean free path of a hydrogen molecule under this condition, assuming  $\sigma = 2.38 \times 10^{-8}$  cm.

**Exercise 3.** Set up a relation\* between the pressure of a gas and its mean free path at any temperature.

## 2.14 Law of Distribution of Free Paths\*\*

We shall now calculate  $f(x)$  the probability of a molecule in a gas going a distance  $x$  after the last collision. Evidently, out of  $N$  molecules of the system  $Nf(x)$  will go this distance after this respective last collisions. Now, the probability of a molecule undergoing a collision in going a further distance  $dx$  is proportional to  $dx$  ( $dx$  being very small), i.e., is equal to  $\alpha dx$ ,  $\alpha$  being a constant. Then, out of  $Nf(x)$ ,  $N\alpha f(x)dx$  will suffer collisions between  $x$  and  $x+dx$ . Hence, the number of molecules not suffering a collision between  $x$  and  $x+dx$  is

$$Nf(x) - N\alpha f(x)dx = Nf(x+dx) = Nf(x) + N \frac{df}{dx} dx + \dots \text{ [by Taylor's expansion]} \quad (2.70)$$

$$\text{Therefore, } \frac{df}{dx} = -\alpha f(x). \quad (2.71)$$

On integration of (2.71),

$$f(x) = Ae^{-\alpha x}, \quad (2.72)$$

where  $A$  is a constant of integration. Since for  $x \rightarrow 0$ ,  $f(x) \rightarrow 1$ , we have  $A = 1$ . Hence (2.72) becomes

$$f(x) = e^{-\alpha x}. \quad (2.73)$$

Now, evidently  $x$  may be taken as the free path of  $N\alpha f(x)dx$  molecules. Then, the mean free path

$$\begin{aligned}\bar{\lambda} &= \frac{\text{Sum of all free paths}}{\text{Total no. of free paths (i.e., collisions)}} = \frac{\int_0^\infty x \cdot N\alpha f(x)dx}{\int_0^\infty N\alpha f(x)dx} \\ &= \frac{\int_0^\infty xe^{-\alpha x}dx}{\int_0^\infty e^{-\alpha x}dx} = \frac{1}{\alpha}.\end{aligned}\quad (2.74)$$

Then, from (2.73) and (2.74),

$$f(x) = e^{-x/\bar{\lambda}}. \quad (2.75)$$

\*See section 2.15 and Problem 8.

\*\*Robert and Miller, *loc.cit.*, P. 85.

(2.75) represents the law of distribution of free paths of molecules in a system.

It is evident from (2.75) that the probability of a molecule describing very long free paths (i.e.,  $x$  being very large) is extremely small. In fact, only one in about 150 is as large as  $5\bar{\lambda}$ .

Also we note from (2.75) that if  $n_0$  molecules of velocity  $c$  are incident on the gas at  $x = 0$ , then only  $n_0 e^{-x/\bar{\lambda}_c}$  molecules will travel the distance  $x$  without collision. If, however, these molecules have velocities distributed according to Maxwell's law, then we shall have to integrate\* this expression for all values of  $c$  from 0 to  $\infty$ .

## 2.15 Born's Experiment on $\bar{\lambda}$

(2.69) shows that if  $n$  and  $\sigma$  are known,  $\bar{\lambda}$  may be easily calculated. But this is not a direct method and, till 1920, there was no direct technique for finding  $\bar{\lambda}$ . In 1920, Born\*\* developed a method for direct determination of  $\bar{\lambda}$ . His arrangement is shown in Fig. 2.11.  $T$  is a quartz tube which can be evacuated to any desired pressure and the pressure is known from a McLeod gauge or a Knudsen manometer. At the bottom of the quartz tube, silver is vaporized by electrical heating. Silver atoms escape through the narrow slit  $S$  and then pass through a circular hole in each of the four brass discs  $D_1$ ,  $D_2$ ,  $D_3$ ,  $D_4$ , the distance between  $D_1$  and  $D_2$  or  $D_2$  and  $D_3$  or  $D_3$  and  $D_4$  being 1 cm. Each of these discs carries a glass quadrant such that the tip of the quadrant lies at the centre of the hole (shown separately). Also the four quadrants on the four discs are so arranged that the quadrant on a disc is displaced by a right angle with respect to that on the next upper or lower disc. A quadrant evidently receives only one-fourth of the beam of silver atoms incident on the whole disc due to collisions with the gas molecules existing inside the quartz tube. The discs are cooled by a cooling mixture,  $M$ , so that the silver atoms incident on the quadrants may get deposited.

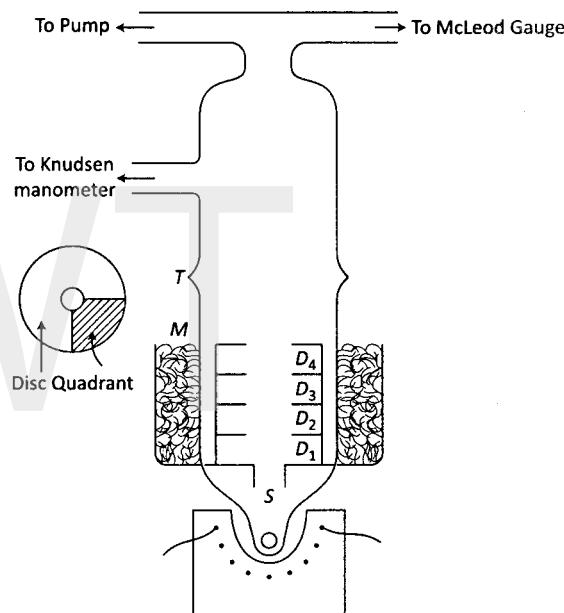


Fig. 2.11: Born's apparatus

First, the density of silver deposit,  $d_{10}$ , on a quadrant is obtained after pumping out almost all the gas in the tube so that the free path is about the length of the tube. Next, the gas is introduced to some definite pressure producing the mean free path  $\bar{\lambda}$ , and then the density  $d_1$  on the same quadrant is determined. Then, the probability of a silver atom reaching this quadrant at a distance  $x_1$  from the slit  $S$  is  $d_1/d_{10}$  and this is equal to  $e^{-x_1/\bar{\lambda}}$  by (2.75). That is,

$$d_1 = d_{10} e^{-x_1/\bar{\lambda}}. \quad (2.76)$$

The validity of this equation may be made clear from the fact that when the quartz tube is almost evacuated,  $\bar{\lambda} \rightarrow$  very large (= length of the tube) so that  $x_1/\bar{\lambda} \rightarrow 0$ . In that case, evidently  $d_1$  should tend to  $d_{10}$ . This is exactly satisfied in (2.76).

\*See, for details, J. Jeans, *Kinetic Theory of Gases* (1940), P. 144.

\*\*Phys. Zeits., 21, 578, (1920); Saha and Srivastava, loc. cit., Pp. 159–61.

For another quadrant at a distance  $x_2$  from  $S$ , we may write an equation similar to (2.76),

$$d_2 = d_{20} e^{-x_2/\bar{\lambda}}. \quad (2.77)$$

Combining (2.76) and (2.77),

$$\bar{\lambda} = (x_2 - x_1) / \log_e \left( \frac{d_1 d_{20}}{d_{10} d_2} \right). \quad (2.78)$$

In Born's experiment,  $(x_2 - x_1)$  was 1 cm, because deposits on two successive quadrants were observed. It was found\* that in one case for  $P = 5.8 \times 10^{-3}$  mm of Hg,  $\bar{\lambda} = 1.7$  cm and in another case for  $P = 4.5 \times 10^{-3}$  mm of Hg,  $\bar{\lambda} = 2.4$  cm. Hence, the product  $P\bar{\lambda}$  is constant, as is expected from theory by combining (2.4) and (2.69). Thus, not only is it possible to determine  $\bar{\lambda}$ , but also the law (2.75) is verified. It should, however, be noted here that the mean free path of silver atoms in a gas has been studied in this experiment.

**Exercise :** Employ the law of distribution of free paths to solve Exercises 1 and 2 under section 2.6.

Look, for solution, into Problem No. 8 at the end of this chapter.

## 2.16 Viscosity of Gases

If the different layers of a fluid are in relative motion in a certain direction, then along unit area of a fluid plane parallel to this motion is experienced a force equal to

$$F = \eta \frac{dV}{dz}, \quad (2.79)$$

where  $\frac{dV}{dz}$  is the velocity gradient in the fluid and  $\eta$  the coefficient of viscosity. This force, acting along unit area of a faster-moving layer, retards it, but this force, acting along unit area of a slower-moving layer, accelerates it.

Maxwell was the first to explain the viscosity of gases on the kinetic theory in 1860. When a gas has its different layers in relative motion, a molecule of any layer possesses, at the same time, two velocities—(a) the mass or stream velocity  $V$  equal to the velocity of the layer and (b) the random molecular velocity  $c$ . The kinetic theory explains the viscosity of gases in the following manner\*\*. The molecules over a given plane taken parallel to mass motion possess, say, a greater mass (or stream) momentum than those below it. Approximately equal numbers of molecules will cross, due to random molecular motion, unit area of the plane in both directions (i.e., from the faster side to the slower side and *vice versa*) per second. As a result, at the expense of the upper region of the medium, the lower region will gain mass (or stream) momentum per second. This rate of gain of mass momentum will appear as the accelerating force experienced by the whole of the gas below the given plane. On the other hand, the whole of the gas above the given plane will lose mass momentum at the same rate and will thus experience a retarding force of the same magnitude.

**Detailed Calculation†† :** Let us suppose, the gas has mass motion along  $x$ -direction and the mass velocity  $V$  increases upward along  $z$ -direction. Let us consider exchange of momentum across the  $AB$ -plane (Fig. 2.12) where the mass velocity is  $V$ . We assume†† that a molecule crossing

\*These results have been taken from Saha and Srivastava, *loc.cit.*

\*\*See W. Wilson, *loc.cit.*, P. 237, for a lucid exposition.

†Calculation, presented here, broadly follows Jeans, *Dynamical Theory of Gases*, Pp. 244–6 (1904). For Maxwell's deduction, see Loeb, *Ibid*, Pp. 182–5.

†For an alternative rigorous deduction, see Appendix-6.

‡Kennard, *Kinetic Theory of Gases*, P. 139 (1938); W. Wilson *loc.cit.*, P. 237.

the  $AB$ -plane after a collision at  $P$ , will carry, besides the random momentum ( $\equiv mu, mv, mw$  due to random motion), a momentum  $mV$  appropriate to the layer at  $P$ . It should, however, be noted that the net transfer of random momentum downward (or upward) is nil, because  $mu, mv$  and  $mw$  have all possible positive and negative values. So we shall leave out of account from the beginning the transfer of random momentum, and shall consider only the transport of mass momentum across  $AB$ -plane.

We first consider those molecules which, after suffering collisions at different layers above  $AB$ -plane, pass through  $AB$ -plane with molecular velocity  $c$  in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$ . In the present problem, since the gas is not in a steady, equilibrium state, we cannot apply Maxwell's law here. Then, following (2.1), we may write the number of molecules passing through unit area of  $AB$ -plane per second from above and having velocities between  $c$  and  $c + dc$  in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$  as

$$dn_{c\theta\phi} \times c \cos \theta = \left( n f(c) dc \times \frac{\sin \theta d\theta d\phi}{4\pi} \right) \times c \cos \theta. \quad (2.80)$$

Here,  $dn_c = n f(c) dc$ , but since the state is not Maxwellian,  $4\pi a^3 e^{-bc^2} c^2 dc$  of (2.29) is replaced by non-Maxwellian  $f(c) dc$ . Now, since these molecules travel different distances (i.e., different free paths)  $\lambda_c$  to reach  $AB$ -plane (Fig. 2.12), we take the mean value of these distances, i.e., the mean free path  $\bar{\lambda}_c$ . Then, because each such molecule carries downward an average momentum\*

$$m \left( V_0 + \bar{\lambda}_c \cos \theta \frac{dV}{dz} \right), \quad V_0 = \text{mass velocity at } AB\text{-plane},$$

the total momentum carried through unit area of  $AB$ -plane per second by  $c$ -molecules in directions specified above is, from (2.80),

$$= \frac{1}{4\pi} nm \left( V_0 + \bar{\lambda}_c \cos \theta \frac{dV}{dz} \right) f(c) c dc \sin \theta \cos \theta d\theta d\phi. \quad (2.81)$$

Then, the net momentum\*\* transported below  $AB$ -plane through unit area per second is

$$\begin{aligned} &= \frac{1}{4\pi} nm \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} \int_0^{\infty} \left( V_0 + \bar{\lambda}_c \cos \theta \frac{dV}{dz} \right) f(c) c dc \sin \theta d\theta d\phi \\ &= \frac{1}{3} nm \frac{dV}{dz} \int_0^{\infty} \bar{\lambda}_c f(c) c dc \\ &= \frac{1}{3} nm \frac{dV}{dz} \overline{(c \bar{\lambda}_c)} \quad [\text{from (2.57)}]^\dagger \\ &= \frac{1}{3} nm \bar{c} \bar{\lambda} \frac{dV}{dz}, \end{aligned} \quad (2.82)$$

where we have put  $\overline{(c \bar{\lambda}_c)} = \bar{c} \cdot \bar{\lambda}$ . (2.83)

\*Note that we have used  $\bar{\lambda}_c$ , and not  $\lambda_c$  here.

\*\*Integration over  $\theta$  from 0 to  $\pi/2$  only corresponds to downward transport and from  $\pi/2$  to  $\pi$  only corresponds to upward transport so that integration over  $\theta$  from 0 to  $\pi$  gives the net transport downward, because molecules from the upper layers carry larger mass-momenta than those from the lower layers.

† $f(c) dc$  plays here the role of (but is not equal to) the Maxwellian  $4\pi a^3 e^{-bc^2} c^2 dc$  which is the probability of a molecule having velocity  $c$  and therefore is the very probability of occurrence of  $c$  and  $\bar{\lambda}_c$ .

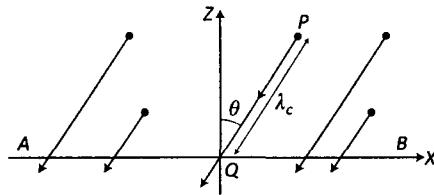


Fig. 2.12: Transport of mass momentum

Here  $\bar{\lambda}$  (mean of all  $\bar{\lambda}_c$ 's for different values of  $c$ ) should be so defined as to satisfy (2.83)\*.

Since  $\frac{1}{3}nm\bar{c}\bar{\lambda}\frac{dV}{dz}$  is the rate of gain of mass momentum per unit area of the medium below  $AB$ -plane, this is the accelerating force experienced by unit area of this medium. Also, since  $\frac{1}{3}nm\bar{c}\bar{\lambda}\frac{dV}{dz}$  is evidently also the rate of loss of mass momentum per unit area of the medium above  $AB$ -plane, this is the retarding force experienced by unit area of this medium. Hence, equating (2.79) to (2.82),

$$\frac{1}{3}nm\bar{c}\bar{\lambda}\frac{dV}{dz} = F = \eta \frac{dV}{dz}$$

$$\text{i.e., } \eta = \frac{1}{3}nm\bar{c}\bar{\lambda}. \quad (2.84)$$

## 2.17 Discussion on (2.84)

Combining (2.69) and (2.84),

$$\eta = \frac{1}{3\sqrt{2}} \frac{m\bar{c}}{\pi\sigma^2}. \quad (2.85)$$

Chapman\*\* modifies (2.85) as

$$\eta = \frac{0.499}{\sqrt{2}} \frac{m\bar{c}}{\pi\sigma^2}. \quad (2.86)$$

According to (2.85) [or (2.86)],  $\eta$  depends on  $\bar{c}$ ,  $m$  and  $\sigma$  only. This means that  $\eta$  should vary as  $\sqrt{T}$  [See (2.36)] but should be independent of pressure or density of the gas. This result was first predicted by Maxwell from theoretical considerations. Experiments by Meyer, Maxwell and others showed that  $\eta$  indeed is independent of pressure from a few mm of Hg to several atmospheres. This law, however, fails at low pressures. This is due to the fact that at low pressures,  $\bar{\lambda}$  becomes comparable with the size of the vessel and, therefore, becomes a constant. Then, as (2.84) shows,  $\eta$  decreases with density or pressure. Also at very high pressures, for certain gases such as carbon dioxide,  $\eta$  is found to vary with pressure. This is explained by the fact that the intermolecular forces, which become very important at very high pressures, have not been taken into account in developing the theory in the foregoing section.

Again, although  $\eta$ , as stated above, should vary as  $\sqrt{T}$ , in practice it varies with  $T$  to a greater extent than as  $\sqrt{T}$ . This is due to the fact that as two molecules collide with high energy at a high temperature, their centres come nearer so that  $\sigma$ , which appears in theory as the distance between molecular centres during collision, is decreased. Thus, from (2.84) [or (2.86)],  $\eta$  depends on temperature not only through  $\bar{c}$  but also through  $\sigma$ . Sutherland† has shown that

$$\eta = \eta_0 \left( \frac{T_0 + K}{T + K} \right) \left( \frac{T}{T_0} \right)^{3/2} \quad (2.87)$$

where  $K$  is a constant characteristic of the gas and  $T_0K$  is just 0 °C. (2.87) is found to accord well with experiment.

Finally, since  $\eta$  can be determined experimentally, the value of  $\sigma$  can be calculated from (2.86). Good agreement is observed between the values of molecular diameter calculated in this way and those found by other methods.

\*Detailed calculations show that with  $f(c)$  as Maxwellian  $\bar{\lambda}$  is 1.051 times Maxwell's mean free path given by (2.69).

\*\* *Idem.*, Proc. Roy. Soc., A, 93, 1 (1916).

†Sutherland, Phil. Mag., 5, 36, 507 (1893).

## 2.18 Thermal Conductivity of Gases

Let us consider conduction in a gas, contained between two infinite parallel plane plates perpendicular to  $z$ -axis (Fig. 2.12), the upper plate being at a higher temperature so that there is no convection effect at all. Then, we may divide the gas into layers having temperature increasing upward. There will, therefore, be a flow of heat in the downward direction. The thermal conductivity observed in such a case is defined by

$$Q = K \frac{dT}{dz}, \quad (2.88)$$

where  $Q$  is the quantity of heat flowing through unit area per unit time in the downward direction.

Now, the kinetic theory identifies heat with the kinetic energy of molecules. Then, we may say that the average kinetic energy of a molecule increases with temperature  $T$  from layer to layer in the upward direction. Now, due to random molecular motion as molecules move from layers of higher temperature to layers of lower temperature and *vice versa* through a given plane (taken perpendicular to  $z$ -axis), there will be a net gain of heat energy by the gas below the plane and an equal net loss of heat energy by the gas above the plane, assuming, of course, that equal numbers of molecules cross unit area of the plane in both directions per second. This is the kinetic interpretation of gaseous conduction.

Let  $E_0$  be the average kinetic energy of a molecule in the  $AB$ -plane (Fig. 2.12)\*. The number of molecules which cross, with a mean velocity  $\bar{c}$ , unit area of this plane per second in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$  is (from (2.1))

$$\left( n \times \frac{\sin \theta d\theta d\phi}{4\pi} \right) \times \bar{c} \cos \theta. \quad (2.89)$$

Now, if  $\bar{\lambda}$  is the mean free path, each of these molecules carries downward an average energy

$$E_0 + \bar{\lambda} \cos \theta \frac{dE}{dz},$$

where  $E$  is average kinetic energy of a molecule of any layer  $z = \text{const}$ . Then, the total energy carried downward through unit area of  $AB$ -plane per second by these molecules is

$$\frac{1}{4\pi} n \bar{c} \left( E_0 + \bar{\lambda} \cos \theta \frac{dE}{dz} \right) \sin \theta d\theta d\phi. \quad (2.90)$$

Now, integrating (2.90) over  $\phi$  from 0 to  $2\pi$  and over  $\theta$  from 0 to  $\pi$ , we obtain the net energy transported downward per unit area of  $AB$ -plane per second (as explained in foot-note, P. 47) as

$$\begin{aligned} \frac{1}{4\pi} n \bar{c} \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} \left( E_0 + \bar{\lambda} \cos \theta \frac{dE}{dz} \right) \sin \theta d\theta d\phi &= \frac{1}{3} n \bar{c} \bar{\lambda} \frac{dE}{dz} \\ &= \frac{1}{3} n \bar{c} \bar{\lambda} \frac{dE}{dT} \frac{dT}{dz}. \end{aligned} \quad (2.91)$$

Then, comparing (2.88) and (2.91)\*\*,

$$K = \frac{1}{3} n \bar{c} \bar{\lambda} \frac{dE}{dT}. \quad (2.92)$$

\*Since this deduction is basically similar to that presented in section 2.16, only salient steps will be worked out here. For an alternative rigorous deduction, see Appendix-6.

\*\* $E$  is expressed here in heat unit.

If  $m$  is the mass of one molecule, the number of molecules in unit mass is  $1/m$  and the specific heat at constant volume per unit mass is given by

$$c_v dT = dE \times \frac{1}{m} \quad (\because dE = \text{change in energy per molecule})$$

or,  $c_v = \frac{1}{m} \frac{dE}{dT}$ . (2.93)

From (2.92) and (2.93),

$$K = \frac{1}{3} mn \bar{\lambda} \bar{c} c_v = \eta c_v. (2.94)$$

Experiment confirms the proportionality between  $K$  and  $\eta$  (since  $c_v$  hardly varies with temperature and pressure) indicated by (2.94) and also confirms the fact that these two quantities vary in the same manner with temperature, but there is agreement up to this point only. It is found from experiment that actually

$$K = \alpha \eta c_v, (2.95)$$

where  $\alpha$  is equal to about 2.5 for monatomic gases like helium and argon, 1.9 for diatomic gases like hydrogen, oxygen and nitrogen, and still smaller values for more complex molecules. The form of  $\alpha$  as given by Eucken\* considering transport of translational and other forms of energy is

$$\frac{K}{\eta c_v} = \alpha = \frac{1}{4}(9\gamma - 5), (2.96)$$

where  $\gamma$  = ratio of specific heats of a gas. From (2.96), we obtain exactly  $\alpha = 2.5$  for monatomic gases, 1.9 for diatomic gases, and 1.68 for triatomic gases like  $\text{CO}_2$  and  $\text{N}_2\text{O}$ .

## 2.19 Diffusion of Gases

Let us consider a mixture of two gases, 1 and 2, such that  $n_1$ , the molecular concentration of gas 1 (= no. of molecules of gas 1/cc) increases in the upward direction along  $z$ -axis, (Fig. 2.12) and  $n_2$ , the molecular concentration of gas 2 increases in the downward direction. Due to random motion, the molecules of the gases will increase in concentration of gas 1 below the  $AB$ -plane (Fig. 2.12) and there is a net increase in concentration of gas 2 above that plane. This is known as the process of diffusion—gas 1 diffusing into gas 2 downward and gas 2 diffusing into gas 1 upward. This process continues till the composition of the mixture is the same throughout. Experiments on gases (also on liquids) give the law of diffusion as

$$G_1 = -D_{12} \frac{dn_1}{dz} (2.97)$$

(where  $G_1$  is the net number of molecules of gas 1 passing through unit area of  $AB$ -plane per second in the downward direction) and as

$$G_2 = -D_{21} \frac{dn_2}{dz} (2.98)$$

(where  $G_2$  is the net number of molecules of gas 2 passing through unit area of  $AB$ -plane per second in the upward direction).  $D_{12}$  is the coefficient of diffusion of gas 1 into gas 2 and  $D_{21}$  that of gas 2 into gas 1.

\*Phys. Ziets, 14, 324, (1913)

Since the pressure and temperature are kept constant in the usual experiments on diffusion, it follows from Avogadro's law on perfect gases that for all layers, the total number of molecules/cc is

$$n_1 + n_2 = \text{constant} \quad (2.99)$$

$$\text{so that } +\frac{dn_1}{dz} = -\frac{dn_2}{dz}, \quad (2.100a)$$

$$\text{i.e., } \left| \frac{dn_1}{dz} \right| = \left| \frac{dn_2}{dz} \right|^*. \quad (2.100b)$$

From (2.99), it is clear that

$$G_1 + G_2 = 0, \quad (2.101)$$

i.e., the net transport of molecules of both kinds must be nil. From (2.97), (2.98), (2.100) and (2.101), therefore,

$$D_{12} = D_{21}. \quad (2.102)$$

Let  $n_{10}$  be the concentration of gas 1 at the  $AB$ -plane. Then, if a molecule of gas 1, after suffering a collision at  $P$  above  $AB$ -plane, travels with velocity  $c$  along a free path  $\lambda_{1c_1}$  at an angle  $\theta$  to pass through the plane, then the concentration at the layer at  $P$  is

$$n_{10} + \lambda_{1c_1} \cos \theta \frac{dn_1}{dz}.$$

Since these molecules, with velocity  $c$ , travel different distances (i.e., free paths), we may consider them to be coming from a layer of mean concentration

$$n_{10} + \bar{\lambda}_{1c_1} \cos \theta \frac{dn_1}{dz}. \quad (2.103)$$

Then, the number of such molecules of velocity  $c$  passing through unit area of  $AB$ -plane per second in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$  is [See (2.80)]

$$\left\{ \left( n_{10} + \bar{\lambda}_{1c_1} \cos \theta \frac{dn_1}{dz} \right) f(c_1) dc_1 \frac{\sin \theta d\theta d\phi}{4\pi} \right\} \times c_1 \cos \theta \quad (2.104)$$

so that the net number of molecules transported downward per unit area of  $AB$ -plane per second is

$$\begin{aligned} \nu_1 &= - \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} \int_0^{\infty} \frac{1}{4\pi} \left( n_{10} + \bar{\lambda}_{1c_1} \cos \theta \frac{dn_1}{dz} \right) f(c_1) dc_1 \sin \theta d\theta d\phi \\ &\quad (-\text{ve sign, because this transport is in the -ve } z\text{-direction}) \\ &= -\frac{1}{3} \bar{c}_1 \bar{\lambda}_1 \frac{dn_1}{dz}, \text{ (See (2.82) and (2.83))} \end{aligned} \quad (2.105)$$

where  $\bar{c}_1$  and  $\bar{\lambda}_1$  are respectively the mean molecular velocity and mean free path (taking into account all possible values of  $c_1$ ) of gas 1.

\*When we write a quantity  $x$  as  $|x|$ , we mean its magnitude only, irrespective of its sign.

Proceeding in the same manner for gas 2, the net number of molecules transported upward per unit area of  $AB$ -plane per second is

$$\nu_2 = +\frac{1}{3}\bar{c}_2\bar{\lambda}_2 \frac{dn_2}{dz}. \quad (2.106)$$

Since, in general,  $|\nu_1| \neq |\nu_2|$ , there would be a tendency for a net transfer of molecules equal to, say,  $|\nu_1| - |\nu_2|$  (if  $|\nu_1|$  is  $> |\nu_2|$ ) in the downward direction. This would produce differences of pressure in the gas which, however, cannot exist as the pressure is maintained constant in experiments. So, to counteract these pressure differences, the gas develops a slow mass motion and carries the same number of molecules, i.e.,  $|\nu_1| - |\nu_2|$  molecules in the upward direction. Since the concentrations of the two kinds of molecules are in the ratio  $n_1 : n_2$ , the gas, due to its mass motion, carries upwards  $\frac{n_1}{n_1+n_2} \times (|\nu_1| - |\nu_2|)$  molecules of gas 1 and  $\frac{n_2}{n_1+n_2} \times (|\nu_1| - |\nu_2|)$  molecules of gas 2 through unit area of  $AB$ -plane per second. Then, the net downward transport of molecules of gas 1 per unit area per second is, from (2.105) and (2.106),

$$\begin{aligned} -\frac{1}{3}\bar{c}_1\bar{\lambda}_1 \frac{dn_1}{dz} + \frac{n_1}{n_1+n_2}(|\nu_1| - |\nu_2|) &= -\frac{1}{3}\bar{c}_1\bar{\lambda}_1 \frac{dn_1}{dz} + \frac{n_1}{n_1+n_2} \times \frac{1}{3} \left( \left| \bar{c}_1\bar{\lambda}_1 \frac{dn_1}{dz} \right| - \left| \bar{c}_2\bar{\lambda}_2 \frac{dn_2}{dz} \right| \right) \\ &= -\frac{1}{3} \frac{n_1\bar{c}_2\bar{\lambda}_2 + n_2\bar{c}_1\bar{\lambda}_1}{n_1+n_2} \frac{dn_1}{dz}, \end{aligned} \quad (2.107)$$

where we have utilised the fact that  $|\frac{dn_1}{dz}|$  and  $|\frac{dn_2}{dz}|$  are equal, as shown in (2.100).

Comparing (2.97) and (2.107), we find

$$D_{12} = \frac{1}{3} \frac{n_1\bar{c}_2\bar{\lambda}_2 + n_2\bar{c}_1\bar{\lambda}_1}{n_1+n_2}. \quad (2.108)$$

Proceeding in the same manner for gas 2, we also find

$$D_{21} = \frac{1}{3} \frac{n_2\bar{c}_1\bar{\lambda}_1 + n_1\bar{c}_2\bar{\lambda}_2}{n_1+n_2} = D_{12}. \quad (2.109)$$

(2.108) (or (2.109)) is generally known as Meyer's formula.

If the molecules of the two gases are approximately of the same size and mass, the  $\bar{\lambda}$  and  $\bar{c}$  are same for both gases. Then, from (2.108),

$$D = \frac{1}{3}\bar{\lambda}\bar{c} = \frac{\eta}{\rho}. \quad [\text{from (2.84)}] \quad (2.110)$$

$D$  is called the coefficient of self-diffusion of the gas. Detailed analysis by Chapman\* and Enskog has modified (2.110) as

$$D = \frac{\epsilon\eta}{\rho}. \quad (2.111)$$

Now, since  $\bar{\lambda} \propto \frac{1}{n} \propto \frac{T}{P}$  and  $\bar{c} \propto \sqrt{T}$ , it is evident from (2.108) and (2.110) that

$$D \propto \frac{T^{3/2}}{P}. \quad (2.112)$$

Experimental observations confirm the dependence of  $D$  upon  $P$  as given in (2.112). But it is found that

$$D \propto T^\alpha, \quad (2.113)$$

where  $\alpha$  lies between 1.75 and 2.

\* Phil. Trans. 217, 166 (1917); Jeans, *Dynamical Theory of Gases*, Chap. XIII (4th edition).

## 2.20 Effusion vs Diffusion\*

*Effusion* : Effusion is a mass phenomenon. It is the process of streaming of a gas through apertures, which, though small, are wide enough to permit the flow of enormous numbers of molecules. Now, if the aperture is very short, the velocity in the emerging stream of gas is given approximately by Bernoulli's theorem :

$$P_1 + \frac{1}{2}\rho v_1^2 + h\rho g = P_2 + \frac{1}{2}\rho v_2^2 + h\rho g, \quad (2.114)$$

where  $P_1$ ,  $P_2$  and  $v_1$ ,  $v_2$  are the pressures and stream velocities at the two ends of the aperture along a stream line. Here,  $\rho$  has approximately been taken to be the density all through the aperture. If  $P_1$  is taken as the pressure in the interior of a large vessel where  $v_1$  is practically zero, and if  $P_2$  is taken as the pressure just outside the aperture, we have for the velocity of effusion  $v$ ,

$$\begin{aligned} P_1 - P_2 &= \frac{1}{2}\rho v^2 \\ \text{or, } v &= \sqrt{\frac{2(P_1 - P_2)}{\rho}}. \end{aligned} \quad (2.115)$$

If, however, the aperture is in the nature of a long tube, the streaming of a gas through it is governed approximately by Poiseuilli's formula :

$$P_1 V_1 = \frac{(P_1^2 - P_2^2)\pi a^4}{16\eta l}, \quad (2.116)$$

where  $V_1$  = volume of gas entering the tube per second at pressure  $P_1$ ,  $a$  = radius of the tube,  $l$  = length of the tube,  $\eta$  = coefficient of viscosity of gas.

It is evident from (2.115) and (2.116) that in the case of effusion, there cannot be separation of individual gases from a mixture. Because, it is the total pressure, and not the partial pressure of a gas mixture that occurs in (2.115) and (2.116).

*Diffusion* : We speak of diffusion of a gas through a membrane, if its apertures are so minute that they allow just one or two molecules to pass through them at a time. Thus, diffusion is a molecular phenomenon depending on the motions of individual molecules.

It has been shown in *Exercise 1* under section 2.6 that the number of molecules hitting unit area of the wall of a vessel per second is

$$\nu = \frac{1}{2}n\bar{c}. \quad (2.117)$$

If there is a fine aperture in the wall, then this is also the number of molecules that pass through unit area of the aperture per second.

If, now, there is in the vessel another gas having the same number of molecules  $n$  per unit volume then the number of molecules of this second gas passing through unit area of the aperture per second is

$$\nu' = \frac{1}{4}n\bar{c}'. \quad (2.118)$$

\*W. Wilson, *loc. cit.*, Pp. 243-244 (1931).

Now, since the gases are in the same vessel, they are at the same temperature. Then, from (2.36),

$$\frac{\nu}{\nu'} = \frac{\bar{c}}{\bar{c}'} = \sqrt{\frac{m'}{m}} = \sqrt{\frac{nm'}{nm}} = \sqrt{\frac{\rho'}{\rho}} \quad (2.119)$$

i.e.,  $\nu \propto \sqrt{\frac{1}{\rho}}$ . (2.120)

This means that the rate of diffusion through a porous membrane is higher for a gas of lower density but lower for a gas of higher density. Hence, diffusion gives a method of separating the constituents of a gas mixture. (2.119) [or (2.120)] corresponds to the experimental fact known as *Graham's law*.

## 2.21 Electrical Conductivity of Metals

On the basis of kinetic theory, we shall discuss here the electrical conductivity of metals. This problem was first discussed by Riecke\* and later in more detail by Drude\*\*. An electrical conductor is distinguished from an insulator by the fact that in an insulator electrons are strongly bound to the atom, whereas in a metal, one or more electrons leave the atom and move about inside the conductor like gas molecules. So, if an electric field is applied through the conductor by means of an electric cell, the free electrons shall have a systematic drift in the direction of the field (actually in the opposite direction, because the electrons are negatively charged). Now, as an electron moves, it collides, from time to time, with the ions of the conductor. We assume that after each collision, the electron starts afresh with the mean velocity  $\bar{c}$  corresponding to the temperature of the metal. Then, during the interval between two consecutive collisions, the electron will develop, in addition to  $\bar{c}$ , some velocity caused by the acceleration.

$$f_E = \frac{Ee}{m} \quad (2.121)$$

parallel to the field  $E$ . Here  $m$  and  $e$  are respectively mass and charge of the electron.

Now, different electrons will travel different distances (i.e., free paths) between two collisions so that we shall take the mean free path,  $\bar{\lambda}$ , for our calculation. Evidently, the time taken to travel a distance  $\bar{\lambda}$  is  $t = \bar{\lambda}/\bar{c}$ . Then, the distance traversed during this time in the field direction due to the acceleration  $f_E$  is

$$s = \frac{1}{2} f_E t^2 = \frac{1}{2} \cdot \frac{Ee}{m} \cdot \left(\frac{\bar{\lambda}}{\bar{c}}\right)^2 \quad (2.122)$$

so that the average velocity in the field direction is

$$\bar{v}_E = \frac{s}{t} = \frac{1}{2} \frac{Ee\bar{\lambda}}{m\bar{c}}. \quad (2.123)$$

From (2.36),

$$m = \frac{8kT}{\pi(\bar{c})^2}. \quad (2.124)$$

Therefore, from (2.123) and (2.124),

$$\bar{v}_E = \frac{\pi E e \bar{\lambda} \bar{c}}{16 k T}. \quad (2.125)$$

\*E. Riecke, *Wied. Ann.* **66**, Pp. 353 & 545 (1898).

\*\*P. Drude, *Ann. der. Phys.*, **1**, P. 566 (1900), and **3**, P. 369 (1900).

If  $n$  be the number of electrons/cc, then the current flowing through unit area of the conductor due to this velocity in the field direction is

$$i = ne\bar{v}_E = \frac{\pi n E e^2 \bar{\lambda} \bar{c}}{16kT}. \quad (2.126)$$

Therefore, conductivity  $\sigma = \frac{i}{E} = \frac{\pi n e^2 \bar{\lambda} \bar{c}}{16kT}$  (2.127)

$$= \frac{ne^2 \bar{\lambda}}{8} \sqrt{\frac{2\pi}{mkT}}. \quad (2.128a)$$

If, however,  $\bar{c}$  is approximately taken  $= \sqrt{\bar{c}^2} = \sqrt{\frac{3kT}{m}}$ , instead of (2.36), then (2.125)–(2.128a) will be accordingly modified, and finally we obtain

$$\sigma = \frac{ne^2 \bar{\lambda} \bar{c}}{6kT} = \frac{ne^2 \bar{\lambda}}{2} \sqrt{\frac{1}{3mkT}}. \quad (2.128b)$$

Quite in keeping with Ohm's law, (2.128) shows that  $\sigma$  depends on the material of the conductor and its temperature. But, whereas (2.128) demands that  $\sigma$  should be inversely proportional to  $\sqrt{T}$ , it is observed for most pure metals that  $\sigma$  varies just inversely as  $T$ . This discrepancy is explained by two facts. First, we should not expect the free electrons because of their density (i.e.,  $n$ ) in metals to behave exactly as an ideal gas. They are so close together that the forces between them always influence their motion. Secondly, when a gas of identical particles is dense, quantum effects become important and should be taken into account.\*

Next,  $n$  and  $\bar{\lambda}$  are the only quantities in (2.128) that may vary from material to material. But,  $\bar{\lambda}$  cannot vary to a large extent from metal to metal. So it is inferred that different metals possess different conductivities due to different values of  $n$  in them.

## 2.22 Thermal Conductivity of Metals

The intimate connection between the electrical and the thermal conductivity of metals is given by the law of Wiedemann and Franz which states that the ratio of thermal conductivity to electrical conductivity at any temperature is same for all metals, and is proportional to the absolute temperature\*\*. Drude's theory of electrons as a gas inside a metal gives an explanation of this law.

On the kinetic theory, thermal conductivity of metals is explained in the following way. Let us suppose, temperature increases upward along  $z$ -axis (Fig. 2.12) inside the metal. Since, the ions inside a metal can have only vibrational energy, it is evident that the average vibrational energy of an ion in an upper layer (Fig. 2.12) is higher than that of an ion in a lower layer. Now, it has already been stated in section 2.21 that as electrons move about like gas molecules, they collide with ions and exchange energy with them. So, after collision with an ion at an upper layer, as an electron comes downward, it carries heat energy (i.e., kinetic energy) appropriate to that layer. When this electron collides with an ion at a lower layer, it transfers this energy to the ion. Now, a similar process will happen as an electron goes upward. Now, supposing that equal numbers of electrons cross unit area of, say,  $AB$ -plane (Fig. 2.12) in both directions per second, it is evident that there will be a net gain of heat energy by the part of the metal below the  $AB$ -plane and an equal net loss of heat energy by the part of the metal above the  $AB$ -plane. This is the interpretation of thermal conductivity of metals.

\*See Chapter 10.

\*\*Lorentz, *Pogg. Ann.* 147, 429 (1872).

Now, it is clear that the calculations that we carried out in section 2.18 with gas molecules may directly be applied to electron gas inside a metal. So we do not repeat the calculations but write the expression for thermal conductivity from (2.92),

$$K = \frac{1}{3} n \bar{c} \bar{\lambda} \frac{dE}{dT}, \quad (2.129)$$

where  $n$  is the number of electrons/cc inside the metal,  $\bar{c}$  the mean velocity,  $\bar{\lambda}$  the mean free path between collisions with the ions and  $\frac{dE}{dT}$  the rate of change of average (kinetic) energy  $E$  of an electron with  $T^*$ .

Now, since  $E = \frac{1}{2} m \bar{c}^2 = \frac{3}{2} kT$ ,

$$\frac{dE}{dT} = \frac{3}{2} k.$$

Then, (2.129) gives

$$K = \frac{1}{2} k n \bar{c} \bar{\lambda}. \quad (2.130)$$

Hence, from (2.128a) and (2.130),

$$\frac{K}{\sigma} = \left( \frac{k}{e} \right)^2 \cdot \frac{8}{\pi} \cdot T. \quad (2.131)$$

If, however, the approximate formula (2.128b) and (2.130) are taken,

$$\frac{K}{\sigma} = \left( \frac{k}{e} \right)^2 \cdot 3 \cdot T. \quad (2.132)$$

(2.132) gives the law of Wiedemann and Franz.

Let us evaluate  $\frac{K}{\sigma T}$  first from (2.131),

$$\frac{K}{\sigma T} = \left( \frac{k}{e} \right)^2 \times \frac{8}{\pi} = \left( \frac{1.37 \times 10^{-16} \text{ erg K}^{-1}}{1.59 \times 10^{-20} \text{ emu}} \right) \times \frac{8}{3.14} = 1.86 \times 10^8 \text{ erg K}^{-1} \text{ emu}^{-1}. \quad (2.133a)$$

If, however, we take (2.128), then

$$\frac{K}{\sigma T} = \left( \frac{k}{e} \right)^2 \cdot 3 = 2.2 \times 10^8 \text{ erg K}^{-1} \text{ emu}^{-1}. \quad (2.133b)$$

The experimentally observed values of  $\frac{K}{\sigma T}$  for different metals are found to be larger than the above theoretical values at ordinary temperatures. Further, contrary to theoretical prediction,  $\frac{K}{\sigma T}$  is found to fall with temperature. Now, it is well known that both electrical and thermal conductivities increase at low temperatures. So, it is evident that as temperature falls  $K$  and  $\sigma$  do not increase in the same manner. In fact,  $\sigma$  increases more rapidly than  $K$ . The variation of  $\frac{K}{\sigma T}$  with temperature is partly accounted for by the fact that the thermal conductivity of metals is not entirely due to electrons but takes place by a mechanism similar to heat conduction in insulators\*\*. Raman<sup>†</sup> has also suggested a quantum mechanism for thermal conduction in solids (See section 8.9).

Further aspects of thermal conduction will be taken up in Chapter 4.

\*An electron in an upper layer will have its average kinetic energy higher than an electron at a lower layer (Fig. 2.12).

\*\*Haas and Nobel, *Physica*, **5**, 449, (1938).

<sup>†</sup>Raman, C. V. Proc. Ind. Acad. Sc., **43**, Pp. 327–35 (1956).

## 2.23 Brownian Motion

In 1827, botanist, Robert Brown, observed that the pollen grains of *clarkia pulchella*, when suspended in water, were in a constant state of agitation, i.e., in a constant state of zigzag motion. Further investigations have shown that this sort of constant zig-zag motion, called *Brownian motion*, is not confined to pollen grains or to living particles. It can be observed with any kind of small particles suspended in a liquid or gas. It is a common experience to see smoke or dust particles moving about constantly in air. Christian Wiener was the first to conclude in 1863 that the Brownian motion is due to collisions on the suspended particles (also called *Brownian particles*) by the molecules of the liquid or gas medium (Fig. 2.13). This directly means that the molecules of the liquid and the gas are in constant agitation themselves and this is, therefore, a definite evidence in favour of the kinetic theory of matter. We may observe conveniently under a high power microscope or an ultramicroscope the zigzag motion of particles suspended in a colloidal solution. The Brownian movement is more violent in the case of small particles than in the case of large particles.

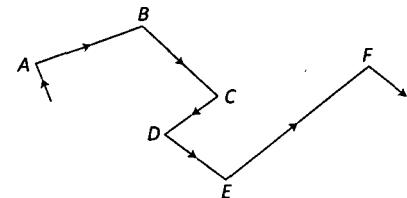


Fig. 2.13: Brownian motion

**(A) Einstein's Theory :** In 1905 Einstein\* (and also Smoluchowski independently in 1906) gave a complete analysis of the phenomenon. Einstein's theory is based on the idea that the Brownian particles, on account of their random motions, tend to diffuse into the fluid medium in the course of time from the region of higher concentration of the suspended particles to the region of lower concentration.

Suppose that the number density,  $n$ , of particles suspended in a fluid medium diminishes along the  $x$ -axis. The number,  $\nu$ , of particles diffusing through unit area of a plane perpendicular to the  $x$ -axis per second is defined by the following relation :

$$\nu = -D \frac{dn}{dx}, \quad (2.134)$$

where  $D$  is called the coefficient of diffusion.  $\frac{dn}{dx}$  is negative because  $n$  decreases as  $x$  increases.

Einstein's theory of Brownian motion is based on the calculation of  $D$  for the suspended Brownian particles in the following two ways and then equating the two results :

- (1) from the random motion of the suspended particles and
- (2) from the difference in osmotic pressure between different parts due to differences in concentration of the suspended particles which are responsible for diffusion.

### First Calculation of $D$

If we observe the  $x$ -component of displacement  $\Delta x$  of a Brownian particle (along the  $x$ -axis) over a time  $\tau$ , then the average of this displacement taken over a large number of Brownian particles would obviously be zero. If, however, we take the square of  $\Delta x$  over a time  $\tau$ , and the average is taken over a large number of Brownian particles, then the square root of  $(\Delta x)^2$ , i.e.,  $\sqrt{(\Delta x)^2} \equiv \Delta$ , may reasonably be taken as a measure of the mean displacement over a time  $\tau$  for the purpose of our calculation.

Refer to Fig. 2.14. Let us imagine a cylinder of cross section  $\alpha$  along the  $x$ -axis. Let us consider a segment of length  $\Delta$  defined above. Then, the average speed of a particle is  $\frac{\Delta}{\tau}$ .

\* Einstein, *Investigations on the Theory of Brownian Movement* edited by Fürth and Cowper, Pp. 68-81.

Suppose, the number density of the suspended particles is  $n_1$ , at the end  $S_1$  of the segment  $\Delta$  and is  $n_2$  at the end  $S_2$  with  $n_1 > n_2$ . Then, the number of particles entering at the end  $S_1$  in time  $\tau$  is

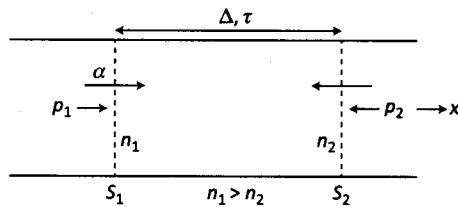


Fig. 2.14

$$\left[ \left( \frac{1}{2}n_1 \right) \times \left( \frac{\Delta}{\tau} \right) \times \alpha \right] \times \tau = \frac{1}{2}n_1 \Delta \alpha$$

and entering at the end  $S_2$  in time  $\tau$  is

$$\left[ \left( \frac{1}{2}n_2 \right) \times \left( \frac{\Delta}{\tau} \right) \times \alpha \right] \times \tau = \frac{1}{2}n_2 \Delta \alpha,$$

where the factor  $\frac{1}{2}$  occurs in each case because as many particles move to the right as to the left due to their random motion.

Hence, the *net number* of particles passing through  $\Delta$  in time  $\tau$  from the left to the right is

$$\frac{1}{2}(n_1 - n_2)\Delta \alpha. \quad (2.135)$$

On the other hand, according to (2.134), this number should be

$$\left( -D \frac{dn}{dx} \right) \times \alpha \times \tau. \quad (2.136)$$

Equating (2.135) and (2.136),

$$\frac{1}{2}(n_1 - n_2)\Delta \alpha = \left( -D \frac{dn}{dx} \right) \times \alpha \times \tau \quad \text{or,} \quad \frac{1}{2} \left[ \frac{n_1 - n_2}{\Delta} \right] \Delta^2 = \left( -D \frac{dn}{dx} \right) \times \tau$$

$$\text{or,} \quad \frac{1}{2} \left( -\frac{dn}{dx} \right) \Delta^2 = \left( -D \frac{dn}{dx} \right) \times \tau.$$

$$\therefore D = \frac{\Delta^2}{2\tau}. \quad (2.137)$$

### Second Calculation of $D$

We know that corresponding to the number density  $n$  of a perfect gas at temperature  $T$  the pressure is

$$P = nkT. \quad (2.138)$$

Now, assuming the suspended particles to behave like a perfect gas, the pressure at the end,  $S_1$ , is

$$P_1 = n_1 kT \quad (2.139a)$$

and that at the end,  $S_2$ , is

$$P_2 = n_2 kT. \quad (2.139b)$$

Then the *net force* on the particles in the segment  $\Delta$  is

$$F = (P_1 - P_2) \times \alpha = (n_1 - n_2)kT \times \alpha. \quad (2.140)$$

Now, if the average number density of particles in  $\Delta$  is taken to be  $n$ , then the total number of particles in  $\Delta$  is

$$n \times (\Delta \alpha) = n \Delta \alpha. \quad (2.141)$$

Then the force on one particle is

$$f = \frac{F}{n\Delta\alpha} = \frac{(n_1 - n_2)}{\Delta} \frac{kT}{n} = \left( -\frac{dn}{dx} \right) \frac{kT}{n}. \quad (2.142)$$

Applying Stokes' law,

$$f = 6\pi\eta rv = \left( -D \frac{dn}{dx} \right) \frac{kT}{n}, \quad v \text{ being the speed of a particle and } r \text{ its radius}$$

or,  $nv = \left( -\frac{kT}{6\pi\eta r} \frac{dn}{dx} \right), \quad (2.143)$

where  $\eta$  = coefficient of viscosity of the fluid medium.

Now applying (2.134) to (2.143), since  $v = nv$  here, we see that

$$D = \frac{kT}{6\pi\eta r} = \frac{RT}{6\pi\eta r N}. \quad (2.144)$$

Now we obtain Einstein's formula by equating (2.137) to (2.144) :

$$\Delta^2 = \frac{RT}{N} \frac{1}{3\pi\eta r}. \quad (2.145)$$

**(B) Langevin's Simplified Treatment\*** : Langevin gave a much simpler derivation of Einstein's formula (2.145). As stated at the beginning of this section, a Brownian particle is bombarded from all sides by the molecules of the fluid. As a result of these molecular collisions on the particle, two forces act on it—(i) a retarding force,  $F_r$  and (ii) an accelerating force,  $F_a$ . The retarding force,  $F_r$ , arises out of those collisions which transfer energy from the Brownian particle to the molecules. Hence the particle is slowed down. This retarding force is, therefore, the viscous force. The other force, i.e., the accelerating force  $F_a$ , arises out of those collisions which transfer energy from the colliding molecules to the Brownian particle and hence the particle gets a forward push in some direction. This forward force,  $F_a$ , does not act all the time but casually whereas the viscous force,  $F_r$ , acts, on the average, systematically all the time.

Here also, as in Einstein's treatment, we consider the components of Brownian displacements along a horizontal axis, say,  $x$ -axis so that the gravity effects are avoided.

Then, from Newton's law, we write the equation for the  $x$ -component of motion

$$m \frac{d^2x}{dt^2} = X - \delta \frac{dx}{dt} \quad (2.146)$$

where  $m$  = mass of the particle of radius  $r$ ,  $X = (F_a)_x$  and  $\delta \frac{dx}{dt}^{**} = (F_r)_x$ ,  $\delta$  being  $= 6\pi\eta r$  from Stokes' law.

At this point there are two alternative ways to proceed further with the calculation.

#### Alternative 1

Multiplying throughout by  $x$  ( $x$ -coordinate of the particle) and remembering that

$$x \frac{d^2x}{dt^2} = \frac{1}{2} \frac{d^2}{dt^2}(x^2) - \left( \frac{dx}{dt} \right)^2,$$

\*Langevin, Comptes Rendus, 146, 530 (1908) or see Loeb, ibid, Pp. 348–51.

\*\*The viscous force on a body is  $\propto$  to its velocity, so that  $\delta$  is here the constant of proportionality.

we obtain from (2.146)

$$\frac{1}{2}m \frac{d^2}{dt^2}(x^2) - m \left( \frac{dx}{dt} \right)^2 + \frac{1}{2}\delta \frac{d}{dt}(x^2) = Xx. \quad (2.147)$$

We write such equations of motion for a very large number  $\nu$  of particles of the same mass and size :

$$\left. \begin{aligned} \frac{1}{2}m \frac{d^2}{dt^2}(x'^2) - m \left( \frac{dx'}{dt} \right)^2 + \frac{1}{2}\delta \frac{d}{dt}(x'^2) &= X'x' \\ \frac{1}{2}m \frac{d^2}{dt^2}(x''^2) - m \left( \frac{dx''}{dt} \right)^2 + \frac{1}{2}\delta \frac{d}{dt}(x''^2) &= X''x'' \\ \dots & \\ \dots & \end{aligned} \right\} \quad (2.148)$$

Adding all these equations in (2.148), and dividing throughout by  $\nu$ ,

$$\frac{1}{2}m \frac{d^2}{dt^2} \left( \frac{x'^2 + x''^2 + x'''^2 + \dots}{\nu} \right) - m \left\{ \frac{\left( \frac{dx'}{dt} \right)^2 + \left( \frac{dx''}{dt} \right)^2 + \left( \frac{dx'''}{dt} \right)^2 + \dots}{\nu} \right\}$$

$$+ \frac{1}{2}\delta \frac{d}{dt} \left( \frac{x'^2 + x''^2 + x'''^2 + \dots}{\nu} \right) = \frac{X'x' + X''x'' + X'''x''' + \dots}{\nu}$$

$$\text{i.e., } \frac{1}{2}m \frac{d^2}{dt^2}(\bar{x}^2) - m \overline{\left( \frac{dx}{dt} \right)^2} + \frac{1}{2}\delta \frac{d}{dt}(\bar{x}^2) = 0. \quad (2.149)$$

Here  $\bar{x}^2$  means the mean square  $x$ -coordinate of a Brownian particle and  $\overline{\left( \frac{dx}{dt} \right)^2}$  is the mean square  $x$ -component of velocity. Further, we have put the right-hand side equal to zero, because  $X'$ ,  $X''$ ,  $X'''$ , ... have got all possible +ve and -ve values (+ve values when they push the particle in +ve  $x$ -direction and -ve values when they push it in -ve  $x$ -direction) so that the mean value approaches zero.

Assuming that we can apply the law of equipartition of energy to Brownian particles, we obtain from (2.45)

$$\frac{1}{2}m \overline{\left( \frac{dx}{dt} \right)^2} = \bar{E}_x = \frac{1}{2}kT = \frac{1}{2} \frac{RT}{N}. \quad (2.150)$$

Then, from (2.149) and (2.150),

$$\frac{1}{2}m \frac{d\alpha}{dt} - \frac{RT}{N} + \frac{1}{2}\delta\alpha = 0, \quad (2.151)$$

$$\text{where } \alpha = \frac{d}{dt}(\bar{x}^2). \quad (2.152)$$

$$\text{Writing (2.151) as } \frac{d(\alpha - \frac{2RT}{N\delta})}{(\alpha - \frac{2RT}{N\delta})} = -\frac{\delta}{m} dt$$

or, integrating,

$$\log_e \left( \alpha - \frac{2RT}{N\delta} \right) = -\frac{\delta}{m} t + \log_e C \text{ (constant)}$$

$$\text{i.e., } \alpha = \frac{2RT}{N\delta} + Ce^{-\frac{\delta}{m}t}. \quad (2.153)$$

Since, usually,  $\frac{\delta}{m}$  is large\*, after a short time  $t$  the second term on the right side of (2.153) vanishes. Hence, (2.153) gives, with (2.152),

$$\frac{d}{dt}(\bar{x^2}) = \frac{RT}{3\pi\eta r N}. \quad (2.154)$$

Integrating between  $t = 0$  and  $t = t$ ,

$$[\bar{x^2}]_0^t = \frac{RT}{3\pi\eta r N}t$$

$$\text{i.e., } [\bar{x^2}]_{t=0} - [\bar{x^2}]_{t=0} = \frac{RT}{3\pi\eta r N}t. \quad (2.155)$$

Now,  $(\bar{x^2})_{t=0}$  and  $(\bar{x^2})_{t=t}$  mean the mean square  $x$ -coordinates of a Brownian particle at  $t = 0$  and  $t = t$  respectively. If we assume that for all particles,  $x = 0$  at  $t = 0$ , i.e., wherever the different particles may exist at  $t = 0$ , if we take the  $x$ -coordinates of their respective positions at that moment equal to zero, then  $\bar{x^2} = 0$  at  $t = 0$ . In that case, the  $x$ -coordinates of the different particles at  $t = t$  will just be their displacements along  $x$ -axis measured from their respective positions at  $t = 0$ . Hence,  $(\bar{x^2})_{t=t}$  becomes the mean square displacement of a Brownian particle in time  $t$  under the assumption made here. From (2.155), therefore,

$$(\bar{x^2})_{t=t} = \frac{RT}{3\pi\eta r N}t. \quad (2.156)$$

Evidently (2.156) is exactly Einstein's formula (2.145).

### Alternative 2

Writing  $P_x = m \frac{dx}{dt}$  ( $x$ -component of the momentum of the Brownian particle), we obtain from (2.146)

$$\frac{dP_x}{dt} = X - \delta \frac{dx}{dt}. \quad (2.157)$$

Let us define a function  $\phi$  by

$$\phi = \sum_{i=1}^{\nu} (P_x)_i x_i, \quad (2.158)$$

where the summation is taken over a large number ( $\nu$ ) of identical Brownian particles. Then,

$$\frac{d\phi}{dt} = \sum_{i=1}^{\nu} \left[ \frac{d(P_x)_i}{dt} x_i + (P_x)_i \frac{dx_i}{dt} \right] = \sum_{i=1}^{\nu} \left[ X_i x_i - \delta \frac{dx_i}{dt} x_i + (P_x)_i \frac{dx_i}{dt} \right]. \quad (2.159)$$

Next, we take the time-average of both sides of (2.159) over a time  $\tau$ ,

$$\frac{1}{\tau} \int_0^\tau \left( \frac{d\phi}{dt} \right) dt = \frac{1}{\tau} \int_0^\tau \left[ \left( \sum_i X_i x_i \right) - \delta \left( \sum_i \frac{dx_i}{dt} x_i \right) + \left( \sum_i (P_x)_i \frac{dx_i}{dt} \right) \right] dt. \quad (2.160)$$

\*For a particle of radius  $10^{-4}$  cm and of density unity,  $\frac{\delta}{m} = \frac{6 \times 3.14 \times 0.00018 \times 10^{-4}}{\frac{4}{3} \times 3.14 \times (10^{-4})^3} \text{ sec}^{-1} \approx 10^5 \text{ sec}^{-1}$ .

Here  $\eta$  is taken 0.00018 for air. For a liquid, say, water near 0 °C,  $\delta/m$  will be  $10^7 \text{ sec}^{-1}$ .

Now, we find the value of each term in (2.160).

$$\text{LHS} = \frac{1}{\tau} [\phi_\tau - \phi_0] = \frac{1}{\tau} \left\{ \left[ \sum_i (P_x)_i x_i \right]_\tau - \left[ \sum_i (P_x)_i x_i \right]_0 \right\} = 0 \quad (2.161)$$

if  $\tau$  is large, since  $P_x$  has the equal probability of being positive and negative.

For the same reason also for  $X$ ,

$$\text{first term of RHS} = 0. \quad (2.162)$$

$$\begin{aligned} \text{Next, second term of RHS} &= \frac{\delta}{\tau} \sum_i \int_0^\tau x_i dx_i = \frac{\delta}{2\tau} \sum_i [x_i^2]_\tau = \frac{\delta}{2\pi} \sum_i [(x_i^2)_\tau - (x_i^2)_0] \\ &= \frac{\delta}{2\tau} \sum_i (x_i^2)_\tau \end{aligned} \quad (2.163)$$

assuming that  $x_i = 0$  at  $t = 0$  for each particle so that  $(x_i)_\tau$  will represent the displacement of a Brownian particle at the end of  $\tau$ .

$$\begin{aligned} \text{Finally, third term of RHS} &= \frac{1}{\tau} \sum_i \int_0^\tau (P_x)_i \frac{dx_i}{dt} dt = \frac{1}{\tau} \sum_i \int_0^\tau \left[ m \left( \frac{dx_i}{dt} \right)^2 \right] dt \\ &= \frac{2}{\tau} \sum_i \int_0^\tau \left[ \frac{1}{2} m \left( \frac{dx_i}{dt} \right)^2 \right] dt \\ &= \frac{2}{\tau} \int_0^\tau E_x dt, \quad \text{where } E_x = \sum_i \left[ \frac{1}{2} m \left( \frac{dx_i}{dt} \right)^2 \right] = \text{total kinetic energy of the Brownian particles for the } x\text{-component of motion} \\ &= 2\bar{E}_x \\ &= 2 \times (\text{time-average of } E_x \text{ of a Brownian particle}). \end{aligned} \quad (2.164)$$

Using (2.161)–(2.164) in (2.160),

$$2\bar{E}_x = \frac{\delta}{2\tau} \sum_i (x_i^2)_\tau \quad (2.165)$$

Taking mean over the  $\nu$  particles

$$2 \left( \frac{\bar{E}_x}{\nu} \right) = \frac{\delta}{2\tau} \frac{\sum_i (x_i^2)_\tau}{\nu}$$

$$\text{or, } 2 \left( \frac{1}{2} kT \right) = \frac{\delta}{2\tau} \overline{(x^2)_\tau}$$

[applying the law of equipartition of energy to the Brownian particles.]

$$\text{or, } \overline{(x^2)_\tau} = \frac{2kT}{\delta} \tau = \frac{2RT}{N(6\pi\eta a)} \tau$$

[using Stokes' law, where  $a = \text{radius of each Brownian particle}$ ]

$$\text{or, } \overline{(x^2)_\tau} = \frac{2RT}{3\pi N \eta a} \tau. \quad (2.166)$$

$(\bar{x^2})$  is called the mean square displacement of a Brownian particle at the end of time  $\tau$ . (2.166) is the well-known Einstein formula and was later verified by Perrin.

**Perrin's Experiments :** Perrin\* carried out a variety of experiments on Einstein's formula which not only settled any question as to the nature of Brownian motion, but confirmed the validity of kinetic theory of matter.

The principle of Perrin's experimental arrangement—microscope with camera lucida—is shown in Fig. 2.15(a). Light from a graph paper GP [shown also separately in Fig. 2.15(b)] is totally reflected in prism P, then passes through lens L (used for suitably focussing graph paper), then passes through glass plates G (used for adjusting the intensity of light) and is finally reflected upwards at the half-silvered plane HSP in the double prism DP and reaches the eye. On the other hand, light also comes from the Brownian particles suspended in a liquid in the vessel V, then passes through a microscope M and finally through the double prism DP and reaches the eye. This arrangement is such that the eye observes the motion of the particles against the background of the graph paper.

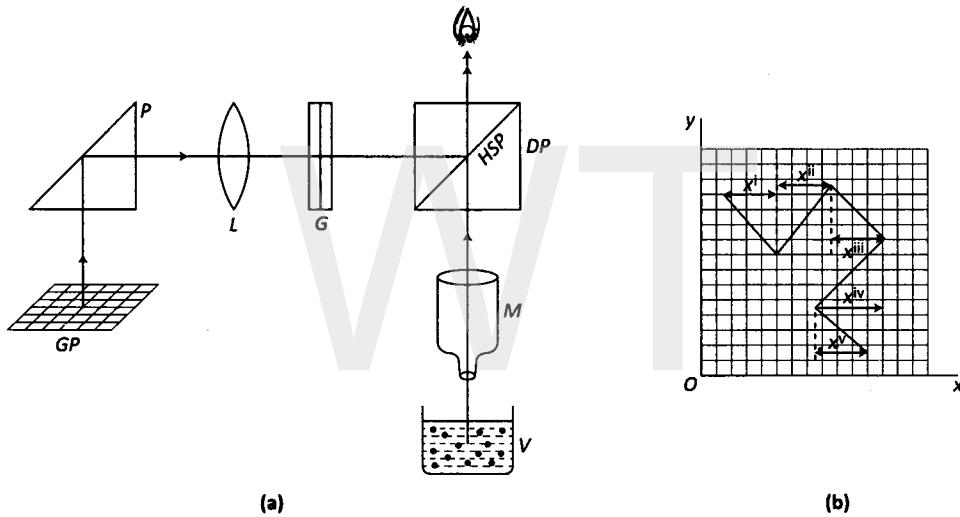


Fig. 2.15: (a) Perrin's camera lucida arrangement and (b) Measurement of  $(\bar{x^2})$

It is evident that because of the random nature of Brownian motion, the observation of a large number  $\nu$  of Brownian particles for an interval  $t$  is quite equivalent to the observation of a single particle  $\nu$  times, each time for an interval  $t$ . Besides, the observation of a large number of particles simultaneously with the eye is difficult. Perrin, therefore, watched the motion of a single particle, thus eliminating the errors due to slight differences in size, which might have occurred from observations on different particles. He took a graph paper of which 16 divisions were equal to  $5.0 \times 10^{-3}$  cm and observed a single particle at intervals of  $t = 30$  sec over a very long time. In this way, Perrin obtained  $(\bar{x^2})$  and putting the values of this and other quantities in (2.156) [or (2.145)], he found for  $N$  (Avogadro number) values ranging from  $5.5 \times 10^{23}$  to  $8 \times 10^{23}$ , his mean value being  $6.88 \times 10^{23}$ .

The importance of these results does not lie, of course, in the precision of the numerical results, but in the confirmation they furnished of the essential soundness of kinetic theory, namely, (a) molecular constitution of matter and (b) incessant random motion of molecules.

\*Jean Perrin, *Les Atomes* (Felix Alcan).

## 2.24 Vapour Pressure

Boltzmann showed from classical statistics\* that Maxwell's law of distribution of velocities (2.29) is a special case of a general law\*\* which gives the distribution of any kind of energy  $E$ , kinetic or potential or both, among the molecules in a system :

$$n_E = Ae^{-E/kT}, \quad (2.167)$$

where  $n_E$  is the number of molecules/cc each having energy  $E$ , and  $A$  is a constant.

**(a) Vapour Pressure over a Flat Surface :** Let us consider a liquid in contact with its vapour in an enclosure at temperature  $T$ . We shall consider the liquid and vapour molecules as forming together a single system and shall find in this system how many molecules per unit volume possess each an amount of potential energy  $E$  due to escaping from the liquid surface against attraction by the surface molecules. From (2.167), we obtain immediately

$$n_v = n_l e^{-E/kT}, \quad (2.168)$$

where  $n_v$  is the number of molecules/cc in vapour each of which possesses this potential energy  $E$  and  $n_l$  is the number of molecules/cc in liquid, none of which possesses this energy. Assuming that the pressure exerted by vapour molecules (i.e., vapour pressure) is given by

$$P = n_v kT. \quad (2.169)$$

we obtain from (2.168) and (2.169)

$$P_\infty = n_l kTe^{-E/kT}. \quad (2.170)$$

Here we write the vapour pressure as  $P_\infty$ , for, this pressure is exerted in the present case over a flat surface of infinite radius of curvature.

If  $L$  is the gram-molecular latent of the liquid, then it is the energy required by  $N$  (= Avogadro number) molecules to leave the liquid surface. Evidently,  $L$  is also equal to the potential energy possessed by these molecules when they have escaped into the vaporous state from the liquid surface. Hence,

$$L = NE$$

$$\text{i.e., } E = \frac{L}{N}, \quad (2.171)$$

Combining (2.170) and (2.171),

$$P_\infty = n_l kTe^{-L/NkT}. \quad (2.172)$$

**(b) Vapour Pressure over a Curved Surface :** Comparing Fig. 2.16(a) and Fig. 2.16(b), it is evident that for a molecule it is easier to escape from a convex liquid surface than from a plane liquid surface, because, the molecules on the convex surface being further down than those on the plane surface, the downward pull on the escaping molecule is weaker for the convex surface. So, at the same temperature, there will be a larger density of vapour molecules over the convex surface than that over the plane surface. Hence, the equilibrium vapour pressure over the convex surface is larger than that on the plane surface. Again, comparing Fig. 2.16(a) and Fig. 2.16(c), and following similar reasoning, it is evident that the equilibrium vapour pressure

\*This is discussed in Chapter 9.

\*\*See (9.13) under section 9.3.

over the concave surface is smaller than that over the plane surface, because the downward pull on the escaping molecule is stronger for the concave surface. Thus, we find that the vapour pressure depends on the curvature of a liquid surface, being a maximum for a convex surface and a minimum for concave surface. We now proceed to build up a relationship between the vapour pressure  $P_r$  over a liquid surface and its radius of curvature  $r$ .

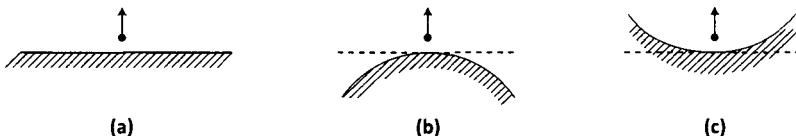


Fig. 2.16: (a) Flat surface, (b) Convex surface and (c) Concave surface

Let us consider a liquid drop of radius  $r$  and of surface tension  $S$  at temperature  $T$ . Then, the total surface energy, i.e., the total potential energy of all the molecules at the surface of the drop is  $4\pi r^2 S^*$ . When some liquid evaporates from the surface,  $r$  is diminished by  $dr$  and hence, the surface potential energy also diminishes by

$$d(4\pi r^2 S) = 8\pi S r dr \quad (2.173)$$

If the mass of the drop is  $\mu$ , it is also diminished by

$$d\mu = d(4/3\pi r^3 \rho) = 4\pi \rho r^2 dr, \quad (2.174)$$

where  $\rho$  is the density of the drop.

Thus, the surface potential energy decreases by  $(8\pi S r dr)/(4\pi \rho r^2 dr) = 2S/\rho r$ , when just unit mass of the drop evaporates. Then, when a molecule of mass  $m$  leaves the surface, the surface loses potential energy by an amount  $2Sm/\rho r$ . Conversely, we may say (and this statement is also equally valid) that as a molecule of mass  $m$  leaves a curved surface of radius  $r$ , the surface loses potential energy by  $2Sm/\rho r^{**}$ . Now, evidently when a molecule will leave a flat surface of infinite radius ( $r \rightarrow \infty$ ), the loss of this potential energy for the molecule is zero, but it will only gain a potential energy of  $E$ , as explained earlier. Thus, we find that when a molecule of mass  $m$  leaves a curved surface, it will not only gain a potential energy of  $E$  (as it should reasonably) but also will lose an amount of potential energy equal to  $2Sm/\rho r$ . Hence, for such a molecule, the net gain of potential energy is

$$E - 2Sm/\rho r = \frac{L}{N} - \frac{2SM}{N\rho r}, \quad (2.175)$$

where  $m = \frac{M}{N}$ .

Hence, for this case, (2.172) has to be modified by replacing  $\frac{L}{N}$  by  $\frac{L}{N} - \frac{2SM}{N\rho r}$  in the exponential index. Thus, the equilibrium vapour pressure over the drop is

$$\begin{aligned} P_r &= n_l k T e^{-(L-2SM/\rho r)/NkT} = n_l k T e^{-\frac{L}{NkT}} e^{(2SM/\rho r)/NkT} \\ &= P_\infty e^{\frac{2SM}{\rho r NkT}}. \end{aligned} \quad (2.176)$$

\* A molecule on or near the liquid surface is acted upon by a force towards the interior of the liquid. So, as it comes to the surface (in fact, there is a constant exchange of molecules between the interior and the surface), it develops potential energy due to the work it has to do against this inward pull.

\*\* Due to separation or approach between two bodies, in fact, the gain or loss of potential energy may be attributed to any one of the two relative to the other.

Since the exponential index in (2.176) is +ve,  $P_r > P_\infty$ . So, we find, as anticipated earlier, that the vapour pressure over a convex surface is larger than that over a flat surface. For a concave surface,  $r$  should be taken as -ve, because now the curvature is just the opposite. Then the exponential index in (2.176) is -ve, and  $P_r > P_\infty$ , because

$$P_r = \frac{P_\infty}{e^{\frac{2\pi M}{r N k T}}}. \quad (2.177)$$

**(c) Formation of Cloud and Fog :** Now we are in a position to understand how the cloud and fog drops are formed in the atmosphere. It is evident from (2.176) that  $P_r$  is large for small  $r$  and is small for large  $r$ . Let us suppose that there are three water drops of radii  $r_1$ ,  $r$ ,  $r_2$  ( $r_1 > r > r_2$ ) in the atmosphere where the existing vapour pressure is  $P_r$ . Then,  $P_{r_1}$ , the necessary equilibrium vapour pressure for the drop of radius  $r_1$  ( $r_1 > r$ ) being less than  $P_r$ , this drop, so far as it is concerned, is in a supersaturated atmosphere and will, therefore, tend to grow due to condensation of supersaturated vapour on it. On the other hand, the drop of radius  $r$  will be quite stable

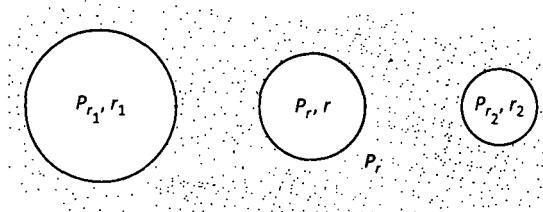


Fig. 2.17

because the vapour pressure  $P_r$  is just right for it. But  $P_{r_2}$ , the necessary equilibrium vapour pressure for the drop of radius  $r_2$  ( $r_2 < r$ ) being larger than  $P_r$ , this drop, so far as it is concerned, is in an unsaturated atmosphere and will continue to evaporate and will ultimately vanish\*.

Now, we come to an interesting question. If a small drop of radius  $r_2$  cannot be stable under the existing vapour pressure  $P_r$ , how is a cloud or fog drop formed at all? Because, when a drop is just formed, its size is definitely extremely small at the beginning. One cannot imagine that at a certain chosen moment a very large number of molecules will come from different directions with the intent of forming a stable, large drop. The answer, in fact, lies in the presence of dust and charged particles in the atmosphere. They serve as the nuclei for the drops to be formed. When some vapour condenses on a nucleus due to adhesive forces, a liquid surface of some curvature is obtained. If, now, the radius of the liquid surface is such that it corresponds to an equilibrium vapour pressure less than the existing vapour pressure, then the liquid surface will immediately evaporate off. If, however, the radius of the surface corresponds exactly to the existing vapour pressure, the liquid surface becomes just stable. Finally, if the radius of the surface corresponds to an equilibrium vapour pressure larger than the existing vapour pressure, the liquid surface will grow, as explained above, into a drop. And this is exactly how cloud and fog drops are formed. When the cloud drops grow too big to remain hanging in the atmosphere, they come down as rain drops.

It is evident from the above discussion that if the atmosphere is completely free from nuclei the drop formation becomes impossible. In fact, all these ideas explained here form the basis

\*When a liquid is in contact with its vapour, there is always exchange of molecules between the liquid phase and the vapour phase. When, however, the liquid is in equilibrium with the vapour (and then the pressure is the equilibrium pressure), the number of molecules leaving the liquid surface per unit time is equal to the number returning during the same time. But if the vapour pressure is less than the equilibrium pressure, the density of vapour molecules becomes comparatively low so that the number of molecules leaving the surface per unit time is larger than the number returning during the same time. Thus, the net effect is evaporation. The net effect is condensation when, however, the pressure is higher than the equilibrium pressure and now more molecules return to the liquid than leave it.

of artificial rain-making and also led C.T.R. Wilson to devise his well-known cloud-chamber which is so important for nuclear and cosmic ray investigations.

## 2.25 Cooling by Adiabatic Demagnetisation

Up to 1932, using the method of boiling liquid helium under reduced pressure, the lowest temperature reached was 0.726 K (Keesom, 1932). And it was found that it was almost impossible, because of practical difficulties, to go below this temperature.

On the other hand, Debye\*, in 1926, suggested theoretically that much lower temperature could be attained by the adiabatic demagnetisation of paramagnetic salts. A simple physical insight into the mechanism of this process may be gained by an application of the kinetic theory of matter\*\*. A paramagnetic substance contains atoms with magnetic moments (i.e., atomic magnets). When unmagnetised, these atomic magnets are oriented at random due to thermal agitation which is in the form of vibrations in this case. When a strong magnetic field is applied, all the atomic magnets get aligned in the direction of the field. In fact, the magnetic field applies mechanical moments (i.e., couples) on the atomic magnets and rotates them through various angles to bring them into alignment. Thus, a certain amount of work is done on the atomic magnets which, therefore, have a corresponding increase in their vibration energy<sup>†</sup>. This increase in the vibrational energy results in a rise in temperature of the substance.

Next, with the help of some heat exchanger, the temperature is brought down to the initial value.

Finally, the magnetic field is reduced to some small value or to zero value. Now, the atomic magnets due to their thermal agitation (i.e., vibrations) break away from the diminishing field and, therefore, do work against the field. Due to this work done by the atomic magnets, they lose some vibrational energy and, therefore, there is a fall in temperature. This is known as cooling by adiabatic demagnetisation.

The cooling in adiabatic demagnetisation may approximately be given by<sup>‡</sup>

$$\Delta T = T_i - T_f = \frac{CV}{2C_H T_i} H^2, \quad (2.178)$$

where  $C$  is a constant of the paramagnetic substance,  $V$  its volume,  $C_H$  the specific heat under constant magnetic field,  $H$  the magnetic field which has been ultimately reduced to zero in the experiment (described below),  $T_i$  the initial temperature and  $T_f$  the final temperature.

**Giauque's Experiment :** In 1927, Giauque also independently put forward the same suggestion as Debye did in 1926. Immediately afterwards, Giauque followed up the suggestion by demonstrating the cooling by adiabatic demagnetisation experimentally.

The experiment was performed in 1931 by Giauque and McDougall on a paramagnetic salt, gadolinium sulphate ( $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ). The salt is powdered and then pressed into the form of a cylinder or a prolate spheroid  $A$  (Fig. 2.18).  $A$  is suspended in the chamber  $B$  which can be filled with helium gas or evacuated. A test coil  $C$  is wound over  $B$ . This coil is connected to one arm of an A.C. (alternating current) bridge to measure its self-inductance.  $B$  is put in liquid helium in a vacuum vessel which is again surrounded by another vessel containing liquid hydrogen. A powerful electromagnet supplies the strong magnetic field.

\* *Ann. der. Physik*, **81**, 1154 (1926)

\*\* Feynman, Leighton and Sands, *Feynman Lectures*, Vol-II, Pp. 35-9 (1964).

<sup>†</sup> These vibrations have a rotational character about axes perpendicular to the field direction.

<sup>‡</sup> This has been derived in section 6.11.

\* *Jour. Amer. Chem. Soc.*, **49**, 1864, 1870 (1927).

First, the chamber  $B$  is filled with helium gas to attain thermal contact with the outer bath containing liquid helium so that the temperature comes down to about 1.50 K. Then,

a magnetic field of the order of 8,000 oersted is produced. The heat developed in the salt (specimen) due to magnetisation is conducted away by the helium gas. Finally, the chamber  $B$  is evacuated and the magnetic field is reduced to zero. This results in a fall in temperature.

Knowing the self-inductance of the test coil in the final condition from the A.C. bridge,  $\chi$ , the susceptibility of the salt, can be found. Then, the final temperature can be found. The final temperature can be determined from Curie's law :

$$\chi = \frac{C}{T}$$

Giauque and McDougall reached a temperature as low as 0.25 K. Later (1933), de Haas, Wiersma and Kramers went further down to 0.0034 K, using a mixture of chrome-potassium alum and aluminium-potassium alum.

Fig. 2.18: Giauque-McDougall arrangement

**Exercise :** In a series of experiments on gadolinium sulphate with  $T_1 = 1.36$  K, Giauque and McDougall obtained the following results\*

$$\begin{array}{l|l|l|l} H_i & 4575 & 6200 & 6860 & 7920 \text{ in oersted} \\ \hline T_f & 0.492 & 0.346 & 0.315 & 0.258 \text{ in K} \end{array}$$

Analyse these results and comment on the validity of (2.178).

## PROBLEMS

1. 'In all considerations of kinetic theory of gases the change in gravitational potential energy is ignored'. Why ?
  2. Is there any deviation of the experimental values of the ratio  $\gamma (= C_p/C_v)$  from the theoretical values in the case of diatomic and polyatomic gases? If so, explain the reason thereof.
  3. Calculate the root mean square velocity of oxygen if its density at N.T.P. is 0.00144 gm/cc [Density of mercury = 13.6 gm/cc and  $g = 980$  cm/s<sup>2</sup>]
  4. If the mean velocity of molecules of oxygen at 40 °C is 0.50 km/sec, find the mean velocity of molecules of hydrogen at 40 °C and 100 °C.
  5. The molecular diameter of a gas is  $3 \times 10^{-8}$  cm. Find its mean free path if there are  $3 \times 10^{19}$  molecules/cc.
  6. Calculate the root mean square speed of dust particles of mass  $4.0 \times 10^{-14}$  gm in air at N.T.P.
  7. It is found experimentally at 15 °C and at atmospheric pressure that the ratio of specific heats is 1.667 for argon, 1.405 for hydrogen, 1.355 for chlorine, 1.340 for sulphuretted hydrogen, 1.235 for carbon disulphide and 1.264 for sulphur dioxide. How do you account for these values?
  8. Derive an expression for the pressure of a gas introducing the concept of mean free path. [C.U.]
- Solution :** Let us denote by  $d n_c$  the number of molecules per unit volume having velocities between  $c$  and  $c + dc$ . Then, if  $P_c$  be the collision probability of such a molecule per unit time, then  $P_c d n_c$  molecules will suffer collisions in unit volume per unit time (i.e., per second) and after

\*These are taken from Saha and Srivastava, loc. cit., P. 535 (1958).

collisions they will proceed in all possible directions. Since  $c/\bar{\lambda}$  (= number of collisions suffered by a  $c$ -molecule per unit time) is evidently a measure of collision probability per unit time, this number may be written as  $dn_c c / \bar{\lambda}$ .

Let us now take an area  $dA$  on the wall of the containing vessel and find first the number of molecules hitting this area per unit time. Let us consider an elementary volume  $r^2 dr \sin \theta d\theta d\phi$  [cf. Fig. 2.4(b)]\* which is between  $r$  and  $r + dr$  from  $dA$  and subtends a solid angle  $d\omega = r^2 dr \sin \theta d\theta d\phi / r^2$  [cf. Fig. 2.2(a)] =  $\sin \theta d\theta d\phi$  at  $dA$ . Evidently, after collisions in this volume  $(dn_c c / \bar{\lambda}) \times r^2 dr \sin \theta d\theta d\phi$  molecules will proceed in all possible directions per unit time. Of these, a number  $(\frac{1}{4\pi} \cdot \frac{dA \cos \theta}{r^2}) \times (dn_c c r^2 dr \sin \theta d\theta d\phi / \bar{\lambda})$  will proceed towards  $dA$  per unit time,  $\frac{dA \cos \theta}{r^2}$  being the solid angle subtended by  $dA$  at the elementary volume. Out of this number again, only  $e^{-r/\bar{\lambda}} \times (\frac{1}{4\pi} \cdot \frac{dA \cos \theta}{r^2}) \times (dn_c c r^2 dr \sin \theta d\theta d\phi / \bar{\lambda})$  will actually reach  $dA$  per unit time,  $e^{-r/\bar{\lambda}}$  being the probability of a free path,  $r$ . Hence, considering all free paths, all velocities and all possible directions, the number of molecules hitting  $dA$  in unit time is

$$\begin{aligned} \frac{dA}{4\pi\bar{\lambda}} \int_0^\infty dn_c c \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta d\theta \int_0^\infty e^{-r/\bar{\lambda}} dr &= \frac{1}{4} dA \int_0^\infty dn_c c \\ &= \frac{1}{4} dAn \left[ \left( \int_0^\infty dn_c c \right) / n \right] = \frac{1}{4} n \bar{c} dA. \end{aligned}$$

Hence, the number of molecules hitting unit area of the wall per unit time =  $\frac{1}{4} n \bar{c}$  (a)

Next, we find the pressure exerted by the molecules on  $dA$ . It is evident that the momentum imparted to  $dA$  per unit time by  $[e^{-r/\bar{\lambda}} \times (\frac{1}{4\pi} \frac{dA \cos \theta}{r^2}) \times (dn_c c r^2 dr \sin \theta d\theta d\phi / \bar{\lambda})]$  molecules is

$$\left[ e^{-r/\bar{\lambda}} \times \left( \frac{1}{4\pi} \frac{dA \cos \theta}{r^2} \right) \times (dn_c c r^2 dr \sin \theta d\theta d\phi / \bar{\lambda}) \right] \times 2mc \cos \theta.$$

$$\begin{aligned} \text{Hence the total force exerted on } dA &= \frac{mdA}{2\pi\bar{\lambda}} \int_0^\infty dn_c c^2 \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin \theta \cos^2 \theta d\theta \int_0^\infty e^{-r/\bar{\lambda}} dr \\ &= \left( \frac{1}{3} mdA \right) n \left[ \left( \int_0^\infty dn_c c^2 \right) / n \right] = \left( \frac{1}{3} mnc \bar{c}^2 \right) dA. \end{aligned}$$

Therefore, the pressure is =  $\frac{1}{3} mnc \bar{c}^2$ . (b)

\*Also see Appendix-6.

## Chapter 3

# Real Gases

### 3.1 Preliminary Remarks

In the foregoing chapter, we have derived Boyle's law from the kinetic theory on two assumptions : (i) molecules of a gas are like point-particles and (ii) inter-molecular forces are absent. These assumptions are thus the conditions under which this law is valid. Boyle who gave his law in 1660 was aware of these limitations, because he himself found that the law holds under only ideal conditions (i) at low pressure (when intermolecular attraction hardly comes into play because of large distances between molecules, and encounters between molecules become as rare as if they were point-particles) and (ii) at high temperature (when intermolecular forces become as ineffective because of high kinetic energy of molecules as if these forces were absent, and also due to highly energetic collisions, molecular diameters are effectively reduced).

However, investigations on the validity of Boyle's law were started pretty before the kinetic theory (1857) exposed its limitations. In the following three consecutive sections, we shall deal with these investigations rather in a chronological order. And it is the results of these experiments that induced J. D. van der Waals to modify Boyle's law, or rather the perfect gas equation

$$PV = RT. \quad (3.1)$$

### 3.2 Regnault's Experiments

Regnault\* was perhaps the first to carry out most extensive experiments on Boyle's law. He applied pressures up to 30 atmospheres and varied temperatures between 0 °C and 100 °C. Although according to Boyle's law, a curve for  $PV$  drawn against  $P$  at a temperature should be parallel to the  $P$ -axis, Regnault observed that such curves for a number of gases are inclined to  $P$ -axis. In fact, he found that the product  $PV$  decreases with increasing  $P$  for air, nitrogen and CO<sub>2</sub> while it increases for hydrogen. Regnault, therefore, concluded that no gas accurately obeys Boyle's law and that air, nitrogen and CO<sub>2</sub> are less than perfect while H<sub>2</sub> is more than perfect.

Regnault was followed in these investigations by Amagat (1870). He applied pressures up to 3,000 atmospheres. He found that  $PV$  for hydrogen rises steadily with  $P$  at any temperature while for nitrogen  $PV$  first decreases, reaches a minimum and then increases with  $P$  at any temperature. Amagat also observed that the behaviour of CO<sub>2</sub> at high temperatures is quite similar to that of nitrogen. But at low temperatures,  $PV$  first diminishes rapidly with  $P$  till it reaches minimum, then it rises but not rapidly (See Fig. 3.6).

### 3.3 Joule-Thomson Effect

Next to Regnault, Joule and Thomson\*\* (later Lord Kelvin) attacked the problem in 1852 from a different angle. We shall give here first a theory of their experiment on the basis of (3.1) as this was the only gas law known at that time. Later in this chapter will be presented a more realistic theory on the basis of van der Waals gas equation.

\* *Mem. Acad. Sciences*, Vol. 21 (1847).

\*\* *Phil. Mag.*, Vol. 14 (1852).

**Theory :** In a cylinder (Fig. 3.1), a porous plug  $A$  is fitted. Through this plug, a gram-molecule of a gas is pushed from a higher pressure  $P_1$  to a lower pressure  $P_2$ .  $P_1, P_2$  are maintained constant.

As the gas passes through the orifices of the plug, the molecules are drawn apart from one another. Thus, the plug ensures that the gas issues rather turbulently, and not in the form of a jet. Because, if the gas streams through a single jet, the energy supplied to it at the higher pressure side would appear as the kinetic energy of the jet as a whole, and would not be added to the internal energy of random (thermal) molecular agitation. In this experiment, we propose to investigate the nature of internal energy of gas molecules and, therefore, we are not at all interested in jets.

Now, let us suppose that the gas initially has the volume  $V_1 = \text{cross section } S \times \text{length } x_1$ . Then, the force applied by the piston on the gas is  $P_1 \times S$  and the work done in pushing the gas to the other side  $= P_1 \times S \times x_1 = P_1 V_1$ . As the gas comes to the other side, it pushes the piston with a force  $= P_2 \times S$ . When the entire gas comes to the lower pressure side, it does work  $= P_2 \times S \times x_2 = P_2 V_2$ . Then, if  $U_1, U_2$  are the initial and final internal energies of the gas, then any net work done by the gas in this process will be at the cost of its internal energy, i.e.,

$$U_1 - U_2 = P_2 V_2 - P_1 V_1 \quad (3.2)$$

$$\text{i.e., } P_1 V_1 + U_1 = P_2 V_2 + U_2. \quad (3.3)$$

Thus, we find that in this experiment, the total heat function or enthalpy  $PV + U = \text{constant}$ . If the fall of temperature due to the work done here is  $(T_1 - T_2) = dT$ , then, from (3.1)

$$C_v dT = U_1 - U_2 = P_2 V_2 - P_1 V_1 = R(T_2 - T_1)$$

$$\text{i.e., } C_v dT = -RdT$$

$$\text{or, } C_p dT = 0 \quad (\text{from } C_p - C_v = R)$$

$$\text{i.e., } dT = 0. \quad (3.4)$$

Thus, we find that a gas obeying Boyle's law or the perfect gas law (3.1) should not show any change of temperature in this experiment. Let us now see how the actual experiment agrees with this theoretical prediction.

### Joule-Thomson Experiment

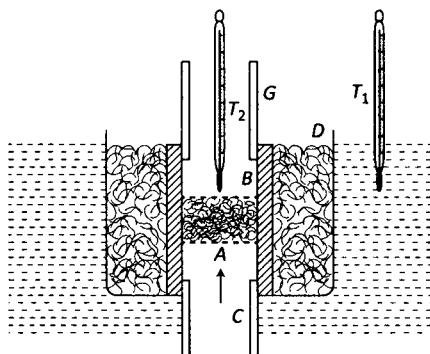


Fig. 3.2: Joule-Thomson experiment

The gas is passed slowly and uniformly under a definite high pressure  $P_1$  through a long copper spiral  $C$  (only top-part shown) immersed in a water bath. At the top of the copper tube is a short box-wood tube  $B$  containing the porous plug  $A$  (cotton wool or silk fibres) placed between two perforated brass plates. Outside the box-wood tube is an insulation provided by cotton wool  $D$ . The gas issues on the other side of the plug pushing up the atmospheric pressure  $P_2$ . To the top of the box-wood is fitted a glass tube  $G$  in which a thermometer  $T_2$  is kept to read the final temperature, while the initial temperature is given by the thermometer  $T_1$  immersed in the water bath.

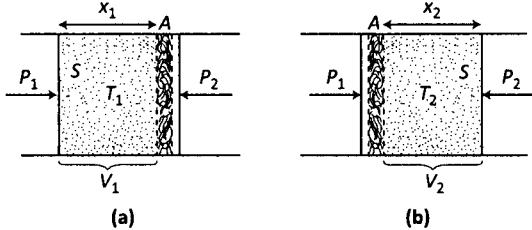


Fig. 3.1: Porous plug

The most significant result of the experiment is that all the gases show a change in temperature on passing through the plug, contrary to (3.4). This shows that the gases do not obey the perfect gas law (3.1). This result—change of temperature on passage through the plug—is known as the *Joule-Thomson* (also *Joule-Kelvin*) effect. The following are characteristics of this result :

- This change in temperature is proportional to  $(P_1 - P_2)$ , the difference between the pressures on the two sides of the porous plug.
- At ordinary temperatures, all the gases examined by Joule and Thomson showed a cooling effect but only hydrogen showed a heating effect.
- Later experiments showed that there is an *inversion temperature* for every gas. If a gas is initially above this temperature, the temperature of the gas increases on passing through the plug. But, if a gas is initially below this temperature, it shows a cooling effect. The inversion temperature for hydrogen is about 190 K and for helium is 30 K. For all other gases, it is well above ordinary temperature. Hence, they show a cooling effect at ordinary temperatures.

As stated earlier, an attempt will be made to explain these results on van der Waals' theory after we get familiar with it.

### 3.4 Andrews' Experiments

The third most significant step in the series of investigations on the validity of Boyle's law is Andrews' experiments\* conducted in 1869 on carbon dioxide.

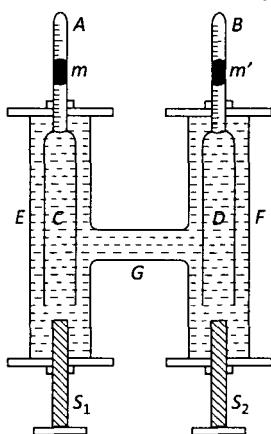


Fig. 3.3: Andrews' experiment

Andrews' experimental arrangement is shown in Fig. 3.3. Carbon dioxide is enclosed by a pellet of mercury  $m$  in a graduated glass tube  $A$ , the lower part  $C$  of which is wider and open and is immersed in water inside a copper cylinder  $E$ . Air is similarly enclosed by a pellet of mercury  $m'$  in a graduated glass tube  $B$ , the lower part  $D$  of which is immersed in water inside another copper cylinder  $F$ .  $F$  is in communication with  $E$  through a tube  $G$  so that air and carbon dioxide are always under the same pressure which may be increased or decreased by rotating the screws  $S_1$ ,  $S_2$ . The air column in  $B$  is calibrated beforehand so that from its volume at a temperature, the pressure may be immediately known. The tube  $A$  is surrounded by a suitable constant temperature bath (not shown in Fig. 3.3) so that the relationship between pressure  $P$  and volume  $V$  of carbon dioxide may be studied at a definite temperature.

The results of Andrews' experiments are shown in the form of curves in Fig. 3.4. These curves may broadly divided into two classes :

- Curves below  $31.1^\circ\text{C}$**  : These curves are characterised by two kinks joined by a straight line nearly parallel to  $V$ -axis. Let us consider one such curve, say, that at  $13.1^\circ\text{C}$ .  $LM$  corresponds to  $\text{CO}_2$  in the gaseous state. At  $M$ , the gas is just saturated so that on further compression,  $P$  remains constant, but  $V$  diminishes accompanied with liquefaction. This continues till  $N$  is reached when all the gas has been converted into the liquid state. Due to high incompressibility, the volume of the liquid is almost unchanged with increase of pressure so that  $NO$  is almost parallel to  $P$ -axis.

\* Phil Trans. CLIX P. 575 (1869).

Now, it is evident from Fig. 3.4 that the straight part (nearly parallel to  $V$ -axis) of any curve below  $31.1\text{ }^{\circ}\text{C}$  which corresponds to the process of liquefaction diminishes in length as the temperature rises and finally is reduced to a point, as pointed out by Andrews, at  $30.92\text{ }^{\circ}\text{C}^*$  (curve for  $30.92\text{ }^{\circ}\text{C}$  not shown in Fig. 3.4). While all curves drawn at different temperatures are isothermals, the one at  $30.92\text{ }^{\circ}\text{C}$  is called the critical isothermal and  $30.92\text{ }^{\circ}\text{C}$  is called the *critical temperature* ( $T_c$ ). There is a point  $Q$  on the curve  $30.92\text{ }^{\circ}\text{C}$ , on the right side of which  $\text{CO}_2$  is in the gaseous state and on the left side of which it is the liquid state. This point,  $Q$ , is the peak of the dotted curve  $MQN$  in the figure and is called the *critical point*. The pressure corresponding to this point is called the *critical pressure* ( $P_c$ ) and the *critical volume* ( $V_c$ ) is the volume at that point.

(b) **Curves from  $31.1\text{ }^{\circ}\text{C}$  Upward :** No curve above  $30.92\text{ }^{\circ}\text{C}$  (critical temperature) possesses any straight part nearly parallel to  $V$ -axis so that it is impossible to obtain the liquid state by mere application of pressure. It is evident that the kinks in the curves from  $31.1\text{ }^{\circ}\text{C}$  upward gradually straighten up and are not at all seen at  $48.1\text{ }^{\circ}\text{C}$ . The curve at  $48.1\text{ }^{\circ}\text{C}$  for  $\text{CO}_2$  is exactly similar to those obtained in a class-room experiment for air at ordinary temperatures.

From the above results on  $\text{CO}_2$  it is clear that there should be a critical temperature for any gas below which it may be liquefied by mere application of pressure.

### Continuity of State

One may be apt to believe from the above discussion that in order to reach the liquid state, say,  $O$  at  $13.1\text{ }^{\circ}\text{C}$  from the gaseous state denoted by  $L$ , one must pass through the straight part  $MN$ , which corresponds to the liquid and the gas existing together and thus giving rise to a sort of inhomogeneity or heterogeneity in the system. But it may be easily shown that it is not essential to pass through this heterogeneity (also called *discontinuity of state*, because the system breaks up in this case into two states—the gaseous state above the liquid state) to reach  $O$  at  $13.1\text{ }^{\circ}\text{C}$  from  $L$ . Keeping the volume fixed, let us heat the gas and adjust pressure suitably till  $R$  is reached from  $L$ . Now, keeping the pressure fixed, let us cool the gas and compress the gas till  $O$  is reached from  $R$ . Now, in this process, the gas is immediately converted into liquid as the isothermal at  $31.1\text{ }^{\circ}\text{C}$  is crossed at  $K$ . At no state of this operation, any discontinuity of state appears. Andrews, therefore, concluded that there exists a continuity between liquid and gaseous states, i.e., there can be a smooth transition for any substance from the gaseous to the liquid state (or *vice versa*) through a series of steady and continuous changes in the internal condition of the system so that no inhomogeneity or discontinuity occurs in the process.

### 3.5 James Thomson's Hypothesis\*\*

In 1871, James Thomson extended Andrews' idea of continuity of state to the isothermals below  $31.1\text{ }^{\circ}\text{C}$ . His speculation was inspired by (i) the form of the isothermals at  $31.1\text{ }^{\circ}\text{C}$ ,  $32.5\text{ }^{\circ}\text{C}$  and  $35.5\text{ }^{\circ}\text{C}$  and (ii) the assumption that all transformations in nature are essentially continuous. He suggested that the straight part, say,  $MN$  at  $13.1\text{ }^{\circ}\text{C}$  (corresponding to discontinuity of

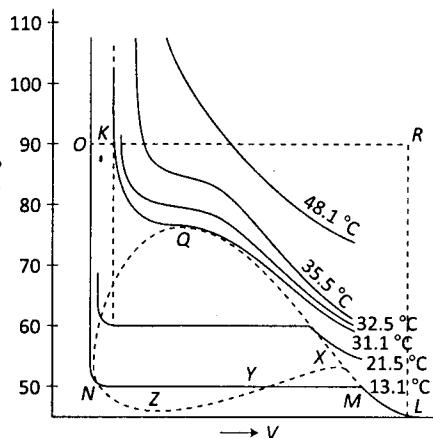


Fig. 3.4: Andrews' results

\* J. Jeans, *loc. cit.*, P. 134 (1904).

\*\* W. Wilson, *ibid.*, Pp. 248-49.

state), should be replaced by  $MXYZN$  (Fig. 3.4) so that the whole isothermal  $LMXYZNO$  becomes continuous. Thomson pointed out that if the isothermals of a substance below the critical temperature are assumed to possess this form, then the well-known phenomena of supersaturated vapour and superheated liquid may be explained. In fact, if the gas is free from dust or charged particles, it will on compression reach the state  $X$ .  $M$ , therefore, corresponds to supersaturation. Again, if the liquid at  $N$  is free from dust or charged particles it will not start evaporation at  $N$ , on release of pressure, but will reach the state  $Z$ .  $NZ$ , therefore, corresponds to superheating. Between  $X$  and  $Z$ , the pressure decreases with volume. This is, of course, an unstable condition and is not observed in practice.

It will be found that the isothermals below the critical temperature obtained from van der Waals' theory are exactly similar to the form predicted by Thomson.

### 3.6 Van der Waals' Theory

The investigations discussed in the preceding sections have put in bold relief the inadequacies of Boyle's law [or the perfect gas law (3.1)] which is derived from kinetic theory on two ideal assumptions—(i) molecules are like point-particles and (ii) intermolecular attraction is absent. J. D. van der Waals\* was the first (1873) to attempt a modification of Boyle's law, or rather the perfect gas law (3.1), taking into account (a) size of molecules and (b) inter-molecular attraction. Van der Waals' equation, however, expresses deviations from Boyle's law to a first approximation only, yet it is widely used for its simplicity. Other attempts to modify Boyle's law will be discussed later.

**(a) Van der Waals' Correction for Molecular Size\*\* :** Let there be  $N$  ( $=$  Avogadro number) molecules in a vessel of volume  $V$ . Let  $\sigma$  be the diameter of each molecule. Imagine the centre of each molecule surrounded by a sphere of radius  $\sigma$  and therefore of volume  $\frac{4}{3}\pi\sigma^3$ . We shall call this sphere the *covering sphere* of the molecule, after Boltzmann. It is evident that the covering sphere of one molecule,  $A$ , can never be penetrated by the centre of another molecule  $B$  [Fig. 3.5(a)]. So, the space available for the centre of any particular molecule in the vessel is

$$V - (N - 1)\frac{4}{3}\pi\sigma^3 \approx V - N\frac{4}{3}\pi\sigma^3 \text{ (nearly).}$$

This expression, of course, requires correction for two or more of the  $(N - 1)$  covering spheres overlapping one another, because due to this overlapping the space available for the centre of a molecule will be more than  $V - N\frac{4}{3}\pi\sigma^3$ . But this is a correction over the correction that is under consideration here and, therefore, may be neglected.

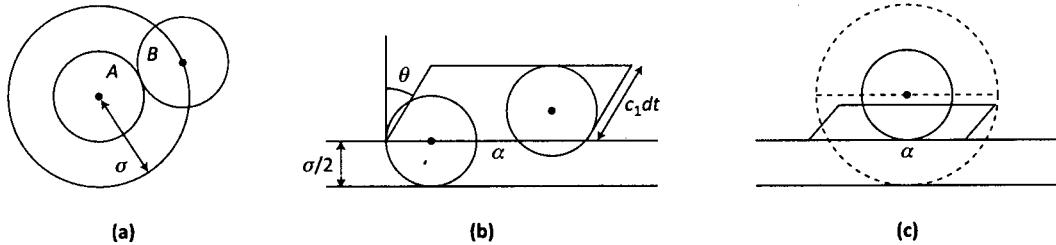


Fig. 3.5

\*Van der Waals' essay "On the Continuity of the Liquid and Gaseous States" was published in 1873 in Dutch by Sighoff, Leyden. It was translated into English in 1890 in *Physical Memoirs*.

\*\*We follow here Boltzmann's treatment of van der Waals' correction in his *Gas theorie*, II. See Jeans *Dynamical Theory of Gases*, Pp. 115–16 (1904); W. Wilson *loc.cit.*, Pp. 244–46.

The expression  $V - N \frac{4}{3} \pi \sigma^3$  requires a further correction since the centre of a molecule cannot reach the wall closer than  $\sigma/2$  [Fig. 3.5(b)]. This requires  $V$  to be reduced to the extent of the volume of a layer of thickness  $\sigma/2$  taken round the wall of the containing vessel. But this correction may be also neglected provided  $\sigma$  is negligible compared to the dimension of the vessel.

[But this should not mean that in that case we may neglect  $N \frac{4}{3} \pi \sigma^3$  also compared to  $V$  and write  $V - N \frac{4}{3} \pi \sigma^3 \approx V$ . We may explain this point by an illustration. Let us take a cubic vessel of volume  $V = 1$  litre and take  $\sigma \approx 3 \times 10^{-8}$  cm for an air molecule and  $n \approx 3 \times 10^{19}$  air molecules/cc at N.T.P. Then,

$$\frac{\text{volume of boundary layer of thickness } \sigma/2}{\text{volume of vessel}} \approx \frac{6 \times 100 \times 3 \times 10^{-8}/2}{1000} = 9.0 \times 10^{-9},$$

$$\text{but } \frac{\text{total volume of covering spheres}}{\text{volume of vessel}} = \frac{1000 \times 3 \times 10^{19} \times \frac{4}{3} \times 3.14 \times 27 \times 10^{-24}}{1000} = 3.39 \times 10^{-3}.$$

Evidently,  $9.0 \times 10^{-9}$  is negligible compared to  $3.39 \times 10^{-3}$ .]

We now proceed to revise, in the light of finite molecular size, our calculation of pressure of a gas (already carried out in section 2.3). If  $N_{c_1}$  is the total number of molecules of velocity  $c_1$  in the vessel, the total number of centres of such molecules in any unit volume of the *net space available* in the vessel is not  $n_{c_1} = N_{c_1}/V$  as before, but

$$n'_{c_1} = \frac{N_{c_1}}{V - N \frac{4}{3} \pi \sigma^3}. \quad (3.5)$$

Now, corresponding to Fig. 2.1, if we take here an inclined cylinder on an area  $\alpha$  of length  $c_1 dt$ , then its volume (Fig. 3.5(b)) is

$$dV = c_1 dt \alpha \cos \theta. \quad (3.6)$$

We have taken this cylinder at a distance  $\frac{\sigma}{2}$  from the wall, because the centre of no molecule, while hitting the wall, can go within a distance  $\frac{\sigma}{2}$  of the wall. All  $c_1$  molecules which have their centres within  $dV$  and which are moving in  $\theta$ -direction towards the wall will hit the area  $\alpha$  of the wall in time  $dt$ .

Now, supposing that  $dV$  is not within the covering sphere of any molecule, the number of centres of  $c_1$ -molecules within  $dV$  coming in directions between  $\theta$  and  $\theta + d\theta$  and  $\phi$  and  $\phi + d\phi$  and hitting area  $\alpha$  in time  $dt$  is, from (2.1) of Chapter 2 and from (3.5) above,

$$\begin{aligned} dn'_{c_1 \theta \phi} &= \left( \frac{\sin \theta d\theta d\phi}{4\pi} \right) \times n'_{c_1} c_1 dt \alpha \cos \theta \\ &= \left( \frac{\sin \theta d\theta d\phi}{4\pi} \right) \times \frac{N_{c_1}}{V - N \frac{4}{3} \pi \sigma^3} dV. \end{aligned} \quad (3.7)$$

This is, however, not a correct result. Because if  $dV$  is taken at random near the wall, it may lie in the covering sphere of a molecule [Fig. 3.5(c)]. In that case,  $dV$  will not contain the centre of any molecule that may at all hit the wall to exert pressure. So, to get a correct and realistic result, we must multiply (3.7) by the probability that  $dV$  will not lie within any of the covering spheres. It is clear from Fig. 3.5(c) that if  $dV$  (near the wall) lies in the covering sphere of a molecule, it must lie in that half (of volume  $= \frac{2}{3}\pi\sigma^3$ ) of the covering sphere which is nearer the wall. Now, the probability that  $dV$ , taken at random near the wall will, lie in the

covering sphere of a molecule (so that the centre of any molecule may not at all lie in  $dV$ ) is given by

$$\frac{\frac{2}{3}\pi\sigma^3}{V}.$$

Hence, the probability that  $dV$  (taken at random near the wall) will lie in the covering sphere of any of the  $(N - 1)$  molecules (so that the centre of any molecule may not at all lie in  $dV$ ) is

$$(N - 1) \times \frac{\frac{2}{3}\pi\sigma^3}{V}.$$

Therefore, the probability that  $dV$  will not lie in the covering sphere of any of the  $(N - 1)$  molecules (so that the centre of any molecule may now lie in  $dV$ ) is

$$1 - (N - 1) \frac{\frac{2}{3}\pi\sigma^3}{V} \approx 1 - \frac{N \frac{2}{3}\pi\sigma^3}{V}. \quad (3.8)$$

Hence, the correct and realistic value of  $dn'_{c_1\theta\phi}$  is, from (3.7) and (3.8),

$$\begin{aligned} & \left\{ \left( \frac{\sin \theta d\theta d\phi}{4\pi} \right) \times \frac{N_{c_1}}{V - N \frac{2}{3}\pi\sigma^3} dV \right\} \times \left( 1 - \frac{N \frac{2}{3}\pi\sigma^3}{V} \right) \approx \left( \frac{\sin \theta d\theta d\phi}{4\pi} \right) \frac{N_{c_1} dV}{V} \frac{1 - N \frac{2}{3}\pi\sigma^3/V}{(1 - N \frac{2}{3}\pi\sigma^3/V)^2} \\ & \qquad \qquad \qquad \text{considering } \left( N \frac{2}{3}\pi\sigma^3/V \right)^2 \text{ negligible} \\ & = \frac{\sin \theta d\theta d\phi}{4\pi} \frac{N_{c_1}}{V - N \frac{2}{3}\pi\sigma^3} c_1 dt \alpha \cos \theta. \quad (3.9) \end{aligned}$$

Now (proceeding as in section 2.3), each of these molecules will impart a momentum on the wall equal to

$$2mc_1 \cos \theta. \quad (3.10)$$

Hence, the total momentum imparted per unit area per second on the wall is, from (3.9) and (3.10),

$$P_{c_1} = \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi/2} \frac{\sin \theta d\theta d\phi}{4\pi} \frac{N_{c_1}}{V - N \frac{2}{3}\pi\sigma^3} 2mc_1^2 \cos^2 \theta = \frac{1}{3}m \frac{N_{c_1} c_1^2}{V - N \frac{2}{3}\pi\sigma^3}.$$

The total pressure is

$$P = P_{c_1} + P_{c_2} + \dots = \frac{1}{3} \frac{mN}{V - N \frac{2}{3}\pi\sigma^3} \frac{(N_{c_1} c_1^2 + N_{c_2} c_2^2 + \dots)}{N} = \frac{1}{3}m \frac{N}{V - N \frac{2}{3}\pi\sigma^3} \bar{c}^2$$

$$\text{or, } P \left( V - N \frac{2}{3}\pi\sigma^3 \right) = N \left( \frac{1}{3}m \bar{c}^2 \right) = NkT \quad \left( \because \frac{1}{2}mc\bar{c}^2 = \frac{3}{2}kT \right)$$

$$\text{i.e., } P(V - b) = RT. \quad (3.11)$$

$$\text{where } b = N \frac{2}{3}\pi\sigma^3 = 4Nv \left( v = \frac{4}{3}\pi r^3 = \text{volume of a molecule} \right).$$

The use of the calculus of probabilities made in the above analysis is probably open to criticism. But, we shall find later in this chapter that we arrive at the same result by an entirely different method due to Clausius.

**(b) Van der Waals' Correction for Intermolecular Attraction :** This correction is based on the assumption that molecules exert on one another attractive forces which are appreciable up to a certain, very small distance  $d_0$ . Any molecule  $A$  in the interior of the gas will, therefore, be under the influence of all those molecules which exist in the sphere of radius  $d_0$  described about this molecule  $A$  as the centre. It is evident that the resultant force exerted on  $A$  will be practically zero. But it is different in the case of a molecule  $B$  near the wall of the vessel. In this case, the attracting gas molecules are all, or mostly only in one half of the sphere of radius  $d_0$  around  $B$ .  $B$  will, therefore, experience a resultant force  $f$  towards the interior of the vessel. If  $\nu$  be the number of molecules hitting unit area of the wall per second, the total inward force on these molecules is  $p = \nu f$ . It is again these  $\nu$  molecules which exert on the wall a pressure  $P$  (this is exactly the pressure observed by any instrument). Now, by Newton's third law,  $P$  is also the pressure applied inward to the gas by the wall. Hence, the total pressure experienced inward by the molecules near the wall is

$$P + p = P + \nu f. \quad (3.12)$$

Evidently, this will also be the pressure throughout the gas. Now,  $\nu$  and  $f$  are each directly proportional to the number of molecules per unit volume,  $n$ . This means that

$$\begin{aligned} p &\propto n^2 \\ \text{i.e., } p &= Cn^2 = C \frac{N^2}{V^2} = \frac{a}{V^2} \end{aligned} \quad (3.13)$$

where  $a = CN^2$ , ( $C$  = a constant of proportionality).

So, finally, we find on combining (3.11), (3.12) and (3.13),

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT. \quad (3.14)$$

This is the celebrated van der Waals equation.

### 3.7 Discussion on van der Waals' Theory

Before proceeding to a discussion on (3.14), we require a knowledge of  $a$  and  $b$  for a gas. A simple and accurate method\* is to consider variation of  $P$  with  $T$  at constant  $V$  over a narrow range. Then, from (3.14),

$$\left( \frac{dP}{dT} \right)_V = \frac{R}{V - b}, \text{ i.e., } b = V - \frac{R}{\left( \frac{dP}{dT} \right)_V}. \quad (3.15)$$

From the  $P-T$  graph,  $\left( \frac{dP}{dT} \right)_V$  can be known for the narrow range in question. Putting the value of  $\left( \frac{dP}{dT} \right)_V$  in (3.15),  $b$  for a gas may be calculated. Again, knowing  $b$  from (3.15) we can find  $a$  from (3.14),

$$a = V^2 \left[ T \left( \frac{dP}{dT} \right)_V - P \right] \quad (3.16)$$

for the range under consideration.

In subsection (b), we shall present another method to evaluate  $a$  and  $b$  in terms of  $P_c$ ,  $V_c$  and  $T_c$  of a gas.

\*For a detailed discussion of different methods of finding  $a$  and  $b$ , see Saha and Srivastava, *ibid*, Pp. 406–10.

**(a) Comparison with Experiments by Regnault and Amagat\*** : Writing  $\eta = PV$  and  $V = \eta/P$  we have from (3.14)

$$\eta^3 - (RT + bP)\eta^2 + aP\eta - abP^2 = 0. \quad (3.17)$$

For a gas, with the help of (3.15) and (3.16), we can plot  $\eta$  against  $P$  at constant temperatures from (3.17) (Fig. 3.6, upper curves corresponding to higher temperatures). It is

noticed that the curves below  $BC$  have each got a minimum, the minimum for  $BC$  being situated at  $B$  itself. The curve  $OAB$  passing through these minima is obtained by differentiating  $\eta$  with respect to  $P$  (keeping  $T$  constant) and then equating  $\frac{d\eta}{dP}$  to 0. From (3.17),

$$\frac{d\eta}{dP}[3\eta^2 - 2(RT + bP)\eta + aP] - b\eta^2 + a\eta - 2abP = 0.$$

For  $\frac{d\eta}{dP} = 0$ ,

$$\eta^2 - \frac{a}{b}\eta + 2aP = 0. \quad (3.18)$$

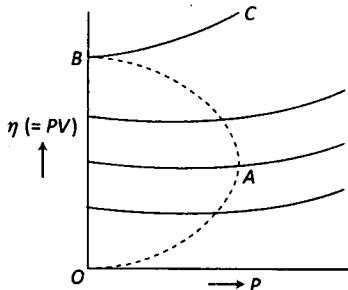


Fig. 3.6:  $PV$  vs  $P$

This equation represents a parabola as the curve  $OAB$  indeed is as found in the figure.

Qualitatively, all these conclusions from van der Waals' theory are in agreement with the results obtained by Regnault and Amagat. Thus, van der Waals' equation represents reality better than the perfect gas equation (3.1). Too much, however, should not be read into this statement. Because, deviations of van der Waals' theory from reality become apparent on some quantitative analysis. For example, let us calculate the coordinates of  $A$  and  $B$  (i.e., values of  $\eta$ ,  $P$ ,  $V$  and  $T$  at  $A$  and  $B$ ) and compare them with experimental values. Since  $A$  corresponds to a maximum for  $P$  in  $OAB$  curve, we obtain the coordinates of  $A$  from (3.18) by differentiating  $P$  with respect to  $\eta$  and then equating  $\frac{dP}{d\eta}$  to 0. We find at  $A$

$$\eta_A = \frac{a}{2b} \quad (3.19)$$

$$\text{so that } P_A = \frac{a}{8b^2} \quad (3.20)$$

$$V_A = 4b \quad (\because \eta_A = P_A V_A) \quad (3.21)$$

$$\text{and } T_A = \frac{9a}{16Rb} \quad [\text{from (3.14), (3.20) and (3.21)}]. \quad (3.22)$$

Further, at  $B$ ,  $P_B = 0$  so that from (3.18),

$$\eta_B = \frac{a}{b} \quad (3.23)$$

$$\text{so that } V_B = \infty \quad (3.24)$$

$$T_B = \frac{a}{Rb}. \quad (3.25)$$

These theoretical values of  $\eta$ ,  $P$ ,  $V$  and  $T$  for  $A$  and  $B$  do not agree satisfactorily with experimental values for any gas.

\*See W. Wilson, *ibid*, Pp. 251–53.

(b) Comparison with Andrews' Experiments\* : We may write (3.14) as

$$P = \frac{RT}{V - b} - \frac{a}{V^2}. \quad (3.26)$$

For carbon dioxide, the values of  $a$  and  $b$  are

$$\left. \begin{array}{l} a = 0.00718 \text{ atmos} \\ b = 0.00190 \text{ cc} \end{array} \right\} \quad (3.27)$$

in terms of 1 cc of gas at N.T.P. obtained from (3.15) and (3.16).

Now, from (3.26) and (3.27), we can plot  $P$  against  $V$  for carbon dioxide at constant temperatures (Fig. 3.7, continuous and dotted curves being respectively Andrews' experimental and van der Waals' theoretical curves). Two discrepancies are noticed between experimental and theoretical curves :

(i) Theoretical curves are displaced from the experimental curves—more so below 31.1 °C than above.

(ii) Also theoretical curves differ in shape from experimental curves more conspicuously below 31.1 °C than above. Below 31.1 °C, the straight part (parallel to  $V$ -axis) of an experimental curve is replaced by a maximum and a minimum. This, however, exactly corresponds to James Thomson's speculation explained in section 3.5. Take, for example, the theoretical curve at 13.1 °C. As discussed in that section,  $AB$  (corresponding to supersaturated vapour) and  $DE$  (corresponding to superheated liquid) may be observed in practice, provided care is taken to remove all nuclei (dust or charged particles) which cause condensation and boiling. But  $BCD$  represents an unstable condition—pressure falling with decreasing volume.

In this case, volume decreases on its own since the pressure is not needed to maintain the small volume. It is not surprising that  $BCD$  cannot be studied experimentally. In fact, as soon as  $B$  is reached from  $A$ , the system gets into a state of unstable equilibrium with a tendency for the volume to decrease spontaneously. It is thus obvious that it is impossible to carry out any accurate measurements in the region  $BCD$ . The failure to find experimentally even the maxima and minima of the theoretical curves is not, however, a weakness of the theory but lies in technical difficulties caused by dust or charged particles and even by the walls (it is also the adhesive forces of the walls which act to cause condensation of the gas as liquid on them before the maximum  $B$  is reached from  $A$ ). This discrepancy between theoretical and experimental curves disappears above 31.1 °C (i.e., above critical temperature). No liquid state is formed above 31.1 °C and, therefore, there is better agreement between theory and experiment at high temperatures.

Now, given a van der Waals isothermal curve, say, at 13.1 °C, how do we draw the straight part  $ACE$  corresponding to actual liquefaction at constant temperature and pressure? This can be understood by thermodynamical reasoning\*\*. [Consider the closed cycle  $ABCDEA$ . If

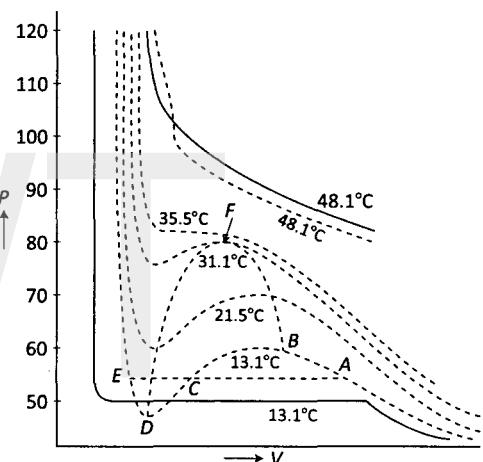


Fig. 3.7: Van der Waals' theoretical curves

\*See Loeb, *loc.cit.*, Pp. 147-58.

\*\*The thermodynamical reasoning given within the brackets will be understood on going through Chapter 5.

we take the substance round this cycle, the net work done would be equal to the difference between the areas  $ABC$  and  $CDE$ . The cycle, however, takes place at a constant temperature and, so, by the second law of thermodynamics, the net work must be nil.] This tells us that the straight part  $ACE$  should be so drawn that the area  $ABC =$  the area  $CDE$ . As  $T$  increases, the points  $A$  and  $E$  approach each other, coinciding at  $F$  at the critical temperature  $T_c$ .

The maxima and minima approach each other as  $T$  increases, coinciding at  $F$  at the critical temperature  $T_c$  and tracing out the curve  $BFD$ . We obtain this curve by differentiating  $P$  in (3.26) with respect to  $V$  at constant  $T$  and putting  $\frac{dP}{dV}$  equal to 0 and then eliminating  $T$  by (3.26). Thus,

$$\frac{dP}{dV} = 0 = \frac{2a}{V^3} - \frac{RT}{(V - b)^2}. \quad (3.28)$$

Eliminating  $T$  from (3.28) by (3.26),

$$P = \frac{a}{V^3} - \frac{2ab}{V^3}. \quad (3.29)$$

This equation represents the curve  $BFD$ . The critical point  $F$  is the maximum of this curve. We find it from (3.29) by putting  $\frac{dP}{dV} = 0$ . Thus,

$$\frac{dP}{dV} = 0 = \frac{2a}{V^3} - \frac{6ab}{V^4}$$

i.e.,  $V_c = 3b$ . (3.30)

From (3.29) and (3.30),

$$P_c = \frac{a}{27b^2}. \quad (3.31)$$

Finally, from (3.26), (3.29) and (3.30),

$$T_c = \frac{8a}{27Rb}. \quad (3.32)$$

Thus, we obtain the critical constants  $V_c$ ,  $P_c$ ,  $T_c$  in terms of van der Waals constants  $a$  and  $b$ . This is evidently, as mentioned earlier in this section, a method for evaluating  $a$  and  $b$  of a gas.

Andrews obtained for  $\text{CO}_2$   $T_c = 31.1^\circ\text{C}$  (strictly  $30.92^\circ\text{C}$ , as stated in section 3.4),  $P_c = 73$  atmospheres and  $V_c = 0.0066$  cc for 1 cc of gas at N.T.P. Then, from (3.31) and (3.32) [with  $R = 1/273$ ],

$$a = \frac{27R^2T_c^2}{64P_c} = 0.00717 \text{ atmos. cm}^6 \quad \text{and} \quad b = \frac{RT_c}{8P_c} = 0.00191 \text{ cc.}$$

This gives  $V_c = 3b = 0.00573$  cc, as against the observed value 0.0066 cc. The discrepancy between the theoretical and observed values of  $V_c$  may be partly due to errors in measuring  $b$  and partly due to defects in the theory discussed in subsection (e) below.

**(c) Law of Corresponding States :** Expressing the pressure, volume and temperature in terms of the corresponding critical values as units,

$$\pi = \frac{P}{P_c}, \quad \phi = \frac{V}{V_c}, \quad \theta = \frac{T}{T_c}$$

we obtain from (3.30), (3.31) and (3.32)

$$P = \frac{a}{27b^2}\pi, \quad V = 3b\phi, \quad T = \frac{8a}{27Rb}\theta. \quad (3.33)$$

Then, from (3.14) and (3.33),

$$\left(\pi + \frac{3}{\phi^2}\right)\left(\phi - \frac{1}{3}\right) = \frac{8}{3}\theta. \quad (3.34)$$

This is an equation from which the constants  $a$  and  $b$ , which distinguish one gas from another, have disappeared. In this sense, this equation is on the same footing as the perfect gas equation (3.1).  $\pi$ ,  $\phi$  and  $\theta$  are called the *reduced pressure*, *volume* and *temperature* respectively. Any two gases for which  $\pi$ ,  $\phi$  and  $\theta$  have equal values are said to be in *corresponding states* and, therefore, (3.34) is called the *law of corresponding states*. This law means that a relation

$$f(\pi, \phi, \theta) = 0$$

exists, in which  $f$  is the same function for all gases. Evidently,

$$f = \left(\pi + \frac{3}{\phi^2}\right)\left(\phi - \frac{1}{3}\right) - \frac{8}{3}\theta.$$

**(d) Interpretation of Joule-Thomson Effect\*** : We found in section 3.3 that the perfect gas law (3.1) fails to account for the change of temperature that occurs in Joule-Thomson effect. Now, we apply the more realistic van der Waals theory to comprehend the results of the experiment.

Let the initial state of the gas before passing through the porous plug be denoted by  $P_1$ ,  $V_1$ ,  $T_1$ , and the final state after passing through the porous plug by  $P_2$ ,  $V_2$ ,  $T_2$ . Then, the net work done by the gas in the process is

$$W = (P_2 V_2 - P_1 V_1) + \int_{V_1}^{V_2} \frac{a}{V^2} dV. \quad (3.35)$$

The first term within brackets on the right-hand is the net external work done by the gas (already discussed in section 3.3). The second term represents the work done in expanding from  $V_1$  to  $V_2$  against intermolecular attraction, i.e., against the inward attractive pressure  $\frac{a}{V^2}$ , as may easily be visualised in Fig. 3.8.

On integration,

$$W = P_2 V_2 - P_1 V_1 + \frac{a}{V_1} - \frac{a}{V_2}. \quad (3.36)$$

Now, from (3.14),

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT. \quad (3.37)$$

Neglecting  $ab$  as a small quantity of the second order and substituting the approximate value  $P/RT$  for  $1/V$ , we obtain from (3.37)

$$PV = RT - \frac{aP}{RT} + Pb \quad (3.38)$$

(3.38) gives

$$\left. \begin{aligned} P_1 V_1 &= RT_1 - \frac{aP_1}{RT_1} + P_1 b \\ P_2 V_2 &= RT_2 - \frac{aP_2}{RT_2} + P_2 b \end{aligned} \right\} \quad (3.39)$$

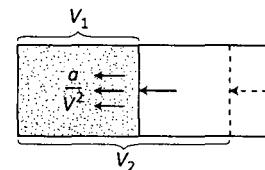


Fig. 3.8

\*Loeb, loc.cit., Pp. 163-69.

From (3.36) and (3.39),

$$W = R(T_2 - T_1) + \frac{a}{RT_1}(P_1 - P_2) - b(P_1 - P_2) + \frac{a}{V_1} - \frac{a}{V_2}, \quad (3.40)$$

where in the denominator of r.h.s. the second term  $T_1$  has been taken  $\approx T_2$ , for small change of temperature.

Again, substituting as before the approximate value  $P/RT$  for  $1/V$ , (3.40) is reduced to the form :

$$W = R(T_2 - T_1) + \left( \frac{2a}{RT_1} - b \right) (P_1 - P_2). \quad (3.41)$$

Since this work has been done at the cost of the internal energy of the gas, we have from (3.41)

$$C_v \Delta T = -R \Delta T + \left( \frac{2a}{RT_1} - b \right) (P_1 - P_2), \quad (3.42)$$

where  $T_1 = T$  and  $T_2 = T - \Delta T$  and  $C_v$  is the sp. heat of the gas at constant volume.

Using  $C_p - C_v = R$  in (3.42),

$$\Delta T = \frac{1}{C_p} \left( \frac{2a}{RT} - b \right) (P_1 - P_2) = \frac{1}{C_p} \left( \frac{2a}{RT} - b \right) \Delta P. \quad (3.43)$$

Thus, we find, as observed by Joule and Thomson, that  $\Delta T$  is proportional to  $\Delta P$ . (3.43) indeed holds well for not too large values of pressure. For higher pressures, the neglect of some of the terms in the derivation lead to disagreement with experiment. [Thermodynamical treatment of the problem on the basis of van der Waals' equation (which has been taken up in section 6.12) leads to a more exact expression for  $\Delta T$  :

$$\Delta T = \frac{1}{C_p} \left( \frac{2a}{RT} - \frac{3abP}{R^2T^2} - b \right) \Delta P.$$

This differs from (3.43) in the negative term  $-\frac{3abP}{R^2T^2}$ . Thus, for large values of  $P$ ,  $\Delta T/\Delta P$  should decrease with increasing pressure, as it is, indeed, observed.]

However, it is evident from (3.43) that  $\Delta T$  should vary with  $1/C_p$ . This is not surprising, because the larger the value of  $C_p$ , the less will be the change of temperature produced by a certain amount of heat or work. Further, if  $\frac{2a}{RT} > b$ ,  $\Delta T$  is +ve, i.e., there is cooling. Again, if  $\frac{2a}{RT} < b$ ,  $\Delta T$  is -ve, i.e., there is heating. Finally, if  $\frac{2a}{RT} = b$ ,  $\Delta T$  is 0. Now, this temperature

$$T_i = \frac{2a}{Rb}$$

is called the *temperature of inversion*. It is clear that when  $\frac{2a}{RT} > b$ , i.e.,  $\frac{2a}{Rb} > T$  for cooling effect, indeed  $T_i > T$ . Also, when  $\frac{2a}{RT} < b$ , i.e.,  $\frac{2a}{Rb} < T$  for heating effect,  $T_i < T$ .

At low pressures, all these conclusions agree fairly with the results obtained by Joule and Thomson. Let us take a few cases. For air, taking  $a = 0.00257$  atmos  $\text{cm}^6$ ,  $b = 0.00156$  cc for 1 cc of gas at N.T.P.,  $C_p = 0.000307$  cal per gm,  $R = 1/273$  and  $T = 273$  K, we obtain

$$\frac{\Delta T}{\Delta P} = 0.274.$$

Joule found for air a mean value of  $\frac{\Delta T}{\Delta P} = 0.259$ . For  $H_2$ , taking  $a = 0.00038 \text{ atm os cm}^6$ ,  $b = 0.001025 \text{ cc}$  for 1 cc of gas at N.T.P.,  $C_p = 0.000305 \text{ cal per gm}$ ,  $R = 1/273$  and  $T = 273 \text{ K}$ , we obtain

$$\frac{\Delta T}{\Delta P} = -0.029.$$

Joule found a value of  $\frac{\Delta T}{\Delta P} = -0.039$ , i.e., the gas is heated by about  $0.03 \text{ }^\circ\text{C}$  per atmosphere pressure difference.

Now, for  $H_2$  the temperature of inversion from the above data is

$$T_i = \frac{2a}{Rb} = \frac{2 \times 0.00038}{0.001025} \times 273 \text{ K} = 202 \text{ K} \quad \text{or, } -71 \text{ }^\circ\text{C}.$$

Hence, below  $-71 \text{ }^\circ\text{C}$ ,  $H_2$  should show a cooling effect, Indeed, Olszewski\* found the temperature of inversion at  $-80.5 \text{ }^\circ\text{C}$ .

**(e) Limitations of van der Waals' Theory :** Inspite of general agreement, van der Waals' equation shows serious deviations from experimental results.

(i) Although van der Waals assumed  $a$  and  $b$  to be constants, they are found to vary with temperature. The variation of  $b$  with temperature may be easily understood from the fact that  $b$  depends upon  $\sigma$  which, due to high energy collisions at high temperatures, gets reduced effectively. However, the variation of  $a$  with temperature may be visualised after we get some idea of its form in the next section.

(ii) Van der Waals' theory gives for all gases

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.66.$$

But it is found to vary from gas to gas, ranging from 3.28 for  $H_2$  to 4.99 for acetic acid. It appears, therefore, to depend on the molecular structure of the gas.

(iii) Finally, the van der Waals equation puts  $V_c = 3b$ , but experiments put  $V_c$  more nearly to  $2b$ .

**Exercise 1.** Prove that for a van der Waals gas  $C_p - C_v \approx R \left( 1 + \frac{2a}{RTV} \right)$ .

**Solution :** For an amount of heat  $dQ$  added to such a gas at constant pressure, (see equation (2.1) of Chapter 2),

$$dQ = C_p dT = C_v dT + \left( P + \frac{a}{V^2} \right) dV. \quad (3.44)$$

Now, from (3.14), at constant pressure,

$$dV = \frac{R}{P - \frac{a}{V^2} - \frac{2ab}{V^3}} dT = \frac{R}{\left( P + \frac{a}{V^2} \right) - \frac{2a(V-b)}{V^3}} dT. \quad (3.45)$$

For (3.44) and (3.45),

$$C_p - C_v = \frac{R \left( P + \frac{a}{V^2} \right)}{\left( P + \frac{a}{V^2} \right) - \frac{2a(V-b)}{V^3}}$$

\*K. Jellinek, *Lehrbuch der Physikalischen Chemie*, Vol I, Part I, P. 408.

$$= R \frac{\frac{RT}{(V-b)}}{\left\{ \frac{RT}{(V-b)} \right\} + \frac{2a(V-b)}{V^3}}, \text{ from (3.14)}$$

$$= \frac{R}{1 - \frac{2a(V-b)^2}{RTV^3}} \quad (3.46)$$

$$\approx R \left\{ 1 + \frac{2a(V-b)^2}{RTV^3} \right\} \quad (3.47)$$

$$\approx R \left( 1 + \frac{2a}{RTV} \right). \quad (3.48)$$

**Exercise 2.** Find isothermal elasticity ( $K$ ) of a van der Waals gas.

**Solution :** From (3.14) at constant  $T$ ,

$$\left( \frac{dP}{dV} - \frac{2a}{V^3} \right) (V - b) + \left( P + \frac{a}{V^2} \right) = 0$$

$$\text{Hence, } K = -\frac{dP}{\frac{dV}{V}} = \left( \frac{P + \frac{a}{V^2}}{V - b} \right) V - \frac{2a}{V^2} \quad (3.49)$$

$$\approx \left( P + \frac{a}{V^2} \right) \left( 1 + \frac{b}{V} \right) - \frac{2a}{V^2} \quad (3.50)$$

$$\approx P + \frac{Pb}{V} - \frac{a}{V^2}. \quad (3.51)$$

**Exercise 3.** Set up the laws of adiabatic transformations for a van der Waals gas.

**Solution :** For adiabatic change in a van der Waals gas,

$$\begin{aligned} -C_v dT &= \left( P + \frac{a}{V^2} \right) dV \\ &= \frac{RT}{V-b} dV, \text{ from (3.14)} \end{aligned}$$

$$\text{or, } -C_v \frac{dT}{T} = R \frac{dV}{V-b}.$$

On integration

$$C_v \log_e T + R \log_e (V - b) = \log_e A \text{ (constant)}$$

$$\text{or } T^{C_v} (V - b)^R = A, \text{ i.e., } T(V - b)^{\frac{R}{C_v}} = \text{constant.}$$

Proceeding now as usual,

$$\left( P + \frac{a}{V^2} \right) (V - b)^{\frac{R}{C_v} + 1} = \text{constant} \quad \text{and} \quad T \left( P + \frac{a}{V^2} \right)^{-\frac{R}{(R+C_v)}} = \text{constant.}$$

**Exercise 4.** For  $\text{CO}_2$ , take  $a = 0.00874 \text{ atmos cm}^6$ ,  $b = 0.0023 \text{ cc}$ ,  $C_p = 0.00039 \text{ cal per gram and } T = 273 \text{ K. Calculate the Joule-Thomson effect per atmosphere pressure difference.}$

[Hints : See end of sub-section 3.6(d)] [Ans.  $0.925 \text{ }^\circ\text{C}$ ]

### 3.8 Clausius' Theory

Clausius built up a relation between the pressure, volume and temperature of a gas on the basis of his virial theorem\*. We shall first establish this theorem.

*Virial Theorem* : Let  $x, y, z$  be the coordinates of the centre of a molecule and  $X, Y, Z$  the components of the forces acting on the molecule. Then, applying the law of dynamics,

$$m \frac{d^2x}{dt^2} = X, \quad m \frac{d^2y}{dt^2} = Y, \quad m \frac{d^2z}{dt^2} = Z, \quad (3.52)$$

where  $m$  is the mass of the molecule. Multiplying these equations by the coordinates  $x, y, z$  respectively

$$mx \frac{d^2x}{dt^2} = Xx, \quad my \frac{d^2y}{dt^2} = YY, \quad mz \frac{d^2z}{dt^2} = ZZ. \quad (3.53)$$

Now, since  $mx \frac{d^2x}{dt^2} = \frac{1}{2}m \frac{d^2(x^2)}{dt^2} - m \left( \frac{dx}{dt} \right)^2$ , etc.

we have from (3.53),

$$\frac{1}{2}m \left( \frac{dx}{dt} \right)^2 = \frac{m}{4} \frac{d^2(x^2)}{dt^2} - \frac{1}{2}Xx$$

$$\frac{1}{2}m \left( \frac{dy}{dt} \right)^2 = \frac{m}{4} \frac{d^2(y^2)}{dt^2} - \frac{1}{2}Yy$$

$$\frac{1}{2}m \left( \frac{dz}{dt} \right)^2 = \frac{m}{4} \frac{d^2(z^2)}{dt^2} - \frac{1}{2}Zz.$$

Adding these together,

$$\begin{aligned} \frac{1}{2}m \left[ \left( \frac{dx}{dt} \right)^2 + \left( \frac{dy}{dt} \right)^2 + \left( \frac{dz}{dt} \right)^2 \right] &= \frac{m}{4} \left[ \frac{d^2(x^2)}{dt^2} + \frac{d^2(y^2)}{dt^2} + \frac{d^2(z^2)}{dt^2} \right] \\ &\quad - \frac{1}{2}[Xx + Yy + Zz]. \end{aligned} \quad (3.54)$$

This equation applies to one molecule. Summing up for all molecules in the system,

$$\frac{1}{2} \sum mc^2 = \frac{m}{4} \sum \frac{d^2}{dt^2}(x^2 + y^2 + z^2) - \frac{1}{2} \sum (Xx + Yy + Zz). \quad (3.55)$$

Now, we take time-average of the equation over a sufficiently long time  $\tau$  :

$$\begin{aligned} \frac{1}{2} \frac{1}{\tau} \int_0^\tau \left[ \sum mc^2 \right] dt &= \frac{m}{4} \frac{1}{\tau} \int_0^\tau \left[ \sum \frac{d^2}{dt^2}(x^2 + y^2 + z^2) \right] dt \\ &\quad - \frac{1}{2} \frac{1}{\tau} \int_0^\tau \left[ \sum (Xx + Yy + Zz) \right] dt. \end{aligned} \quad (3.56)$$

$$\text{That is, } \frac{1}{2} \overline{\sum mc^2}^\tau = \frac{m}{2} \frac{1}{\tau} \sum \left[ x \frac{dx}{dt} + y \frac{dy}{dt} + z \frac{dz}{dt} \right]_0^\tau - \frac{1}{2} \overline{\sum [Xx + Yy + Zz]}^\tau. \quad (3.57)$$

If the gas is in a steady state at constant temperature, constant pressure and uniform molecular distribution (3.56) gives

\* Phil. Mag., August, (1870), Ann. Physik, **2**, 124, 141, (1870)

$$\left(\frac{1}{2} \sum mc^2\right) \cdot \frac{1}{\tau} \int_0^\tau dt = \frac{m}{2} \frac{1}{\tau} \sum \left[ x \frac{dx}{dt} + y \frac{dy}{dt} + z \frac{dz}{dt} \right]_0^\tau - \frac{1}{2} \sum [Xx + Yy + Zz] \frac{1}{\tau} \int_0^\tau dt$$

$$\text{i.e., } \frac{1}{2} \sum mc^2 = \frac{m}{2} \frac{1}{\tau} \sum \left[ x \frac{dx}{dt} + y \frac{dy}{dt} + z \frac{dz}{dt} \right]_0^\tau - \frac{1}{2} \sum [Xx + Yy + Zz], \quad (3.58)$$

Because, in the steady state,  $\frac{1}{2} mc^2$  is constant for constant temperature and  $\frac{1}{2} \sum [Xx + Yy + Zz]$  is constant for constant pressure and uniform molecular distribution in the system (as will be seen presently). Again while  $x, y, z$  are finite for any molecule of a gas confined in a vessel,  $\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}$  will, at any instant be positive for as many molecules as they will be negative. Evidently, then, for a sufficiently large value of  $\tau$ , the first term of the right-hand side will approach zero value\*. Then from (3.58),

$$\frac{1}{2} \sum mc^2 = -\frac{1}{2} \sum [Xx + Yy + Zz] \quad (3.59)$$

for the equilibrium of the system.

Clausius called the quantity  $-\frac{1}{2} \sum [Xx + Yy + Zz]^\tau$  the virial of the system. (3.59) states that the total kinetic energy of the system is, in the steady state, equal to the virial of the same. This is the famous *Virial Theorem*.

### Derivation of Gas Law\*\*

The virial depends only on the forces acting upon the molecules. In the case of a gas, these forces consist of (a) the pressure exerted upon the gas by the walls of the containing vessel and (b) the intermolecular forces which are repulsive for intermolecular distance for  $r \approx \sigma$  and attractive for  $r > \sigma$ . The virial of the system will, therefore, contain two parts—(i) for pressure and (ii) for intermolecular (repulsive and attractive) forces. First, we proceed to calculate the contribution of pressure to the virial.

**(a) Contribution of Pressure to the Virial :** Let  $dS$  be an element of the surface of the containing vessel, and  $l, m, n$  be the direction cosines of its outward normal (which has the same direction as the pressure  $P$  exerted by the gas on the element). Then the pressure of the element  $dS$  (same as  $P$  but opposite in direction, by Newton's third law) exerts on the gas a force  $-PdS$  with components  $-lPdS, -mPdS, -nPdS$ . Hence, the contribution to  $\sum Xx$  from pressure is  $\iint -lxPdS$ . If we assume that the pressure is the same at all points of the containing vessel, then the total contribution to the virial from the pressure is, for the whole vessel,

$$\begin{aligned} \frac{1}{2} P \iint (lx + my + nz) dS &= \frac{1}{2} P \iiint \left( \frac{dx}{dx} + \frac{dy}{dy} + \frac{dz}{dz} \right) dx dy dz, \text{ by Green's theorem} \\ &= \frac{3}{2} P \iiint dx dy dz = \frac{3}{2} PV, \end{aligned} \quad (3.60)$$

where  $V$  is the volume of the vessel.

\* Alternatively,  $\sum m(x^2 + y^2 + z^2) = \sum mr^2$  = moment of the gas about the origin and in the steady state, this must remain almost constant for all time if the gas is confined in a vessel. Then,  $\sum m \frac{d}{dt}(x^2 + y^2 + z^2)$  becomes very small. This makes the first term of the right-hand side of (3.58) vanish for large  $\tau$  (i.e.,  $\tau$  large compared to mean interval between two collisions =  $10^{-5} \text{ cm}/10^4 \text{ cm/sec} = 10^{-9} \text{ sec}$ ).

\*\* We follow here broadly the treatment of Jeans, *Dynamical Theory of Gases*, Pp. 144–48 (1904).

**(b) Contribution of Intermolecular Forces to the Virial :** Let us suppose that the force between two molecules at distance  $r$  is a short range function of  $r$ ,  $\phi(r)$ . If the centres of the molecules are at  $x, y, z$  and  $x', y', z'$  and if  $X, Y, Z$  and  $X', Y', Z'$  are the components of the forces on the molecules, then

$$\begin{aligned} X &= \phi(r) \frac{x - x'}{r}, & Y &= \phi(r) \frac{y - y'}{r}, & Z &= \phi(r) \frac{z - z'}{r} \\ X' &= \phi(r) \frac{x' - x}{r}, & Y' &= \phi(r) \frac{y' - y}{r}, & Z' &= \phi(r) \frac{z' - z}{r}. \end{aligned}$$

The contribution to  $\sum Xx$  from these forces between the two molecules is

$$Xx + X'x' = \phi(r) \frac{(x - x')^2}{r}.$$

Therefore, the contribution to

$$\sum (Xx + Yy + Zz) = \frac{\phi(r)}{r} \{(x - x')^2 + (y - y')^2 + (z - z')^2\} = r\phi(r) \quad (3.61)$$

so that the part of the virial arising from intermolecular forces is

$$-\frac{1}{2} \sum \sum r\phi(r), \quad (3.62)$$

where the double summation extends over all pairs of molecules in the system\*.

Now, combining (3.59), (3.60) and (3.61),

$$\frac{1}{2} \sum mc^2 = \frac{3}{2} PV - \frac{1}{2} \sum \sum r\phi(r).$$

So the pressure is given by

$$PV = \frac{1}{3} \sum mc^2 + \frac{1}{2} \sum \sum r\phi(r).$$

Now, this is the general form of equation of state derived from the virial theorem. If we had a complete knowledge of  $\phi(r)$ , we could exactly evaluate (3.62) and obtain a correct equation of state. Unfortunately, this is not possible, since  $\phi(r)$  is not known precisely.

If there were no intermolecular forces in the system the number of molecules at distances between  $r$  and  $r + dr$ , from a particular molecule  $A$  would be

$$\nu_r^0 = \frac{N}{V} 4\pi r^2 dr \quad (3.64)$$

where  $N$  is the total number of molecules (= Avogadro number) in the system. If, however, the intermolecular force  $\phi(r)$  acts, then each of the molecules between  $r$  and  $r + dr$  from  $A$  will have potential energy between  $E_r$  ( $= \int_{\infty}^r \phi(r) dr$ ) and  $E_r + dE_r$ . Then, applying Maxwell-Boltzmann's law [(2.167) of section 2.24], the number of molecules between  $r$  and  $r + dr$  from  $A$  is

$$\nu_r = \nu_r^0 e^{-\frac{E_r}{kT}}. \quad (3.65)$$

\*  $\phi(r)$  will be taken as +ve, for  $r \approx \sigma$  (in case of repulsion) and -ve for  $r > \sigma$  (in case of attraction). But here we have considered  $\phi(r)$  to be of any kind (repulsive or attractive) so that we have been indifferent here to the sign of  $\phi(r)$  or, precisely speaking, have taken  $\phi(r)$  to be +ve.

Because, in the absence of intermolecular forces, i.e., for  $E_r = 0$ ,  $\nu_r$  becomes evidently  $\nu_r^0$ . Then, from (3.64) and (3.65),

$$\nu_r = \frac{N}{V} 4\pi e^{-\frac{E_r}{kT}} r^2 dr. \quad (3.66)$$

$\nu_r$  is evidently equal to the number of pairs of molecules such that one molecule in each pair is  $A$  separated from the other (of the pair) by a distance between  $r$  and  $r + dr$ . Then, the total number of such pairs of molecules in the whole system with one molecule of each pair separated from the other (of the pair) by a distance between  $r$  and  $r + dr$  is

$$\frac{1}{2}(N \times \nu_r) = 2\pi \frac{N^2}{V} e^{-\frac{E_r}{kT}} r^2 dr. \quad (3.67)$$

Here, we have first multiplied  $\nu_r$  by  $N$ , but since in that case every pair of molecules is counted twice, we have again divided  $N \times \nu_r$  by 2. Now (3.67) gives the number of pairs of molecules of which each pair makes a contribution  $r\phi(r)$  [according to (3.61)] to  $\sum \sum r\phi(r)$  of (3.63). Hence, multiplying (3.67) by  $r\phi(r)$  and integrating over all values of  $r$ , we obtain

$$\frac{1}{3} \sum \sum r\phi(r) = \frac{2\pi}{3} \frac{N^2}{V} \int_0^\infty \phi(r) e^{-\frac{E_r}{kT}} r^3 dr. \quad (3.68)$$

Let us first consider intermolecular attraction. In this case, since  $\phi(r)$  is not known, we keep (3.68) in its form but only put ( $\because r \geq \sigma$  for intermolecular attraction)

$$a = \frac{2}{3}\pi N^2 \int_0^\infty \phi(r) e^{-\frac{E_r}{kT}} r^3 dr.$$

Then, for intermolecular attraction, the contribution to  $\frac{1}{3} \sum \sum r\phi(r)$  is  $-\frac{a}{V}$  (−ve sign, because  $\phi(r)$  is negative for attraction).

Next, we consider intermolecular repulsion when the centres of two molecules approach a distance  $r \simeq \sigma$  (molecular diameter). Evidently, the contribution to  $\frac{1}{3} \sum \sum r\phi(r)$  in this case becomes appreciable, when  $r \simeq \sigma$ . Writing  $E_r = \int_\infty^r \phi(r) dr$ ,  $dE_r = -\phi(r) dr$ , we obtain for the contribution to  $\frac{1}{3} \sum \sum r\phi(r)$  from (3.68)

$$\begin{aligned} & -\frac{2}{3}\pi \frac{N^2}{V} \int_\infty^0 r^3 e^{-\frac{E_r}{kT}} dE_r \text{ [since, as } r \rightarrow 0 \text{ and } \infty, E_r \rightarrow \infty \text{ and } 0 \text{ respectively]} \\ &= \frac{2}{3}\pi \frac{N^2}{V} \sigma^3 \int_0^\infty e^{-\frac{E_r}{kT}} dE_r \end{aligned}$$

[since, in fact,  $E_r$  changes from 0 to  $\infty$  in an infinitesimal range at the value of  $r \simeq \sigma$ ]

$$= \frac{2}{3}\pi \frac{N^2}{V} \sigma^3 kT = \frac{bRT}{V}, \text{ where } b = \frac{2}{3}\pi N \sigma^3.$$

Hence, taking into account the above contributions from intermolecular forces in (3.63), we find

$$\begin{aligned} PV &= \frac{1}{3} \sum mc^2 - \frac{a}{V} + \frac{bRT}{V} \\ &= RT + \frac{RT}{V} \left( b - \frac{a}{RT} \right) \quad \left( \because \frac{1}{3} \sum mc^2 = \frac{1}{3} N m \bar{c^2} = NkT = RT \right) \end{aligned} \quad (3.69)$$

$b$  is the same as van der Waals' constant.  $a$  is clearly positive. From (3.69),

$$PV = RT \left( 1 + \frac{b}{V} \right) - \frac{a}{V}$$

i.e.,  $\left( P + \frac{a}{V^2} \right) V \left( 1 + \frac{b}{V} \right)^{-1} = RT.$

Expanding  $\left( 1 + \frac{b}{V} \right)^{-1}$  up to first order in  $b/V$ ,

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT. \quad (3.70)$$

This is exactly van der Waals' equation. Still, it may be noted that (3.69) and (3.70) are not exactly identical. Because, for transition from (3.69) to (3.70), we have retained the expansion of  $\left( 1 + \frac{b}{V} \right)^{-1}$  only up to first order. This may be seen in an alternative manner also. From (3.26),

$$P = \frac{RT}{V - b} - \frac{a}{V^2} = \frac{RT}{V} \left( 1 - \frac{b}{V} \right)^{-1} - \frac{a}{V^2}$$

or,  $PV = RT + \frac{RT}{V} \left( b - \frac{a}{RT} \right) + RT \left( \frac{b}{V} \right)^2 + \dots \quad (3.71)$

Evidently (3.71) agrees with (3.69) only up to the second term on the right-hand side. Since the present derivation is more rigorous than the one we undertook to obtain van der Waals' equation, we may say that (3.71) is theoretically correct up to the second term of the right-hand side. It is, therefore, more correct to use (3.69) than (3.70), i.e., (3.14). The fact that (3.69) is found to hold fairly well shows that van der Waals' assumptions approach truth to a good extent.

### Variation of $a$ and $b$

From the explicit form of  $a$  presented above, it is evident that  $a$  depends on temperature. Further, since  $E_r$  is negative for attraction, it is evident that  $a$  will diminish with rise of temperature but will ultimately become a constant for very high temperatures.

Since  $b$  is the same as van der Waals' constant the explanation for its variation with temperature is the same as presented in subsection 3.7(e).

## 3.9 Other Equations of State

It has been stated in section 3.7 that according to experiments  $V_c$  is more nearly equal to  $2b$  than  $3b$  and  $RT_c$  is more nearly equal to  $3.7 P_c V_c$  than  $2.66 P_c V_c$ . So any other equation of state must satisfy these results and its validity will, in fact, be determined by the extent to which it approaches these conditions. Over fifty equations of state have so far been proposed\*. Here, however, we shall consider only a few of them.

There have been two approaches towards improvement of van der Waals' equation. One is addition of suitable constants in van der Waals' equation empirically. The other is more rigorous deduction of the equation taking into account variations of  $a$  and  $b$  with temperature and otherwise.

\*See Partington and Shilling, *Specific Heat of Gases*.

(a) **Clausius' Equation\*** : Clausius modified van der Waals' equation empirically as below :

$$\left\{ P + \frac{a}{T(V+c)^2} \right\} (V-b) = RT. \quad (3.72)$$

Proceeding as in subsection 3.7(b), we obtain

$$T_c^2 = \frac{8a}{27R(b+c)}, \quad P_c^2 = \frac{aR}{216(b+c)^3}, \quad V_c = 3b + 2c. \quad (3.73)$$

$$\text{Now, } \frac{P_c V_c}{RT_c} = \frac{3}{8} \frac{1 + (\frac{2c}{3b})}{1 + (\frac{c}{b})} \quad (3.74)$$

and this depends on  $c/b$ .

The following is a comparative study of the values of  $T_c$ ,  $P_c$ ,  $V_c$  obtained theoretically from van der Waals' equation [See (3.30), (3.31) and (3.32)] and Clausius' equation [See (3.73)] for  $\text{CO}_2^{**}$ .

	$T_c$	$V_c$	$P_c$
van der Waals	32.5 °C	3.49 cc/gm	61 atmos
Clausius	31 °C	2.27 cc/gm	77 atmos
Experimental	31 °C	2.22 cc/gm	73 atmos

Apparently, Clausius' equation gives values closer to the experimental results here. This equation, however, gives a poorer fit at low densities for  $\text{CO}_2$ . For other gases, it is even less successful.

(b) **Kammerlingh Onnes' Equation†** : We have seen from experiments by Regnault and Amagat at any temperature  $T$ ,

$$PV = f(T, P). \quad (3.75)$$

Also, we know that (3.75) is reduced to the perfect gas law (3.1) at low pressure, i.e., for  $P \rightarrow 0$ . So, Kammerlingh Onnes was led to the following Taylor expansion of  $f(T, P)$ , i.e.,  $PV$ ,

$$PV = A(T) + B(T)P + C(T)P^2 + D(T)P^3 + \dots \quad (3.76)$$

$A$ ,  $B$ , etc. which depend upon  $T$  are called first, second, etc. virial coefficients. Since for  $P \rightarrow 0$ , (3.76) is reduced to (3.1),  $A$  is just  $RT$ . However, at moderate pressures  $B$  is very important and at very high pressures  $C$ ,  $D$  ... are to be taken into account.

$B$ , the second virial coefficient, has got interesting significance in that for all gases  $B$  varies with temperature in a similar way. At low temperatures,  $B$  has large negative values. As the temperature is increased, the magnitude of  $B$  increases through zero to positive values. The temperature at which  $B$  becomes zero for a gas is called the *Boyle temperature*  $T_B$  of the gas. The reason for this is that  $C$ ,  $D$ , ... being all small compared to  $B$ , the terms in (3.76) involving them are important at high pressures. So, when  $C$ ,  $D$ , ... are negligible, we have from (3.76)

$$PV = A(T) + B(T)P = RT + B(T)P. \quad (3.77)$$

\* Wiedem. Ann, 9, 337, (1880).

\*\*These data are taken from R. A. Smith, *Physical Principles of Thermodynamics*, P. 112, (1952).

† Leiden Commun, No. 71, (1901).

Now, at  $T = T_B$  (as stated just now),  $B \rightarrow 0$  so that from (3.77)

$$PV = RT_B. \quad (3.78)$$

That is, if the gas is studied at a constant temperature  $T_B$ , the gas will follow Boyle's law with considerable accuracy up to comparatively high pressures.

We can find the Boyle temperature  $T_B$  for a van der Waals gas. From van der Waals' equation (3.71), with  $P \approx \frac{RT}{V}$  approximately in higher terms,

$$PV = RT + \left( b - \frac{a}{RT} \right) P + \dots \quad (3.79)$$

$$\text{Thus, } B_V = b - \frac{a}{RT}. \quad (3.80)$$

From (3.80), the Boyle temperature for a van der Waals gas is

$$T_B = \frac{a}{Rb}. \quad (3.81)$$

From (3.32) and (3.81),

$$\frac{T_B}{T_c} = \frac{27}{8} = 3.375 \text{ (a constant for all gases).}$$

But agreement with experiment is not satisfactory. This ratio is 3.65 for He, 3.15 for H<sub>2</sub>, 3.00 for Ne, 2.56 for N<sub>2</sub>, 2.67 for air, 2.73 for A and 2.72 for O<sub>2</sub>\*

**Exercise :** Show for Clausius' equation (3.72),  $B(T) = b - (a/RT^2)$  and  $T_B = \sqrt{a/Rb}$ .

(c) **Berthelot's Equation :** The third and last empirical equation of state we would consider here is due to Berthelot. It is

$$\left( P + \frac{a}{TV^2} \right) (V - b) = RT. \quad (3.82)$$

This equation fails at the critical point just like van der Waals' equation. But at moderate pressures it represents experiment better than van der Waals' equation. Proceeding as in subsection 3.7(b), we obtain

$$V_c = 3b, \quad P_c = \left( \frac{RT_c}{2b} - \frac{a}{9T_c b^2} \right), \quad T_c^2 = \frac{8a}{27Rb}. \quad (3.83)$$

In terms of the critical constants,

$$a = 3P_c V_c^2 T_c, \quad b = \frac{V_c}{3}. \quad (3.84)$$

From (3.82) and (3.84),

$$\left( P + \frac{3P_c}{\theta\phi^2} \right) \left( V - \frac{V_c}{3} \right) = RT, \quad (3.85)$$

where  $\theta$  and  $\phi$  are the reduced temperature and volume respectively. Starting from (3.85), Berthelot has given an equation which may be applied to gases and vapours over a very wide range of temperatures but at small pressures. Further, the constants appearing in the modified

\*These data are taken from Roberts and Miller, *Heat and Thermodynamics*, P. 116 (1962).

equation are not  $a$  and  $b$ , but  $P_c$  and  $T_c$  so that the values of the critical constants are not predicted by the equation but are adopted from experiment.

Berthelot found from a large number of results that in (3.85)  $V_c/3$  should be replaced by  $V_c/4$  and in the first factor of the left-hand side  $16/3$  should be substituted for 3. Thus, we obtain from (3.85),

$$PV \left( 1 + \frac{16}{3} \frac{1}{\pi \theta \phi^2} \right) \left( 1 - \frac{1}{4\phi} \right) = RT$$

or,  $PV = RT \left( 1 - \frac{16}{3} \frac{1}{\pi \theta \phi^2} + \frac{1}{4\phi} \right).$  (3.86)

neglecting squares and products of the correction terms which are small compared to unity. Berthelot also observed for a large number of gases that

$$P_c V_c \approx \frac{9}{32} R T_c. \quad (3.87)$$

Now, since we are going to use the equation for low pressures at which Boyle's law approximately holds, we have

$$PV \approx RT. \quad (3.88)$$

From (3.87) and (3.88)

$$\pi \phi \approx \frac{32}{9} \theta. \quad (3.89)$$

Substitution the value of  $\phi$  from (3.89) in (3.86),

$$PV = RT \left\{ 1 + \frac{9}{128} \frac{\pi}{\theta} \left( 1 - \frac{6}{\theta^2} \right) \right\} \quad (3.90)$$

$$\text{i.e., } PV = RT \left\{ 1 + \frac{9}{128} \frac{T_c}{P_c} \frac{P}{T} \left( 1 - \frac{6T_c^2}{T^2} \right) \right\} \quad (3.91)$$

This is the final form of Berthelot's modified equation and is often employed for practical purposes, because it gives better agreement at all temperatures for comparatively small pressures for gases and vapours.

Writing (3.91) as

$$PV = RT + \frac{9}{128} \frac{RT_c}{P_c} \left( 1 - \frac{6T_c^2}{T^2} \right) P$$

we find the second virial coefficient for this equation to be

$$B = \frac{9}{128} \frac{RT_c}{P_c} \left( 1 - \frac{6T_c^2}{T^2} \right).$$

Then, the Boyle temperature for a Berthelot gas is given by  $B = 0$ , i.e.,

$$\frac{T_B}{T_c} = \sqrt{6} = 2.45.$$

This is, on the whole, in slightly better agreement with experiment than the ratio predicted by van der Waals' equation (See the proceeding subsection).

(d) Dieterici's Equation : The equation  $P = \frac{RT}{V - b} e^{-\frac{a}{RTV}}$  (3.92)

was first empirically proposed by Dieterici\* and was later put on a rigorous theoretical basis by Jeans.\*\* (3.92) may also be written as

$$Pe^{\frac{a}{RTV}} = \frac{RT}{V - b}. \quad (3.93)$$

For small  $a$  and  $b$ , we may have from (3.93)

$$P \left(1 + \frac{a}{RTV}\right) (V - b) = RT$$

and also may substitute  $PV$  for  $RT$  (approx) in the first factor of the left-hand side. Then,

$$\left(P + \frac{a}{V^2}\right) (V - b) = RT. \quad (3.94)$$

Thus, we obtain van der Waals' equation. As Jeans pointed out, theoretically (3.92) has a range of validity no better than van der Waals' equation at high pressures. It gives for  $V_c$  a theoretical value of  $2b$  which is in better agreement with experiment, while  $\frac{RT_c}{PV_c} = \frac{e^2}{2} = 3.695$  which is closer to the experimental values than 2.66 given by van der Waals' equation. In fact, it was to obtain these numerical values that Dieterici set up his original equation.

(e) Reinganum's Equation<sup>†</sup> : On a rigorous application of the virial theorem, Reinganum deduced the equation

$$PV = RT \left(1 + \frac{be^{\frac{c}{T}}}{V}\right) + \frac{2\pi N^2}{3V} f(T) \quad (3.95)$$

$$\text{i.e., } \left(P - \frac{2\pi N^2 f(T)}{3V^2}\right) V \left(1 + \frac{be^{\frac{c}{T}}}{V}\right)^{-1} = RT. \quad (3.96)$$

Now, if  $\frac{be^{c/T}}{V}$  be considered small compared to unity, then

$$\left(P - \frac{2\pi N^2 f(T)}{3V^2}\right) (V - be^{\frac{c}{T}}) = RT. \quad (3.97)$$

Thus,  $-\frac{2\pi N^2 f(T)}{3}$  is equivalent to van der Waals'  $a$  and  $be^{c/T}$  is equivalent to van der Waals'  $b$ . Since the intermolecular forces are not precisely known,  $f(T)$  and  $c$  are to be determined from experiment. So, by adjusting the values of  $f(T)$  and  $c$  from experiment suitably, (3.95) is more easily fitted to the results than (3.92) and is perhaps a bit more accurate. It must, however, be remembered that Reinganum deduced his equation for relatively low pressures only.

(f) Equation of Saha and Bose<sup>‡</sup> : Saha and Bose deduced from thermodynamical considerations and the theory of probability the equation

$$P = -\frac{RT}{2b} e^{-\frac{a}{RTV}} \log_e \left(\frac{V - 2b}{V}\right). \quad (3.98)$$

\* Wiedem Ann., 66, P. 826 (1898). 69, P. 685 (1899), Drud. Ann. 5, P. 51 (1901).

\*\* Jeans, Dynamical Theory of Gases, P. 161 (1921).

<sup>†</sup> Phys. Zeits, 2, P. 241 (1901); Ann. der. Phys., 10, P. 334 (1903).

<sup>‡</sup> Phil. Mag., 36, P. 199 (1918).

Van der Waals' equation may be obtained as a special case of (3.98), proceeding as in the preceding cases. This equation gives  $RT_c/P_c V_c = 3.53$ , which agrees better with experiment for simple gases than in the case of van der Waals' equation.

## PROBLEMS

1. A gas is allowed to expand at constant temperature from  $V_1$  to  $V_2$ . Calculate the amount of work done according to (a) van der Waals' equation, (b) Berthelot's equation, (c) Dieterici's equation and (d) equation of Saha and Bose.
2. Expand the above equations of state in the form  $PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots\right)$  and find the second virial coefficient  $B$  in each case.
3. Show that corresponding to Dieterici's equation, the reduced equation of state is

$$\pi(2\phi - 1) = \theta e^{2\left(1 - \frac{1}{\phi}\right)},$$

where  $P = \pi P_c$ ,  $V = \phi V_c$  and  $T = \theta T_c$ .

[Use the values of  $P_c$ ,  $V_c$  and  $T_c$  from the following problem.]

4. Using Dieterici's equation show that  $P_c = \frac{a}{4e^2 b^2}$ ,  $V_c = 2b$ ,  $T_c = \frac{a}{4Rb}$ .  
Hence, find the value of  $\frac{RT_c}{P_c V_c}$ .



## Chapter 4

# Thermal Conduction

### 4.1 Definition of Conductivity

In Chapter 2, we have seen how we can understand the thermal conductivity of gases and metals from a *microscopic* point of view, that is, in terms of molecular and electronic motions respectively, on the kinetic theory. In this chapter, however, we shall only study the *macroscopic* aspects of thermal conductivity of solids, liquids and gases.

Fourier\* was the first to give a precise definition of conductivity. Let us consider flow of heat through a cross-section  $A$  of a material of thickness  $\Delta x$ , the temperature at the two faces at  $x$  and  $x + \Delta x$  being  $\theta_1$  and  $\theta_2$  ( $\theta_1 > \theta_2$ ). If  $Q$  be the quantity of heat flowing from the hotter to the colder face in time  $t$ , then it is found from experiment that

$$Q = KA \frac{(\theta_1 - \theta_2)}{\Delta x} \cdot t. \quad (4.1)$$

$K$  is a quantity depending on the nature of the material and is called its *thermal conductivity* or simply *conductivity*. In analogy with electrical conduction,  $1/K$  is called *thermal resistivity*.

In mathematical investigations, it is often necessary to write down the quantity of heat  $dQ$  passing through area  $A$  at  $x$  in time  $dt$ . For this purpose, we take, instead of  $\Delta x$ , an infinitesimal thickness  $dx$  at  $x$  so that the temperatures are  $\theta$  at  $x$  and  $\theta + d\theta$  at  $x + dx$ . Then, from (4.1),

$$dQ = KA \frac{\theta - (\theta + d\theta)}{dx} dt = -KA \frac{d\theta}{dx} dt. \quad (4.2)$$

Since, in fact,  $\theta$  falls along  $x$ ,  $\frac{d\theta}{dx}$  is itself  $-ve$  making  $dQ +ve$ .

In the following sections, we shall first consider some important methods\*\* to measure conductivity of solids, liquids and gases, and then proceed to the mathematical investigation of flow of heat.

### 4.2 Conductivity of Good Conductors

Out of a large number of methods for determination of conductivity of good conductors, we shall discuss in this section only three important methods due to (a) Donaldson, (b) Lees and (c) Kohlrausch.

(a) **Donaldson's Method<sup>†</sup>** : The specimen in the form of a rod  $A$  is placed on a metallic base  $E$  which is electrically heated (Fig. 4.1).  $A$  is surrounded by a cylindrical guard-sheath  $B$  (of the same material) also on the same base. At the other end, around both  $A$  and  $B$  water is so circulated through the tubes  $CC$  and  $DD$  respectively that the temperatures at the same level in the rod  $A$  and the sheath  $B$  are steadily identical and there is therefore no loss of heat

\* *Theorie Analytique de la Chaleur* (1822).

\*\* For a more detailed discussion of these methods, see Saha and Srivastava, *loc. cit.*, Roberts and Miller, *loc. cit.* and other advanced treatises.

<sup>†</sup> See Jacob, *Zeits. f. Metallkde*, **18**, P. 55 (1926).

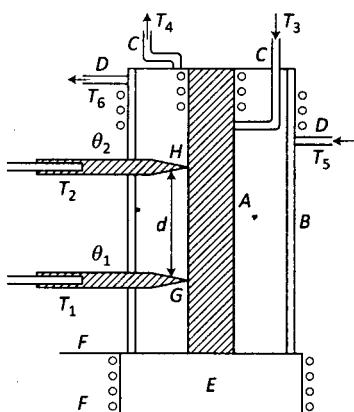


Fig. 4.1: Donaldson's experiment

from  $A$  side-ways. When such a steady state has been attained, the average of the readings of thermometers,  $T_3, T_4$  becomes equal to the average of the readings of thermometers  $T_5, T_6$ . The temperatures  $\theta_1, \theta_2$  at  $G$  and  $H$  on the rod  $A$  separated by a distance  $d$  are known (in the steady state) from the thermocouples  $T_1, T_2$ . Then, from (4.1),

$$Q = KA \frac{\theta_1 - \theta_2}{d} \cdot t.$$

$Q$ , the heat passing from  $G$  to  $H$  in time  $t$ , is determined in the steady state from the heat carried off in time  $t$  by water circulating through the tube  $CC$ , because in the steady state any heat that enters  $A$  at the base reaches the other end straight away and is carried off by the circulating water.

(b) Lees' Method : Variation of  $K$  with Temperature : Lees\* gave a method to measure of conductivity of a metal at any temperature from  $18^\circ\text{C}$  to  $-170^\circ\text{C}$ .  $D$  is a Dewar vessel in which a small copper cylinder  $C$  is supported on a wire frame  $F$  (Fig. 4.2).  $C$  is wound over with a heating coil  $H_2$ . Inside the cylinder  $C$ , the specimen in the form of a short rod  $A$  is fitted. At the upper end of  $A$  there is a heating coil  $H_1$ , of resistance equal to that of  $H_2$ .  $T_1, T_2$  are two platinum thermometers at a distance  $d$  apart.

The cylinder  $C$  is immersed in liquid air inside the Dewar vessel  $D$  or heated electrically by the heating coil  $H_2$  so as to attain the desired temperature at which the value of  $K$  of the material  $A$  is to be determined. Next the rod  $A$  is heated electrically by the heating coil  $H_1$ . The current  $I$  through  $H_1$  and the potential difference  $V$  across it are measured. If  $\theta_1, \theta_2$  are the temperatures given by  $T_1, T_2$ , then the heat produced in time  $t$  is

$$Q = \frac{VIt}{J} = KA \frac{\theta_1 - \theta_2}{d} t = KA \frac{\delta\theta}{d} t$$

i.e.,  $K = \frac{VId}{JA\delta\theta}$ , since  $(\theta_1 - \theta_2)$  is small.

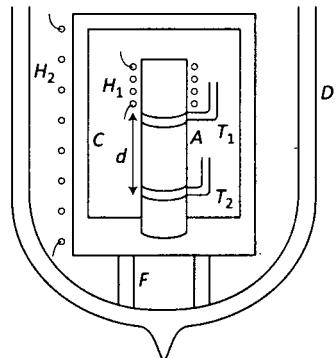


Fig. 4.2: Lees' experiment

A very important correction is necessary in this experiment. When the rod  $A$  is heated by the coil  $H_1$ , some of the heat passes along the rod to  $C$  and the balance raises the temperature of the rod itself so that no steady state is attained at all. On this account the observed value of  $\theta_1 - \theta_2$  ( $= \delta\theta$ ) will, in fact, be less than what it would have been if the whole amount of heat had passed to  $C$  and thus the steady state were exactly attained. Hence,  $\delta\theta$  requires some correction. For this purpose, before performing the experiment, the current  $I$  which is to be passed through  $H_1$  during the experiment is passed through  $H_2$ . Since the resistances of  $H_1$  and  $H_2$  are equal, heat is produced in  $H_2$  at the same rate as in  $H_1$ . But the heat that now reaches the rod flows into it from the lower end. This heat is all used to raise the temperature of the rod and it does so at the same average rate as if the rod were heated by  $H_1$ . The difference of temperature  $d\theta_i$  between  $T_2$  and  $T_1$  ( $T_2$  now being the hotter side) is noted. The same observation is repeated after the experiment, i.e., after the current  $I$  has been passed through

\* Phil. Trans., A, Vol. 208, P. 381 (1908).

$H_1$ , and now again the new temperature difference  $d\theta_f$  is noted. The corrected temperature difference is then

$$\delta\theta + \frac{d\theta_i + d\theta_f}{2}$$

(See for details the original paper). This value is used in the above equation to find  $K$  at temperature  $\theta_1$ .

A steady state can, however, be reached if one end of the rod is continuously cooled. By doing so, and by using high vacuum to reduce lateral loss, Grüneisen and Goens (1927) eliminated two chief sources of error—one due to the state being unsteady and the other due to the absence of high vacuum in Lees' experiment. Since loss of heat by radiation is very small at low temperatures, no correction was needed for such heat loss.

(c) **Kohlrausch's Method** : Kohlrausch\* gave a good method of finding the ratio of the thermal to the electrical conductivity and this method was experimentally carried out by Jaeger and Diesselhorst\*\*. Further, from a knowledge of this ratio and of electrical conductivity, the thermal conductivity may be found out.

When an electric current is passed through a straight metallic rod, it is heated and the heat flows sideways as well as along the length of the rod. We shall, however, suppose that the loss of heat from the sides is prevented by some cylindrical sheath (as in Donaldson's experiment) and also the ends of the rod are maintained at definite temperatures. Then, the flow of heat is parallel to the axis, say,  $x$ -axis, of the rod. Let the temperature and electric potential at  $x$  be  $\theta$  and  $V$  respectively and let the corresponding values be  $\theta + d\theta$  and  $V + dV$  at  $x + dx$ . Let  $A$  be the cross-section of the rod,  $K$  its thermal conductivity and  $\sigma$  its electrical conductivity. Both  $K$  and  $\sigma$  depend on temperature and, therefore, vary with  $x$  (Fig. 4.3).

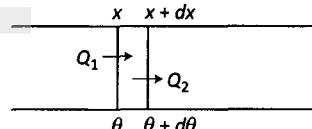


Fig. 4.3

According to (4.2) the amount of heat flowing in unit time into the section at  $x$  is

$$Q_1 = -KA \frac{d\theta}{dx}$$

and the amount of heat flowing in unit time out of the section at  $x + dx$  is

$$Q_2 = - \left[ KA \frac{d\theta}{dx} + \frac{d}{dx} \left( KA \frac{d\theta}{dx} \right) dx \right].$$

Hence, the net gain of heat by conduction in unit time by the element  $dx$  between  $x$  and  $x + dx$  is

$$dQ = Q_1 - Q_2 = A \frac{d}{dx} \left( K \frac{d\theta}{dx} \right) dx, \quad (4.3)$$

assuming  $A$  to be uniform along the rod.

If  $dR$  is the resistance of the element  $dx$  and  $i$  is the current, then the gain in heat due to the electrical energy per unit time supplied is

$$i^2 dR = \left( -\frac{dV}{dx} A\sigma \right)^2 \frac{dx}{A\sigma} = A\sigma \left( \frac{dV}{dx} \right)^2 dx. \quad (4.4)$$

When a steady state has been reached, the total rate of gain of heat by the element must be zero so that from (4.3) and (4.4),

\* Ann. der Phys., 1, P. 132 (1900).

\*\* Abhand. d. Reichsanstalt, 3, P. 269 (1900).

$$A \frac{d}{dx} \left( K \frac{d\theta}{dx} \right) dx + A\sigma \left( \frac{dV}{dx} \right)^2 dx = 0$$

i.e.,  $\frac{dK}{dx} \frac{d\theta}{dx} + K \frac{d^2\theta}{dx^2} + \sigma \left( \frac{dV}{dx} \right)^2 = 0. \quad (4.5)$

Now,  $\frac{d\theta}{dx} = \frac{d\theta}{dV} \frac{dV}{dx}$

so that  $\frac{d^2\theta}{dx^2} = \frac{d^2\theta}{dV^2} \left( \frac{dV}{dx} \right)^2 + \frac{d\theta}{dV} \frac{d^2V}{dx^2}. \quad (4.6)$

From (4.5) and (4.6),

$$\frac{dK}{d\theta} \left( \frac{d\theta}{dx} \right)^2 + K \frac{d^2\theta}{dV^2} \left( \frac{dV}{dx} \right)^2 + K \frac{d\theta}{dV} \frac{d^2V}{dx^2} + \sigma \left( \frac{dV}{dx} \right)^2 = 0$$

i.e.,  $\frac{dK}{d\theta} \left( \frac{d\theta}{dV} \right)^2 \left( \frac{dV}{dx} \right)^2 + K \frac{d^2\theta}{dV^2} \left( \frac{dV}{dx} \right)^2 + K \frac{d\theta}{dV} \frac{d^2V}{dx^2} + \sigma \left( \frac{dV}{dx} \right)^2 = 0. \quad (4.7)$

Since  $i = -A\sigma \frac{dV}{dx}$  at  $x$  as stated in (4.4), and also since  $A$  is constant and  $\frac{di}{dx} = 0$ ,

$$0 = \frac{di}{dx} = -A \frac{d}{dx} \left( \sigma \frac{dV}{dx} \right), \text{ i.e., } \frac{d\sigma}{dx} \frac{dV}{dx} + \sigma \frac{d^2V}{dx^2} = 0$$

or,  $\frac{d\sigma}{d\theta} \frac{d\theta}{dV} \left( \frac{dV}{dx} \right)^2 + \sigma \frac{d^2V}{dx^2} = 0. \quad (4.8)$

Combining (4.7) and (4.8),

$$\frac{\sigma}{K} + \left( \frac{1}{K} \frac{dK}{d\theta} - \frac{1}{\sigma} \frac{d\sigma}{d\theta} \right) \left( \frac{d\theta}{dV} \right)^2 + \frac{d^2\theta}{dV^2} = 0. \quad (4.9)$$

This is Kohlrausch's general equation. This may also be written as

$$\frac{\sigma}{K} + \frac{d}{d\theta} \left[ \log_e \left( \frac{K}{\sigma} \right) \right] \left( \frac{d\theta}{dV} \right)^2 + \frac{d^2\theta}{dV^2} = 0. \quad (4.10)$$

Jaeger and Diesselhorst applied this equation to find  $K/\sigma$  for a large number of metals. Let  $V_1, V_2, \theta_1, \theta_2$  be the potentials and temperatures at the two ends of the rod and  $V_0, \theta_0$  be the corresponding values in the middle of the rod. They, however, took in their experiment  $\theta_1 = \theta_2$ . Further, on account of symmetry,  $V_0 = (V_1 + V_2)/2$ .

Now, if  $\overline{(K/\sigma)}$ , the average value of  $(K/\sigma)$  of the rod for the  $\theta_1 - \theta_0$  range, is considered in (4.10), then from (4.10),

$$\frac{1}{\overline{(K/\sigma)}} + \frac{d^2\theta}{dV^2} = 0. \quad (4.11)$$

The solution of this equation, considering  $\overline{(K/\sigma)}$  constant under the condition of the experiment, is

$$\left( \frac{K}{\sigma} \right) \theta = -\frac{1}{2} V^2 + \alpha V + \beta, \quad (4.12)$$

where  $\alpha$  and  $\beta$  are the constants of integration.

From (4.12) three equations will be obtained using in the equation the three sets of values of  $(\theta, V)$ , i.e.,  $(\theta_1, V_1)$ ,  $(\theta_0, V_0)$  and  $(\theta_2, V_2)$ .

Eliminating  $\alpha$  and  $\beta$  between the three equations,

$$\begin{aligned} \left(\frac{K}{\sigma}\right) &= \frac{1}{2} \frac{(V_1 - V_0)(V_0 - V_2)(V_2 - V_1)}{\theta_1(V_0 - V_2) + \theta_0(V_2 - V_1) + \theta_2(V_1 - V_0)} \\ &= \frac{1}{8} \frac{(V_2 - V_1)^3}{-\frac{\theta_1}{2}(V_2 - V_1) + \theta_0(V_2 - V_1) - \frac{\theta_2}{2}(V_2 - V_1)} \\ &= \frac{1}{8} \frac{(V_2 - V_1)^2}{(\theta_0 - \theta_1)}. \end{aligned} \quad (4.13)$$

Thus,  $(\overline{K/\sigma})$  can be determined from a measurement of the potential difference between the two ends of the rod, and of the temperature difference between the middle and either end of the rod.

In the original apparatus of Jaeger and Diesselhorst, the experimental rod was surrounded by a constant temperature bath. So (4.13) was corrected for the radial flow of heat from the sides of the rod.

### 4.3 Conductivity of Bad Conductors

For finding the conductivity of bad conductors, we shall consider here two methods : (a) Poensgen's method and (b) cylindrical shell method.

**(a) Poensgen's Method :** Poensgen\*, in fact, improved a method originally devised by Lees\*\*.  $A$  and  $C$  are two identical plates of the material of which the conductivity is to be found (Fig. 4.4).  $B$  is a plate heated electrically and is surrounded by a ring  $E$  (of the same material as  $B$ ) also heated electrically and maintained at the same temperature as that of  $B$ . Consequently, all the heat developed in  $B$  flows only through  $A$  and  $C$  and is ultimately carried off by water circulating through the plates  $D_1$ ,  $D_2$ . The whole system is enclosed in a chamber  $F$  filled with some badly conducting substance such as cork-shavings, etc. The temperature  $\theta_1$  of the plate  $B$  and the temperature  $\theta_2$  of the plates  $D_1$ ,  $D_2$  are measured by thermoelements attached to their surfaces. If  $Q$  is the amount of heat supplied electrically by  $B$  in time  $t$ , then

$$\frac{Q}{2} = KA \frac{\theta_1 - \theta_2}{d} t, \text{ i.e., } K = \frac{Qd}{2A(\theta_1 - \theta_2)t},$$

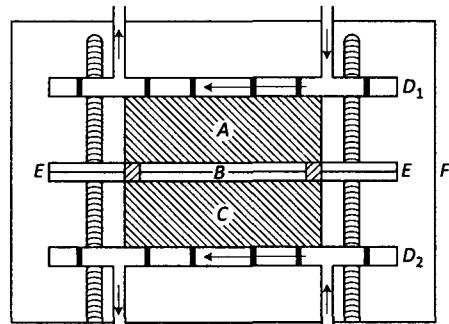


Fig. 4.4: Poensgen's experiment

where  $A$  is the area of the plates  $A$ ,  $C$  and  $d$  their thickness. In the above equation,  $Q$  has been divided by 2 because half of  $Q$  supplied by  $B$  flows through each of  $A$  and  $C$ .

**(b) Cylindrical Shell Method :** Let us consider a cylindrical shell of which the inner surface is maintained at a temperature  $\theta_1$  and the outer surface at a lower temperature  $\theta_2$  so that there is a radial flow of heat from the inside to the outside of the shell. It is evident that in this case the isothermal surfaces are cylindrical. Then, from (4.2), the amount of heat  $Q$

\* Forschungsarbeiten, herausgeg, Ver d. Ing., 130, P. 25 (1912); Zeits. d. Ver. d. Ing., 56, P. 1653, (1912).

\*\* Phil. Trans., 191, P. 399 (1898).

flowing through a cylindrical surface of radius  $r$  in unit time is

$$Q = -K \cdot 2\pi r l \cdot \frac{d\theta}{dr},$$

where  $l$  is the length of the cylindrical shell. Assuming that the steady state has been attained so that  $Q$  is the amount of heat flowing through every cylindrical surface, the above equation may be integrated :

$$Q \int_{r_1}^{r_2} \frac{dr}{r} = -2\pi K l \int_{\theta_1}^{\theta_2} d\theta$$

$$\text{or, } K = \frac{Q}{2\pi l} \frac{\log_e(r_2/r_1)}{\theta_1 - \theta_2}, \quad (4.14)$$

where  $r_1, r_2$  are the inner and outer radii of the cylindrical shell.

We shall discuss here the experimental method devised by Stephens\* on the basis of the above theory.

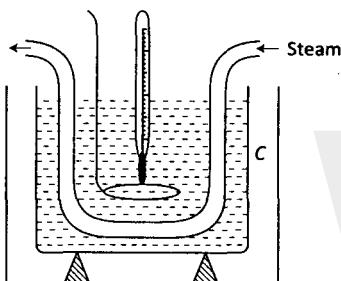


Fig. 4.5: Conductivity of rubber

First we consider the experiment to find the conductivity of rubber (Fig. 4.5). A known length  $l$  of a rubber tube is immersed in water contained in a calorimeter  $C$ . Steam is passed through the tube for time  $t$  and the rise in temperature of the calorimeter from the initial temperature  $\theta_1$  to the final temperature  $\theta_2$  is noted. Thus, the outer surface of the rubber tube changes from  $\theta_1$  to  $\theta_2$  whereas the inner surface of the tube gets the same temperature  $\theta$  as that of steam. Then, from (4.14), we have

$$K = \frac{Q}{2\pi l} \frac{\log_e(r_2/r_1)}{\left(\theta - \frac{\theta_1 + \theta_2}{2}\right)}, \quad (4.15)$$

where  $\frac{\theta_1 + \theta_2}{2}$  is the average temperature of the outer surface of the rubber tube and  $Q$  is the average rate of flow of heat through the wall of the tube obtained from

$$Q = \frac{(m + w)(\theta_2 - \theta_1)}{t}$$

Here  $m$  is the mass of water in the calorimeter and  $w$  is the water-equivalent of the calorimeter.

Next we consider the experiment to find the conductivity of glass. The specimen is a tube  $A$  (Fig. 4.6) of length  $l$  through which a steady current of water passes through a constant-head supply. Surrounding the specimen in an outer jacket  $J$  through which steam is passed for time  $t$ . Thus, in this experiment the outer surface of glass tube  $A$  is at a higher temperature  $\theta$  equal to that of steam.  $K$  for glass is found from a formula exactly same as (4.15), but here

$$Q = \frac{m(\theta_2 - \theta_1)}{t}$$

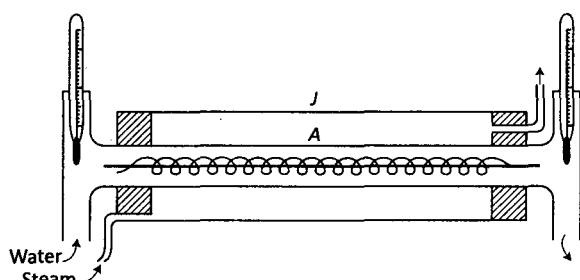


Fig. 4.6: Conductivity of glass

and the inner surface temperature is taken as  $\frac{\theta_1 + \theta_2}{2}$ , where  $m$  is the mass of water flowing in time  $t$  with temperature  $\theta_1$  at the entrance and temperature  $\theta_2$  at the exit.

\*Phil. Mag., 15, P. 857 (1933).

#### 4.4 Conductivity of Crystals : Eueken's Method

We have so far discussed experiments to find the conductivity of isotropic bodies, i.e., the bodies for which conductivity is same in all directions. But the conductivity of crystalline and anisotropic bodies is different in different directions. We shall describe a method due to Eucken\* to determine conductivity of crystals.

The crystal *B* placed between two plates of copper *A* and *C* (Fig. 4.7). *A* is heated electrically and is the source of heat for the experiment. The temperatures of *A* and *C* are measured by thermocouples. The two junctions of another thermocouple are inserted (as shown in the figure) into two small holes *X*, *Y* bored in the crystal *B* so as to give the temperature gradient in it. Above *C* there is a copper block *D*. *A* rests on a pinewood support *E* which again stands on a copper plate *F*. Below *F* there is a copper block *G*. The whole apparatus is fitted in a copper vessel *H* with a copper lid *LL*.

Eucken carried out experiments at low temperatures down to  $-252^{\circ}\text{C}$ . When working at low temperatures, it is not possible to use a liquid to improve contacts between different surfaces. Eucken, therefore, used a gas (filling the whole apparatus) for the purpose. It is evident that the correction necessary for the temperature drop at the contacts and also the correction necessary for loss of heat by conduction from the sides of the crystal depend on the conductivity of the gas filling the apparatus. Eucken found out the conductivity of the gas at the temperature of the experiment by a separate experiment.

Correction is also made for the heat conducted by the pinewood support *E* and for the heat loss by radiation from the surface of the crystal.

The results of the experiments show that *the thermal conductivity of such bodies is inversely proportional to the absolute temperature*. Debye\*\* was the first to give a theoretical explanation of this law. He worked out the kinetic theory of the transfer of heat in such bodies from the point of view of the propagation of elastic waves in a continuous medium. Peierls† further improved the theory taking into account, according to Pauli‡, the atomic nature of the solid lattice as opposed to continuum assumed by Debye and obtained satisfactory agreement with the experimental results.

#### 4.5 Conductivity of Liquids

The effect of convection must be eliminated if the coefficient of thermal conductivity of a liquid is to be measured. This can be done by using a fairly thin horizontal layer of liquid heated from above.

We consider here Lees' method§ to find the conductivity of a liquid. The liquid *L* is enclosed between two copper discs *C*<sub>1</sub>, *C*<sub>2</sub> by an ebonite ring *E* (Fig. 4.8). A glass disc *G* of known conductivity is placed above *C*<sub>2</sub>, and above *G* is another copper disc *C*<sub>3</sub>. Between *C*<sub>3</sub> and

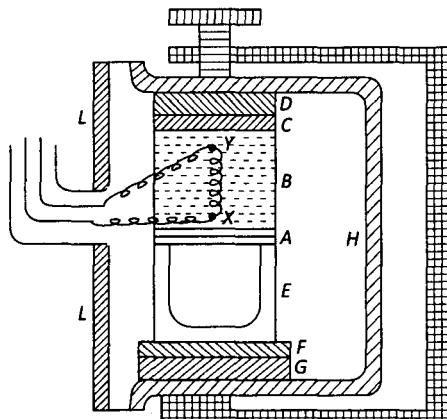


Fig. 4.7: Conductivity of a crystal

\* Ann. d. Phys., 34, P. 185 (1911).

\*\* Walfakehl-Vorträge zu Göttingen, Leipzig (1914).

† Ann. d. Phys., 3, P. 1055 (1929).

‡ Verh. d. dents, phys., Ges., 6, P. 10 (1925).

§ Phil. Trans., 191, P. 418 (1898).

another copper disc  $C_4$  is placed the heating coil  $H$ .  $H$  is insulated from  $C_3$  and  $C_4$  by mica sheets. The whole system thus built up is varnished to give it a uniform and known emissivity (i.e., power of emission of radiation) and enclosed in an air-bath maintained at constant temperature. Thermocouples are used (as shown in the figure) to know the temperatures of the upper and lower surfaces of  $G$  and  $L$ .

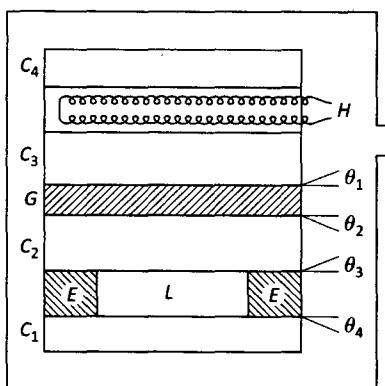


Fig. 4.8: Conductivity of a liquid

After switching on the current in the heating coil  $H$ , when the steady state has been attained the thermocouples give  $\theta_1$ ,  $\theta_2$  as the temperatures of the surfaces of  $G$  and  $L$ ,  $\theta_3$ ,  $\theta_4$  as the temperatures of the surfaces of  $L$ . We take  $K$ ,  $A$ ,  $d$  as the conductivity, cross-section and thickness of the liquid  $L$ ,  $K_1$ ,  $A_1$ ,  $d_1$ , the corresponding quantities of  $G$  and  $K_2$ ,  $A_2$ ,  $d_2$  those of the ebonite ring  $E$ .

$$\text{Evidently, the heat flowing through } G \text{ per second} = K_1 A_1 \frac{\theta_1 - \theta_2}{d_1}.$$

This will be equal to the total amount of heat passing through  $L$  and  $E$  per second

$$= K A \frac{\theta_3 - \theta_4}{d} + K_2 A_2 \frac{\theta_3 - \theta_4}{d_2}.$$

$$\text{Hence, } K_1 A_1 \frac{\theta_1 - \theta_2}{d_1} = K A \frac{\theta_3 - \theta_4}{d} + K_2 A_2 \frac{\theta_3 - \theta_4}{d_2}.$$

Knowing other quantities,  $K$  is obtained from the above equation. However, correction will have to be made for the heat radiated from the sides of  $G$ ,  $C_2$  and  $E$ .

## 4.6 Conductivity of Gases

The measurement of conductivity of gases is extremely difficult because it is so small that it is generally masked by the effects of convection and radiation. The most satisfactory method for measuring the conductivity of gases is that of Hercus and Laby\*. Their method is based on the same principle as applied by Lees to find the conductivity of liquids.

$B$  is a copper plate electrically heated (Fig. 4.9). From  $B$ , heat flows by conduction downward through the experimental gas to the copper plate  $C$  which is water-cooled. The surfaces of  $B$  and  $C$  are silver-plated so as to minimise radiation.  $B$  is surrounded by a guard-ring  $D$  heated electrically, both being maintained at the same temperature so that there is no heat loss from the lateral sides of  $B$ . Further,  $B$  is supported from  $D$  by three I-shaped ivory buttons (not shown in the figure). To prevent any loss of heat from the upper surface of  $B$ , another copper plate  $A$  is electrically maintained at the same temperature\*\* as  $B$  itself. The temperatures of all the copper plates,  $A$ ,  $B$ ,  $C$  and  $D$ , are measured at various points by attaching constantan

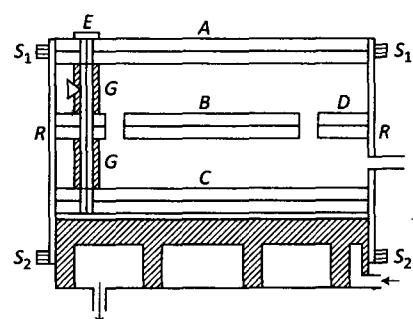


Fig. 4.9: Conductivity of a gas

\* Proc. Roy. Soc., 95, P. 190 (1919); Proc. Roy. Soc. A. 145, P. 599, (1934)

\*\* In fact  $A$  is maintained at a slightly higher temperature than  $B$  so as to prevent any convection occurring between  $A$  and  $B$ . For this, however, some correction is made for the small quantity of heat gained by  $B$  from  $A$ .

wires to them—in fact, these wires form thermocouples with the plates themselves and each of the plates has a copper lead attached to it. All the plates are held together by three bolts (one,  $E$ , is shown) passing through glass distance-pieces  $G$ . The whole apparatus is made gas-tight by a stout rubber ring  $RR$  clamped to  $A$  and  $C$  by two steel bands  $S_1S_1$ ,  $S_2S_2$ .

It is evident that in the steady state all the heat generated in  $B$  flows to  $C$  and this is measured from the electrical energy supplied to the heating coil in  $B$ . If  $V$  is the potential difference across this coil and  $I$  the current flowing through it then the heat generated in time  $t$  is

$$Q = \frac{VIt}{J} = KA \frac{\theta_1 - \theta_2}{d} t, \text{ i.e., } K = \frac{VId}{JA(\theta_1 - \theta_2)},$$

where  $d$  is the distance between  $B$  and  $C$  and  $\theta_1, \theta_2$  are their temperatures. Some heat passes from  $B$  to  $C$  by radiation also. So some correction is done on this account.

The method of Hercus and Laby has the advantage that due to downward flow of heat from  $B$  to  $C$ , there is no convection. Ubbink and de Haas\* modified this method suitably to find the conductivity at low temperatures of gases like hydrogen, helium and air.

#### 4.7 Mathematical Theory of Rectilinear Flow of Heat: Forbes Method

Let us consider flow of heat through a thin metal bar of cross-section  $A$  with its hot end (temperature =  $\theta_1$ ) at  $x = 0$  and cold end (temperature =  $\theta_2$ ) at  $x = l$ . Let us take an element between  $x$  and  $x + \delta x$  and let the temperature at  $x$  and  $x + \delta x$  be  $\theta$  and  $\theta + \delta\theta$  respectively (Fig. 4.10). Since the heat flowing in unit time through a section at  $x$  is practically the same as the heat passing in unit time through an element of infinitesimal thickness  $dx$  at  $x$ , we obtain for this amount of heat from (4.2)

$$Q_1 = -KA \frac{d\theta}{dx}. \quad (4.16)$$

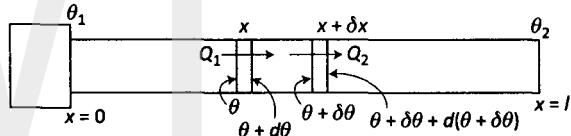


Fig. 4.10: Bar

In a similar manner, the quantity of heat  $Q_2$ , passing in unit time through the section at  $x + \delta x$  is

$$\begin{aligned} Q_2 &= -KA \frac{d}{dx}(\theta + \delta\theta) = -KA \frac{d\theta}{dx} - KA \frac{d}{dx} \left( \frac{d\theta}{dx} \delta x \right) \\ &= -KA \frac{d\theta}{dx} - KA \frac{d^2\theta}{dx^2} \delta x. \end{aligned} \quad (4.17)$$

Hence, the gain of heat per unit time by the element  $\delta x$  is

$$\delta Q = Q_1 - Q_2 = KA \frac{d^2\theta}{dx^2} \delta x. \quad (4.18)$$

In general, part of this heat,  $\delta Q'$ , is used up to raise the temperature of the element and a part of it,  $\delta Q''$ , is radiated from the sides of the element. If  $\rho$  be the density of the material of the metal bar, then

$$\delta Q' = \rho A \delta x c \frac{d\theta}{dt}, \quad (4.19)$$

where  $c$  is the specific heat of the bar. If  $p$  be the perimeter of the bar, then  $p\delta x$  is the surface area of the element. Now  $\delta Q''$  is proportional to  $p\delta x$  and, assuming Newton's law of cooling, is

\* Leiden Comm. 266c, d; Physica, 10, P. 451 (1943).

also proportional to  $(\theta - \theta_0)$ , where  $\theta_0$  is the temperature of the surroundings. Thus,

$$\delta Q'' = Ep\delta x(\theta - \theta_0), \quad (4.20)$$

where  $E$  is the constant of proportionality and is called the *emissive power* of the surface. Combining (4.18), (4.19) and (4.20),

$$KA \frac{d^2\theta}{dx^2} \delta x = \rho A \delta x c \frac{d\theta}{dt} + Ep\delta x(\theta - \theta_0)$$

$$\text{or, } \frac{d\phi}{dt} = h \frac{d^2\phi}{dx^2} - \mu\phi, \quad (4.21)$$

where  $h (= K/\rho c)$  has been called *diffusivity* by Kelvin and *thermometric conductivity* by Maxwell,  $\mu$  is equal to  $Ep/\rho Ac$  and  $\phi = \theta - \theta_0$ .

(4.21) is the standard Fourier equation for one-dimensional flow of heat and this equation has to be solved to investigate any problem in thermal conduction along a bar, taking into account appropriate boundary conditions.

Let us consider some special cases of (4.21).

(a) If the bar is covered so that there is no radiation loss, then (4.21) is reduced to the form :

$$\frac{d\phi}{dt} = h \frac{d^2\phi}{dx^2}. \quad (4.22)$$

Solutions of (4.22) have been considered in sections **4.9** and **4.10**.

(b) If there is no radiation loss and at the same time the steady state has been attained (say, as in Donaldson's experiment), then (4.21) takes the form :

$$\frac{d^2\phi}{dx^2} = 0. \quad (4.23)$$

The solution of this equation yields

$$\phi = \alpha x + \beta,$$

where the constants  $\alpha$  and  $\beta$  are to be determined from the boundary conditions :  $\phi = \phi_1 = \theta_1 - \theta_0$  at  $x = 0$  and  $\phi = \phi_2 = \theta_2 - \theta_0$  at  $x = l$ . Then, it can easily be seen that

$$\phi = \phi_1 - \frac{\phi_1 - \phi_2}{l}x. \quad (4.24)$$

(c) If the steady state has been attained and there is also radiation loss, then from (4.21),

$$\frac{d^2\phi}{dx^2} = \frac{Ep}{KA}\phi = m^2\phi \text{ (say).} \quad (4.25)$$

The general solution of (4.25) is of the form :

$$\phi = Pe^{mx} + Qe^{-mx}, \quad (4.26)$$

where  $P$  and  $Q$  are two constants to be determined from boundary conditions. If the bar is of infinite (i.e., very large) length, then  $\theta_2 \rightarrow \theta_0$  so that  $\phi_2 \rightarrow 0$ . But, from (4.26), it is seen that for such a bar at  $x = l$  (very large),  $\phi_2 \rightarrow$  a very large value because of the first term on the right-hand side. So, on the physical ground we must put  $P = 0$ . Then (4.26) gives

$$\phi = Qe^{-mx}. \quad (4.27)$$

Now, at  $x = 0$ ,  $\phi = \phi_1$ , so that

$$\phi_1 = Q. \quad (4.28)$$

Hence, we have from (4.27) and (4.28),

$$\phi = \phi_1 e^{-mx}. \quad (4.29)$$

If, however, the bar is not of infinite length but the temperature of the cold end is the same as that of the surroundings ( $\phi_2 = 0$ ), then for this case no heat flows out from the cold end and the temperature gradient at the cold end is zero. That is,

$$\frac{d\theta}{dx} = \frac{d\phi}{dx} = 0 \text{ at } x = l.$$

Under this condition, we obtain from (4.26),

$$Pe^{ml} - Qe^{-ml} = 0. \quad (4.30)$$

Also at  $x = 0$ ,

$$P + Q = \phi_1. \quad (4.31)$$

Now, solving (4.30) and (4.31),

$$P = \frac{\phi_1}{1 + e^{2ml}}, \quad Q = \frac{\phi_1}{1 + e^{-2ml}}. \quad (4.32)$$

Hence, from (4.26) and (4.32),

$$\phi = \phi_1 \left[ \frac{e^{mx}}{1 + e^{2ml}} + \frac{e^{-mx}}{1 + e^{-2ml}} \right]. \quad (4.33)$$

It is evident that for  $l$  very large, (4.33) is reduced to (4.29).

**Ingen-Hausz's Experiment :** In 1789, Ingen-Hausz performed an experiment (now usually shown as a demonstration experiment) to compare the conductivity of different metals. The results of this experiment can be easily understood from (4.29). Long thin bars of different materials having equal length, same area of cross-section and identical surface finish (i.e., electroplated and polished in the same manner) are taken. The bars are coated with wax and one end of each is immersed in a hot bath of oil or water. After a steady state has been reached, the wax is observed to have melted to distances  $x_1, x_2, x_3, \dots$  (measured from the hot end) along bars of conductivities  $K_1, K_2, K_3, \dots$

Let  $\phi_m$  correspond to the melting point  $\theta_m$  of wax. Then,  $\phi_m$  corresponds to  $x = x_1$  of bar of conductivity  $K_1$ , to  $x = x_2$  of bar of conductivity  $K_2$ , .....

Thus, we obtain from (4.29)

$$\phi_m = \phi_1 e^{-m_1 x_1} = \phi_1 e^{-m_2 x_2} = \phi_1 e^{-m_3 x_3} = \dots$$

That is,  $m_1 x_1 = m_2 x_2 = m_3 x_3 = \dots$

$$\text{But } m_1 = \sqrt{\frac{Ep}{K_1 A}}, \quad m_2 = \sqrt{\frac{Ep}{K_2 A}}, \quad m_3 = \sqrt{\frac{Ep}{K_3 A}}, \dots$$

$E, p$  and  $A$  being same for all bars.

$$\text{Hence, } \frac{x_1}{\sqrt{K_1}} = \frac{x_2}{\sqrt{K_2}} = \frac{x_3}{\sqrt{K_3}} = \dots$$

$$\text{or, } \frac{K_1}{x_1^2} = \frac{K_2}{x_2^2} = \frac{K_3}{x_3^2} = \dots \quad (4.34)$$

This theory holds quite well for very long bars. In practice, however, bars, up to about 20 cm long with diameters of a few mm, are used so that this theory does not apply to the actual experimental arrangements, as usually used in demonstrations. Ashford\* gave the correct treatment of the experiment. We must, in fact, use (4.33) instead of (4.29) so that we have now

$$\phi_m = \phi_1 \left[ \frac{e^{mx}}{1 + e^{2ml}} + \frac{e^{-mx}}{1 + e^{-2ml}} \right]$$

at the point  $x$  up to which wax has melted along a bar of length  $l$ . Then, for bars of lengths  $l_1, l_2, l_3, \dots$  with corresponding conductivities  $K_1, K_2, K_3, \dots$

$$\begin{aligned} \phi_m &= \phi_1 \left[ \frac{e^{m_1 x_1}}{1 + e^{2m_1 l_1}} + \frac{e^{-m_1 x_1}}{1 + e^{-2m_1 l_1}} \right] = \phi_1 \left[ \frac{e^{m_2 x_2}}{1 + e^{2m_2 l_2}} + \frac{e^{-m_2 x_2}}{1 + e^{-2m_2 l_2}} \right] \\ &= \phi_1 \left[ \frac{e^{m_3 x_3}}{1 + e^{2m_3 l_3}} + \frac{e^{-m_3 x_3}}{1 + e^{-2m_3 l_3}} \right] = \dots \end{aligned}$$

This is satisfied for all bars, if and only if

$$(1) m_1 x_1 = m_2 x_2 = m_3 x_3 = \dots \quad \text{or, } \frac{K_1}{x_1^2} = \frac{K_2}{x_2^2} = \frac{K_3}{x_3^2} = \dots \text{ as in (4.34)}$$

and (2) either (a)  $l_1, l_2, l_3, \dots$  are infinite as in Ingen-Hausz's experiment, or (b)  $m_1 l_1 = m_2 l_2 = m_3 l_3 = \dots$

$$\text{or, } \frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \dots \text{ for finite lengths of bars.}$$

It is evident that for finite lengths of bars, conditions (4.1) and (4.26) must be satisfied, that is, combining these two conditions the ultimate condition to be satisfied is

$$\frac{l_1}{x_1} = \frac{l_2}{x_2} = \frac{l_3}{x_3} = \dots \quad (4.35)$$

It must, however, be remembered that (4.33), from which (4.35) has been derived, comes from the assumption that

$$\frac{d\theta}{dx} = \frac{d\phi}{dx} = 0 \text{ at } x = l.$$

## 4.8 Theory of Periodic Rectilinear Flow of Heat : Ångström's Experiments

Ångström was the first to determine the conductivity of a bar by periodically heating and cooling it. For this purpose, a periodic solution of the Fourier equation

$$\frac{d\phi}{dx} = h \frac{d^2\phi}{dx^2} - \mu\phi \quad (4.21)$$

\*School Science Review, 21, P. 83

is necessary. If the bar is heated and cooled alternately in a smooth and continuous manner,  $\theta$  (i.e.,  $\phi$ ) will be exactly a simple harmonic function representing a temperature wave as shown in Figs. 4.11(a) and (b).

But Ångström heated and cooled one end of the bar periodically and not simple harmonically\*. So  $\phi$  is a periodic (and not a simple harmonic) function. But it is well known that from Fourier's theorem, we may expand  $\phi$  into a Fourier series. Hence, the general periodic solution of (4.21) is

$$\phi = \sum_{n=0}^{n=\infty} A_n e^{-\alpha_n x} \sin(n\omega t + \beta_n x + \gamma_n). \quad (4.36)$$

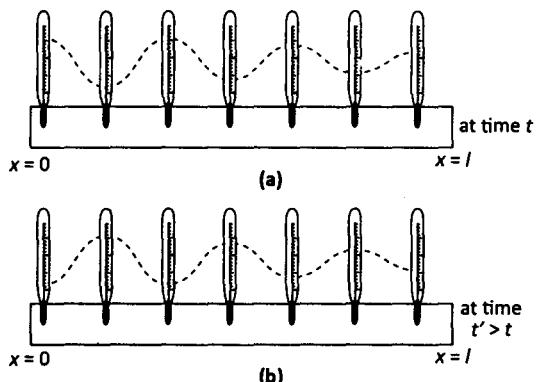


Fig. 4.11: Ångström's experiment

The exponential factor appears because the amplitude of  $\phi$  diminishes as  $x$  increases (See eq. (4.26)).

Now, substituting (4.36) in (4.21), we get

$$\left. \begin{aligned} \alpha_n \beta_n &= -\frac{n\omega}{2h} \\ \alpha_n^2 - \beta_n^2 &= \frac{\mu}{h} \end{aligned} \right\} \quad (4.37)$$

If  $\alpha_n, \beta_n$  are known, then from (4.37)  $h$ , i.e.,  $K$  can be found out. For this purpose, temperatures at two points  $x = x_0$  and  $x = x_0 + d$  along the bar are determined at regular intervals of time. From (4.36), these temperatures are given by

$$\phi_{x_0} = \sum_{n=0}^{n=\infty} B_n \sin(n\omega t + \delta_n) \quad (4.38)$$

$$\text{and } \phi_{x_0+d} = \sum_{n=0}^{n=\infty} B'_n \sin(n\omega t + \delta'_n), \quad (4.39)$$

where  $B_n, B'_n, \delta_n, \delta'_n$  are constants at the two points and are given by

$$B_n = A_n e^{-\alpha_n x_0}, \quad B'_n = A_n e^{-\alpha_n (x_0+d)} \quad (4.40)$$

$$\delta_n = \beta_n x_0 + \gamma_n, \quad \delta'_n = \beta_n (x_0 + d) + \gamma_n. \quad (4.41)$$

$$\text{Hence, } \alpha_n d = \log_e(B_n/B'_n), \quad \beta_n d = \delta'_n - \delta_n \quad (4.42)$$

$$\text{and } \alpha_n \beta_n = \frac{(\delta'_n - \delta_n) \log_e(B_n/B'_n)}{d^2}. \quad (4.43)$$

From (4.37) and (4.43),

$$h = \frac{n\pi d^2}{T(\delta_n - \delta'_n) \log_e(B_n/B'_n)}$$

\*King modified Ångström's method and heated one end of the bar electrically, the heating current being varied simple-harmonically by means of a cam. See, for details, *Phys. Rev. II*, 6, P. 437 (1915).

$$\text{i.e., } K = \frac{n\pi\rho cd^2}{T(\delta_n - \delta'_n) \log_e(B_n/B'_n)}, \quad (4.44)$$

where  $T = \frac{2\pi}{\omega}$  = period of heating and cooling.

Thus, to find  $K$ , we must know  $\delta_n$ ,  $\delta'_n$ ,  $B_n$  and  $B'_n$ . It is evident from (4.44) that we obtain as many independent values of  $K$  as there are terms in (4.36). In practice, the first two or three terms are important as the coefficients diminish rapidly. In this discussion, therefore, we shall retain only three terms in (4.38) and (4.39) with  $n = 0, 1, 2$ .

$$\phi_{x_0} = B_0 + B_1 \sin(\omega t + \delta_1) + B_2 \sin(2\omega t + \delta_2) \quad (4.45)$$

$$\text{and } \phi_{x_0+d} = B'_0 + B'_1 \sin(\omega t + \delta'_1) + B'_2 \sin(2\omega t + \delta'_2). \quad (4.46)$$

From these two equations,  $B$ 's and  $\delta$ 's—ten quantities in all—are to be determined in order to find  $K$  from (4.44) for  $n = 1$  and  $n = 2$ .

In his later experiments, Ångström enclosed the end of the bar in a chamber through which steam and cold water were alternately passed. The bar was heated for 12 minutes and cooled also for 12 minutes, the total period  $T$  being 24 minutes. Temperatures were observed every minute (i.e., 24 times in a period) at points  $x = x_0$  and  $x = x_0 + d$  by means of thermocouples. Thus, 24 sets of values are obtained from the thermocouples for  $\phi_{x_0}$  and  $\phi_{x_0+d}$ . Hence, 24 equations follow from each of (4.45) and (4.46) and from them all  $B$ 's and  $\delta$ 's are found. Putting their values in (4.44) two values of  $K$  (one for  $n = 1$  and the other for  $n = 2$ ) are calculated and the mean value is obtained.

## 4.9 Conductivity of Earth's Crust

Ångström's investigations have got an important application to the earth which is heated during day and cooled during night. This alternate heating and cooling give rise to a diurnal temperature wave into the earth's crust. Approximately, this wave may be considered as simple harmonic with a period of 24 hours. Then, for this case which corresponds to an infinite wall heated and cooled at one end or to a bar periodically heated and cooled at one end and covered with a guard-sheath, we have the equation from (4.22)

$$\frac{d\theta}{dt} = h \frac{d^2\theta}{dx^2} \quad (4.47)$$

for which the simplest solution should be of the form\* :

$$\theta = \theta_0 e^{-\alpha x} \sin(\omega t + \beta x), \quad (4.48)$$

where  $\theta_0$  is evidently the temperature at  $x = 0$ , i.e., at the surface of the earth. Now, as before, substituting (4.48) in (4.47),

$$\left. \begin{aligned} \alpha^2 &= \beta^2 \\ \text{and } \alpha\beta &= -\frac{\omega}{2h} \end{aligned} \right\} \quad (4.49)$$

As (4.48) is supposed to represent a progressive temperature wave of wave length  $\lambda$  (say),

$$\beta = -\frac{2\pi}{\lambda} \quad (4.50)$$

\*The exponential factor appears because the amplitude of  $\theta$  diminishes as  $x$  increases (See Eq. (4.36)).

so that from (4.49),

$$\alpha = \frac{2\pi}{\lambda} = -\beta. \quad (4.51)$$

Hence, from (4.49),

$$h = \frac{\omega}{2\alpha^2} = \frac{\lambda^2}{4\pi T} \quad (4.52)$$

$$\text{i.e., } K = \frac{\rho c \lambda^2}{4\pi T}. \quad (4.53)$$

The velocity of the temperature wave is, from (4.53),

$$v = \frac{\lambda}{T} = 2\sqrt{\frac{\pi K}{\rho c T}} \quad (4.54)$$

so that the time,  $t$ , taken by the wave to travel a depth  $x$ , is

$$t = \frac{x}{v} = \frac{x}{2} \sqrt{\frac{\rho c T}{\pi K}}. \quad (4.55)$$

In order to know  $K$  from (4.53), a number of thermometers are embedded at different depths in the earth and from the readings of the thermometers the wavelength  $\lambda$  is determined (vide Fig. 4.11). Then  $K$  can easily be calculated from (4.53), other quantities being known from subsidiary experiments.

**Exercise 1.** Taking  $h = 0.0050$  for the crust of the earth, calculate (a)  $\lambda$ , (b)  $v$  and (c)  $t$  (time) required by a maximum of the diurnal temperature wave to reach a depth  $x = 60$  cm.

**Exercise 2.** Taking  $h = 0.0058$  for concrete, find at which hour of the day the maximum of the diurnal temperature wave, starting at 2 P.M. from the outer surface of a house wall of thickness 40 cm, would reach the inner surface of the same.

## 4.10 Age of the Earth

Kelvin made an estimate of the age of the earth from its conductivity and the present temperature gradient on its surface. He solved the equation

$$\frac{d\theta}{dt} = h \frac{d^2\theta}{dx^2} \quad [\text{Vide (4.47)}]$$

under the boundary conditions : (a) at  $x = 0$ , i.e., at the surface of the earth,  $\theta = 0$ ; (b) at  $x = \infty$ , i.e., at a large depth,  $\theta = \theta_0$ ; and (c) at  $t = 0$ , i.e., the moment the earth began to solidify,  $\theta = \theta_0$ .

Let us make the substitution,

$$y = \frac{x}{2\sqrt{ht}} \quad (4.56)$$

and thus obtain from (4.47)

$$\frac{d^2\theta}{dy^2} + 2y \frac{d\theta}{dy} = 0. \quad (4.57)$$

The solution of this equation is easily seen to be

$$\theta = A \int_0^y e^{-y^2} dy + B, \quad (4.58)$$

where  $A$  and  $B$  are constants of integration. From the boundary condition (a), we find that  $B = 0$ . From the boundary condition (b), we find from (4.58)

$$\theta_0 = A \int_0^\infty e^{-y^2} dy = A \frac{\sqrt{\pi}}{2} \quad [\text{See Appendix 1}]$$

$$\text{i.e., } A = \theta_0 \frac{2}{\sqrt{\pi}}. \quad (4.59)$$

From (4.58) and (4.59),

$$\theta = \theta_0 \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy. \quad (4.60)$$

This  $\theta$  gives the temperature at a depth  $x$  at a moment  $t$ . On differentiation of (4.60) at  $x = 0$ , i.e., at the surface of the earth,

$$\begin{aligned} \left( \frac{d\theta}{dx} \right)_{x=0} &= \frac{\theta_0}{\sqrt{\pi h t}}. \\ \therefore t &= \frac{\theta_0^2}{\pi h \left( \frac{d\theta}{dx} \right)_{x=0}}. \end{aligned} \quad (4.61)$$

If we put for  $(\frac{d\theta}{dx})_{x=0}$  the present value, then  $t$  will give the present age of the earth counted from the moment the process of solidification started. Kelvin put  $\theta_0 = 3900$  °C,  $h = 0.01178$  and  $(\frac{d\theta}{dx})_{x=0} = \frac{1}{2776}$  and obtained for  $t$  a value of 100 million years. This estimate, however, falls short of the value given by geologists. This is accounted for by the heat continuously generated by radioactive bodies inside the earth. Thus the cooling of the earth is retarded and a lower value of the age of the earth is obtained.

**Exercise 1.** Calculate time  $t_0$ , required by a layer of ice of thickness  $d$  to be formed on the surface of a lake, the air above being at  $-\theta$  °C.

**Solution :** Let  $\rho$ ,  $L$ ,  $K$  be respectively the density, latent heat and conductivity of ice. Let us suppose, a thickness of ice =  $x$  has formed in time  $t$ . Then, if  $dt$  be the time required to form a further thickness  $dx$  at the bottom of the layer of ice already formed, we have from the principle of calorimetry and the law of conductivity,

$$L\rho \frac{dx}{dt} = \frac{K\{0 - (-\theta)\}}{x} = \frac{K\theta}{x}$$

taking the temperature of ice to be 0 °C. Hence, on integration,

$$\int_0^a x dx = \frac{K\theta}{L\rho} \int_0^{t_0} dt$$

$$\text{i.e., } d^2 = \frac{2K\theta}{L\rho} t_0 \quad (4.62)$$

$$\text{or, } t_0 = \frac{L\rho d^2}{2K\theta}. \quad (4.63)$$

**Exercise 2.** Calculate the quantity of heat flowing in unit time per unit area of a composite wall consisting of  $n$  layers of thicknesses  $d_1, d_2, d_3, \dots$  and conductivities  $K_1, K_2, K_3; \dots, \theta_1$  and  $\theta_2$  being the temperatures of the hot and the cold face respectively.

**Solution :** Let  $Q$  be the quantity of heat to be calculated. Let  $\theta', \theta'', \theta''', \dots$  be the temperatures of the first interface, second interface, third interface, ... so that

$$Q = \frac{\theta_1 - \theta'}{\left(\frac{d_1}{K_1}\right)} = \frac{\theta' - \theta''}{\left(\frac{d_2}{K_2}\right)} = \frac{\theta'' - \theta'''}{\left(\frac{d_3}{K_3}\right)} = \dots = \frac{\theta^{n-1} - \theta_n}{\left(\frac{d_n}{K_n}\right)} \cdot$$

or,  $Q = \frac{(\theta_1 - \theta') + (\theta' - \theta'') + \dots + (\theta^{n-1} - \theta_n)}{\left(\frac{d_1}{K_1} + \frac{d_2}{K_2} + \dots + \frac{d_n}{K_n}\right)} = \frac{\theta_1 - \theta_n}{\sum\left(\frac{d}{K}\right)}. \quad (4.64)$

**Exercise 3.** Find an expression for the conductivity of a material in the form of a hollow spherical shell.

**Solution :** Let  $r_1, r_2$  be the inner and outer radii of the spherical shell and  $\theta_1, \theta_2$  be the temperatures of the inner and the outer surface respectively ( $\theta_1 > \theta_2$ ). Consider an infinitesimally thin spherical shell of radii  $r$  and  $r + dr$ . Then, from (4.2), the heat flowing through this thin shell per unit time is

$$Q = -KA \frac{d\theta}{dr} = -K4\pi r^2 \frac{d\theta}{dr}.$$

In the steady state,  $Q$  is constant so that on integration

$$\int_{r_1}^{r_2} \frac{dr}{r^2} = -\frac{4\pi K}{Q} \int_{\theta_1}^{\theta_2} d\theta$$

i.e.,  $K = \frac{Q(r_2 - r_1)}{4\pi r_1 r_2 (\theta_1 - \theta_2)}. \quad (4.65)$

## PROBLEMS

- Steam at 100 °C is passed through a rubber tube 14.6 cm length of which is immersed in 440 gm of water in a copper calorimeter of thermal capacity 23 cal. The temperature of the water and calorimeter is found to rise at the rate 0.019 °C every second when they are at the room temperature 22 °C. The external and internal diameters of the tube are 1.00 cm and 0.75 cm respectively. Calculate the conductivity of rubber. [Gau.U.]
- Find the time required to form a thickness of 2 cm of ice on a lake, when the atmosphere above it is at a temperature of -10 °C. [conductivity of ice =  $5.25 \times 10^{-3}$  cal/cm sec deg C, density of ice = 0.92 gm/cc, latent heat of ice = 80 cal/gm.] [Gau.U.]
- A pipe, whose temperature and radius are  $\theta_1$  and  $r_1$  respectively, is covered by  $n$  concentric cylindrical shells of different materials and thicknesses. If the temperature of the outer surface of the  $n$ th (i.e., the outermost) shell is  $\theta_2$ , show that the heat conducted per unit length per unit time is

$$Q = \frac{2\pi(\theta_1 - \theta_2)}{\frac{1}{K_1} \log_e \frac{r_2}{r_1} + \frac{1}{K_2} \log_e \frac{r_3}{r_2} + \dots + \frac{1}{K_n} \log_e \frac{r_{n+1}}{r_n}}.$$

- In estimating the rate of cooling of the earth, Kelvin used the following data. Conductivity of earth's crust = 0.005 calorie per sq. cm per unit centigrade temperature gradient per second. Thermal capacity of surface rock per cc = 0.5 calorie per degree centigrade. Temperature gradient at the surface = 1 °C per 30 metres. Radius of earth =  $6 \times 10^8$  cm. Assuming the earth to be homogeneous, find the annual cooling.

5. The thickness of ice on a lake is 5 cm and the temperature of the air is  $-15^{\circ}\text{C}$ . At what rate is the thickness of the ice increasing, and approximately how long will it take for the thickness of the ice to be doubled? [Take data from Problem No. 2.]
6.  $A$  is a compound slab made up of two layers, one of thickness  $d_1$ , and thermal conductivity  $K_1$ , and the other of thickness  $d_2$  and thermal conductivity  $K_2$ .  $B$  is a slab of thickness  $d_1 + d_2$  and thermal conductivity  $K$ . One face of each slab is maintained at  $\theta_1^{\circ}\text{C}$ , and the other at  $\theta_2^{\circ}\text{C}$  until a steady state is reached. If the rate of conduction of heat per unit area through the two slabs is the same, find the relation between  $K_1$  and  $K_2$ .

WT

## Chapter 5

# Second Law of Thermodynamics

### 5.1 Conditions of Reversibility

A process is said to be *reversible* if all that happens in direct operations of the process is exactly reversed when these operations are carried out in the reverse order. The reversibility of a cyclic process\* is also defined in the same manner. We shall discuss here the conditions\*\* under which a process may become reversible.

Let us take a gas in a non-conducting cylinder with a light, movable piston carrying some weights (See Fig. 1.1). Ordinarily friction takes place when the piston moves up or down. So, when some small weight is removed from the piston, the gas expands and does work against both gravity and friction. Next, if the weight is restored in order to reverse the process, what happens? Gravity does work to compress the gas and also does work against friction. Thus, work is done in both cases against friction and heat is generated. Friction, however, never does work and is, therefore, irreversible. It is now evident that in order to make the process reversible, the movement of the piston must be *frictionless*.

Now, we shall assume that the movement of the piston is frictionless. If a finite (i.e., not small) weight is removed from the piston, the gas expands quickly and not only does work against gravity but also generates kinetic energy of mass motion in the form of eddies and whirls<sup>†</sup> (turbulent motion) which, due to dissipative forces like viscosity and friction, gradually subside with the transformation of kinetic energy of mass motion into heat. Next, if the weight is restored in order to reverse the process, gravity does work to compress the gas and also produces eddies and whirls with the ultimate production of heat in the system. Thus, the formation of eddies and whirls accompanying quick and large expansion or compression of the gas is irreversible. This may, however, be avoided if the weights are removed or added in infinitesimally small steps so that the difference between the gas pressure and the piston pressure is extremely small and the expansion or compression of the gas is balanced, i.e., infinitely slow. Such slow changes of the system are often referred to as *quasi-static*.

So we shall assume that the piston is free from friction and also the expansion (or compression) of the gas is infinitely slow. Now, we shall consider the gas to be contained in a conducting cylinder so that there may be exchange of heat between the gas and the surroundings. Let the surroundings, for example, be at a finitely higher temperature than the gas. Then, there will be a continuous conduction of heat into the gas from outside till the temperature is the same both inside and outside. Now, part of the heat has raised the temperature of the gas and the balance has been used up for work done in slow expansion of the gas against a constant piston pressure

\*When a system comes back to the original state in the course of a series of changes, it is said to have performed a cyclic process, or simply, a cycle.

\*\*For an exhaustive discussion, see Saha and Srivastava, *A Treatise on Heat*, Pp. 234–38 (1958), Epstein, *Text Book of Thermodynamics*, Pp. 35–37 (1954).

<sup>†</sup>On removal or addition of a finite weight on the piston, there is an immediate rarefaction or compression beneath the piston. Because of the lag in propagation of stresses in the system, this gives rise to mass motion in the form of eddies and whirls. See Epstein, *loc. cit.*

(i.e., a constant gravity force in our arrangement). Now, it is impossible to conceive of a means to reverse the whole process so that all the heat that has come from outside may flow out and also the gas may go back to the initial state under the same constant pressure as before. Thus, we find that conduction of heat under finite differences of temperature is irreversible. This may, however, be avoided if the temperature differences are infinitesimally small, i.e., if the changes in the system are *isothermal*. In that case, the same amount of heat will be received at a given stage of expansion as will be given out at the corresponding stage of compression and also the work done on the gas in compression will equal that done by it in the corresponding expansion.

One may readily enumerate a number of conditions which *must not* hold for a particular process to be reversible. It is, however, much more difficult to exhaust all the conditions which *must* hold for the process to be reversible. All processes occurring in nature have some irreversible element but, with care, may be made to approximate fairly well to an ideal reversible process.

## 5.2 Carnot's Work\*

Thermodynamics, in fact, owes its origin to the young French engineer Sadi Carnot who published in 1824 his remarkable essay, *Réflexions sur la puissance motrice du feu, et sur les machines propres à développer cette puissance*, making an exhaustive theoretical investigation of the efficiency of heat engines. The practical problem of the conversion of heat into work by heat engines had, however, been solved already without any theoretical understanding. But this essay, which is so fundamentally important in physics, was entirely ignored for more than twenty years, when its merits were first recognised by Kelvin (then William Thomson). Carnot enunciated, for the first time, the second law of thermodynamics in this essay. It may thus appear that the second law of thermodynamics was discovered earlier than the first law. But in justice to Carnot it should be stated that a precise and clear statement of the first law of thermodynamics was found after his death in his unpublished notes. The value of the mechanical equivalent of heat he obtained was 0.37 kilogram-metre per gram-calorie. Thus, the discovery of the first law of thermodynamics should also be accredited to Carnot, although this is commonly ascribed to J. R. Mayer who, in 1842, evaluated  $J$  from the equation :

$$C_p - C_v = \frac{R}{J}.$$

Carnot was the first to introduce the concept of a cyclic process and the concept of reversibility already discussed in the preceding section. He showed that the most efficient heat engine is one in which all the operations are made under reversible conditions. He conceived theoretically the idea of a perfect engine in which these conditions hold. The cycle which this engine performs is known as Carnot's cycle. We shall now study in some details Carnot's investigations.

## 5.3 Carnot's Engine

Carnot's theoretical engine consists of a cylinder  $A$  and a frictionless piston  $B$ , both made of a perfectly non-conducting material (Fig. 5.1). The base  $C$  of the cylinder is made of a perfectly conducting material.  $S_1$  is a source of heat maintained at temperature  $\theta_1$ , (expressed in any arbitrary scale) and is supposed to be perfectly conducting.  $S_2$  is a sink maintained at temperature  $\theta_2$  ( $\theta_1 > \theta_2$ ) and is also supposed to be perfectly conducting.  $S$  is a perfectly non-conducting body. No particular assumptions are made regarding the nature of the working

\*See W. Wilson, *Theoretical Physics*, Vol. I, Pp. 272, 280, 288 (1931); Allen and Maxwell, *A Text Book of Heat*, Part II, Pp. 596-97 (1952).

substance taken inside the cylinder except that it must be capable of exerting pressure on the piston. It may be a gas, a mixture of water and its vapour, or anything else that may operate an actual engine. Let us suppose, at the beginning, the working substance is in a state denoted by  $L$  (Fig. 5.2) at temperature  $\theta_1$ . Now, the cylinder is placed on  $S_1$ , and the weights are slowly removed from the piston in infinitesimally small steps so that the working substance expands isothermally in a quasi-static manner from the state  $L$  to the state  $M$ . In this case the work done by the working substance on the piston is

$$W_1 = \int_{V_1}^{V_2} P dV = \text{area } LMM'L'. \quad (5.1)$$

This must be equal to  $Q_1$ , heat absorbed from the source, since the temperature has been constant in the process.

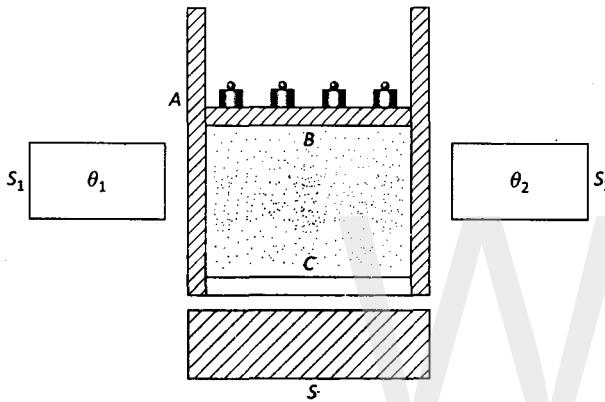


Fig. 5.1: Carnot engine

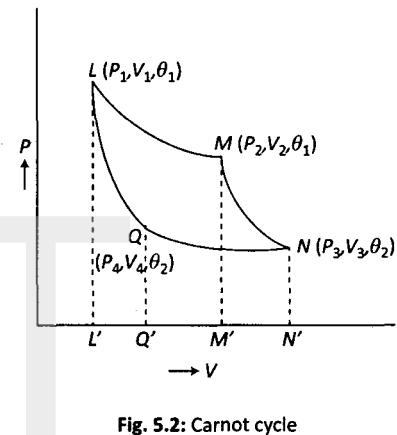


Fig. 5.2: Carnot cycle

Next, the cylinder is placed on  $S$  and again the weights are slowly removed from the piston in infinitesimally small steps so that now the working substance expands adiabatically in a quasi-static manner from the state  $M$  to the state  $N$  doing on the piston a further amount of work

$$W_2 = \int_{V_2}^{V_3} P dV = \text{area } MNN'M'. \quad (5.2)$$

This work has, of course, been done at the cost of internal energy of the system of which now the temperature has gone down from  $\theta_1$  to  $\theta_2$ .

Next, the cylinder is put on the sink  $S_2$  and the weights are slowly added to the piston in infinitesimally small steps so that the working substance is isothermally compressed in a quasi-static manner from the state  $N$  to the state  $Q$ . In this case, the work done on the system by the piston is

$$W_3 = \int_{V_4}^{V_3} P dV = \text{area } QNN'Q'. \quad (5.3)$$

This must be equal to  $Q_2$ , heat generated in the system and rejected to the sink, since the temperature has been constant in the process.

Finally, the cylinder is again put on  $S$  and the weights are again added slowly to the piston in infinitesimally small steps so that the working substance is adiabatically compressed in a quasi-static manner from the state  $Q$  back to the state  $L$ . Now a further amount of work is

done by the piston on the working substance and that is

$$W_4 = \int_{V_1}^{V_4} PdV = \text{area } LQQ'L'. \quad (5.4)$$

This work will increase the internal energy of the system of which now the temperature has gone up from  $\theta_2$  to  $\theta_1$ .

It is evident that in the cycle (called *Carnot's cycle*) just performed the net work done by the system is

$$\begin{aligned} W &= (W_1 + W_2) - (W_3 + W_4) \\ &= (\text{area } LMM'L' + \text{area } MNN'M') - (\text{area } QNN'Q' + \text{area } LQQ'L') \\ &= \text{area } LMNQ. \end{aligned} \quad (5.5)$$

From the first law of thermodynamics, this must be equal to the net amount of heat absorbed during the cycle. Thus,

$$W = Q_1 - Q_2 \quad (5.6)$$

so that the efficiency of the engine is

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} \quad (5.7)$$

To sum up the cycle, an amount of heat  $Q_1$  has been taken at a higher temperature  $\theta_1$ , out of this an amount of work  $W (= Q_1 - Q_2)$  has been performed during the cycle and the balance  $Q_2$  has been rejected at a lower temperature  $\theta_2$ .

Since all the conditions of reversibility (already discussed in section 5.1) are satisfied by Carnot's engine in all operations during the cycle, we may also work the cycle backwards, i.e., along  $L \rightarrow Q \rightarrow N \rightarrow M \rightarrow L$ . Now, the working substance receives an amount of heat  $Q_2$  from  $S_2$  at the lower temperature  $\theta_2$  and rejects an amount of heat  $Q_1$  to  $S_1$ , at the higher temperature  $\theta_1$ . Thus, to carry out the reverse cycle, a net amount of work  $W = Q_1 - Q_2$  will have to be done on the engine. Carnot's engine working in a reverse cycle is called a *refrigerator*.

#### 5.4 Carnot's Cycle with a Perfect Gas

Consider a Carnot cycle performed with a gram-molecule of a perfect gas as the working substance. Suppose that  $\theta_1$  and  $\theta_2$  correspond to  $T_1$  and  $T_2$  respectively on the perfect gas scale defined by the equation

$$PV = RT. \quad (5.8)$$

It has been shown in section 1.5 that the equation for adiabatic change in a perfect gas is

$$PV^\gamma = C \text{ (a constant).} \quad (5.9)$$

Now, we are in a position to evaluate  $W_1$ ,  $W_2$ ,  $W_3$  and  $W_4$  of the preceding section (Fig. 5.2). From (5.1) and (5.8),

$$Q_1 = W_1 = \int_{V_1}^{V_2} PdV = RT_1 \int_{V_1}^{V_2} \frac{dV}{V} = RT_1 \log_e \left( \frac{V_2}{V_1} \right). \quad (5.10)$$

From (5.2) and (5.9),

$$\begin{aligned}
 W_2 &= \int_{V_2}^{V_3} P dV = C \int_{V_2}^{V_3} \frac{dV}{V^\gamma} = \frac{C}{1-\gamma} [V_3^{1-\gamma} - V_2^{1-\gamma}] \\
 &= \frac{1}{1-\gamma} [P_3 V_3^\gamma V_3^{1-\gamma} - P_2 V_2^\gamma V_2^{1-\gamma}] \quad (\because PV_2^\gamma = C = P_2 V_3^\gamma) \\
 &= \frac{R}{1-\gamma} (T_2 - T_1) \quad [\text{from (5.8)}] \\
 &= \frac{R(T_1 - T_2)}{\gamma - 1}.
 \end{aligned} \tag{5.11}$$

Next, from (5.3) and (5.8), [as in (5.10)],

$$Q_2 = W_3 = \int_{V_4}^{V_3} P dV = RT_2 \log_e \left( \frac{V_3}{V_4} \right). \tag{5.12}$$

Finally, from (5.4) and (5.9), [as in (5.11)],

$$W_4 = \int_{V_1}^{V_4} P dV = \frac{R(T_1 - T_2)}{\gamma - 1}. \tag{5.13}$$

Since, from (5.11) and (5.13)  $W_2 = W_4$ , the net work done by the engine is

$$W = W_1 + W_2 - W_3 - W_4 = W_1 - W_3 = Q_1 - Q_2. \tag{5.14}$$

Another relation for adiabatic change in a perfect gas is

$$TV^{\gamma-1} = C' \quad (\text{a constant}). \tag{5.15}$$

Applying (5.15) to the adiabatic changes from  $M$  to  $N$  and from  $Q$  to  $L$  (Fig. 5.2), we have

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}, \quad \text{i.e., } \frac{V_2}{V_3} = \left( \frac{T_2}{T_1} \right)^{\frac{1}{\gamma-1}} \tag{5.16}$$

$$\text{and } T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}, \quad \text{i.e., } \frac{V_1}{V_4} = \left( \frac{T_2}{T_1} \right)^{\frac{1}{\gamma-1}} \tag{5.17}$$

Combining (5.16) and (5.17),

$$\frac{V_2}{V_3} = \frac{V_1}{V_4}, \quad \text{i.e., } \frac{V_2}{V_1} = \frac{V_3}{V_4}. \tag{5.18}$$

Hence, (5.10), (5.12) and (5.18) give

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \tag{5.19}$$

The efficiency of a Carnot engine with a perfect gas as the working substance is, from (5.7) and (5.19),

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}. \tag{5.20}$$

Thus, the efficiency of a Carnot engine with a perfect gas is a function of  $T_1$  and  $T_2$  only. We shall show in sections 5.6 and 5.7 that the efficiency of all reversible engines, whatever may be the working substance, is a function of the source temperature ( $\theta_1$ ) and the sink temperature ( $\theta_2$ ).

## 5.5 Second Law of Thermodynamics

In his essay referred to in section 5.2, Carnot made the statement "... *mais à son transport d'un corps chaud à un corps froid ...*". This statement constitutes the earliest expression of the second law of thermodynamics. Carnot observed, as explained in section 5.3, that a heat engine, in doing work, not only abstracts heat from a source at a higher temperature but also gives up a part of heat to a sink at a lower temperature. It is found in practice to be impossible to consume heat from a source in doing work, without giving up some of it to a sink at a lower temperature. It is, however, true that a *limited amount* of work can be done simply at the expense of heat taken from a source without giving up any heat to any sink, for example, during expansion of a gas. But it must be remembered that an expansion cannot be continued indefinitely so that work cannot be done in such a case continuously. On the other hand, a heat engine is a machine that works in a cyclic fashion receiving heat from some source in one part of the cycle and rejecting some of this heat in another part of the cycle to a sink. Carnot further observed that if a heat engine works in reverse order receiving heat from a sink at a lower temperature and rejecting heat to a source at a higher temperature, an amount of work must be done on the engine for the purpose by some external agency.

All these observations form the basis on which Clausius, Kelvin and Planck formulated the second law of thermodynamics. Clausius stated it in the form :

*It is not possible for a self-acting machine working in a cyclical process, unaided by any external agency, to make heat pass from one body to another at a higher temperature.*

This is clear from the fact that for an engine to carry heat from a colder (sink) to a hotter body (source), some work will have to be done on it by some external agency, as explained above.

Kelvin\* gave the law in the following language : *It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coolest body of its surroundings.*

This can be understood from the fact that for a heat engine to do work, it must receive heat from a hotter body (source) and reject part of it to a colder body (sink). If it so happens that the body from which the engine takes heat has been cooled below the temperature of the coldest body of the surroundings, then not a single body will be available under the circumstances to serve as the sink. In that case, it becomes impossible for the engine to do any work.

Planck stated it in the form : *It is impossible to construct an engine abstracting heat from a single body and converting the whole of it to work, without leaving changes in the working system.*

The meaning of this statement is that it is not possible for an engine to do work just by taking heat from a body without affecting anything else. Because, as has already been seen above, if the body serves as the source, then there must be a sink at a lower temperature for rejection of some of the heat taken from the source.

Hamtil\*\* has shown by formal logic that the statements of Clausius and Planck are equivalent, while Ehrenfest-Afanassjewa† has most thoroughly examined the logical relationships between all the three above statements of the second law of thermodynamics. [See also Appendix 2.]

It must be remembered that Carnot's theoretical observations out of which the second law of thermodynamics evolved were, in fact, inspired by experience, i.e., by the performances

\*Math. and Phys. Papers, 1, P. 179.

\*\* Amer. Journ. Physics, 22, P. 93 (1954).

† Ziets. f. Physik, 33, P. 933 (1925), see also Zemansky, M. W., *Heat and Thermodynamics*, for equivalence between statements of Clausius and Planck.

of actual heat engines. [He attributed ideal conditions, i.e., conditions of reversibility, to his engine in order to obtain the highest possible limit of efficiency of a heat engine. It is, therefore, evident that no actual engine can do what Carnot's engine cannot do.] However, the second law of thermodynamics which is thus based on experience cannot be proved by direct test. But truth of this law is established by the correctness of deductions made from it on change of state, primary electric cells, thermo-electricity, chemical reactions, etc.

Regarding the applicability of this law it must be pointed out that since it has been discovered in connection with the cyclic operations of heat engines, it applies only to cyclical or continuous processes.

We close this section showing the distinction between the first and the second law of thermodynamics. The first law is just the principle of conservation of energy applied to heat. It states that heat and work are mutually convertible on the basis of  $W = JQ$ . Thus we know from the first law that if a body can be made to yield up an amount of heat  $Q_1$ , then on conversion of work, an amount of work  $= JQ_1$  should be obtained. But this law does not tell us if this amount of work ( $= JQ_1$ ) will at all be obtained. This question is answered by the second law of thermodynamics which is based on the performances of heat engines. We know from the second law that out of  $Q_1$ , only a part is converted into work  $W$ , the balance  $Q_2$  being rejected to some sink. Thus, one law is quite distinct from the other, but no doubt they are complementary to each other in problems of conversion of heat into work.

**Exercise :** *Apply second law of thermodynamics to show that friction is an irreversible process.*

**Hints :** Use the system of bodies heated due to work done against friction as the source and a colder body as the sink. Now employ Carnot's engine between the source and the sink. Evidently Carnot's engine cannot convert back into work all the heat produced by friction, because it has to reject a part of the same to the sink.

## 5.6 Carnot's Theorem

From a consideration of reversible heat engines, Carnot established that *no heat engine can be more efficient than a reversible engine working between the same temperature limits*. This is known as Carnot's theorem. We now give the proof of this theorem following Carnot.

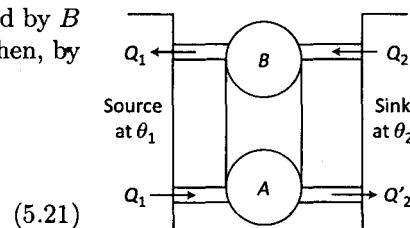
Let us suppose that we have a heat engine  $A$  which is more efficient than a reversible engine  $B$ , both working between the same temperatures  $\theta_1, \theta_2$  (Fig. 5.3).

Let  $Q_1, Q_2$  be the amounts of heat taken in and rejected by  $B$  at  $\theta_1, \theta_2$  and  $Q_1, Q'_2$  the corresponding quantities for  $A$ . Then, by hypothesis,

$$\frac{Q_1 - Q_2}{Q_1} < \frac{Q_1 - Q'_2}{Q_1}$$

i.e.,  $Q_1 - Q_2 < Q_1 - Q'_2$

or,  $Q_2 > Q'_2$ .



(5.21)

Fig. 5.3: Coupled engine

Now, according to (5.21), we may couple  $A$  and  $B$  so that  $A$  derives  $B$  in reverse order. In that case, the net gain or loss of heat by the source will be nil, but the sink will lose, according to (5.22), a net amount of heat  $= Q_2 - Q'_2$  and the net amount of work available for utilisation for any purpose is also equal to  $Q_2 - Q'_2$ , since the difference between the total work done by  $A$  during a cycle and the total work required by  $B$  to be driven backward during a cycle is

$= (Q_1 - Q'_1) - (Q_1 - Q_2) = Q_2 - Q'_2$ . Thus we have, with  $A$  and  $B$  coupled together, a self-acting machine which abstracts heat from a single body, i.e., the sink, and converts the whole of it into work without affecting any other body. But this is contrary to all experience as expressed in the second law of thermodynamics (See Kelvin's statement, for example) and is, therefore, impossible. So  $A$  cannot be more efficient than  $B$ . Thus we conclude that no engine can be more efficient than a reversible engine working between the same temperature limits. This is Carnot's theorem.

As a corollary to this theorem, we can prove, following the same above procedure, that if  $A$  and  $B$  are two reversible engines working between the same temperature limits, then one cannot be more efficient than the other, that is, *all reversible heat engines working between the same temperature limits have got the same efficiency*.

These results show that reversibility is the criterion of perfection in a heat engine in the sense that no engine can convert a greater proportion of the heat supplied into work than a reversible engine. Further, the nature of the working substance is immaterial if the criterion of reversibility is satisfied since no assumptions have been made in this regard in our discussions.

## 5.7 Efficiency of a Reversible Heat Engine : Kelvin's Absolute or Thermodynamic Scale of Temperature

It is evident from the preceding section that all reversible heat engines working between the same temperature limits have the same efficiency and this is independent of the nature of the working substance. So the only factors which can determine the efficiency are the temperature limits between which the engine works, because the engine cannot do any work unless there are a source and a sink with a temperature difference between them. Then, from (5.7), we have

$$\eta = 1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2), \quad \text{i.e., } \frac{Q_2}{Q_1} = 1 - f(\theta_1, \theta_2)$$

$$\text{or, } \frac{Q_1}{Q_2} = \frac{1}{1 - f(\theta_1, \theta_2)} = F(\theta_1, \theta_2), \text{ say,} \quad (5.23)$$

where  $\theta_1, \theta_2$  are the temperatures (measured on any scale) of the source and sink respectively.

Now, suppose we have three reversible engines, the first taking in heat  $Q_1$  at  $\theta_1$ , and rejecting heat  $Q_2$  at  $\theta_2$ , the second taking in heat  $Q_2$  at  $\theta_2$  and rejecting heat  $Q_3$  at  $\theta_3$ , and the third taking in heat  $Q_1$  at  $\theta_1$  and rejecting heat  $Q_3$  at  $\theta_3$ . Then, from (5.23) we obtain

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2), \quad \frac{Q_2}{Q_3} = F(\theta_2, \theta_3), \quad \frac{Q_1}{Q_3} = F(\theta_1, \theta_3). \quad (5.24)$$

Multiplying the first two equations of (5.24),

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3). \quad (5.25)$$

Comparing the last equation of (5.24) with (5.25)

$$F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3). \quad (5.26)$$

That is,  $\theta_2$  must disappear from the right-hand side of (5.26). In order that this may happen  $F(\theta_1, \theta_2)$  must be of the form :

$$F(\theta_1, \theta_2) = \frac{\psi(\theta_1)}{\psi(\theta_2)}. \quad (5.27)$$

From (5.23) and (5.27),

$$\frac{Q_1}{Q_2} = \frac{\psi(\theta_1)}{\psi(\theta_2)}. \quad (5.28)$$

As  $Q_1$  is greater than  $Q_2$ ,  $\psi(\theta_1)$  must be greater than  $\psi(\theta_2)$ , i.e., the function  $\psi(\theta)$  is such that its magnitude increases with increase in temperature.

Kelvin\* (then Thomson) was the first to realise that the important formula (5.28) for a reversible heat engine might be used to compare the two temperatures  $\theta_1, \theta_2$ . It is well known that any property that depends upon temperature may be used to define a temperature scale. Then, since  $\psi(\theta)$  is a function of temperature only, it may be used to define a new scale of temperature. Denoting  $\psi(\theta)$  by  $\tau$ , we have from (5.28),

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2}. \quad (5.29)$$

$\tau$  defined by (5.29) is called the *absolute* or *thermodynamic temperature* or *Kelvin temperature* after Kelvin who introduced it. As we see from (5.29), the ratio of any two temperatures on this scale is the same as the ratio of the heat taken in to the heat rejected by a reversible engine working between these temperatures as source and sink respectively. Since (5.29) is independent of the nature of the working substance (as already explained at the end of the preceding section or at the beginning of this section), the new scale does not depend upon the properties of any particular substance.

The definition of the new scale by (5.29) directly leads to the concept of an absolute zero. If  $Q_2$ , the heat rejected by a reversible engine, is zero, then by (5.29)  $\tau_2$  is also zero. This means that all the heat supplied at  $\tau_1$  has been converted into work under this condition and the efficiency of the engine is unity.  $\tau_2$  cannot be less than zero value, i.e., cannot be negative, because in that case  $Q_2$  will also be negative, meaning that heat is abstracted by the engine from both the source and the sink and is wholly converted into work. This is contrary to all experience as expressed by the second law of thermodynamics (See Kelvin's and Planck's statements, for example). Thus the zero on the new scale is the lowest possible limit of temperature. Thus, the absolute zero need not be the temperature at which all molecular motions should cease to exist as predicted by the elementary kinetic theory (See section 2.5).

After knowing the zero on the thermodynamic scale, the only other thing to find is the size of the degree. In conformity with general practice, we assume now that the interval between the ice-point and the steam-point of water is equal to 100 divisions on this new scale. Now we shall show that the thermodynamic scale is identical with the perfect gas scale.

For this purpose, let us suppose that the temperature of the source is  $T + dT$  on the perfect gas scale and  $\tau + d\tau$  on the thermodynamic scale, and the temperature of the sink is  $T$  on the perfect gas scale and  $\tau$  on the thermodynamic scale. Then, from (5.19) and (5.24),

$$\frac{Q + dQ}{Q} = \frac{T + dT}{T} = \frac{\tau + d\tau}{\tau}, \quad \text{i.e., } \frac{dT}{T} = \frac{d\tau}{\tau}.$$

On integration,  $\log_e T = \log_e \tau + \log_e A$  (a constant), i.e.,  $T = A\tau$ . (5.30)

Now, if the ice-point of water is  $T_0$  and  $\tau_0$  on the perfect gas scale and the thermodynamic scale respectively, then the steam-point is  $T_0 + 100$  and  $\tau_0 + 100$  respectively on these scales since the interval between these points has been taken to be equal to 100 divisions. Then, from (5.30),

\*Math. and Phys. Papers, 1, Pp. 104, 235, Phil. Mag., 1848; Trans. Roy. Soc. Edin., 1854.

$$T_0 = A\tau_0 \quad (5.31)$$

$$T_0 + 100 = A(\tau_0 + 100). \quad (5.32)$$

Subtracting (5.31) from (5.32),  $100 = A100$ , i.e.,  $A = 1$ .

Hence,  $T = \tau$ . (5.33)

That is, the two scales are identical. So from now onwards, the symbol  $T$  will be used to represent either scale.

## 5.8 Realisation of Absolute Scale

If we could have a perfect gas, then the temperature scale provided by it would be the same as the absolute thermodynamic scale. But no gas is really perfect. We can, however, consider the deviation of a real gas from a perfect gas and compute the correction to be applied to the reading of a real gas thermometer of the constant-volume or the constant-pressure type.

At pressures used in gas thermometry, the terms in the virial expansion (3.76) of Chapter 3 containing the square and higher powers of  $P$  are negligibly small. Then, we have only

$$PV = A + BP \quad (5.34)$$

to represent the behaviour of the gas at pressures used in gas thermometry.

**(a) Constant-volume Gas Thermometer :** We first consider the correction to be applied to the readings of a constant-volume thermometer so as to obtain the corresponding readings at vanishingly low pressure ( $P \rightarrow 0$ ), i.e., on the perfect gas scale\*. Let the constant volume be  $V_0$ . Then, at  $0^\circ\text{C}$ ,  $100^\circ\text{C}$  and  $t^\circ\text{C}$ , (5.34) gives

$$\left. \begin{aligned} P_0 V_0 &= A_0 + B_0 P_0 \\ P_{100} V_0 &= A_{100} + B_{100} P_{100} \\ P_t V_0 &= A_t + B_t P_t \end{aligned} \right\} \quad (5.35)$$

The temperature  $t_v$  on the constant-volume scale is defined by

$$\begin{aligned} t_v &= 100 \times \frac{P_t - P_0}{P_{100} - P_0} \\ &= 100 \times \frac{P_t V_0 - P_0 V_0}{P_{100} V_0 - P_0 V_0} \end{aligned} \quad (5.36)$$

$$\begin{aligned} &= 100 \times \frac{A_t - A_0 + B_t P_t - B_0 P_0}{A_{100} - A_0 + B_{100} P_{100} - B_0 P_0}, \text{ from (5.35)} \\ &= 100 \times \frac{A_t - A_0}{A_{100} - A_0} \times \left\{ \frac{1 + (B_t P_t - B_0 P_0)/(A_t - A_0)}{1 + (B_{100} P_{100} - B_0 P_0)/(A_{100} - A_0)} \right\}. \end{aligned} \quad (5.37)$$

Now, expanding the right-hand side of (5.37) (neglecting the square and higher powers of  $P$ ),

$$t_v = t_{P \rightarrow 0} \left\{ 1 + \frac{B_t P_t - B_0 P_0}{A_t - A_0} - \frac{B_{100} P_{100} - B_0 P_0}{A_{100} - A_0} \right\}, \quad (5.38)$$

where  $t_{P \rightarrow 0} \left( = 100 \times \frac{A_t - A_0}{A_{100} - A_0} \right)$  evidently gives the reading on the perfect gas scale.

\*(5.34) is reduced to the perfect gas equation (5.8) for  $P \rightarrow 0$ .

From (5.38), on transposition,

$$t_{P \rightarrow 0} - t_v = t_{P \rightarrow 0} \left\{ \frac{B_{100}P_{100} - B_0P_0}{A_{100} - A_0} - \frac{B_tP_t - B_0P_0}{A_t - A_0} \right\} \quad (5.39)$$

$$\approx t_v \left\{ \frac{B_{100}P_{100} - B_0P_0}{A_{100} - A_0} - \frac{B_tP_t - B_0P_0}{A_t - A_0} \right\} \quad (5.40)$$

Since the right-hand side gives the correction, we have replaced  $t_{P \rightarrow 0}$  by  $t_v$  in (5.40) and since all quantities on the right-hand side may be known from experiment, the correction to be applied to  $t_v$  is determined easily.

The value of the correction is found according to (5.40) at a large number of temperatures. Then, a curve is drawn from which the correction at any temperature can be known immediately.

**(b) Constant-pressure Gas Thermometer :** We now consider the correction for the readings of a constant-pressure thermometer. Let the constant pressure be  $P_0$ . Then at 0 °C, 100 °C and  $t$  °C, (5.34) gives

$$\left. \begin{aligned} P_0V_0 &= A_0 + B_0P_0 \\ P_0V_{100} &= A_{100} + B_{100}P_0 \\ P_0V_t &= A_t + B_tP_0 \end{aligned} \right\} \quad (5.41)$$

Now, the temperature  $t_p$  on the constant-pressure scale is defined by

$$\begin{aligned} t_p &= 100 \times \frac{V_t - V_0}{V_{100} - V_0} \\ &= 100 \times \frac{P_0V_t - P_0V_0}{P_0V_{100} - P_0V_0} \end{aligned} \quad (5.42)$$

$$= 100 \times \frac{A_t - A_0 + P_0(B_t - B_0)}{A_{100} - A_0 + P_0(B_{100} - B_0)}, \text{ from (5.41)}$$

$$= 100 \times \frac{A_t - A_0}{A_{100} - A_0} \times \left\{ \frac{1 + P_0(B_t - B_0)/(A_t - A_0)}{1 + P_0(B_{100} - B_0)/(A_{100} - A_0)} \right\} \quad (5.43)$$

$$= t_{P \rightarrow 0} \left\{ 1 + P_0 \frac{B_t - B_0}{A_t - A_0} - P_0 \frac{B_{100} - B_0}{A_{100} - A_0} \right\}, \quad (5.44)$$

expanding the right-hand side of (5.43) as before. Hence, the correction is

$$\begin{aligned} t_{P \rightarrow 0} - t_p &= t_{P \rightarrow 0}P_0 \left\{ \frac{B_{100} - B_0}{A_{100} - A_0} - \frac{B_t - B_0}{A_t - A_0} \right\} \\ &\approx t_pP_0 \left\{ \frac{B_{100} - B_0}{A_{100} - A_0} - \frac{B_t - B_0}{A_t - A_0} \right\}. \end{aligned} \quad (5.45)$$

In this case also a curve for the correction at a number of temperatures is drawn to find the correction at any temperature.

## 5.9 Theorem of Clausius

For a Carnot cycle, we have

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}. \quad (5.46)$$

[See (5.29) and (5.33)]. This can be written as

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0, \quad (5.47)$$

if  $Q_1$  (heat absorbed) is considered positive and  $Q_2$  (heat rejected) is negative.

Now, for a general reversible cycle  $ABCDA$  (Fig. 5.4) the heat is not all absorbed and rejected at two definite temperatures, but is taken in and given out at continuously varying temperatures. Clausius extended the above result (5.47) for a Carnot cycle to the general reversible cycle.

Instead of following the smooth curve  $ABCDA$  first, we replace it by a series of infinitesimal

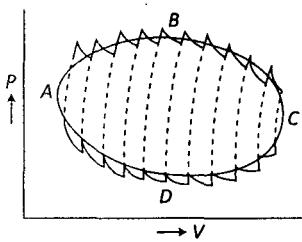


Fig. 5.4: General reversible cycle

isothermal changes shown by the zigzag curve. By drawing adiabatic (dotted) lines across the closed curve it can be divided into an infinite number of extremely small Carnot cycles. Making the isothermal sufficiently small the zigzag curve will approximate closely to the continuous curve. For any small Carnot cycle, if  $\delta Q_1$  is the heat absorbed at  $T_1$  and  $-\delta Q_2$  the heat rejected at  $T_2$ , then from (5.47),

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0. \quad (5.48)$$

Taking the sum for all the small cycles,

$$\sum \frac{\delta Q}{T} = 0. \quad (5.49)$$

Assuming the isothermals to be infinitesimally small so as to coincide with the smooth curve  $ABCDA$ , (5.49) becomes

$$\oint \frac{dQ}{T} = 0. \quad (5.50)$$

This relation is true for any reversible cyclic change. This result is known as the *theorem of Clausius*.

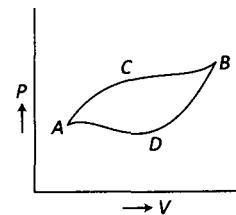
## 5.10 Entropy

Let  $A$  and  $B$  represent respectively the initial and final states of a thermodynamic system. Let  $ACB$  and  $ADB$  be any two reversible paths (i.e., curves) connecting  $A$  and  $B$  (Fig. 5.5). Considering  $ACBDA$  as a closed reversible cycle, we have from (5.50)

$$\int_{ACB} \frac{dQ}{T} + \int_{BDA} \frac{dQ}{T} = 0$$

$$\text{or, } \int_{ACB} \frac{dQ}{T} = - \int_{BDA} \frac{dQ}{T} = \int_{ADB} \frac{dQ}{T}$$

$$\text{i.e., } C \int_A^B \frac{dQ}{T} = D \int_A^B \frac{dQ}{T}.$$



(5.51) Fig. 5.5: Closed reversible cycle

This means that the value of the integral

$$\int_A^B \frac{dQ}{T} \quad (5.52)$$

is independent of the reversible path  $ACB$  or  $ADB$ , along which the system is carried. The value of the integral (5.52) must, therefore, depend only on the coordinates of the end points  $A$  and  $B$ . We can, therefore, write :

$$\int_A^B \frac{dQ}{T} = S(P_B, V_B) - S(P_A, V_A), \quad (5.53)$$

where  $S(P_B, V_B)$  and  $S(P_A, V_A)$  are values for the upper and the lower limit respectively. From (5.53), we can write :

$$\frac{dQ}{T} = dS(P, V). \quad (5.54)$$

It is evident that  $S$ , defined by (5.53) and (5.54), is a function of the variables  $P, V$  defining the state of the system.  $S$  is thus a function of state like the internal energy  $U$ . Clausius called it the *entropy* of the system. (5.53) or (5.54) does not give the absolute value of entropy but only gives the change in entropy with which we are generally concerned. It should, however, be remembered that to calculate the change in entropy of a system as it passes from an initial state  $A$  to a final state  $B$ , we should connect the two states by a suitable reversible path and calculate the value of the integral  $\int_A^B \frac{dQ}{T}$  along this path.

From (5.53) and (5.54), it is clear that since the left-hand side is proportional to mass, the right-hand side is also proportional to mass. Thus, if  $s$  refers to unit mass,  $S = ms$ , where  $m$  is the mass of the system. This idea may be further extended to show in a similar manner that if we have a system of bodies in *thermodynamic equilibrium*, then the entropy of the whole system is

$$S = S_1 + S_2 + \dots, \quad (5.55)$$

where  $S_1, S_2, \dots$  are the entropies of the individual bodies.

Further, in a reversible adiabatic process, no change in entropy takes place because in this case  $dQ$  is zero.

**Exercise :** Calculate the change in entropy in heating a gram-molecule of water from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ , under constant pressure.

**Solution :** From (5.53),  $\Delta S = \int_{0^\circ\text{C}}^{100^\circ\text{C}} \frac{dQ}{T} = C_p \int_{0^\circ\text{C}}^{100^\circ\text{C}} \frac{dT}{T} = C_p \log_e \left( \frac{373}{273} \right)$

$$= 18 \times 2.3 \times \log_{10} \left( \frac{373}{273} \right) \text{ cal/K} \approx 5.6 \text{ cal/K.}$$

Since the gm-molecular weight of water is 18 gm,  $C_p$  is 18 cal/K here.

## 5.11 Clausius' Inequality

For an irreversible cycle divided into a large number of small cycles as in Fig. 5.4, let  $\delta Q_1, \delta Q_2$  be the heats taken in at  $T_1$  and given out at  $T_2$  for a small cycle. Then, since the efficiency is less than that for a reversible cycle,

$$\frac{\delta Q_1 - \delta Q_2}{\delta Q_1} < \frac{T_1 - T_2}{T_1} \quad \text{or,} \quad \frac{\delta Q_1}{T_1} < \frac{\delta Q_2}{T_2}$$

i.e.,  $\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} < 0$ ,

considering  $\delta Q_1$  positive and  $\delta Q_2$  negative as before.

Summing for all the small cycles and proceeding to the limit,

$$\oint \frac{dQ}{T} < 0. \quad (5.56)$$

This is called *Clausius' inequality* in contrast with (5.50).

## 5.12 Temperature-Entropy Diagram

Since the entropy  $S$  is a function of state it may be substituted for any one of the variables  $P$ ,  $V$ ,  $T$ . For many practical purposes it is more convenient to use  $T$  and  $S$  (instead of  $P$  and  $V$ ) as the two variables describing the state of a system.

Let the system pass from the initial state  $A$  to the final state  $B$  via  $C$  (Fig. 5.6) by the reversible path  $ACB$ . The heat taken in this process is, from (5.54),

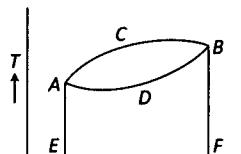


Fig. 5.6

$$Q = C \int_A^B dQ = C \int_A^B T dS = \text{Area } ACBFEA. \quad (5.57)$$

Similarly, the heat given out passing from  $B$  to  $A$  via  $D$  is

$$Q' = D \int_B^A T dS = \text{Area } BDAEFA. \quad (5.58)$$

The net heat absorbed during the cyclic process  $ACBDA$  is, therefore, equal to the area enclosed by the cycle in the  $T$ - $S$  diagram. As the internal energy of the system is unchanged at the end of the cycle, the net heat absorbed must all be used up in doing external work. This means that the enclosed area  $ACBDA$  on the  $T$ - $S$  diagram gives the work done in the cycle.

**Exercise :** Indicate the form of a Carnot cycle on a  $T$ - $S$  diagram.

## 5.13 Entropy in Reversible Processes

It can be seen from some examples that the total entropy of all systems taking part in a reversible process remains constant. Take the reversible Carnot engine. If  $Q_1$  be the heat absorbed from the source at  $T_1$ , then the gain in entropy by the working substance at  $T_1$  is  $+\frac{Q_1}{T_1}$  and the loss in entropy by the source is  $-\frac{Q_1}{T_1}$  so that the net gain in entropy by the whole system—source and working substance—is

$$+\frac{Q_1}{T_1} - \frac{Q_1}{T_1} = 0.$$

Again, if  $Q_2$  be the heat rejected at the sink at  $T_2$ , then the gain in entropy by the sink is  $+\frac{Q_2}{T_2}$ . The total change in entropy in the whole system—source and sink taken together—in a complete Carnot cycle is

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad [\text{by (5.47)}].$$

Since the working substance comes back to the initial state at the end of a cycle, the change in entropy for it in a cycle is nil (entropy being a function of state).

## 5.14 Entropy in Irreversible Processes

We consider an engine operating in an irreversible cycle of the Carnot type, together with its source and sink, as an isolated system. We so arrange that the process of taking in heat

from the source by the working substance and that of giving heat up to the sink are carried out reversibly and that irreversible processes take place only in the cycle of the engine. Let  $Q_1$  and  $Q_2$  be the quantities of heat taken in and given out at temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ ).

Now, since the engine is irreversible, the efficiency is less than that of a reversible engine. From (5.20) and Carnot's theorem the efficiency of the irreversible engine is

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1}$$

or,  $\frac{Q_2}{T_2} > \frac{Q_1}{T_1}$ . (5.59)

Since the working substance has returned to the original state, its entropy is unchanged. But the source has lost entropy by  $\frac{Q_1}{T_1}$  and the sink has gained entropy by  $\frac{Q_2}{T_2}$ . Thus, there is a net gain in entropy by

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1}. (5.60)$$

These arguments may be applied to any cyclic process. We then have the general result that for any isolated system, the occurrence of irreversible cyclic processes tends to increase the entropy during each cycle.

But this result can be further generalised to include non-cyclic processes also. Suppose, we have an isolated system and a process takes place irreversibly from a state  $A$  to a state  $B$  such that a certain part of the system only changes irreversibly while all other changes in the system are reversible. Now, the whole system is brought back to the original state  $A$  by a reversible process. The entire cycle so formed is irreversible and, according to the result of the preceding paragraph, the total entropy increases during the cycle. But since according to the result of the preceding section, the entropy of the whole system will remain unchanged during the reversible return to the initial  $A$ , all the increase in entropy must take place during the irreversible change from  $A$  to  $B$ . We, therefore, obtain the most general result that the entropy increases during any irreversible change of an isolated system.

Since all natural processes are irreversible, any change in nature leads to an increase in entropy. This led Clausius to say that the *entropy of the universe tends towards a maximum*. In some of the following sections we shall consider some natural processes such as the conduction of heat from a hotter to a colder body, Joule's expansion and diffusion of one gas into another to illustrate the truth of this statement.

## 5.15 Increase of Entropy in Conduction

Let us put in contact two bodies  $A$  and  $B$  with thermal capacities  $C_1$  and  $C_2$  and at temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ ). Let  $T$  be the final temperature. Then, since

$$C_1(T_1 - T) = C_2(T - T_2) \quad \text{or, } T = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}. (5.61)$$

The conduction that has taken place spontaneously here is an irreversible process. In order to calculate the change in entropy, we shall have to consider equivalent reversible processes (See section 5.10). Since the entropy is a function of state, the change in entropy will be the same as that which will take place if we bring  $A$  from  $T_1$  to  $T$  by a reversible process and also  $B$  from  $T_2$  to  $T$  by a reversible process. The entropy changes are

$$\int_{T_1}^T \frac{dQ}{T} = \int_{T_1}^T \frac{C_1 dT}{T} = C_1 \log_e \left( \frac{T}{T_1} \right) = -C_1 \log_e \left( \frac{T_1}{T} \right) \quad (5.62)$$

and  $\int_{T_2}^T \frac{dQ}{T} = \int_{T_2}^T \frac{C_2 dT}{T} = C_2 \log_e \left( \frac{T}{T_2} \right).$  (5.63)

The total change in entropy is, therefore  $= C_2 \log_e \left( \frac{T}{T_2} \right) - C_1 \log_e \left( \frac{T_1}{T} \right)$   
 $= (C_1 + C_2) \log_e \left( \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2} \right)$   
 $- (C_1 + C_2) \log_e (T_1^{C_1} T_2^{C_2})^{\frac{1}{C_1 + C_2}}.$  (5.64)

There is a theorem in algebra\* which states that for  $a, b, x, y > 0$ , the weighted arithmetic mean is greater than the weighted geometric mean, i.e.,

$$\frac{ax + by}{a + b} > (x^a y^b)^{\frac{1}{a+b}}. \quad (5.65)$$

This means that in conduction there is a net gain in entropy.

**Exercise :** Use the second law of thermodynamics to show that conduction is an irreversible process.

**Hints :** Suppose,  $dQ$  is the heat that has flown from the hot body  $A$  to the cold body  $B$ . Now, use  $A$  as the source and  $B$  as the sink and employ a Carnot engine backward so that it takes an amount of heat  $dQ$  from  $B$ . Evidently, the heat rejected to  $A$  will not be  $dQ$  but greater than  $dQ$  owing to the work done on the engine for the backward cycle. Initial conditions of  $A$  and  $B$  cannot, therefore, be restored altogether.

## 5.16 Joule's Expansion

Let us consider a perfect gas in a vessel of volume  $V_1$  rushing into an evacuated vessel so that the final volume of the gas is  $V_2$ . Since the gas is perfect, the average internal kinetic energy of a molecule, i.e., the temperature does not change in this process. The change in entropy may be calculated along any reversible path connecting the initial and the final state, say, by considering an isothermal expansion of the gas from volume  $V_1$  to volume  $V_2$ .

Thus, the change in entropy is  $= \int_{V_1}^{V_2} \frac{dQ}{T} = \frac{1}{T} \int_{V_1}^{V_2} P dV = R \int_{V_1}^{V_2} \frac{dV}{V}$

(since the heat added at constant temperature must be equal to work done)

$$= R \log_e \left( \frac{V_2}{V_1} \right). \quad (5.66)$$

This is positive and there is, therefore, an increase in entropy.

**Exercise :** Show by argument that Joule's expansion is an irreversible process.

**Hints :** In order to bring the gas back from the final to the initial state after Joule's expansion, it must be compressed under isothermal condition. For this purpose, work must be done on the gas by some external agency (say, by a Carnot engine) and at the same time heat developed in the gas must be removed. Thus, for return to the initial state, other bodies are affected whereas during change from the initial to the final state no other body is affected at all.

\*Durell, C. V. and Robson, A, *Advanced Algebra*, Vol. III, P. 375.

## 5.17 Entropy of a Perfect Gas

Let us take a gram-molecule of a perfect gas. For a quantity of heat  $dQ$  added in a reversible manner to it, we have

$$dQ = C_v dT + P dV. \quad (5.67)$$

From (5.54) and (5.67),

$$dS = \frac{C_v}{T} dT + \frac{P}{T} dV.$$

Substituting in the second term of the right-hand side from the perfect gas equation,  $PV = RT$ ,

$$dS = \frac{C_v}{T} dT + R \frac{dV}{V}. \quad (5.68)$$

On integration,

$$S = \int^T \frac{C_v}{T} dT + T \log_e V + S_0, \quad (5.69)$$

where  $S_0$  is a constant of integration.

If we assume that the specific heat at constant volume is independent of temperature, then from (5.69),

$$S = C_v \log_e T + R \log_e V + S_0. \quad (5.70)$$

From (5.68) and the relation,  $C_p = C_v + R$ ,

$$dS = \frac{C_p}{T} dT - \frac{R}{T} dT + R \frac{dV}{V}.$$

On integration,

$$S = \int^T \frac{C_p}{T} dT - \frac{R}{T} \log_e P + S'_0, \quad (5.71)$$

using the perfect gas equation.

Again, if we assume that the specific heat at constant pressure is independent of temperature, then from (5.71),

$$S = C_p \log_e T - R \log_e P + S'_0. \quad (5.72)$$

**Exercise 1.** Show that the entropy of a perfect gas may also be expressed by

$$S = C_p \log_e V + C_v \log_e P + \text{constant}$$

**Exercise 2.** A gas has the equation of state  $PV = RT(1 + \frac{b}{V})$ , where  $b$  is a constant. Show that the entropy is given by

$$S = \int^f \frac{C_v}{T} dT + R \log_e V - R \frac{b}{V} + S_0.$$

**Exercise 3.** The equation of state of a solid may be given by

$$V = V_0(1 + 3\alpha T - \beta P),$$

where  $V_0$  is a constant, and  $\alpha$ ,  $\beta$  are respectively the temperature-coefficient of linear expansion and the compressibility. The internal energy is given by

$$U = U_0 + \gamma T + \frac{1}{2\beta} \frac{(V - V_0)^2}{V_0}.$$

Now, show that

- $S = S_0 + \gamma \log_e T + 3\alpha(V - V_0)/\beta$
- $C_v = \gamma$
- $C_p = \gamma + 9\alpha^2 TV_0/\beta.$

## 5.18 Entropy of a Mixture of Gases

In order to calculate the entropy of a mixture of two perfect gases, let us consider some reversible means of separating them. For this purpose, let us have the gases  $X$  and  $Y$  in a

cylinder (Fig. 5.7). The walls  $A, A'$  are fixed and while  $A'$  is impermeable to either gas,  $A$  is permeable to  $X$  only. On the other hand, the walls  $B, B'$  are coupled together and are frictionlessly movable in such a manner that the space between  $B$  and  $B'$  remains fixed and equal to the space between  $A$  and  $A'$ . Besides, while  $B$  is impermeable to either gas,  $B'$  is permeable to  $Y$  only.

At the beginning,  $B$  and  $B'$  are in contact with  $A$  and  $A'$  respectively and the intervening space contains the mixture of the gases  $X$  and  $Y$ . Let

us suppose that above  $B$  there is vacuum. Now, if the coupled pistons  $B$  and  $B'$  are given a slight motion, they will continue to rise slowly and the gas  $X$  will pass into the space between  $A$  and  $B$  and the gas  $Y$  will pass into the space between  $A'$  and  $B'$ . During this motion, no external work will be done, because the net pressure on the pistons  $B$  and  $B'$  is nil. This is evident from the fact that the pressure on  $B$  due to  $X$  is neutralised by that on  $B'$  due to  $X$  and also the pressure on one side of  $B'$  due to  $Y$  is balanced by that on the other side of  $B'$  due to  $Y$ . When  $B'$  comes into contact with  $A$ , the gases get completely separated. If the whole system is isolated, no energy change can take place during this process so that the total energy is unchanged and the temperature of the gases is the same as was that of the mixture. Since there has been no heat exchange, and also the process has been carried out infinitely slowly and, therefore, reversibly, the net change of entropy is zero. This means that the entropy of a mixture of gases is the same as the sum of the entropies of the two gases if each gas has, before mixing, the same temperature and the same volume as the mixture itself.

Then, from (5.71), we write the entropy of a mixture of perfect gases as

$$S = \sum_r n_r \left\{ \int^T \frac{(C_p)_r}{T} dT - R \log_e P_r + (S'_0)_r \right\}, \quad (5.73)$$

where  $(C_p)_r$  is the gm-molecular specific heat,  $P_r$  the partial pressure and  $n_r$  the number of gram-molecules of the  $r$ th gas present in the mixture.

By Dalton's law of partial pressures, the total pressure of the mixture is

$$P = \sum P_r$$

Also, according to the equation,

$$P_r V = n_r RT.$$

The partial pressure  $P_r$  is proportional to  $n_r$ , since  $V$  and  $T$  are same for every constituent of the mixture. Then,

$$P_1 : P_2 : P_3 : \dots = n_1 : n_2 : n_3 : \dots$$

$$\text{giving } P_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots} P, P_2 = \frac{n_2}{n_1 + n_2 + n_3 + \dots} P, \text{ etc.}$$

Now, writing  $c_1 = \frac{n_1}{\sum n_r}$ ,  $c_2 = \frac{n_2}{\sum n_r}$ , etc. where  $c_1, c_2, \dots$  are the concentrations, we obtain,

$$P_1 = c_1 P, \quad P_2 = c_2 P, \quad P_3 = c_3 P, \dots \text{ etc.} \quad (5.74)$$

Then, from (5.73) and (5.74)

$$\begin{aligned} S &= \sum_r n_r \left\{ \int^T \frac{(C_p)_r}{T} dT - R \log_e (c_r P) + (S'_0)_r \right\} \\ &= \sum_r n_r \left\{ \int^T \frac{(C_p)_r}{T} dT - R \log_e c_r - R \log_e P + (S'_0)_r \right\}. \end{aligned} \quad (5.75)$$

### 5.19 Increase of Entropy in Diffusion

Now we can immediately calculate the change of entropy when two gases diffuse into one another. Let  $n_1, n_2$  be the number of gram-molecules of the first and the second gas respectively. If the gases diffuse into each other at the same temperature  $T$  and the same pressure  $P$ , then the total entropy before diffusion is, from (5.71),

$$S_1 = n_1 \left\{ \int^T \frac{(C_p)_1}{T} dT - R \log_e P + (S'_0)_1 \right\} + n_2 \left\{ \int^T \frac{(C_p)_2}{T} dT - R \log_e P + (S'_0)_2 \right\}. \quad (5.76)$$

After diffusion, the entropy of the mixture is, from (5.75),

$$\begin{aligned} S_2 &= n_1 \left\{ \int^T \frac{(C_p)_1}{T} dT - R \log_e c_1 - R \log_e P + (S'_0)_1 \right\} \\ &\quad + n_2 \left\{ \int^T \frac{(C_p)_2}{T} dT - R \log_e c_2 - R \log_e P + (S'_0)_2 \right\}. \end{aligned} \quad (5.77)$$

From (5.76) and (5.77), the change of entropy on diffusion is

$$S_2 - S_1 = -R \{n_1 \log_e c_1 + n_2 \log_e c_2\}. \quad (5.78)$$

Now, since  $c_1, c_2$  are fractions, the change of entropy is a positive quantity, i.e., there is a net increase of entropy in diffusion.

We close this section with a paradox known as *Gibbs' paradox*. Suppose, we take a gram-molecule of each of the two gases. Then, as they get mixed by diffusion, the gain in entropy is  $2R \log_e 2$  from (5.78). But if we take, instead, two gram-molecules of the same gas, then on diffusion there is, of course, no change of state and there should, therefore, be no change of entropy, the total entropy being just twice that of each gram-molecule of the gas. This remarkable difference between the two cases is called *Gibbs' paradox*.

**Exercise 1.** A vessel of volume  $2V$  is divided into two equal chambers by a partition. Both chambers are filled with a perfect gas—at temperature  $T_1$  and pressure  $P_1$  in one chamber and at temperature  $T_2$  and pressure  $P_2$  in the other. Now show that if the two parts of the gas on the two sides of the partition are allowed to mix slowly, no exchange of heat taking place, then the gain of entropy is

$$V \left[ \left( \frac{C_p}{R} \right) \left\{ \frac{P_1}{T_1} \log_e \frac{T}{T_1} + \frac{P_2}{T_2} \log_e \frac{T}{T_2} \right\} - \frac{P_1}{T_1} \log_e \frac{P}{P_1} - \frac{P_2}{T_2} \log_e \frac{P}{P_2} \right],$$

where  $T, P$  are the final temperature and pressure respectively.

**Exercise 2. Entropy of Steam :** Find the change of entropy as one gram of ice at  $T_1$  K is heated into steam at  $T_2$  K at normal pressure.

*Hints :* Let  $T_m$ ,  $T_b$  be respectively the melting point of ice and the boiling point of water. Also let  $L_f$ ,  $L_v$  be respectively the latent heat of fusion of ice and the latent heat of vaporization of water.

Now, the change of entropy in question = change of entropy for (rise of temp. of ice from  $T_1$  to  $T_m$  + conversion of ice into water + rise of temp. of water from  $T_m$  to  $T_b$  + conversion of water into steam + rise of temp. of steam from  $T_b$  to  $T_2$ )

$$= \int_{T_1}^{T_m} \frac{(C_p)_{\text{ice}}}{T} dT + \frac{L_f}{T_m} + \int_{T_m}^{T_b} \frac{(C_p)_{\text{water}}}{T} dT + \frac{L_v}{T_b} + \int_{T_b}^{T_2} \frac{(C_p)_{\text{steam}}}{T} dT.$$

## 5.20 Mathematical Formulation of Second Law\*

It has been seen in section 5.5 how the second law of thermodynamics is intimately associated with the operations of reversible engines. For this reason, the following equation :

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad (5.46)$$

is adopted as an equivalent (mathematical) form of the second law. But this equation is not of much use for finding out the direction in which a chemical or physical change takes place. Clausius, therefore, developed from (5.46) (See sections 5.9 and 5.10) the concept of entropy which is a function of state of a substance. The change of entropy of a substance gives a measure of the thermodynamic change in a certain process. So the following equation :

$$dS = \frac{dQ}{T} \quad (5.47)$$

has been adopted as the most useful mathematical form of the second law of thermodynamics.

*Since the entropy increases in all natural processes, we may also call this principle of increase of entropy itself the second law of thermodynamics.*

## 5.21 Statistical Interpretation of Entropy : Boltzmann's Law

Boltzmann showed (See Chapter 9) that Maxwell's law of velocity distribution in a gas in the steady state represents just the most probable distribution, i.e., the equilibrium state of a gaseous system is the state which has got the maximum probability under the existing conditions of pressure and temperature. On the other hand, we have already seen in this chapter that the entropy increases in all natural processes. This means that in a certain process the equilibrium condition is reached when the entropy attains a maximum value. This led Boltzmann to infer that the entropy must be a function of the probability of the state of the system.

Boltzmann, therefore, wrote down the equation :

$$S = f(P), \quad (5.79)$$

where  $P$  is the probability of a state of a system having entropy  $S$ . Now if we have two independent systems  $X$  and  $Y$  with entropies  $S_x$  and  $S_y$ , then the entropy of the combined

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\*See Saha and Srivastava, *A Treatise on Heat*, Pp. 319–20, (1958); Wilson, *Theoretical Physics*, Vol. 1, Pp. 293, 298–99, (1931).

system\* is  $S_x + S_y$ . If the probability of  $X$  be  $P_x$  and that of  $Y$  be  $P_y$ , then the probability of the combined system is  $P_x \times P_y$ . Hence, we find, since  $S_x + S_y = f(P_x) + f(P_y)$  and also  $S_x + S_y = f(P_x \times P_y)$ ,

$$f(P_x \times P_y) = f(P_x) + f(P_y). \quad (5.80)$$

Differentiating (5.80) with respect to  $P_x$ , keeping  $P_y$  constant,

$$P_y f'(P_x \times P_y) = f'(P_x). \quad (5.81)$$

Similarly, differentiating (5.80) with respect to  $P_y$ , keeping  $P_x$  constant,

$$P_x f'(P_x \times P_y) = f'(P_y). \quad (5.82)$$

From (5.81) and (5.82),

$$\begin{aligned} P_x f'(P_x) &= P_y f'(P_y) = P_x P_y f'(P_x \times P_y), \text{ i.e., } P f'(P) = \text{constant} \\ f(P) &= k \log_e P + C, \end{aligned} \quad (5.83)$$

on integration. Here  $k$  is a universal constant known as *Boltzmann's constant* and  $C$  is also a constant but is different for different systems. From (5.79) and (5.83),

$$S = k \log_e P + C. \quad (5.84)$$

This is the form in which Boltzmann gave his law.

Following Planck, we may put  $C$  equal to zero. This is permissible because the entropy is indeterminate to the extent of an additive constant [See, for example, (5.69)]\*\*. Hence, from (5.84),

$$S = k \log_e P. \quad (5.85)$$

Further development of this subject will be taken up in Chapter 11.

## PROBLEMS

- Take a Carnot engine containing a perfect gas in the state represented by  $P_1$ ,  $V_1$ ,  $T_1$ . The temperature of the gas is first raised to  $T_2$  at constant volume and then the gas is expanded adiabatically to  $T_1$ . Finally, it is compressed isothermally to its original volume  $V_1$ . Draw a  $P$ - $V$  diagram for the whole cycle. Find the efficiency of the cycle.
- Heat is absorbed from a source and is completely converted into work
  - in an isothermal expansion of a gas, and
  - in an isothermal demagnetisation of a paramagnetic solid.
 Does any violation of the second law of thermodynamics occur in either process?
- Calculate the change of entropy when 200 gm of solid mercury at its melting point is raised to a temperature of 50 °C [Melting point of mercury -39 °C, Latent heat of fusion = 3 cal/gm, Mean specific heat = 0.034]
- A gm-molecule of a perfect gas expands isothermally by 10%. Calculate the change in entropy. What will be the change in entropy if it is subjected to isothermal compression to the same extent?
- 'Heat engines are extremely inefficient engines'. Discuss this statement from the stand point of the second law of thermodynamics.

\*The combined system does not mean that they are mixed up. They are still apart and are not allowed to interact with each other.

\*\*Fermi, E., *Thermodynamics*, P. 59 (1938).

6. The efficiency  $\eta$  of a Carnot engine can be enhanced either by raising the temperature  $T_1$  of the source or by lowering the temperature  $T_2$  of the sink. Which of the two methods is the more effective?

[*Hints* : Compare  $(d\eta/dT_1)_{T_2}$  and  $(d\eta/dT_2)_{T_1}$ ]

7. Clausius summed up the first and the second laws of thermodynamics as follows :

- (i) 'The energy of the universe is constant'.
- (ii) 'The entropy of the universe tends towards a maximum'.

Discuss these statements.

8. 'As a result of natural processes, energy is becoming more unavailable for work'. Discuss the meaning of this statement.



## Chapter 6

# Applications of Thermodynamic Principles

### 6.1 Latent Heat Equations

$XABX'$  and  $YDCY'$  are two isothermals of unit mass of a substance at temperatures  $T+dT$  and  $T$  respectively (Fig. 6.1).  $AB$  and  $DC$  represent the change of the substance from the liquid to the gaseous phase. On the other hand,  $AD$  represents the liquid state just at the point of vaporization and  $BC$  represents just the state of saturated vapour.

Now we take the unit mass of the substance reversibly round the cycle  $ABCDA$ . If the latent heat of vaporization is  $L$  at  $T$  and  $L+dL$  at  $T+dT$ , then  $L$  is the heat rejected at  $T$  and  $L+dL$  is the heat absorbed at  $T+dT$  during the cycle. Also during the cycle,  $c_1dT$  and  $c_2dT$  will be absorbed and rejected in going from  $D$  to  $A$  and from  $B$  to  $C$  respectively, if  $c_1$  is the specific heat of liquid at  $T$  and  $c_2$  is the specific heat of saturated vapour at  $T$ . Hence, the net amount of heat absorbed during the cycle  $ABCDA$  is

$$L + dL - c_2dT - L + c_1dT = \left( c_1 - c_2 + \frac{dL}{dT} \right) dT. \quad (6.1)$$

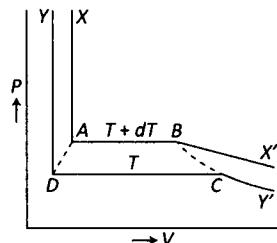


Fig. 6.1: Andrews' curves

Now, the heat absorbed in a reversible cyclic process must be equal to the external work done, i.e., equal to the area of the cycle

$$ABCDA = dP \times (V_2 - V_1) = \left( \frac{dP}{dT} \right)_V dT \times (V_2 - V_1),$$

where  $dP$  is the pressure difference between the curve  $AB$  and the curve  $CD$  and  $V_1$ ,  $V_2$  are the volumes at  $A$  (or  $D$ ) and  $B$  (or  $C$ ) respectively. We have then

$$\begin{aligned} \left( c_1 - c_2 + \frac{dL}{dT} \right) dT &= \left( \frac{dP}{dT} \right)_V (V_2 - V_1) dT \\ \text{i.e., } c_1 - c_2 + \frac{dL}{dT} &= (V_2 - V_1) \left( \frac{dP}{dT} \right)_V \end{aligned} \quad (6.2)$$

Again, since the substance has gone through a closed reversible cycle, the net change of entropy is zero by the theorem of Clausius (because the substance has returned to the initial state at the end of the cycle). Hence,

$$\frac{L + dL}{T + dT} - \frac{c_2dT}{T} - \frac{1}{T} + \frac{c_1dT}{T} = 0, \quad (6.3)$$

where the changes along  $BC$  and  $DA$  have been considered as taking place at  $T$  approximately, since  $dT$  is very small. Now, we can write to first order of small quantities,

$$\frac{L + dL}{T + dT} = \frac{(L + dL)(T - dT)}{T^2 - (dT)^2} = \frac{LT - LdT + TdL}{T^2} = \frac{L}{T} - \frac{L}{T^2}dT + \frac{dL}{T}. \quad (6.4)$$

Combining (6.3) and (6.4),

$$c_1 - c_2 = \frac{L}{T} - \frac{dL}{dT}. \quad (6.5)$$

Now, substituting  $(c_1 - c_2)$  from (6.5) in (6.2),

$$\frac{L}{T} = (V_2 - V_1) \left( \frac{dP}{dT} \right)_V \quad (6.6)$$

(6.6) is called the first latent heat equation or Clapeyron equation (sometimes also Clapeyron-Clausius equation), whereas (6.5) is known as the second latent heat equation or Clausius equation.

**Exercise 1.** Calculate the change in boiling point of water due to a change of pressure by 1 atmosphere ( $L = 536$  cal, volume of 1 gm of water at  $100^\circ\text{C}$  = 1 cc, volume of 1 gm of saturated steam at  $100^\circ\text{C}$  = 1600 cc).

**Solution :** From (6.6),

$$dT = \frac{T(V_2 - V_1)}{L} dP = \left[ \frac{373 \times (1600 - 1) \times 76 \times 13.6 \times 980}{536 \times 4.2 \times 10^7} \right] K = 26.83 \text{ K.}$$

**Exercise 2.** Sulphur has density 2.05 gm/cc before melting and 1.95 gm/cc after melting, the melting point being  $115^\circ\text{C}$  and the latent heat being 9.3 cal. Find the change in melting point for change of pressure by 1 atmosphere.

**Exercise 3.** Specific Heat of Saturated Steam : Calculate the specific heat of saturated steam at  $100^\circ\text{C}$ , given the following data :

$$T = 373 \text{ K}, \quad c_1 = 1.007, \quad L = 540 \text{ cal} \quad \text{and} \quad \frac{dL}{dT} = -0.604 \text{ at } 100^\circ\text{C}.$$

**Solution :** From (6.5),

$$c_2 = c_1 + \frac{dL}{dT} - \frac{L}{T} = \left[ 1.007 - 0.604 - \frac{540}{373} \right] \text{ cal/gm} = -1.044 \text{ cal/gm.}$$

Thus, the specific heat of saturated steam at  $100^\circ\text{C}$  is negative and is  $-1.044 \text{ cal/gm}$ . This means that in raising the temperature of saturated steam from  $100^\circ\text{C}$  to  $101^\circ\text{C}$ , instead of adding any heat, an amount of heat equal to 1.044 cal. is removed. In fact, the temperature of saturated steam is raised from  $100^\circ\text{C}$  to  $101^\circ\text{C}$  just by compression accompanied with removal of heat so that the condition of saturation is satisfied throughout.

## 6.2 Richardson's Equation for Thermionic Emission

O.W. Richardson\* extensively investigated the phenomenon of the emission of electricity from hot bodies and gave the name *thermionics* to the subject and *thermions* to the electrons emitted. M. von Laue\*\* showed that the problem can be treated as a case of evaporation of electrons from the state of condensed phase inside the hot body to state of the gaseous phase. We shall follow this idea in our discussion here.

When a hot body is put in an evacuated chamber, a state of equilibrium is soon reached when as many electrons return to the body as are emitted per unit time. This exactly corresponds

\*O.W. Richardson, *The Emission of Electrons from Hot Bodies* (1922).

\*\*M. von Laue, Ann. d. Phys., **55**, P. 695 (1919).

to a liquid in contact with its vapour. We can, therefore, apply the Clapeyron equation :

$$\frac{L}{T} = (V_2 - V_1) \left( \frac{dP}{dT} \right)_V \quad (6.6)$$

to our present problem. Here  $L$  may be considered as the latent heat of vaporization of electrons from the hot body,  $P$  the equilibrium pressure of the electron gas and  $(V_2 - V_1)$  the change in volume as the electrons come from the condensed phase to the gaseous phase.  $V_1$  may, however, be neglected compared to  $V_2$  and we have from (6.6)

$$\frac{L}{T} = V \frac{dP}{dT} \quad (6.7)$$

(writing  $V$  for  $V_2$  here).

Now considering the concentration of electrons to be small, the effect of mutual repulsion may be neglected. Then, we may apply the gas law :

$$P = nkT \quad (6.8)$$

to the electron gas ( $n$  = number of electrons in unit volume).

We now proceed to evaluate  $L$ . If  $\varepsilon$  is the energy required by one electron to be ejected from the hot body, then the total energy necessary for this purpose for unit mass of electron gas contained in volume  $V$  is  $nV\varepsilon$ . Also this mass of electron gas must carry a further amount of energy to perform external work  $PV$  against the external pressure  $P$ . Hence,

$$L = nV\varepsilon + PV. \quad (6.9)$$

From (6.7) and (6.9), therefore,

$$n\varepsilon + P = T \frac{dP}{dT} \quad (6.10)$$

Again, from (6.8) and (6.10),

$$n\varepsilon = kT^2 \frac{dn}{dT}. \quad (6.11)$$

On integration,

$$n = Ce^{\int^T \frac{k\varepsilon}{kT^2} dT}, \quad (6.12)$$

where  $C$  is an integration constant which can be evaluated on the basis of quantum statistics only [See sections 10.9 and 11.4].

From (2.36) and (2.39) of Chapter 2, the number of gas molecules hitting unit area of the wall per second is

$$n_1 = n \sqrt{\frac{kT}{2\pi m}}. \quad (6.13)$$

Applying this result to our electron gas, we obtain from (6.12) and (6.13) for the number of electrons hitting unit area of the hot body per second

$$n_1 = C \sqrt{\frac{kT}{2\pi m}} e^{\int^T \frac{k\varepsilon}{kT^2} dT}, \quad (6.14)$$

where  $m$  stands for the mass of an electron. Since we are considering here a state of equilibrium, (6.14) also gives the number of electrons emitted per unit area of the hot body per second.

Multiplying both sides of (6.14) by  $q$ , the charge of an electron, we obtain the thermionic current per unit area of the hot body

$$i = Cq \sqrt{\frac{kT}{2\pi m}} e^{\int T \frac{e^{-\epsilon/kT^2}}{kT^2} dT}. \quad (6.15)$$

Richardson has shown from thermodynamic reasoning\* that

$$\epsilon = \epsilon_0 + \frac{3}{2} kT^{**}. \quad (6.16)$$

Substituting  $\epsilon$  from (6.16) in (6.15),

$$i = AT^2 e^{-\alpha/T}, \quad (6.17)$$

where  $A$  and  $\alpha$  are constants independent of  $T$ . (6.17) is Richardson's equation for thermionic emission. Richardson applied the equilibrium condition of electrons near the metals to explain the contact difference of potentials between metals, and the Peltier and Thomson effects. For a detailed account, see his book (referred to earlier).

From (6.17) a straight line should be obtained by plotting  $\log_e i - 2 \log_e T$  against  $1/T$ . This has, in fact, been found from the data obtained by Schlichter<sup>†</sup> for platinum wires.

### 6.3 Surface Tension and Surface Energy

Here we shall set up a relation between surface tension and surface energy. Imagine a heat engine formed by a liquid film stretched on a frame  $YXX'Y'$ . Let one side of the frame,  $ZZ'$ , be such that it can be pulled out by an external force  $F$  or pulled in by surface tension of the film [Fig. 6.2(a)].

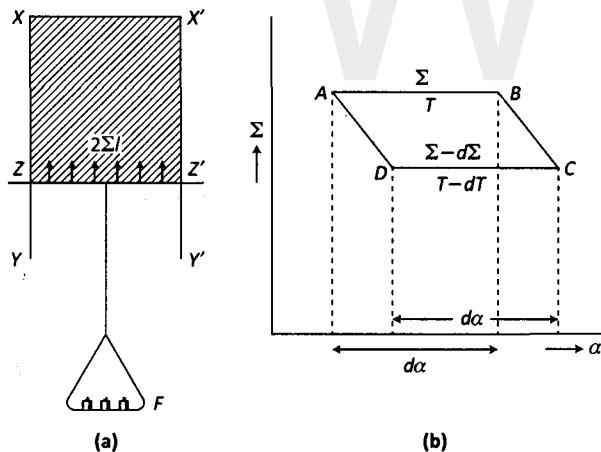


Fig. 6.2

Let the initial temperature of the film be  $T$  and the initial state given by the point  $A$  on the  $\Sigma-\alpha$  diagram [Fig. 6.2(b)] with surface tension  $\Sigma$  and area of the film  $\alpha$ . At the outset we shall assume that  $\Sigma$  increases with  $T$ , although the reverse is the fact. Now, with the frame in a hot chamber maintained at  $T$ , the film is isothermally stretched from the state  $A$  to the state  $B$  by an area  $d\alpha$ . Let the heat absorbed from the hot chamber (serving as the source here) be  $qd\alpha$ , where  $q$  is the heat absorbed when the film is stretched by unit area. Next the frame is placed in an insulated chamber and the film is adiabatically stretched from the state  $B$  to the state  $C$ , the temperature and the surface tension changing from  $T$  and  $\Sigma$  to

\*See, for example, Hoare, F. E., *Thermodynamics*, Pp. 222-25 (1952).

\*\* $\epsilon_0$  is the energy required just for emission and  $\frac{3}{2}kT$  is the average kinetic energy retained by an electron even after emission.

<sup>†</sup>Schlichter, Ann. d. Phys., 47, P. 573 (1915).

$T - dT$  and  $\Sigma - d\Sigma$  respectively. Next, the frame is taken into a cold chamber (serving as the sink) maintained at  $T - dT$  and the film is allowed to contract isothermally from the state  $C$  to the state  $D$ , all the heat generated here being rejected to the cold chamber. Finally, the frame is put again in the insulated chamber and the film is allowed to contract adiabatically so that it returns to the initial state  $A$ .

Considering that the processes taking place here are infinitesimally slow and that the movement of the side  $ZZ'$  is frictionless, the cycle  $ABCDA$  becomes completely reversible and the frame  $YXX'Y'$  with the film and the weight  $F$  behaves like a reversible engine. Then, we have from the second law of thermodynamics [eqn. (5.46) of Chapter 5] :

$$\frac{\text{Net work done by the film during the cycle}}{\text{Heat absorbed from the source}} = \frac{dT}{T}$$

or, 
$$\frac{2(\Sigma - d\Sigma)l \times dx - 2\Sigma l \times dx}{qda} = \frac{dT}{T}, \quad (6.18)$$

where  $dx$  is the displacement of  $ZZ'$  during change from  $A$  to  $B$  or from  $C$  to  $D$ .

Since  $da = 2l \times dx$ , we obtain from (6.18)

$$q = -T \frac{d\Sigma}{dT}. \quad (6.19)$$

Thus, the total gain in surface energy for an increase in surface area by unit area under isothermal condition is

$$E = \Sigma \times 1 + q \times 1$$

$$\text{i.e., } E = \Sigma - T \frac{d\Sigma}{dT} [\text{from 6.191}]. \quad (6.20)$$

Now, since for all liquids the surface tension decreases with temperature, i.e.,  $\frac{d\Sigma}{dT}$  is negative,  $E$  is, in fact, larger than  $\Sigma$  by  $T \frac{d\Sigma}{dT}$ .

#### 6.4 E.M.F. of Reversible Cells

An electric cell is said to be reversible if whatever happens in the cell when it supplies current is exactly reversed on reversing the current from some external source so that the cell comes back to its original condition. By this criterion, a simple cell with dil.  $H_2SO_4$  and with copper anode and zinc cathode is not a reversible cell. For, when the cell delivers the current, zinc goes into solution and hydrogen is evolved at the copper plate. But if a current is passed through the cell from an external source in the reverse direction, copper is dissolved and hydrogen is evolved at the zinc plate. Thus, a reversal of current does not restore the simple cell to the initial state.

On the other hand, a Daniell cell—with zinc cathode immersed in dil.  $H_2SO_4$  in a porous pot outside which there is a saturated solution of  $CuSO_4$  with copper anode immersed in it—is a reversible cell. For, when the cell supplies the current zinc goes into solution and copper is deposited on the copper plate. But, if a current is passed through the cell from an external source in the reverse direction, copper is dissolved and zinc is deposited on the zinc cathode. Thus, the cell comes back to initial state.

There is, however, a common element of irreversibility in an electric cell due to its internal resistance  $r$ . Whenever a current  $i$  flows for a time  $t$ , an amount of work  $i^2rt$  is converted into heat in the cell. This is irreversible, because application of heat will not produce the current.

We may, however, assume  $i$  and  $t$  to be so small that this element of irreversibility may be neglected in our discussion.

Let us consider a reversible cell  $X$  of e.m.f.  $E$  at temperature  $T$  connected to an external electromotive force  $Y$  as shown in Fig. 6.3(a).

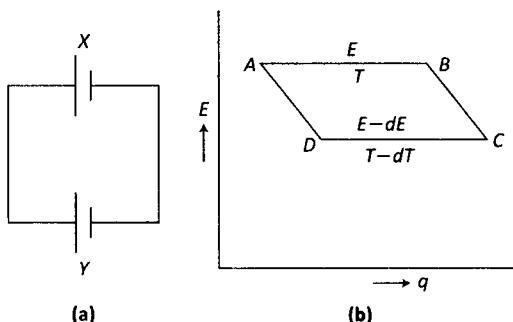


Fig. 6.3

For all the processes carried out here, the differences between the e.m.f.s of  $X$  and  $Y$  are kept infinitesimally small so that infinitesimally small currents may flow through the circuit and the condition of reversibility is satisfied.

Let us suppose that initially the e.m.f. of the reversible cell is  $E$  at  $T$ . Now, it is placed in a hot chamber maintained at  $T$  (serving as the source here) and is allowed to pass a current until a small charge  $dq$  passes round the circuit. On the  $E$ - $q$  diagram in Fig. 6.3(b), this is indicated

by  $AB$  parallel to  $q$ -axis ( $q$  representing the charge that flows), since the e.m.f. is constant at constant temperature. Let  $h$  be the heat absorbed by the cell from the hot source during this process. Next, the cell is placed in an insulated chamber and is allowed to pass a further infinitesimally small charge. In this case, the cell uses up its own energy so that its temperature falls from  $T$  to  $T - dT$ . At the same time, the e.m.f. of the cell also falls from  $E$  to  $E - dE$ . This process is indicated by  $BC$  on the  $E$ - $q$  diagram. Next, the cell is put in a cold chamber maintained at  $T - dT$  (serving as the sink). Now a current is passed by the external source  $Y$  in opposite direction so that a charge  $dq$  passes through the cell. This process is indicated by  $CD$ , parallel to  $q$ -axis. The heat  $h_1$  that is generated in the cell now is rejected to the cold sink. Finally, the cell is again placed in the insulated chamber and a further charge is passed through the cell by the external source  $Y$  so that the cell comes back to initial state  $A$  from  $D$ .

Evidently the cycle  $ABCDA$  is a reversible cycle and the reversible cell behaves like a reversible engine because a net work ( $h - h_1$ ) has been done by it during the cycle. Applying the second law of thermodynamics [Eqn. (5.46) of Chapter 5],

$$\frac{h - h_1}{h} = \frac{dT}{T}. \quad (6.21)$$

Now, since  $h - h_1 = \text{net work done by the cell} = Edq - (E - dE)dq = dq \frac{dE}{dT} dT$ ,

$$\frac{dq \frac{dE}{dT} dT}{h} = \frac{dT}{T}$$

$$\text{i.e., } h = dqT \frac{dE}{dT}. \quad (6.22)$$

Now, the total work  $Edq$  done by the cell in passing a charge  $dq$  at  $T$  is partly at the cost of  $h$  drawn from the hot source and partly at the cost of the energy released by chemical reactions in the cell. If  $H$  be the energy liberated by the chemical processes where a unit charge passes through the cell, then we have

$$Edq = h + Hdq$$

$$\text{i.e., } E = H + T \frac{dE}{dT} \quad [\text{from (6.22)}]. \quad (6.23)$$

This is known as Gibbs-Helmholtz equation.

For a Daniell cell,  $H = 2.587 \text{ cal} = 2.587 \times 4.2 \times 10^7 \text{ C.G.S. unit} = 1.08654 \times 10^8 \text{ C.G.S.}$  and  $E = 1.096 \text{ volts} = 1.096 \times 10^8 \text{ C.G.S.}$ . Then from (6.23) at  $T = 273 \text{ K}$ ,

$$\frac{dE}{dT} = \frac{(1.096 \times 10^8 - 1.08654 \times 10^8) \text{ C.G.S.}}{273 \text{ K}} = 3.465 \times 10^{-5} \text{ volt/K.}$$

Thus, the temperature coefficient  $\frac{dE}{dT}$  for a Daniell cell is very low. This vindicates Lord Kelvin's calculation (1851) on the assumption that the electrical energy of a Daniell cell arises from the chemical changes occurring in the cell.

**Exercise :** A reversible cell is found to have an e.m.f. of 1.0064 volts at 22 °C. The energy liberated by chemical reactions is 0.266 cal per coulomb passing through the cell. Find the change in e.m.f. of the cell when the temperature rises to 28 °C.

## 6.5 Perfect Differentials

Let  $z$  be a function to two independent variables  $x$  and  $y$ , i.e.,

$$z = f(x, y). \quad (6.24)$$

Then, the change in  $z$  due to a small change in  $x$  ( $y$  being constant) is

$$(dz)_y = \left( \frac{\partial z}{\partial x} \right)_y dx. \quad (6.25)$$

Similarly, the change in  $z$  due to a small change in  $y$  ( $x$  being constant) is

$$(dz)_x = \left( \frac{\partial z}{\partial y} \right)_x dy. \quad (6.26)$$

Hence, if both  $x$  and  $y$  vary simultaneously, then the total change in  $z$  is

$$dz = (dz)_y + (dz)_x = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy. \quad (6.27)$$

This  $dz$  is called a *total or perfect differential* in mathematics.

We note here two important properties of a perfect differential which will be useful in subsequent discussions.

(1) It is evident from (6.27) that the total change  $dz$  in  $z$  has the same value whether we first make the change  $(dz)_y$ , i.e., the change  $dx$  in  $x$  and then the change  $(dz)_x$ , i.e., the change  $dy$  in  $y$ , or in the reverse order.

(2) The mixed second derivative of  $z$  is independent of the order of differentiation\*, i.e.,

$$\left[ \frac{d}{dx} \left( \frac{\partial z}{\partial y} \right)_x \right]_y = \left[ \frac{d}{dy} \left( \frac{\partial z}{\partial x} \right)_y \right]_x \quad (6.28)$$

Let us have a differential of the form :

$$dF(x, y) = M(x, y)dx + N(x, y)dy. \quad (6.29)$$

Then, if it is to be perfect or total, we must have, according to (6.27),

$$M(x, y) = \left( \frac{\partial F}{\partial x} \right)_y, \quad N(x, y) = \left( \frac{\partial F}{\partial y} \right)_x \quad (6.30)$$

\*Take an example, say,  $z = Ax^2 + Bxy + Cy^2$  and verify (6.28).

so that according to (6.28),

$$\left(\frac{dM}{dy}\right)_x = \left(\frac{dN}{dx}\right)_y. \quad (6.31)$$

We now consider the relevance of these ideas to thermodynamics. We know that the thermodynamic state of a system is defined by  $P, V, T, S, U$ , etc. That is, at a definite state of the system, each of these variables has a definite value. Further, a state is completely known if any two of these quantities are known. This means that any one of  $P, V, T, S, U$ , ... is completely given by any other two of them. For example, we may write :

$$S = f(U, V), \quad U = F(V, T), \dots \text{etc.} \quad (6.32)$$

which are exactly of the form (6.24). Then, like  $dz$  of (6.27),  $dP, dV, dT, dS, dU$ , etc., are also perfect differentials and we may write from (6.32) :

$$dS = \left(\frac{dS}{dU}\right)_V dU + \left(\frac{dS}{dV}\right)_U dV, \quad (6.33)$$

$$dU = \left(\frac{dU}{dV}\right)_T dV + \left(\frac{dU}{dT}\right)_V dT, \text{ etc.} \quad (6.34)$$

It should, however, be pointed out that  $dW$  (work done) and  $dQ$  (heat added) are not perfect differentials. Because they depend on how or in what order changes take place in the system. And this is a definite violation of the first property of a perfect differential stated above. This imperfect character of  $dW$  and  $dQ$  may be understood by a simple example provided by Carnot cycle of Fig. 5.2. If the system is taken from the state  $L$  to the state  $N$  via  $M$  with an isothermal change  $LM$  followed by an adiabatic change  $MN$ , then the total work done by the engine is given by the area  $LMNN'L'$ . If, instead, the change takes place from  $L$  to  $N$  via  $Q$  with an adiabatic change  $LQ$  followed by an isothermal change  $QN$ , then the work done by the system is given by the area  $LQNN'L'$ . Evidently, the two areas are not equal. Also it is already known that  $Q_1$ , the heat absorbed during change from  $L$  to  $N$  via  $M$ , is not equal to  $Q_2$ , the heat absorbed during change from  $L$  to  $N$  via  $Q$ .

## 6.6 Thermodynamic Functions and Maxwell's Thermodynamic Relations

We have from the first law of thermodynamics :

$$dQ = dU + dW = dU + PdV, \quad (6.35)$$

where the heat  $dQ$  is added reversibly to a system resulting in a change in internal energy  $dU$  and in an amount of work  $PdV$  done.

From the second law of thermodynamics,

$$dQ = TdS. \quad (6.36)$$

From (6.35) and (6.36),

$$dU = TdS - PdV. \quad (6.37)$$

Since  $dU$  is a perfect differential (as explained in the preceding section) and  $U$  is here evidently a function of the independent variables  $S$  and  $V$ , we have from (6.29), (6.30) and (6.37)

$$T = \left(\frac{dU}{dS}\right)_V, \quad -P = \left(\frac{dU}{dV}\right)_S. \quad (6.38)$$

Then, from (6.31) and (6.38),

$$\left(\frac{dT}{dV}\right)_S = - \left(\frac{dP}{dS}\right)_V. \quad (6.39)$$

If  $T$  and  $P$  are constant, then from (6.37),

$$dU = d(TS - PV)$$

$$\text{i.e., } d(U - TS + PV) = 0. \quad (6.40)$$

Thus, for a reversible process at constant temperature and pressure,  $U - TS + PV$  remains constant. This function, which we shall denote by  $G$ , is commonly called the *thermodynamic potential* or *Gibbs' function*.

Then, a general change in  $G$  is given by

$$dG = d(U - TS + PV) = (dU - TdS + PdV) - SdT + VdP$$

$$\text{i.e., } dG = -SdT + VdP \text{ [from (6.37)]} \quad (6.41)$$

$G$  is a function of the variables  $U, S, V, T$  and  $P$ . This means that  $G$  is also a function of state like  $P, V, S$ , etc. Hence  $dG$  is also a perfect differential like  $dP, dV, dS, \dots$

Then from (6.29), (6.30) and (6.41),

$$-S = \left(\frac{dG}{dT}\right)_P, \quad V = \left(\frac{dG}{dP}\right)_T. \quad (6.42)$$

Then, from (6.31) and (6.42),

$$\left(\frac{dS}{dP}\right)_T = - \left(\frac{dV}{dT}\right)_P. \quad (6.43)$$

Next, from (6.37),

$$dW = PdV = -dU + TdS = -d(U - TS) \quad (6.44)$$

at constant temperature. Thus, the external work done during a reversible process at constant temperature is done at the cost of the function  $U - TS$ . This function, which we shall denote by  $F$ , is called the *free* or *available energy* of the system.

Then, a general change in  $F$  is given by

$$dF = d(U - TS) = (dU - TdS + PdV) - SdT - PdV$$

$$\text{i.e., } dF = -SdT - PdV \text{ [from (6.37)].} \quad (6.45)$$

Evidently  $dF$  is also a perfect differential like  $dG$  and we have, therefore, from (6.29), (6.30) and (6.45)

$$-S = \left(\frac{dF}{dT}\right)_V, \quad -P = \left(\frac{dF}{dV}\right)_T. \quad (6.46)$$

Then, from (6.31) and (6.46),

$$\left(\frac{dS}{dV}\right)_T = \left(\frac{dP}{dT}\right)_V. \quad (6.47)$$

Again, from the first relation of (6.46),

$$U - TS = U + T \left(\frac{dF}{dT}\right)_V$$

$$\text{i.e., } F = U + T \left( \frac{dF}{dT} \right)_V. \quad (6.48)$$

This is known as the Gibbs-Helmholtz equation.

Finally, from (6.35) at constant pressure,

$$dQ = d(U + PV). \quad (6.49)$$

Thus, the heat  $dQ$  added reversibly to a system is equal to the change in the function  $(U + PV)$  at constant pressure. This function is denoted here by  $H$  and called the *heat content* or *enthalphy* of the system.

Then, a general change in  $H$  is

$$dH = d(U + PV) = (dU - TdS + PdV) + TdS + VdP$$

$$\text{i. e., } dH = TdS + VdP \quad [\text{from (6.37)}]. \quad (6.50)$$

Evidently,  $dH$  is also a perfect differential and we have from (6.29), (6.30) and (6.50)

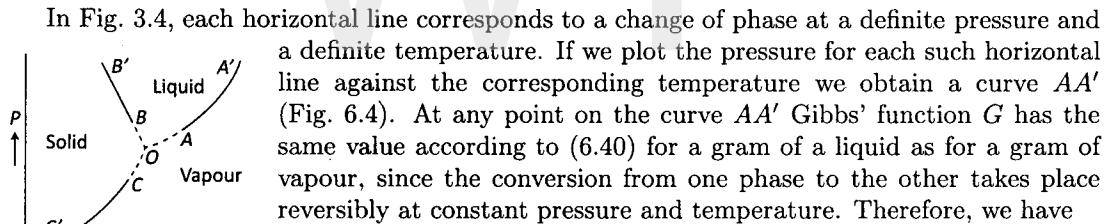
$$T = \left( \frac{dH}{dS} \right)_P, \quad V = \left( \frac{dH}{dP} \right)_S. \quad (6.51)$$

Then, from (6.31) and (6.51),

$$\left( \frac{dT}{dP} \right)_S = \left( \frac{dV}{dS} \right)_P \quad (6.52)$$

(6.39), (6.43), (6.47) and (6.52) are known as Maxwell's thermodynamic relations\*

## 6.7 Triple Point



$$G_L = G_V \quad (6.53)$$

Fig. 6.4: Triple point

at every point on  $AA'$ . Hence, (6.53) represents the curve  $AA'$ .

Similarly, we have the curve  $BB'$  each point on which represents the conversion between the liquid and the solid state at a definite pressure and temperature. For this curve, therefore, we have

$$G_S = G_L. \quad (6.54)$$

In the same manner, we have the curve  $CC'$  each point on which corresponds to the conversion between the solid and the vapour state at a definite pressure and temperature. For this curve, we have

$$G_V = G_S. \quad (6.55)$$

Now the point of intersection of  $AA'(G_L^0, G_V^0)$  and  $BB'(G_S^0, G_V^0)$ , being common to both the curves, must satisfy both the equations (6.53) and (6.54). Hence, for this point, we obtain from (6.53) and (6.54).

\*Maxwell, J.C., *Theory of Heat*.

$$G_S^0 = G_V^0. \quad (6.56)$$

This means from (6.55) that the point of intersection of  $AA'$  and  $BB'$  is also a point on the curve  $CC'$ . In other words, all the three curves intersect at a point which is called the *triple point* and is indicated in the  $P$ - $T$  diagram (Fig. 6.4) as  $O$ . At  $O$  all the three phases exist together.

For water,  $OA'$ ,  $OB'$  and  $OC'$  are called respectively the steam line, the hoar frost line and the ice line.

**Exercise :** Find the triple point ( $P_0, T_0$ ), given that  $L = 80 \text{ cal/gm}$ ;  $J = 4.2 \times 10^7 \text{ ergs/cal}$ ;  $T_0 = 273 \text{ K}$ ,  $V_2 = \text{sp. vol. of water at } 0^\circ\text{C} = 1.000 \text{ cc/gm}$ ,  $V_1 = \text{sp. vol. of ice at } 0^\circ\text{C} = 1.090 \text{ cc/gm}$ , vap. pressure of water at  $0^\circ\text{C} = 4.58 \text{ mm of Hg}$ , melting pressure of ice at  $0^\circ\text{C} = 760 \text{ mm of Hg}$ .

**Solution :** From (6.6) with the above data,

$$\frac{dT}{dP} = -0.0075 \text{ }^\circ\text{C per atmosphere increase of pressure.}$$

Now ice melts at  $0^\circ\text{C}$  under the (atmospheric) pressure of 760 mm of Hg. But at the triple point we have, in an *air-free* vessel, only ice, water and water vapour, the vapour having only a pressure of 4.58 mm of Hg. Thus, the value of  $P$  at the triple point is just 4.58 mm of Hg and the value of  $T$  [which is now the melting point under the vapour pressure of 4.58 mm of Hg] is approximately  $0.0075^\circ\text{C}$  (because in an air-free vessel, a difference of pressure,  $dP = (760 - 4.58)$  mm of Hg, i.e., nearly one atmosphere of pressure, occurs).

## 6.8 Some Alternative Derivations

Some results of the earlier sections of this chapter will be rederived in this section by methods based on the ideas developed in the intervening sections.

### (a) First Latent Heat Equation

**Method 1 :** We have Maxwell's relation

$$\left( \frac{dS}{dV} \right)_T = \left( \frac{dP}{dT} \right)_V. \quad (6.47)$$

Multiplying both sides by  $T$  at which the left-hand side is constant,

$$\begin{aligned} \left( T \frac{dS}{dV} \right)_T &= T \left( \frac{dP}{dT} \right)_V \\ \text{or, } \left( \frac{dQ}{dV} \right)_T &= T \left( \frac{dP}{dT} \right)_V. \end{aligned} \quad (6.57)$$

Now, if unit mass of a substance is considered,  $dQ$  will mean the latent heat  $L$  at  $T$  in a change of phase and  $dV$  will be the difference in the specific volumes in the final and initial phase, i.e.,

$$dV = V_2 - V_1,$$

where  $V_2$ ,  $V_1$ , are the specific volumes in the final and the initial phase respectively. Then, (6.57) takes the form :

$$\frac{L}{T} = (V_2 - V_1) \left( \frac{dP}{dT} \right)_V. \quad (6.58)$$

This is the first latent heat equation.

**Method 2 :** Take two neighbouring points on the curve, say,  $OA$  of Fig. 6.4. Then, by (6.53),

$$G_V = G_L \quad \text{and} \quad G_V + dG_V = G_L + dG_L$$

so that  $dG_V = dG_L$ . (6.59)

Then, from (6.41) and (6.59),

$$-S_V dT + V_V dP = -S_L dT + V_L dP$$

i.e.,  $(S_V - S_L)dT = (V_V - V_L)dP$ . (6.60)

But evidently

$$T(S_V - S_L) = L, \quad (6.61)$$

where  $L$  is the latent heat of evaporation at  $T$ . Hence, from (6.60) and (6.61),

$$\frac{L}{T} = (V_V - V_L) \frac{dP}{dT} \quad (6.62)$$

**Method 3 :** Finally, we start with Gibbs-Helmholtz equation (6.48). For unit mass of liquid as well as of vapour, we have respectively

$$F_L = U_L + T \left( \frac{dF_L}{dT} \right)_V \quad (6.63)$$

$$F_V = U_V + T \left( \frac{dF_V}{dT} \right)_V \quad (6.64)$$

$$\text{so that, } F_V - F_L = U_V - U_L + T \left( \frac{d(F_V - F_L)}{dT} \right)_V. \quad (6.65)$$

But we know from (6.44) that at constant  $T$ ,

$$\text{the external work done} = F_V - F_L = -P(V_V - V_L) \quad (6.66)$$

Combining (6.65) and (6.66),

$$U_V - U_L + P(V_V - V_L) = (V_V - V_L)T \frac{dP}{dT}$$

$$\text{i.e., } L = (V_V - V_L)T \frac{dP}{dT}, \quad (6.67)$$

since  $U_V - U_L + P(V_V - V_L)$  means the total energy  $L$  required for the change of unit mass of liquid into the vapour state.

### (b) Second Latent Heat Equation

For a change of unit mass of a liquid into vapour at  $T$  and  $P$ , we have

$$S_V - S_L = \frac{L}{T}. \quad (6.68)$$

Now, for a change of phase at  $T + dT$  and  $P + dP$ , each term of (6.68) will be changed. We have now

$$(S_V + dS_V) - (S_L + dS_L) = \frac{L}{T} + d \left( \frac{L}{T} \right). \quad (6.69)$$

From (6.68) and (6.69),

$$dS_V - dS_L = d \left( \frac{L}{T} \right) \quad \text{i.e.,} \quad \frac{c_2 dT}{T} - \frac{c_1 dT}{T} = d \left( \frac{L}{T} \right)$$

$$\text{or, } c_2 - c_1 = T \frac{d}{dT} \left( \frac{L}{T} \right), \quad (6.70)$$

where  $c_2, c_1$  are the specific heats of saturated vapour and liquid respectively. (6.70) is evidently the second latent heat equation.

### (c) Surface Energy Equation

Let us stretch a liquid film adiabatically so that there is a temperature change by  $dT$  and a surface area change by  $d\alpha$ . Then, the change in the internal energy of the film is

$$dU = \left( \frac{dU}{dT} \right)_\alpha dT + \left( \frac{dU}{d\alpha} \right)_T d\alpha = cdT + Ed\alpha, \quad (6.71)$$

where  $c$  is the specific heat of the film and  $E$  is the surface energy/area.

Now, if heat is supplied to accomplish this change, then it must be

$$dQ = dU + dW = dU - \Sigma d\alpha, \quad (6.72)$$

since all the external work is done in stretching the film against surface tension  $\Sigma$ . Substituting (6.71) in (6.72),

$$dQ = cdT + (E - \Sigma)d\alpha$$

$$\text{or, } dS = \frac{dQ}{T} = \frac{cdT}{T} + \frac{(E - \Sigma)}{T} d\alpha. \quad (6.73)$$

Since  $dS$  is a perfect differential, from (6.29)-(6.31) and (6.73),

$$\left[ \frac{d\left(\frac{S}{T}\right)}{d\alpha} \right]_T = \left[ \frac{d}{dT} \left( \frac{E - \Sigma}{T} \right) \right]_\alpha$$

$$\text{or, } \left( \frac{dc}{d\alpha} \right)_T = T \left[ \frac{d}{dT} \left( \frac{E - \Sigma}{T} \right) \right]_\alpha, \quad (6.74)$$

since  $T$  is constant on the left-hand side.

Again, since  $dU$  is a perfect differential in (6.71), we have from (6.29)-(6.31)

$$\left( \frac{dc}{d\alpha} \right)_T = \left( \frac{dE}{dT} \right)_\alpha. \quad (6.75)$$

From (6.74) and (6.75),

$$\left( \frac{dE}{dT} \right)_\alpha = T \left[ \frac{d}{dT} \left( \frac{E - \Sigma}{T} \right) \right]_\alpha$$

$$\text{or, } E = \Sigma - T \left( \frac{d\Sigma}{dT} \right)_\alpha. \quad (6.76)$$

This is the surface energy equation derived in section 6.3.

### (d) E.M.F. of Reversible Cells

The e.m.f.  $E$  of an electric cell is the work done for flow of unit charge from one plate to the other. Then,  $E$  at a definite temperature  $T$  should be identified by  $-\Delta F$ , the change in free energy of the cell at that temperature. Further, for flow of unit charge, an amount of internal (chemical) energy  $H$  is used up. Evidently,  $H$  should be  $-\Delta U$ .

Now, we have from Gibbs-Helmholtz equation (6.48) under isothermal condition

$$-\Delta F = -\Delta U + T \left[ \frac{d(-\Delta F)}{dT} \right]_V.$$

On substitution of the values of  $-\Delta F$  and  $-\Delta U$  as explained above,

$$E = H + T \left( \frac{dE}{dT} \right)_V. \quad (6.77)$$

This is the Helmholtz equation (also sometimes called Gibbs-Helmholtz equation).

## 6.9 Some Thermodynamic Relations\*

We shall derive in this section some interesting thermodynamic relations.

### (a) Specific Heat at Constant Volume

We have Maxwell's relation

$$\left( \frac{dS}{dV} \right)_T = \left( \frac{dP}{dT} \right)_V \quad (6.47)$$

Differentiating both sides with respect to  $T$  at constant  $V$ ,

$$\left[ \frac{d}{dT} \left( \frac{dS}{dV} \right)_T \right]_V = \left( \frac{d^2 P}{dT^2} \right)_V$$

or, from (6.28),

$$\left[ \frac{d}{dV} \left( \frac{dS}{dT} \right)_V \right]_T = \left( \frac{d^2 P}{dT^2} \right)_V.$$

Multiplying both sides by  $T$ ,

$$\left[ \frac{d}{dV} \left( T \frac{dS}{dT} \right)_V \right]_T = T \left( \frac{d^2 P}{dT^2} \right)_V. \quad (6.78)$$

Since differentiation w.r.t.  $V$  is carried out at constant  $T$ ,  $T$  can enter inside on the left-hand side. But considering unit mass of the substance,

$$c_v = \left( T \frac{dS}{dT} \right)_V \quad (6.79)$$

so that from (6.78) and (6.79),

$$\left( \frac{dc_v}{dV} \right)_T = T \left( \frac{d^2 P}{dT^2} \right)_V \quad (6.80)$$

### (b) Specific Heat at Constant Pressure

Here we start from Maxwell's relation :

$$\left( \frac{dS}{dP} \right)_T = - \left( \frac{dV}{dT} \right)_P. \quad (6.43)$$

\*For a large number of such relations, see Ewing, *Thermodynamics for Engineers*; Callendar, *Properties of Steam*; Bridgman, Phys. Rev., Vol. 3, P. 273 (1914) and Shaw, A. N., *Phil. Trans. Roy. Soc., A*, Pp. 234, 299 (1935).

Differentiating both sides with respect to  $T$  at constant  $P$  and using (6.28),

$$\left[ \frac{d}{dP} \left( \frac{dS}{dT} \right)_P \right]_T = - \left( \frac{d^2V}{dT^2} \right)_P.$$

Now, multiplying both sides by  $T$  as in case (a),

$$\left[ \frac{d}{dP} \left( T \frac{dS}{dT} \right)_P \right]_T = -T \left( \frac{d^2V}{dT^2} \right)_P. \quad (6.81)$$

For unit mass of the substance under consideration,

$$c_p = \left( T \frac{dS}{dT} \right)_P \quad (6.82)$$

so that from (6.81) and (6.82),

$$\left( \frac{dc_p}{dP} \right)_T = -T \left( \frac{d^2V}{dT^2} \right)_P. \quad (6.83)$$

### (c) Difference of Specific Heats

We have from (6.82)

$$\begin{aligned} c_p &= T \left( \frac{dS}{dT} \right)_P = T \left[ \frac{\left( \frac{dS}{dT} \right)_V dT + \left( \frac{dS}{dV} \right)_T dV}{dT} \right]_P \quad [\text{taking } S = f(T, V)] \\ &= T \left( \frac{dS}{dT} \right)_V + T \left( \frac{dS}{dV} \right)_T \left( \frac{dV}{dT} \right)_P \\ &= c_v + T \left( \frac{dP}{dT} \right)_V \left( \frac{dV}{dT} \right)_P \quad [\text{from (6.79) and (6.47)}] \\ \text{i.e., } c_p - c_v &= T \left( \frac{dP}{dT} \right)_V \left( \frac{dV}{dT} \right)_P. \end{aligned} \quad (6.84)$$

Now, from  $P = f(V, T)$ ,

$$dP = \left( \frac{dP}{dV} \right)_T dV + \left( \frac{dP}{dT} \right)_V dT. \quad (6.85)$$

Now, under isobaric condition, i.e., for  $dP = 0$ ,

$$\begin{aligned} 0 &= \left( \frac{dP}{dV} \right)_T (dV)_P + \left( \frac{dP}{dT} \right)_V (dT)_P \quad \text{or, } 0 = \left( \frac{dP}{dV} \right) \left( \frac{dV}{dT} \right)_P + \left( \frac{dP}{dT} \right)_V \\ \text{i.e., } \left( \frac{dP}{dT} \right)_V &= - \left( \frac{dP}{dV} \right)_T \left( \frac{dV}{dT} \right)_P. \end{aligned} \quad (6.86)$$

From (6.84) and (6.86),

$$c_p - c_v = -T \left( \frac{dP}{dV} \right)_T \left( \frac{dV}{dT} \right)_P^2 \quad (6.87)$$

$$= TV \left( -\frac{dP}{\frac{dV}{V}} \right)_T \left( \frac{dV}{VdT} \right)_P^2 = TV K_T \gamma_P^2, \quad (6.88)$$

where  $K_T$  (isothermal bulk modulus) =  $\left(-\frac{dP}{dV/V}\right)_T$  (6.89)

and  $\gamma_P$  (isobaric volume coefficient of expansion) =  $\left(\frac{dV}{VdT}\right)_P$ . (6.90)

Now, for a solid,  $\gamma_P = 3\alpha$  ( $\alpha$  = coeff. of linear expansion)

so that from (6.88),

$$c_p - c_v = 9TVK_T\alpha^2. \quad (6.91)$$

#### (d) Ratio between Isothermal and Adiabatic Elasticities

From (6.89),

$$K_T \text{ (isothermal elasticity)} = -V \left( \frac{dP}{dV} \right)_T \quad (6.92)$$

and  $K_S$  (adiabatic\* elasticity) =  $-V \left( \frac{dP}{dV} \right)_S$ . (6.93)

Then from (6.92) and (6.93),

$$\begin{aligned} \frac{K_S}{K_T} &= \frac{\left( \frac{dP}{dV} \right)_S}{\left( \frac{dP}{dV} \right)_T} = \frac{\left( \frac{dP}{dT} \right)_S \left( \frac{dT}{dV} \right)_S}{\left( \frac{dP}{dT} \right)_T \left( \frac{dT}{dV} \right)_T} = \frac{\left( \frac{dS}{dT} \right)_T \left( \frac{dT}{dV} \right)_S}{\left( \frac{dP}{dT} \right)_S \left( \frac{dT}{dV} \right)_T} \\ &= \frac{\left( \frac{dP}{dS} \right)_V \left( \frac{dV}{dT} \right)_P}{\left( \frac{dV}{dS} \right)_P \left( \frac{dP}{dT} \right)_V} \quad [\text{from Maxwell's four relations}] \\ &= \frac{\left( \frac{dS}{dT} \right)_P}{\left( \frac{dS}{dT} \right)_V} = \frac{T \left( \frac{dS}{dT} \right)_P}{T \left( \frac{dS}{dT} \right)_V} = \frac{c_p}{c_v} = \gamma \end{aligned} \quad (6.94)$$

#### (e) Ratio between Isobaric and Adiabatic Volume Coefficients of Expansion

From (6.90),

$$\gamma_P \text{ (isobaric volume coefficient of expansion)} = \frac{1}{V} \left( \frac{dV}{dT} \right)_P. \quad (6.95)$$

$\gamma_S$  (adiabatic volume coefficient of expansion)

$$= -\frac{1}{V} \left( \frac{dV}{dT} \right)_S, \quad (-\text{ve sign, because temperature falls with increase in volume under adiabatic condition}) \quad (6.96)$$

Then, from (6.95) and (6.96),

$$\begin{aligned} \frac{\gamma_S}{\gamma_P} &= \frac{-\left( \frac{dV}{dT} \right)_S}{\left( \frac{dV}{dT} \right)_P} = \frac{-1}{\left( \frac{dT}{dV} \right)_S \left( \frac{dV}{dT} \right)_P} = \frac{1}{\left( \frac{dP}{dS} \right)_V \left( \frac{dV}{dT} \right)_P} \quad [\text{from (6.39)}] \\ &= \frac{1}{\left( \frac{dP}{dT} \right)_V \left( \frac{dT}{dS} \right)_V \left( \frac{dV}{dT} \right)_P} = \frac{T \left( \frac{dS}{dT} \right)_V}{T \left( \frac{dP}{dT} \right)_V \left( \frac{dV}{dT} \right)_P} \\ &= \frac{c_v}{c_p - c_v} \quad [\text{from (6.84)}] \\ &= \frac{1}{\gamma - 1}. \end{aligned} \quad (6.97)$$

\*Under adiabatic condition,  $S$  (entropy) does not change, since no heat is added to the system.

## (f) Ratio between Isochoric and Adiabatic Pressure Coefficients

$$\begin{aligned}
 \frac{\beta_S \text{ (adiabatic pr. coeff.)}}{\beta_V \text{ (isochoric pr. coeff.)}} &= \frac{\left(\frac{dP}{dT}\right)_S}{\left(\frac{dP}{dT}\right)_V} = \frac{\left(\frac{dP}{dT}\right)_S}{\left(\frac{dP}{dT}\right)_V} \\
 &= \frac{1}{\left(\frac{dT}{dP}\right)_S \left(\frac{dP}{dT}\right)_V} = \frac{1}{\left(\frac{dV}{dS}\right)_P \left(\frac{dP}{dT}\right)_V} \quad [\text{from (6.52)}] \\
 &= \frac{1}{\left(\frac{dT}{dV}\right)_P \left(\frac{dS}{dT}\right)_P \left(\frac{dP}{dT}\right)_V} = \frac{T \left(\frac{dS}{dT}\right)_P}{T \left(\frac{dV}{dT}\right)_P \left(\frac{dP}{dT}\right)_V} \\
 &= \frac{c_p}{c_p - c_v} \quad [\text{from (6.84)}] \\
 &= \frac{\gamma}{\gamma - 1}. \tag{6.98}
 \end{aligned}$$

**Exercise 1.** Show from (6.84) that

(a) for a gm-molecule of a perfect gas,  $C_P - C_V = R$

and (b) for a gm-molecule of a van der Waals gas,  $C_P - C_V = \frac{R}{1 - \frac{2a}{V^3} \frac{(V-b)^2}{RT}} \approx R \left(1 + \frac{2a}{RTV}\right)$ .

**Exercise 2.** Prove that for a gm-molecule of a van der Waals gas, the change of entropy for a rise of temperature from  $T_1$  to  $T_2$  is

$$\Delta S = C_V \log_e \left( \frac{T_2}{T_1} \right) + R \log_e \left( \frac{V_2 - b}{V_1 - b} \right).$$

**Exercise 3.** Prove the following relations :

$$(a) \text{ (i) } dS = \frac{c_v}{T} dT + \left( \frac{dP}{dT} \right)_V dV \quad \text{ (ii) } dS = \frac{c_p}{T} dT - \left( \frac{dV}{dT} \right)_P dP$$

**Hints :** Use  $dS = \frac{dU}{T} + \frac{P}{T} dV$  and Maxwell's relations.

$$(b) \text{ (i) } \left( \frac{dU}{dV} \right)_P = c_p \left( \frac{dT}{dV} \right)_P - P \quad \text{ (ii) } \left( \frac{dU}{dS} \right)_T = T - P \left( \frac{dT}{dP} \right)_V.$$

**Hints :** Use  $dU = TdS - PdV$

$$(c) \text{ (i) } \left( \frac{dH}{dS} \right)_V = T - V \left( \frac{dT}{dV} \right)_S \quad \text{ (ii) } \left( \frac{dH}{dS} \right)_T = T - V \left( \frac{dT}{dV} \right)_P$$

$$\text{ (iii) } \left( \frac{dH}{dV} \right)_T = T \left( \frac{dP}{dT} \right)_V + V \left( \frac{dP}{dV} \right)_T.$$

**Hints :**  $dH = TdS + VdP$  and Maxwell's relations.

$$(d) \text{ (i) } U = F - T \left( \frac{dF}{dT} \right)_V \quad \text{ (ii) } c_v = -T \left( \frac{d^2 F}{dT^2} \right)_V.$$

**Hints :** Use  $F = U - TS$  and  $dF = -PdV - SdT$ . For (ii) start from (i).

$$(e) (i) H = G - T \left( \frac{dG}{dT} \right)_P \quad (ii) c_p = -T \left( \frac{d^2G}{dT^2} \right)_P.$$

**Hints :** Use  $G = U - TS + PV$  and  $dG = -SdT + VdP$ . For (ii), start from (i).

$$(f) (i) \left( \frac{dU}{dV} \right)_T = T \left( \frac{dP}{dT} \right)_V - P \quad (ii) dU = c_v dT + \left\{ T \left( \frac{dP}{dT} \right)_V - P \right\} dV.$$

**Hints :** Use  $dU = TdS - PdV$  and one of Maxwell's relations. For (ii), make use of (i) also along with  $U = f(V, T)$ .

## 6.10 Thermo-electric Effect

Consider a thermocouple consisting of two metals  $A$  and  $B$  (Fig. 6.5).  $T_2$  at junction 2 is larger than  $T_1$  at junction 1 and the Peltier coefficient\*  $\pi_2$  at  $T_2$  is greater than  $\pi_1$  at  $T_1$ .

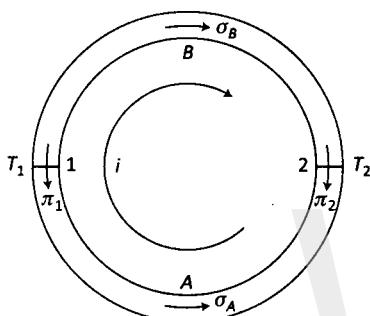


Fig. 6.5: Thermocouple

Thomson coefficients\*\*  $\sigma_A$  and  $\sigma_B$  are considered as positive, i.e., the electromotive forces for Thomson effect are directed from points of lower to points of higher temperature. The total e.m.f. of the circuit is

$$E = \pi_2 - \pi_1 - \int_{T_1}^{T_2} \sigma_A dT + \int_{T_1}^{T_2} \sigma_B dT. \quad (6.99)$$

Now, for this work done (i.e.,  $E$ ) for flow of unit charge through the circuit, an amount of heat  $\pi_2$  is absorbed at junction 2 and  $\int_{T_1}^{T_2} \sigma_B dT$  is absorbed in  $B$  while an amount of heat  $\pi_1$  is rejected at junction 1 and  $\int_{T_1}^{T_2} \sigma_A dT$  is rejected in  $A$ .

Now all these effects are exactly reversed if unit charge is passed through the circuit from some external source in the reverse direction. But although the Peltier and Thomson effects are thus reversible, the Joule effect occurring with the flow of charge is independent of the direction of current and is, therefore, irreversible. But we may not take note of the Joule effect if the resistance of the thermocouple is negligible. Then, the thermocouple behaves as a *reversible heat engine—reversible* because all the effects (neglecting the Joule effect) are reversible and a *heat engine* because work ( $E$  for flow of each unit charge) is done at the cost of heat absorbed. Then, we can apply to the thermocouple the second law of thermodynamics (the law which represents the behaviour of a reversible heat engine) [See equation (5.46)] :

$$\sum \frac{Q}{T} = 0, \quad (6.100)$$

where  $Q$  is the heat absorbed (or rejected) at  $T$  (the sum being considered as algebraic).

Now, considering the flow of unit charge round the circuit, we have from (6.100),

$$\frac{\pi_2}{T_2} - \frac{\pi_1}{T_1} - \int_{T_1}^{T_2} \frac{\sigma_A dT}{T} + \int_{T_1}^{T_2} \frac{\sigma_B dT}{T} = 0. \quad (6.101)$$

\*The Peltier coefficient ( $\pi$ ) for any junction of two dissimilar metals at any temperature is the potential difference at the junction at that temperature. It varies with temperature.

\*\*The Thomson coefficient ( $\sigma$ ) of any conductor is the potential difference generated between any two points of it due to unit degree difference in temperature. If the ends of the conductor are at  $T_2$  and  $T_1$  ( $T_2 > T_1$ ), then the total potential difference due to this cause is  $\int_{T_1}^{T_2} \sigma dT$ .  $\sigma$  is considered as positive if a point at a lower temperature is at a higher potential than a point at a higher temperature.  $\sigma$  is negative under the reverse condition.

Now, for a thermocouple whose junctions are at temperatures  $T (= T_1)$  and  $T + dT (= T_2)$ , (6.99) and (6.101) become respectively

$$dE = d\pi - (\sigma_A - \sigma_B)dT \quad (6.102)$$

$$\text{and } d\left(\frac{\pi}{T}\right) - \frac{\sigma_A - \sigma_B}{T}dT = 0. \quad (6.103)$$

Now, from (6.102) and (6.103),

$$\frac{dE}{dT} = \frac{d\pi}{dT} - T \frac{d}{dT} \left( \frac{\pi}{T} \right) = \frac{\pi}{T} \quad (6.104)$$

$$\text{so that } \pi = T \frac{dE}{dT}. \quad (6.104)$$

Again, from (6.103) and (6.104),

$$\sigma_A - \sigma_B = T \frac{d^2 E}{dT^2}. \quad (6.105)$$

(6.104) and (6.105) give the expressions for the Peltier and the Thomson coefficient respectively for a thermocouple.

## 6.11 Magneto-caloric Effect\*

In section 2.25, we have presented a qualitative theory of this effect. Now, since we are already familiar with the second law of thermodynamics, we shall undertake a detailed calculation here.

Let us consider a gm-molecule of a paramagnetic substance at temperature  $T$ , pressure  $P$ , volume  $V$  and under a magnetic field  $H$  with  $M$  as the induced magnetic moment. Now, if an amount of heat  $dQ$  is added and also if  $H$  increases, at the same time,  $M$  by  $dM$ , then by the first law of thermodynamics, since  $HdM$  is the work done by  $H$  to change  $M$  by  $dM$ ,

$$dQ + HdM = dU + PdV$$

or  $dQ = dU + dW = dU + PdV - HdM. \quad (6.106)$

where  $dW (= PdV - HdM)$  is the net work done by the substance due to the addition of heat  $dQ$ . Now, since in experiments on magnetisation the change in volume is negligible,  $dV = 0$  so that (6.106) becomes

$$dQ = dU - HdM. \quad (6.107)$$

Applying the second law of thermodynamics [eqn. (5.54)] to (6.107),

$$dU = TdS + HdM. \quad (6.108)$$

Now, the state of a magnetised body under a magnetic field  $H$  is defined not only by  $U$ ,  $T$ ,  $S$ , etc. but also by  $H$  and  $M$ , because the state of magnetisation depends on  $H$  and  $M$ . Then, we may define a function of state in the form\*\* :

$$\zeta = U - HM. \quad (6.109)$$

$d\zeta$  at constant  $H$  is  $dU - HdM = dQ$  (heat added to the system). So  $\zeta$  corresponds to enthalpy here.

\*See Saha and Srivastava, *A Treatise on Heat*, Pp. 533–34 (1958); Smith, R. A., *Thermodynamics*, Pp. 75–78, (1952).

\*\*See Hoare, F. E., *Thermodynamics*, Pp. 227–8 (1952).

Now, from (6.108) and (6.109),

$$d\zeta = TdS - MdH. \quad (6.110)$$

Since  $\zeta$  is a function of state by definition,  $d\zeta$  is a perfect differential here so that from (6.29)–(6.31) and (6.110),

$$\left(\frac{dT}{dH}\right)_S = - \left(\frac{dM}{dS}\right)_H. \quad (6.111)$$

With  $T \left(\frac{dS}{dT}\right)_H = C_H$ , the specific heat (gram-molecular) of the substance under constant field  $H$ , we have from (6.111),

$$\left(\frac{dT}{dH}\right)_S = - \left(\frac{dM}{dT}\right)_H / \left(\frac{dS}{dT}\right)_H = - \frac{T}{C_H} \left(\frac{dM}{dT}\right)_H. \quad (6.112)$$

This gives the change in temperature during adiabatic magnetisation or demagnetisation. This phenomenon is called the *magneto-caloric effect*.

On integration of (6.112) from the initial (*i*) to the final (*f*) state,

$$T_f - T_i = - \int_{H_i}^{H_f} \frac{T}{C_H} \left(\frac{dM}{dT}\right)_H dH. \quad (6.113)$$

If  $\chi$  is the susceptibility per cc,

$$M = \chi HV. \quad (6.114)$$

Again,  $\chi$  is related to  $T$  by Curie's law :

$$\chi = \frac{C}{T}, \quad (6.115)$$

where  $C$  is a constant.

From (6.113)–(6.115),

$$T_f - T_i = \frac{CV}{2C_H T_i} (H_f^2 - H_i^2), \quad (6.116)$$

where we have taken  $\overline{C_H}$  for the range of integration and have taken  $T$  approximately as  $T_i$ , assuming the variation of these two quantities to be small compared to the variation of other quantities involved in integration.

For  $H_f = 0$ , the fall in temperature is

$$\Delta T = T_i - T_f = \frac{CV}{2T_i \overline{C_H}} H_i^2 \quad (6.117)$$

**Exercise :** Find the difference between the specific heat under constant field ( $C_H$ ) and that at constant magnetisation ( $C_M$ ).

**Hints :** Comparison of (6.35) and (6.107) shows that in (6.107),  $-H$  and  $M$  play the roles of  $P$  and  $V$ . Then, from (6.84),

$$\begin{aligned} C_H - C_M &= -T \left(\frac{dH}{dT}\right)_M \left(\frac{dM}{dT}\right)_H = \frac{MH}{T} \quad [\text{from (6.114) and (6.115)}] \\ &= \frac{H^2 \chi V}{T}. \end{aligned}$$

## 6.12 Joule-Thomson Effect

We have for the change in enthalpy  $H$

$$dH = TdS + VdP. \quad (6.50)$$

Now, since in Joule-Thomson effect  $H$  remains constant, we have from (6.50)

$$TdS + VdP = 0. \quad (6.118)$$

With  $S = f(P, T)$ ,

$$dS = \left( \frac{dS}{dP} \right)_T dP + \left( \frac{dS}{dT} \right)_P dT = - \left( \frac{dV}{dT} \right)_P dP + \left( \frac{dS}{dT} \right)_P dT \quad (6.119)$$

(from one of Maxwell's relations)

From (6.118) and (6.119),

$$-T \left\{ \left( \frac{dV}{dT} \right)_P dP - \left( \frac{dS}{dT} \right)_P dT \right\} + VdP = 0$$

$$\text{or, } C_p \left( \frac{dT}{dP} \right)_H = T \left( \frac{dV}{dT} \right)_P - V$$

$$\text{i.e., } \left( \frac{dT}{dP} \right)_H = \frac{1}{C_p} \left\{ T \left( \frac{dV}{dT} \right)_P - V \right\}. \quad (6.120)$$

$\left( \frac{dT}{dP} \right)_H$  is a measure of Joule-Thomson cooling. We calculate the value of  $\left( \frac{dT}{dP} \right)_H$  for a van der Waals gas. Writing van der Waals' equation in the form :

$$V = \frac{RT}{P} - \frac{a}{PV} + \frac{ab}{PV^2} + b$$

and simplifying it by replacing  $PV$  by  $RT$ ,

$$V = \frac{RT}{P} - \frac{a}{RT} + \frac{abP}{R^2T^2} + b. \quad (6.121)$$

From (6.121),

$$\left( \frac{dV}{dT} \right)_P = \frac{R}{P} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3}. \quad (6.122)$$

From (6.120) and (6.122),

$$\left( \frac{dT}{dP} \right)_H = \frac{1}{C_p} \left\{ \frac{2a}{RT} - \frac{3abP}{R^2T^2} - b \right\}. \quad (6.123)$$

At low values of  $P$ ,

$$\left( \frac{dT}{dP} \right)_H = \frac{1}{C_p} \left( \frac{2a}{RT} - b \right). \quad (6.124)$$

Next, we undertake an analysis of Joule-Thomson effect. We have from  $H = U + PV$ ,  $dH = dU + PdV + VdP$  so that

$$\left( \frac{dH}{dP} \right)_T = \left( \frac{dU}{dP} \right)_T + P \left( \frac{dV}{dP} \right)_T + V. \quad (6.125)$$

Again from  $dU = TdS - PdV$  [(6.37)]

$$\left(\frac{dU}{dP}\right)_T = T\left(\frac{dS}{dP}\right)_T - P\left(\frac{dV}{dP}\right)_T = -T\left(\frac{dV}{dT}\right)_P - P\left(\frac{dV}{dP}\right)_T. \quad (6.126)$$

(from one of Maxwell's relations)

From (6.125) and (6.126),

$$\left(\frac{dH}{dP}\right)_T = V - T\left(\frac{dV}{dT}\right)_P. \quad (6.127)$$

From (6.120) and (6.127),

$$\left(\frac{dT}{dP}\right)_H = -\frac{1}{C_p}\left(\frac{dH}{dP}\right)_T \quad (6.128)$$

$$= -\frac{1}{C_p} \left\{ \left(\frac{dU}{dP}\right)_T + \left(\frac{d(PV)}{dP}\right)_T \right\}. \quad (6.129)$$

Thus, the Joule-Thomson effect arises from two causes—(1)  $\left(\frac{dU}{dP}\right)_T$  and (2)  $\left(\frac{d(PV)}{dP}\right)_T$ .

$\left(\frac{dU}{dP}\right)_T^*$  represents intermolecular attraction and is always negative because potential energy of the attractive forces between the molecules is diminished by decrease in volume or increase in pressure. This term, therefore, always represents a cooling effect. But the other term, i.e.,  $\left(\frac{d(PV)}{dP}\right)_T^{**}$ , which represents departure from Boyle's law may be a cooling or heating effect.

### 6.13 Correction of a Gas Thermometer by Joule-Thomson Effect

We have just seen above in (6.129) that the Joule-Thomson effect gives an indication of the deviations of a real gas from a perfect gas. Further, in the preceding chapter, it has been found that the perfect gas scale is identical with the thermodynamic scale. So it may be expected that the Joule-Thomson effect will give information as to the difference between a real gas scale and the absolute scale of temperature.

The Joule-Thomson effect is given by

$$C_p \left(\frac{dT}{dP}\right)_H = T \left(\frac{dV}{dT}\right)_P - V, \quad [(6.120)]$$

where  $T$  refers to the absolute thermodynamic scale of temperature.

Now, suppose we have a constant pressure gas thermometer, made with the same gas as used in the Joule-Thomson experiment. It is our object now to find the connection between the indications of this thermometer and the absolute thermodynamic scale.

Let  $\theta$  be the reading of the gas thermometer corresponding to the absolute temperature  $T$ . Now, since  $T$  must be a function of  $\theta$ ,

$$\left(\frac{dV}{dT}\right)_P = \left(\frac{dV}{d\theta} \frac{d\theta}{dT}\right)_P = \frac{d\theta}{dT} \left(\frac{dV}{d\theta}\right)_P \quad (6.130)$$

\*  $U$  = kinetic energy + potential energy. At constant  $T$ , kinetic energy is constant so that  $(dU/dP)_T$  refers potential energy, i.e., intermolecular attraction only.

\*\* It can be seen from (6.121), neglecting the second-order term in  $a, b$  of the right-hand side that  $(d(PV)/dP)_T$  is approximately equal to  $-\frac{a}{RT} + b$ , the value of which may be +ve or -ve depending on  $T$ .

$$\text{and } C_p = \left( \frac{dQ}{dT} \right)_P = \left( \frac{dQ}{d\theta} \frac{d\theta}{dT} \right)_P = C'_p \frac{d\theta}{dT}, \quad (6.131)$$

where  $C'_p$  is the specific heat at constant pressure of the gas on the gas scale itself. Further

$$\left( \frac{dT}{dP} \right)_H = \frac{dT}{d\theta} \left( \frac{d\theta}{dP} \right)_H. \quad (6.132)$$

Then, from (6.120) and (6.130)–(6.132),

$$C'_p \left( \frac{d\theta}{dP} \right)_H + V = T \left( \frac{dV}{d\theta} \right)_P \frac{d\theta}{dT}. \quad (6.133)$$

On integration,

$$\int_{T_0}^T \frac{dT}{T} = \int_{\theta_0}^{\theta} \frac{\left( \frac{dV}{d\theta} \right)_P d\theta}{C'_p \left( \frac{d\theta}{dP} \right)_H + V}$$

i.e.,  $\log_e \frac{T}{T_0} = \int_{\theta_0}^{\theta} \frac{\left( \frac{dV}{d\theta} \right)_P d\theta}{C'_p \left( \frac{d\theta}{dP} \right)_H + V}, \quad (6.134)$

where  $T_0, \theta_0$ , refer to the melting point of ice.

Now, if  $T$  and  $\theta$  correspond to the boiling point of water, (6.134) gives

$$\log_e \left( \frac{T_0 + 100}{T_0} \right) = \int_{\theta_0}^{\theta_0 + 100} \frac{\left( \frac{dV}{d\theta} \right)_P d\theta}{C'_p \left( \frac{d\theta}{dP} \right)_H + V}. \quad (6.135)$$

Now, knowing the different quantities of the right-hand side at different temperatures between  $\theta_0$  and  $\theta_0 + 100$ , the integral can be evaluated graphically and  $T_0$  is determined. Roebuck\* has found from (6.135) the value  $T_0 = 273.160$  K in excellent agreement with the value found by extrapolation to zero pressure (See section 5.8).

Having found  $T_0$  thus, the value of any temperature  $T$  can be obtained from (6.134), provided the different quantities of the right-hand side of this equation are known at different temperatures between  $\theta_0$  and  $\theta$  for graphical evaluation of the integral.

However, the existing data on the Joule-Thomson effect are not sufficient and so the corrections are usually calculated from deviation from the perfect gas law (See section 5.8).

## 6.14 Expression for Saturated Vapour Pressure

By integration of the first latent heat equation, an equation connecting the pressure of a saturated vapour with the temperature may be obtained. We have

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}. \quad [(6.58)]$$

Neglecting  $V_1$ , the specific volume of the condensed (liquid or solid) phase compared to  $V_2$  that of the vapour phase,

$$\frac{dP}{dT} = \frac{L}{TV_2} = \frac{ML}{RT^2} P, \quad (6.136)$$

assuming that the saturated vapour obeys the law of perfect gases ( $M$  = mass of a gm-molecule of vapour).

\*Roebuck, J. R., Phys., Rev. 50, P. 370 (1936).

Now, in order to integrate (6.136), we must find an expression of  $L$ . We now proceed to do so.

Let us start with unit mass of a condensed phase (liquid or solid) at temperature  $T_1$ , and vaporize it at the same temperature. Denoting by  $L_1$ , the latent heat at  $T_1$ , the net gain in internal energy by the vapour phase is

$$L_1 - P_1 V_1,$$

where  $P_1$  is the vapour pressure at  $T_1$ , and  $V_1$  here the specific volume of vapour.  $P_1 V_1$  is the work done by the vapour against  $P_1$  to occupy a volume  $V_1$ . So  $P_1 V_1$  has been subtracted from  $L_1$ . Now, as we have already assumed the vapour to behave like a perfect gas, the above expression may be written as

$$L_1 - \frac{RT_1}{M}.$$

If the vapour is now heated at constant volume from  $T_1$  to  $T_2$ , the internal energy will further increase by

$$\int_{T_1}^{T_2} c_v dT$$

so that the total gain in internal energy of the vapour is

$$L_1 - \frac{RT_1}{M} + \int_{T_1}^{T_2} c_v dT. \quad (6.137)$$

Now, we shall calculate the same quantity in a different way. First we heat the condensed phase from  $T_1$  to  $T_2$  at constant pressure and then allow it to vaporize at  $T_2$ . Neglecting the small amount of work done against the constant external pressure during heating from  $T_1$  to  $T_2^*$ , the total gain in internal energy of the vapour phase is

$$L_2 - \frac{RT_2}{M} + \int_{T_1}^{T_2} (c_p)^c dT, \quad (6.138)$$

where  $L_2$  is the latent heat of vaporization at  $T_2$  and  $(c_p)^c$  is the specific heat of the condensed phase.

Since the vapour has been assumed to obey the perfect gas law, the change in its internal energy will be independent of its volume. Therefore, the two expressions for the gain in internal energy will be equal. Then, equating (6.137) and (6.138),

$$L_2 = L_1 + \int_{T_1}^{T_2} \{c_p - (c_p)^c\} dT \quad (6.139)$$

where  $c_p$  has been put in place of  $c_v + \frac{R}{M}$ .

Now writing  $T_1 = 0$ ,  $T_2 = T$ , we obtain from (6.139)

$$L = L_0 + \int_0^T \{c_p - (c_p)^c\} dT, \quad (6.140)$$

where  $L_0$  is the latent heat at the absolute zero.

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\* Joos, G., *Theoretical Physics*, P. 528 (1956).

Now, putting the value of  $L$  from (6.140) in (6.136),

$$\frac{dP}{P} = \frac{ML_0}{R} \frac{dT}{T^2} + \frac{M}{R} \frac{dT}{T^2} \int_0^T \{c_p - (c_p)^c\} dT.$$

On integration,

$$\log_e P = -\frac{ML_0}{RT} + \int_0^T \frac{M}{R} \frac{dT}{T^2} \int_0^T \{c_p - (c_p)^c\} dT + \text{constant}. \quad (6.141)$$

For most practical purposes, it is convenient to use common logarithms and express pressures in atmospheres. Then, writing  $ML_0 = \lambda_0$ ,  $M c_p = C_p$  and  $M(c_p)^c = C_p^c$ , we have from (6.141)

$$\log_{10} P = -\frac{\lambda_0}{2.302RT} + \frac{1}{2.302R} \int_0^T \frac{dT}{T^2} \int_0^T (C_p - C_p^c) dT + C, \quad (6.142)$$

where  $C$ , the constant of integration, has been called the *chemical constant* by Nernst. If we take for a monatomic substance  $C_p = \frac{5}{2}R$  considering it independent of temperature, then (6.142) becomes

$$\log_{10} P = -\frac{\lambda_0}{2.302RT} + \frac{5}{2} \log_{10} T - \frac{1}{2.302R} \int_0^T \frac{dT}{T^2} \int_0^T C_p^c dT + C \quad (6.143)$$

$C$  cannot be evaluated classically. It will be seen in section 11.7 that this can be done by application of quantum statistics.

## 6.15 Gibbs' Phase Rule

So far in this chapter we have considered the equilibrium between different states of aggregation of a single substance (say, water in three states : solid, liquid and vapour). Now, we proceed to discuss the equilibrium of a heterogeneous system, i.e., the equilibrium between mixtures of various substances. For this purpose, we must, at the outset, familiarise ourselves with a few definitions.

Each distinct, physically homogeneous part of a system is called a *phase*. A phase is bounded by a surface, and is mechanically separable from other parts of the system. There may exist together in a system several liquid phases (e.g., immiscible oil and water constitute two liquid phases in a system), or several solid phases (e.g., a mixture of two solid substances, say, ice and salt make up two solid phases). On the other hand, two gases in contact with one another, but not mixed, can never be in equilibrium. They ultimately get intimately mixed up and, therefore, constitute a single gaseous phase.

Besides the phases, a system is characterised by the number of *components* present in each phase. By the term, *components*, is meant the smallest number of independently variable constituents by means of which the composition of each phase can be completely specified. In simple cases, it may not be difficult to identify the components. For instance, in a solution of salt in water (or in a solution of  $H_2SO_4$  in water) one may say that the independent components are water and salt (or  $H_2SO_4$  and water) and, therefore, the number of components is two. But this task becomes difficult for complicated systems like an aqueous solution of NaCl, NaBr, KCl and KBr, say. There is, however, a simple rule to arrive at the total number of components in a system, simple or complicated. Find the number of chemical elements contained in a certain phase of the system and out of these, reject those elements whose quantitative estimation is dependent on the rest of the elements. First, take the simple example of a solution of NaCl in water. Here the elements are Na, Cl, H and O, but the amount of Cl depends on the amount

of Na and that of O on H. Thus, there are just two independent components. Similarly, in the case of  $H_2SO_4$  solution in water, the elements are H, O and S and out of these three, a knowledge of the masses of H and S exactly fix up the mass of O so that the number of independent components is here also two. It should be pointed out that in whatever manner one may choose the independent components (for instance, we chose earlier NaCl and water in an aqueous solution of NaCl, or  $H_2SO_4$  and water in an aqueous solution of  $H_2SO_4$ , as independent components, but now we have taken Na and O, say, for the first case and H and S, say, for the second case), their number will always be the same. Finally, however, we take up the complicated example, i.e., the solution of NaCl, NaBr, KCl and KBr in water. Evidently, the chemical elements are H, O, Na, K, Cl and Br. If we know the masses of H, Na, K and Cl, then the masses of O and Br may be calculated. Thus, the number of independent components is, in this case, four.

Lastly, we define the number of *degrees of freedom*\* of a system. This is the number of independent variables (such as temperature, pressure and relative concentrations of components) which determine the state of the system and which can be varied without destroying the nature of the system. That is to say, these independent variables can be altered and yet the different phases of the system will be in equilibrium in the new, altered state also.

**Detailed Calculation :** Now we proceed to deduce the *phase rule*—the rule which gives a relationship between the number of phases, the number of independent components and the number of degrees of freedom of a system. This law was first given by Willard Gibbs\*\* in 1875.

Let us consider<sup>†</sup> the equilibrium of a system having  $p$  phases and  $c$  components in each phase at temperature  $T$  and pressure  $P$ . We shall denote the phases by superscripts. and components by subscripts. Now, the total thermodynamic potential  $G$  of the system is given by

$$G = \sum_{r=1}^p G^r, \quad (6.144)$$

where  $G^r$  is the thermodynamic potential of the  $r$ th phase. In any reversible transfer of one or more components from one phase to another under equilibrium condition at a definite temperature  $T$  and a definite pressure  $P$ ,  $G$  remains unaltered so that from (6.40),

$$dG = 0. \quad (6.145)$$

(see the footnote on page 161 marked by \*)

Now, the expression for the thermodynamic potential of the  $r$ th phase is

$$G^r = U^r - TS^r + PV^r. \quad (6.146)$$

It is evident from (6.146) that  $G^r$  depends not only on  $T$  and  $P$ , but also on the masses of the various components of the phase, because the internal energy  $U^r$ , entropy  $S^r$  and volume  $V^r$  are each proportional to mass at a definite temperature and a definite pressure. Thus,

$$G^r = G^r(T, P, m_1^r, m_2^r, \dots, m_c^r). \quad (6.147)$$

It is, therefore, evident from (6.144) and (6.147) that  $G$  is also a function of  $T$ ,  $P$  and masses of various components in the different phases of the system. So at constant  $T$  and  $P$ ,  $G$  will be only a function of masses of various components in the different phases.

\*This is used here in a sense different from that in which it has been used in Chapter 2.

\*\*Gibbs, W., *Collected Works*, Vol. i, P. 55 et seq.

<sup>†</sup>We follow here the deduction given by W. Wilson in his *Theoretical Physics*, Vol. 1, Pp. 321–2, (1931).

Now, since the total mass of each component must be constant,

$$\sum_{r=1}^p m_s^r = \text{const.}, \quad s = 1, 2, \dots, c. \quad (6.148)$$

So in any reversible transfer\* of components from one phase to another under equilibrium condition, there must be a redistribution of mass of each component among the  $p$  phases. This redistribution occurs, say, for the  $s$ th component, by mass variations :

$$dm_s^1, dm_s^2, \dots dm_s^p \quad (6.149)$$

These may be mass increments in some phases and mass decrements in other phases so that the total variation is zero for the component according to (6.148),

$$dm_s^1 + dm_s^2 + \dots + dm_s^p = 0. \quad (6.150)$$

If we know any  $(p - 1)$  of the  $dm_s$ 's arbitrarily, the value of the remaining one is at once fixed up. Thus, for each component, there are  $(p - 1)$  independent mass variations ( $dm$ 's) so that there are altogether  $c(p - 1)$  such quantities. Let us represent all these independent  $c(p - 1)$  mass variations ( $dm$ 's) by

$$dx_1, dx_2, dx_3 \dots dx_{c(p-1)}. \quad (6.151)$$

This means that the independent mass variables in the whole system are

$$x_1, x_2, x_3 \dots x_{c(p-1)}. \quad (6.152)$$

Hence, at constant temperature and pressure,  $G$  is a function of  $x_1, x_2, x_3 \dots x_{c(p-1)}$ . Hence\*\*, from (6.27) and (6.145) for equilibrium,

$$dG = \left( \frac{\partial G}{\partial x_1} \right) dx_1 + \left( \frac{\partial G}{\partial x_2} \right) dx_2 + \dots + \left( \frac{\partial G}{\partial x_{c(p-1)}} \right) dx_{c(p-1)} = 0. \quad (6.153)$$

Now,  $dx$ 's are arbitrary variations, since the mass variations ( $dm$ 's) may have any value though small. Hence, from (6.153),

$$\frac{\partial G}{\partial x_1} = 0, \quad \frac{\partial G}{\partial x_2} = 0, \quad \dots, \quad \frac{\partial G}{\partial x_{c(p-1)}} = 0. \quad (6.154)$$

These  $c(p - 1)$  equations, therefore, represent the equilibrium condition of the system at constant temperature and pressure.

Let us now consider how many data are required to determine the state of the system. Evidently, temperature and pressure are two of these data. Besides these, we require the data determining the composition or constitution of each phase. If the masses of any  $(c - 1)$  components contained in unit mass of the phase are known, the mass of the remaining component is at once fixed up, and thus we know the relative proportions of the masses of all components of the phase, or in other words, the composition of the phase itself†. As there are  $p$  phases, we require  $p(c - 1)$  variables (i.e., quantities) to determine the composition of the

\*Take water in equilibrium with vapour at  $T$  and  $P$ . In this case, as many molecules come from the vapour to the liquid phase as go from the liquid to the vapour phase. This sort of reversible transfer of mass from one phase to another goes on. In either way of transfer of molecules, the total mass remains constant.

\*\*Here,  $\frac{\partial G}{\partial x_1} = \left( \frac{\partial G}{\partial x_1} \right)_{x_2, x_3, \dots, x_{c(p-1)}}$ , etc., etc.

†That is, if the percentages of any  $(c - 1)$  components of a phase are known, that of the remaining component becomes at once known, and thus the composition of the whole phase is also found out.

system. Hence, we require altogether  $2 + p(c - 1)$  quantities to completely describe the state of the system. Now,  $c(p - 1)$  equations in (6.154) which represent the equilibrium state of the system can, however, determine  $c(p - 1)$  quantities out of these  $2 + p(c - 1)$  quantities. Thus, the number of free variables which may be varied arbitrarily, *consistent with the maintenance of  $p$  phases in equilibrium*, is

$$2 + p(c - 1) - c(p - 1).$$

Hence, the number of degrees of freedom is

$$f = 2 + p(c - 1) - c(p - 1) = c - p + 2. \quad (6.155)$$

*This is the phase rule.*

**Applications of Phase Rule :** We consider now applications of the phase rule.

(a) Take water in contact with vapour at, say,  $20^\circ\text{C}$ . Here  $c = 1$  (water),  $p = 2$  so that from (6.155),  $f = 1$ . That is, there is one degree of freedom. The temperature or pressure may be varied arbitrarily (within certain limits\*) consistent with the two phases in equilibrium. At temperature  $= +0.0075^\circ\text{C}$  and  $P = 4.58$  mm (triple point), however, ice appears and now  $p$  being 3,  $f = 0$ . Now, there is no degree of freedom, i.e., no variable can be altered consistent with the three phases in equilibrium. If we raise the temperature, ice disappears and if we lower the temperature water disappears. For variations of pressure also similar things happen. At atmospheric pressure, however, the triple point is at temperature  $= 0^\circ\text{C}$ .

(b) Next take a dilute solution of common salt in water. In this case,  $p = 2$  (solution and vapour) and  $c = 2$  (salt and water) so that  $f = 2$ . Now, there are in this case three variables—temperature, pressure and concentration of the solution. Any two of these can be independently varied and the third variable is at once fixed up. Thus, for instance, a solution of a given concentration at a particular temperature shall have a definite vapour pressure. Suppose, the temperature is brought down to  $0^\circ\text{C}$ , then ice appears. Now,  $p$  being 3,  $f = 1$ . Now, only one of the three variables can be varied independently, consistent with the three phases in equilibrium. At temperature  $= -22^\circ\text{C}$ , vapour pressure  $= 0.73$  mm and concentration  $= 36\%$  (quadruple point or cryohydric point or eutectic point), some salt precipitates out of the solution. Now, there are 4 phases (solution, vapour, ice and solid salt) and  $f = 0$ . In other words, there is no degree of freedom and no variable can be altered consistent with the four phases in equilibrium.

This explains the phenomenon of *freezing mixtures*. When some common salt is mixed with ice, part of the salt dissolves in the layer of water over the ice. Since there are now 4 phases (salt, ice, solution and vapour), the system will be in equilibrium only at the quadruple point. So more salt dissolves and also ice melts, and the system ultimately reaches the quadruple point. Since this is usually done at atmospheric pressure, the temperature at the quadruple point is not exactly  $-22^\circ\text{C}$ , but slightly different from  $-22^\circ\text{C}$ .

## 6.16 Second-Order Phase Transitions

In any ordinary phase transition, corresponding to a change of state at constant temperature and pressure, the thermodynamic potential remains constant according to (6.40). Thus,

$$G_2 - G_1 = 0. \quad (6.156)$$

Further, since some latent heat is required, there is a jump in entropy given by

$$\left( \frac{dG_1}{dT} \right)_P - \left( \frac{dG_2}{dT} \right)_P = S_2 - S_1 = \frac{L}{T} \quad [\text{from (6.42)}]. \quad (6.157)$$

\*Experiment can determine the range of these limits; they cannot be decided by thermodynamics alone.

Also, there is a change in specific volume (and hence a change in density) so that from (6.42),

$$\left(\frac{dG_2}{dT}\right)_P - \left(\frac{dG_1}{dT}\right)_P = V_2 - V_1. \quad (6.158)$$

Finally, there is also a break in specific heat-temperature curve, the specific heat going to infinity on the low-temperature side.

Thus, it is evident from (6.156)–(6.158) that in an ordinary phase transition, while the thermodynamic potential is constant its first-order derivatives with respect to temperature and pressure change discontinuously at the transition point. Such a transition is, therefore, called *first-order transition*. Graphically, the first-order transition is represented in Fig. 6.6.

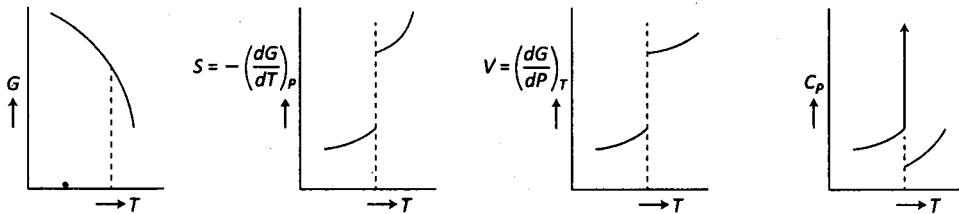


Fig. 6.6: First-order transition

A new type of phase transition is, however, observed when liquid helium I is transformed into liquid helium II at about 2.2 K (called  $\lambda$ -point). The nature of this phase transition is shown in Fig. 6.7.

The density-temperature curve, due to Onnes and Boks\*, shows that there is no change in density (and hence in specific volume), but a discontinuity in the slope at the transition point  $T_\lambda$ . Further, thermal measurements show that no latent heat is required for this transition so that entropy does not change at  $T_\lambda$ . But there is a sharp discontinuity in the specific heat-temperature curve (plotted from measurements by Keesom and his co-workers\*\*). These facts led Ehrenfest† to examine the behaviour of the thermodynamic potential and its derivatives in this new type of transition.

For this transition also, (6.40) holds, i.e.,

$$G_2 - G_1 = 0. \quad (6.159)$$

Since the entropy does not change at transition point,

$$\left(\frac{dG}{dT}\right)_P - \left(\frac{dG_2}{dT}\right)_P = S_2 - S_1 = 0. \quad (6.160)$$

Also, since the density does not change during transition,

$$\left(\frac{dG_2}{dT}\right)_P - \left(\frac{dG_1}{dT}\right)_P = V_2 - V_1 = 0.$$

\*Onnes and Boks, *Leiden Comm.*, No. 170b (1924).

\*\*Keesom, W.H., and Clusius, *Leiden Comm.*, No. 219e (1932); Keesom, W.H., and Keesom, A. P., *ibid*, No. 221d (1932).

†Ehrenfest, *Leiden Comm.*, No. 75b (1933).

From (6.160),

$$S_1 = S_2 \quad (6.161)$$

On differentiating (6.161). considering  $S$  as a function of  $T$  and  $P$ , we have

$$\left( \frac{dS_1}{dT} \right)_P + \left( \frac{dS_1}{dP} \right)_T \frac{dP}{dT} = \left( \frac{dS_2}{dT} \right)_P + \left( \frac{dS_2}{dP} \right)_T \frac{dP}{dT}. \quad (6.162)$$

Now, since  $\left( \frac{dS}{dT} \right)_P = \frac{C_p}{T}$  and  $\left( \frac{dS}{dP} \right)_T = -\left( \frac{dV}{dT} \right)_P$  (one of Maxwell's relations), we obtain from (6.162)

$$\frac{dP}{dT} = \frac{(C_p)_2 - (C_p)_1}{T \left[ \left( \frac{dV_2}{dT} \right)_P - \left( \frac{dV_1}{dT} \right)_P \right]} = \frac{(C_p)_2 - (C_p)_1}{TV(\alpha_2 - \alpha_1)}, \quad (6.163)$$

where  $\alpha$  is the volume-coefficient of expansion. (6.163) is the analogue of Claperyron-Clausius equation in the present case.

Now, in this transition,

$$\left( \frac{dV}{dT} \right)_P \left[ = \left\{ \frac{d}{dT} \left( \frac{dG}{dP} \right)_T \right\}_P \right] \quad \text{and} \quad C_p \left[ = -T \left( \frac{d^2G}{dT^2} \right)_P \right]$$

change discontinuously as shown in Fig. 6.7(a) and (b). Since here the second-order derivatives of the thermodynamic potential change discontinuously (while the first-order derivatives change discontinuously in first-order transitions), this new type of transition is called the *second-order transition*. Graphically, the second-order transition is represented in Fig. 6.8.

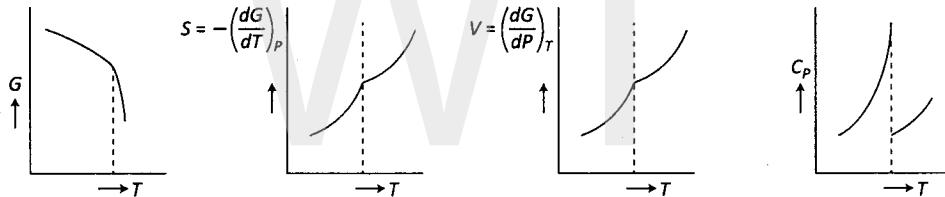


Fig. 6.8: Second-order transition

It is now known that second-order transitions take place at ordinary temperatures as well as at low temperatures. An example is the transition taking place in a ferro-magnetic or ferro-electric substance at the Curie-point. A second example is the transition of a metal from the normal to the superconducting state in the absence of a magnetic field.

**Exercise :** Find  $(\alpha_2 - \alpha_1)$  for liquid helium at  $\lambda$ -point, given that\*

$$\left( \frac{dP}{dT} \right)_\lambda = -81.9 \times 10^6 \text{ dynes cm}^{-2}\text{deg}^{-1}$$

$$(C_p)_2 - (C_p)_1 = 7.37 \times 10^7 \text{ erg gm}^{-1}\text{deg}^{-1} \quad \text{and} \quad \frac{1}{V} = 0.1462 \text{ cm}^{-3}$$

**Solution :** Putting the above data in (6.163),  $\alpha_2 - \alpha_1 = -0.0601 \text{ deg}^{-1}$ .

## 6.17 Thermochemistry : Hess's Law

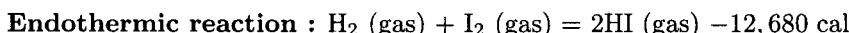
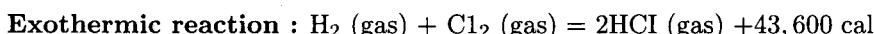
We have seen in section 0.1 that thermodynamics deals with the internal state of a system (say, a gas) in terms of its pressure, volume and temperature, called its thermodynamic

\* Taken from Robert and Miller, *Heat and Thermodynamics*.

coordinates. Thermodynamics is relevant to chemical reactions in as much as they (i.e., chemical reactions) are conditioned by pressure, volume and temperature.

Chemical reactions take place, in general, with the evolution or absorption of heat. The first law of thermodynamics deals with heat changes in chemical reactions. It is interesting to note that many principles of chemical reactions were discovered long before the formulation of the first law of thermodynamics.

Reactions that take place with the evolution of heat are called *exothermic reactions*. On the other hand, reactions which occur with the absorption of heat are called *endothermic reactions*. These two types of reactions can be explained broadly as follows. When two molecules approach each other under mutual attraction they combine to form a new molecule resulting in the transformation of their potential energy into the kinetic energy of the new molecule. The kinetic energy of the newly formed molecules manifests itself as heat. This is an exothermic reaction. On the other hand, two molecules may come together against mutual repulsion on account of their increased kinetic energy due to heating, and form a new molecule. This is an endothermic reaction. The following are examples of the two types of reaction :



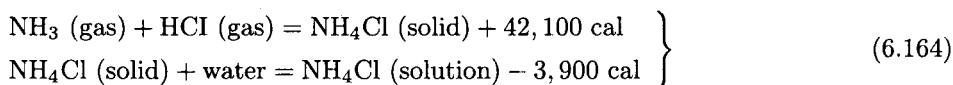
In other words, 1 mole (i.e., gram-molecule) of hydrogen gas reacts with 1 mole of chlorine gas and produces 2 moles of hydrochloric acid gas with the evolution of 43,600 cal. On the other hand, 1 mole of hydrogen gas reacts with 1 mole of iodine gas and produces 2 moles of hydriodic acid gas with the absorption of 12,680 cal.

### 6.17.1 Hess's Law of Constant Summation

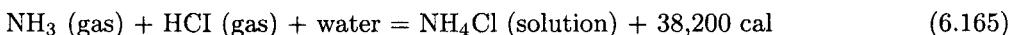
From experiments conducted over a number of years, Hess stated in 1840 the following law, called *Hess's law* (before the formulation of the first law of thermodynamics) : *If a chemical reaction is brought about in a single step, or alternatively, in a number of intermediate steps, the total amount of heat evolved is the same provided the initial and final states are the same in all cases.*

Let us take an example.

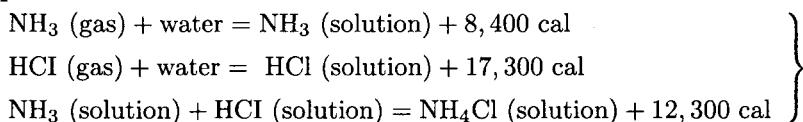
**First process :**



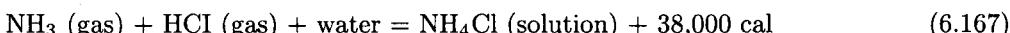
**Summing up :**



**Second process :**



**Summing up :**



Obviously, within limits of experimental error, the net amount of heat evolved is the same in the two processes. Thus, Hess's law is vindicated.

### 6.17.2 Hess's Law from First Law of Thermodynamics

From (6.35), according to the first law of thermodynamics, we have for heat added to a system (say, a gas),

$$dQ = dU + PdV. \quad [(6.35)]$$

If the volume is constant, then

$$dQ_V = dU. \quad (6.168)$$

Since  $dU$  (change of internal energy of the system) obviously represents a change of the state of the system,  $dQ_V$  is equal to this change of state of the system at constant volume and is therefore independent of how this heat change occurs.

Secondly, from (6.49), the change of enthalpy of a system is

$$\begin{aligned} dH &= d(U + PV) = dU + PdV, \text{ at constant pressure} \\ &= dQ_P, \text{ according to the first law of thermodynamics.} \end{aligned} \quad (6.169)$$

Now,  $dH$  represents a change of the state of the system. So  $dQ_P$  is equal to this change of state of the system at constant pressure and is, therefore, independent of how this heat change occurs.

Hence (6.168) and (6.169) represent a vindication of Hess's law.

### 6.18 Chemical Equilibrium of Gaseous Systems : Law of Mass Action

We shall consider here an interesting case of application of thermodynamics to chemistry. Let us have in a vessel a mixture of some reacting (ideal) gases maintained in equilibrium at constant temperature  $T$  and constant pressure  $P$  so that the thermodynamic potential  $G$  of the whole system is constant by (6.40). Hence,

$$dG = 0, \quad (6.170)$$

Let us suppose that in the mixture of reacting gases, there are  $n_1$  gram-molecules of the first gas,  $n_2$  gram-molecules of the second gas, ...  $n_r$ , gram-molecules of the  $r$ th gas...

Now we have

$$G = U - TS + PV. \quad (6.171)$$

Then, since the change in internal energy of a gram-molecule of, say, the  $r$ th ideal gas is given by

$$dU_r = (C_v)_r dT,$$

we have

$$U_r = \int^T (C_v)_r dT + (U_0)_r, \quad (6.172)$$

where  $(U_0)_r$  is an integration constant.

Now, substituting for  $PV$  from  $PV = RT$ , for  $S$  from (5.75) and for  $U$  from (6.172) in (6.171),

$$G = \sum_r n_r \left[ \int^T (C_v)_r dT + (U_0)_r - T \int^T \frac{(C_p)_r}{T} dT + RT \log_e c_r P - (S'_0)_r T + RT \right], \quad (6.173)$$

where  $c_r$  is the concentration of the  $r$ th gas.

But the thermodynamic potential of one gram-molecule of the  $r$ th gas at temperature  $T$  and pressure  $P$  is

$$\begin{aligned} G_r &= U_r - TS_r + PV \\ &= \int^T (C_v)_r dT + (U_0)_r - T \int^T \frac{(C_p)_r}{T} dT + RT \log_e P - (S'_0)_r T + RT, \end{aligned} \quad (6.174)$$

where we have used (5.71), (6.172) and the perfect gas equation. Using  $(C_p)_r - (C_v)_r = R$  in (6.174),

$$G_r = \int^T (C_p)_r dT + (U_0)_r - T \int^T \frac{(C_p)_r}{T} dT + RT \log_e P - (S'_0)_r T. \quad (6.175)$$

Hence, substituting (6.175) in (6.173),

$$G = \sum_r n_r [G_r + RT \log_e c_r]. \quad (6.176)$$

Now, in any reversible chemical change\* (i.e., reaction) under equilibrium condition at constant temperature and pressure, the numbers of gram-molecules of the reacting gases  $n_1, n_2, \dots$  change by  $dn_1, dn_2, \dots$ . Then, from (6.170) and (6.176),

$$dG = \sum_r [G_r + RT \log_e c_r] dn_r + \sum_r n_r d[G_r + RT \log_e c_r] = 0. \quad (6.177)$$

From (6.175), it is evident that  $G_r$  depends only on  $T$  and  $P$ , which are constant here so that

$$dG_r = 0. \quad (6.178)$$

Further, we have

$$\begin{aligned} \sum_r n_r d(\log_e c_r) &= \frac{n_1}{c_1} dc_1 + \frac{n_2}{c_2} dc_2 + \dots \\ &= (n_1 + n_2 + \dots)(dc_1 + dc_2 + \dots) \quad \left[ \because c_r = \frac{n_r}{\sum n_r} \right] = 0 \end{aligned} \quad (6.179)$$

since  $c_1 + c_2 + c_3 + \dots = 1$  and, therefore,  $dc_1 + dc_2 + \dots = 0$ .

Taking into account (6.178) and (6.179), the condition of chemical equilibrium (6.177) becomes

$$\sum_r [G_r + RT \log_e c_r] dn_r = 0. \quad (6.180)$$

Now, the equation for the chemical reaction under consideration may be written as follows :

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \dots = 0. \quad (6.181)$$

where  $A_1, A_2, \dots$  are the molecular formulae of the first, second, etc. gases and  $\nu_1, \nu_2, \dots$  are the numbers of molecules of each of them taking part in the reaction.  $\nu_r$  is positive if the  $r$ th gas is formed during the reaction and is negative if it disappears. For example, the equation representing the formation of water from oxygen and hydrogen :



\*Under equilibrium condition, reversible reactions, i.e.,  $A + B \rightleftharpoons C$  take place though on an infinitesimal scale. In the following calculations, however, we have to adopt just  $A + B \rightarrow C$  or,  $A + B \leftarrow C$ .

may be written according to (6.181) as



Here  $A_1, A_2, A_3$  are respectively  $\text{H}_2\text{O}$ ,  $\text{H}_2$  and  $\text{O}_2$  and  $\nu_1, \nu_2, \nu_3$  are respectively 2, -2, -1. Evidently, we must have

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \cdots = \text{a pure number.}$$

i.e.,  $dn_r = \text{constant} \times \nu_r$ . (6.183)

From (6.180) and (6.183) the equilibrium equation becomes

$$\sum_r \nu_r [G_r + RT \log_e c_r] = 0$$

$$\text{or, } \nu_1 \log_e c_1 + \nu_2 \log_e c_2 + \cdots = -\frac{\nu_1 G_1 + \nu_2 G_2 + \cdots}{RT} \quad (6.184)$$

Now writing in (6.184),

$$\log_e K_c = -\frac{\sum \nu_r G_r}{RT}, \quad (6.185)$$

we obtain

$$\log_e (c_1^{\nu_1} c_2^{\nu_2} c_3^{\nu_3} \cdots) = \log_e K_c$$

$$\text{i.e., } c_1^{\nu_1} c_2^{\nu_2} c_3^{\nu_3} \cdots = K_c, \quad (6.186)$$

where  $K_c$  (called *reaction constant*) depends, for a given reaction, only on the temperature and pressure, and not on the concentrations, as (6.185) shows. (6.186) is the well-known *law of mass action* which was first stated correctly in 1867 by Guldberg and Waage, two Norwegian scientists.

It is sometimes more convenient to express the reaction constant  $K_c$  in terms of partial pressures  $P_r$ , rather than concentrations. From (5.74),  $P_1 = c_1 P$ ,  $P_2 = c_2 P$ , ...

Substituting in (6.186),

$$P_1^{\nu_1} \times P_2^{\nu_2} \times P_3^{\nu_3} \times \cdots = P^{\nu_1 + \nu_2 + \nu_3 + \cdots} \times K_c = K_p, \quad (6.187)$$

where  $K_p$  is the reaction constant expressed in terms of partial pressures, and is a constant for constant temperature and pressure since

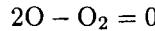
$$\log_e K_p = (\nu_1 + \nu_2 + \cdots) \log_e P + \log_e K_c \quad (6.188)$$

$$= (\nu_1 + \nu_2 + \cdots) \log_e P - \frac{\sum \nu_r G_r}{RT}. \quad (6.189)$$

## 6.19 Applications of Law of Mass Action

We shall consider some examples which will illustrate the use of the law of mass action.

(a) **Dissociation of Oxygen** : The equation of reaction in this case is, according to (6.181),



so that  $\nu_1 = 2$ ,  $\nu_2 = -1$ . Then, according to (6.186),

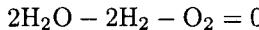
$$c_1^2 c_2^{-1} = \frac{c_1^2}{c_2} = K_c$$

or, since  $c_1 + c_2 = 1$ ,

$$\frac{c_1^2}{1 - c_1^2} = K_c. \quad (6.190)$$

Since  $K_c$  is a function of  $T$  and  $P$  only, we see that the concentrations in this case are determined if  $T$  and  $P$  are known.

(b) **Formation of Water in Gaseous Phase :** The equation for the transformation of  $H_2$  and  $O_2$  into  $H_2O$  in gaseous phase is, like (6.181),



so that  $\nu_1 = 2$ ,  $\nu_2 = -2$ ,  $\nu_3 = -1$ . Then, according to (6.186),

$$\frac{c_1^2}{c_2^2 c_3} = K_c. \quad (6.191)$$

Now, suppose, we start with a mixture of  $n_{20}$  gram-molecules of  $H_2$  with  $n_{30}$  gram-molecules of  $O_2$  and allow the reaction to take place. Then, if  $n_1$  gram-molecules of  $H_2O$  are formed and  $n_2$ ,  $n_3$  gram-molecules of  $H_2$ ,  $O_2$  left, we have

$$\left. \begin{array}{l} n_{20} = n_2 + n_1 \\ n_{30} = n_3 + \frac{1}{2}n_1 \end{array} \right\} \quad (6.192)$$

Hence, we obtain the concentrations in the equilibrium condition :

$$\left. \begin{array}{l} c_1 = \frac{n_1}{n_{20} + n_{30} - \frac{1}{2}n_1} \\ c_2 = \frac{n_{20} - n_1}{n_{20} + n_{30} - \frac{1}{2}n_1} \\ c_3 = \frac{n_{30} - \frac{1}{2}n_1}{n_{20} + n_{30} - \frac{1}{2}n_1} \end{array} \right\} \quad (6.193)$$

since  $n_1 + n_2 + n_3 = n_1 + n_{20} - n_1 + n_{30} - \frac{1}{2}n_1 = n_{20} + n_{30} - \frac{1}{2}n_1$ .

Then, from (6.191) and (6.193),

$$\frac{n_1^2(n_{20} + n_{30} - \frac{1}{2}n_1)}{(n_{20} - n_1)^2(n_{30} - \frac{1}{2}n_1)} = K_c. \quad (6.194)$$

Now, measuring  $n_1$  at a given temperature and pressure,  $K_c$  for that temperature and pressure will be determined from (6.194). Again, (6.194) will then enable us to find the value of  $n_1$ , and hence also of  $n_2$  and  $n_3$  [from (6.192)] for any other amounts of  $H_2$  and  $O_2$  which are mixed at the same temperature and pressure.

(c) **Dissociation of Hydriodic Acid :** This case has been fully investigated by Bodenstein\* and his co-workers. The equation for the reaction is



so that  $\nu_1 = 1$ ,  $\nu_2 = 1$ ,  $\nu_3 = -2$ . If the degree of dissociation is  $x$ , then for each gram-molecule of  $HI$  originally present there will be  $(1 - x)$  gram-molecules of  $HI$  left and  $x/2$  gram-molecules

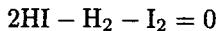
\*Bodenstein, *Ziets. Phys. Chem.*, **13**, P. 56 (1893); **22**, P. 1 (1897); **29**, P. 295 (1899).

of each of  $H_2$  and  $I_2$  produced. Then,  $c_1 = x/2$ ,  $c_2 = x/2$  and  $c_3 = 1 - x$ . Hence, (6.186) gives

$$\frac{c_1 c_2}{c_3^2} = \frac{\frac{x}{2} \cdot \frac{x}{2}}{(1-x)^2} = \frac{x^2}{4(1-x)^2} = K_c. \quad (6.195)$$

By starting with pure hydriodic acid and allowing equilibrium to be reached, and then analyzing the mixture,  $x$  and hence  $K_c$  from (6.195) can be found.

Next, we consider the reverse reaction



with  $\nu_1 = 2$ ,  $\nu_2 = -1$ ,  $\nu_3 = -1$ .

If we start with  $n_{10}$  gram-molecules of  $H_2$  and  $n_{20}$  gram-molecules of  $I_2$  and if equilibrium is reached when  $2n_3$  gram-molecules of HI are formed, then from (6.186),

$$\frac{c_1^2}{c_2 c_3} = \frac{4n_3^2}{(n_{10} - n_3)(n_{20} - n_3)} = K_c. \quad (6.196)$$

(6.196) gives, with a knowledge of  $K_c$  from (6.195), a means of finding how much HI will be formed at the same temperature and pressure when  $H_2$  and  $I_2$  are mixed in any known proportions.

## 6.20 Heat of Reaction

When a chemical reaction takes place at constant temperature, heat is either taken in or given out. This heat is called the *heat of reaction*, the value of which depends on whether the reaction takes place at constant volume or at constant pressure.

Let us first find the heat of reaction at constant volume. No external work is done in this case so that the heat taken in at constant temperature is

$$\Delta Q = U_f - U_i, \quad (6.197)$$

where  $U_i$ ,  $U_f$  are the total internal energy of the system before and after the reaction. If  $\nu_1$ ,  $\nu_2$ , ... gram-molecules of the various reacting gases take part actually in the reaction, then we may write :

$$U_f - U_i = \sum_r \nu_r U_r, \quad (6.198)$$

where  $U_r$  is the internal energy per gram-molecule of the  $r$ th gas taking part in the reaction, the sign of the  $\nu$ 's denoting whether each  $U_r$  is to be added or subtracted. Hence, the heat of reaction at constant temperature and volume is

$$\Delta Q = \Delta U = \sum_r \nu_r U_r. \quad (6.199)$$

In practice, however, reactions take place often at constant pressure  $P$  so that the heat taken in is equal to the change in heat content or enthalpy  $H$ . In this case, external work  $P\Delta V [= P(V_f - V_i)]$  is done. Hence, the heat taken in is

$$\Delta Q = U_f - U_i + P(V_f - V_i) = \Delta U + P\Delta V = H_f - H_i = \Delta H. \quad (6.200)$$

But like  $\Delta U$ ,  $\Delta V$  may also be written as

$$\Delta V = \sum_r \nu_r V_r, \quad (6.201)$$

where  $V_r$  is the volume per gram-molecule of the  $r$ th gas taking part in the reaction at pressure  $P$  and temperature  $T$ . Then, the heat of reaction is, from (6.199), (6.200) and (6.201),

$$\begin{aligned}\Delta H &= \sum_r \nu_r (U_r + PV_r) \\ &= \sum_r \nu_r \left\{ \int^T (C_v)_r dT + (U_0)_r + RT \right\} \quad [\text{from (6.172) and } PV_r = RT] \\ &= \sum_r \nu_r \left\{ \int^T (C_p)_r dT + (U_0)_r \right\}. \end{aligned} \quad (6.202)$$

(from  $C_p - C_v = R$ )

From (6.202) we can at once find the change in the heat of reaction with temperature. If  $(\Delta H)_{T_1}$ ,  $(\Delta H)_{T_2}$  are the heats of reaction at  $T_1$ ,  $T_2$ , then from (6.202),

$$(\Delta H)_{T_2} - (\Delta H)_{T_1} = \sum_r \nu_r \left\{ \int_{T_1}^{T_2} (C_p)_r dT \right\}. \quad (6.203)$$

## 6.21 Variation of Reaction Constant with Pressure and Temperature

From (6.185) we obtain the change of  $K_c$  with pressure at constant temperature :

$$\left( \frac{d \log_e K_c}{dP} \right)_T = -\frac{1}{RT} \sum_r \nu_r \left( \frac{dG_r}{dP} \right)_T.$$

Using (6.175), this gives

$$\left( \frac{d \log_e K_c}{dP} \right)_T = -\frac{1}{RT} \sum_r \nu_r \left( \frac{RT}{P} \right) = -\frac{1}{RT} \sum_r \nu_r V_r = -\frac{\Delta V}{RT}, \quad (6.204)$$

where  $\Delta V$  is the increase in volume when the reaction takes place according to (6.181), taking  $\nu_1, \nu_2, \dots$  here as the numbers of gram-molecules [instead of numbers of molecules as in (6.181)] of the various reacting gases transformed during the reaction. The relation (6.204) means that *increasing the pressure causes the equilibrium to be displaced in such a direction that the reaction proceeds with decrease in volume*.

Again, from (6.185) we obtain the change of  $K_c$  with temperature at constant pressure :

$$\begin{aligned}\left( \frac{d \log_e K_c}{dT} \right)_P &= \frac{1}{RT^2} \sum_r \nu_r G_r - \frac{1}{RT} \left( \nu_1 \frac{dG_1}{dT} + \nu_2 \frac{dG_2}{dT} + \dots \right)_P \\ &= \frac{1}{RT^2} \sum_r \nu_r \left\{ \int^T (C_p)_r dT + (U_0)_r \right\} \quad [\text{from (6.175)}] \\ &= \frac{\Delta H}{RT^2}, \quad [\text{from (6.202)}] \end{aligned} \quad (6.205)$$

where also  $\nu_1, \nu_2, \dots$  are the numbers of gram-molecules of the various reacting gases transformed during the reaction. The relation (6.205) is the well-known equation of Van't Hoff and is usually called *the equation of the isochore of the reaction*. The equation means that *increasing the temperature causes the equilibrium to be displaced in such a direction that the reaction proceeds with absorption of heat from outside*.

From (6.188), we find that

$$\left( \frac{d \log_e K_p}{dT} \right)_P = \left( \frac{d \log_e K_c}{dT} \right)_P = \frac{\Delta H}{RT^2}. \quad (6.206)$$

Thus,  $K_p$  and  $K_c$  vary in the same manner with temperature at constant pressure.

The most important application of Van't Hoff's equation is to determine the heat of reaction from measurements of the equilibrium concentration. For instance, if  $K_c$  or  $K_p$  is determined from the equilibrium concentrations at a number of temperatures, the slope of the  $\log_e K_c - T$  curve gives at once the value of  $\Delta H$  from (6.205).

## 6.22 Principle of Le Chatelier\*

The results expressed in (6.204) and (6.205) are particular cases of a general principle due to Le Chatelier. No direct proof of this principle can be given, but it has been applied to many fields of physics and chemistry and has been found to be a valid law of nature. It may be stated thus : *A change of one of the factors determining the condition of equilibrium causes a rearrangement of the system in such a direction that the factor in question tends to experience a change in a sense opposite to the original change.*

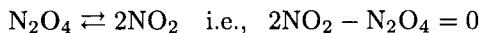
Let us first take an example from physics to illustrate the principle. Suppose, we have a gas contained in a vessel at a definite pressure, volume and temperature. If the pressure is suddenly increased by decreasing the volume of the vessel, then according to Le Chatelier's principle, a change should occur in the system in such a direction as to tend to annul this compression. And actually the gas is heated and hence develops a tendency to expand in volume—this is quite as required by the principle.

Next, let us take an example from chemistry. Suppose, dissociation of a gas occurs with increase in volume. Then, an increase in pressure diminishes the degree of dissociation. In this case, due to the diminution of dissociation, the volume and hence the pressure tend to be decreased. This is just in accord with Le Chatelier's principle.

Further, if the dissociation is accompanied with absorption of heat, then an increase in temperature increases the degree of dissociation. In this case, due to the increase in dissociation, the system will absorb more heat and will thus tend to regain its original temperature\*\*

**Exercise :** Calculate the heat of reaction in the case of dissociation of nitrogen tetroxide.

**Solution :** The equation of dissociation of  $N_2O_4$  is



so that  $\nu_1 = 2$ ,  $\nu_2 = -1$ , and from (6.187),

$$K_p = \frac{P_1^2}{P_2}. \quad (6.207)$$

where  $P_1$  is the partial pressure of  $NO_2$  and  $P_2$  that of  $N_2O_4$ . Therefore, the total pressure is

$$P = P_1 + P_2. \quad (6.208)$$

When the equilibrium condition has been set up, let  $x$  be the degree of dissociation. Then, out of each gram-molecule of  $N_2O_4$ , a fraction  $(1 - x)$  remains undissociated. If  $N$  be the number of molecules in a gram-molecule, then since two molecules of  $NO_2$  are formed out of

\*See Fermi, E., *Thermodynamics*, Pp. 109–12 (1938).

\*\*Rayleigh, *Journ. Chem. Soc.*, **111**, P. 250 (1917).

one molecule of  $\text{N}_2\text{O}_4$ , the ratio of partial pressures is

$$\frac{P_1}{P_2} = \frac{2xN}{(1-x)N} = \frac{2x}{1-x}. \quad (6.209)$$

From (6.208) and (6.209),

$$P_1 = \frac{2x}{1+x}P, \quad P_2 = \frac{1-x}{1+x}P. \quad (6.210)$$

Substituting from (6.120) in (6.207),

$$K_p = \frac{4x^2}{1-x^2}P. \quad (6.211)$$

Now, the ratio of the total number of molecules present in the partially dissociated mixture when the equilibrium has been set up to the number which would have been present at the same temperature and pressure if no dissociation had taken place at all is (in terms of a gram-molecule of  $\text{N}_2\text{O}_4$ ),

$$\frac{(1-x)N + 2xN}{N} = \frac{1+x}{1}. \quad (6.212)$$

Now, by Avogadro's law, at the same temperature and pressure, the number of molecules/volume is the same in all systems, i.e., the total number of molecules is proportional to the volume. Suppose,  $N$  number of  $\text{N}_2\text{O}_4$  molecules, if undissociated, would have volume  $V$ . Then, at the same temperature and pressure,  $\{(1-x)N + 2xN\}$ , i.e.,  $(1+x)N$  molecules of the partially dissociated mixture will have the volume  $(1+x)V$ . Now, the total mass  $M$  being same in either case, the densities of undissociated  $\text{N}_2\text{O}_4$ ,  $\rho_0$ , and of the partially dissociated mixture,  $\rho$ , must be in the ratio

$$\frac{\rho_0}{\rho} = \frac{M/V}{M/(1+x)V} = \frac{1+x}{1}. \quad (6.213)$$

From (6.213),

$$x = \frac{\rho_0 - \rho}{\rho}. \quad (6.214)$$

Substituting from (6.124) in (6.211),

$$K_p = \frac{4(\rho_0 - \rho)^2}{\rho_0(2\rho - \rho_0)}P. \quad (6.215)$$

It is more convenient (without any loss of rigour) to use, instead of the actual densities, the specific gravities referred to air as standard. Then, the value of  $\rho_0$  is equal to the molecular weight of undissociated  $\text{N}_2\text{O}_4$  molecules divided by the average molecular weight of air i.e.,

$$\rho_0 = \frac{92.02}{28.95} = 3.179. \quad (6.216)$$

The partially dissociated mixture has been found to have following specific gravities,  $\rho$ , (defined as above) at  $26.7^\circ\text{C}$  and  $111.3^\circ\text{C}$  at atmospheric pressure :

Temp.	Sp.Gr.	}
$26.7^\circ\text{C}$	2.65	
$111.3^\circ\text{C}$	1.65	

(6.217)

From (6.215)–(6.217), we find the values of  $K_p$  at  $26.7^\circ\text{C}$  and  $111.3^\circ\text{C}$  to be 0.166P and 24.32P respectively.

If we assume that the heat of reaction (dissociation here) remains appreciably constant over the range of temperatures under consideration, then on integration of (6.206),

$$\log_e \left( \frac{(K_p)_1}{(K_p)_2} \right) = \frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right). \quad (6.218)$$

where  $(K_p)_1$ ,  $(K_p)_2$  are the reaction constants at  $T_1$ (26.7 °C) and  $T_2$ (111.3 °C) respectively. Then, putting the values of  $K_p$  in (6.218) and taking  $R = 1.985$  calories,  $\Delta H = 13,480$  calories.

Thus, the complete dissociation of a gram-molecule (i.e., 92.02 gm) of  $N_2O_4$  at constant pressure requires 13,480 calories which is a considerable quantity of heat. The observed value\*, deduced from specific heat measurements on the dissociating gas, is about 13,200 calories. This is indeed a good agreement.

## PROBLEMS

1. For liquid hydrogen the following data have been obtained at 20.4K :

Gram-molecular volume = 28.2 cc,  $\gamma_p = 1.60 \times 10^{-3}$  per deg C and  $K_T = 5.13 \times 10^2$  kg/sq. cm.  
Calculate the difference between its molar specific heats in calories per degree.

2. Prove the following relations :

$$(a) \frac{1}{K_T} - \frac{1}{K_S} = TV \frac{\gamma_p^2}{C_p}$$

[Hint : Use (6.88) and (6.94).]

$$(b) \frac{1}{C_v} - \frac{1}{C_p} = \frac{1}{T} \left( \frac{dV}{dS} \right)_P \left( \frac{dP}{dS} \right)_V$$

[Hint : Use (6.79), (6.82) and (6.84)]

$$(c) \left( \frac{dQ}{dV} \right)_T = T \left( \frac{dP}{dT} \right)_V$$

3. Calculate the specific volume of ether at its boiling point (35 °C)

Given that  $L = 86$  cal/gm.

$$\frac{dP}{dT} = 27 \text{ mm of Hg/K},$$

density of liquid ether = 0.7 gm/cc, density of mercury = 13.6 gm/cc,  $J = 4.2 \times 10^7$  ergs/cal  
and  $g = 981$  cm/sec<sup>2</sup>. [Gau.U.]

4. By how much will the freezing point of water at normal pressure be altered if it is subjected to an additional pressure of 4 atmospheres? The specific volumes of water and ice at 0 °C are 1.0001 cc and 1.0908 cc respectively. [ $L = 80$  cal/gm, 1 atmosphere =  $1.013 \times 10^6$  dynes/sq cm]

5. Show that

$$(a) \left( \frac{dV}{dT} \right)_S = - \frac{C_v}{C_p - C_v} \left( \frac{dV}{dT} \right)_P$$

[Hint : See (6.97).]

$$(b) \left( \frac{dP}{dT} \right)_S = \frac{C_p}{C_p - C_v} \left( \frac{dP}{dT} \right)_V$$

[Hint : See (6.98).]

\*Nernst *Theoretical Chemistry*, P. 753 (1923), the result quoted there refers to the reaction at constant volume and should, therefore, be converted into the heat of reaction at constant pressure by addition of  $RT = R(T_1 + T_2)/2$ .

$$(c) U = -T^2 \left( \frac{d(F/T)}{dT} \right)_V$$

$$(d) C_v = -T \left( \frac{d^2 F}{dT^2} \right)_V$$

$$(e) C_p = -T \left( \frac{d^2 G}{dT^2} \right)_P$$

$$(f) C_p = T \left( \frac{dV}{dT} \right)_P \left( \frac{dP}{dT} \right)_S.$$

[Hint : Use (6.82) and a Maxwell relation.]

6. The theory of *electro-caloric effect* is analogous to that of magneto-caloric effect. Hence, following the treatment of the latter effect, show that the small temperature change caused by a reversible adiabatic change of electric field  $E$  in a dielectric medium is

$$T_f - T_i = \frac{CV}{2C_E T_i} (E_f^2 - E_i^2),$$

where  $C_E$  is the specific heat at constant field  $E$ .

Also show that

$$C_E - C_P = \frac{E^2 \chi V}{T}$$

where  $C_P$  is the specific heat at constant polarisation  $P$  of the medium and  $\chi (= C/T)$  is the electric susceptibility.

7. For a gas with the equation of state  $PV = RT + BP$ , show that

$$C_p - C_v = R + 2 \frac{dB}{dT} P.$$

## Chapter 7

# Thermodynamics of Radiation

### 7.1 Prevost's Theory of Exchanges

Let us first consider two bodies  $A$  and  $B$  in the vicinity of (but not in contact with) each other,  $A$  being hotter than  $B$ . After sometime, the temperature of  $A$  falls and that of  $B$  rises. This means that heat has been transferred from  $A$  to  $B$  by radiation. Next, let us consider  $B$  and another body  $C$  in the vicinity of each other,  $C$  being colder than even  $B$ . Now, it is observed that after sometime, the temperature of  $B$  falls and that of  $C$  rises. This means that now heat has been transferred from  $B$  to  $C$  by radiation. The observations in these two instances can be explained from the idea, first pointed out by Prevost of Geneva in 1792 and known as *Prevost's theory of exchanges*, that *every body radiates heat to and absorbs heat (radian) from every other body and that the hotter body radiates more heat than it absorbs, while the colder one absorbs more than it radiates*. So, in the first instance,  $A$ , being hotter, radiates more heat to and receives less heat from  $B$  by radiation—as a result,  $A$  is cooled and  $B$  is heated. In the second instance, however,  $B$ , being hotter than  $C$ , radiates more heat to and receives less heat from  $C$ —as a result, now  $B$  is cooled and  $C$  is heated.

### 7.2 Emissive and Absorptive Powers of a Body

The amount of radiation,  $dQ_\lambda$ , of wavelengths between  $\lambda$  and  $\lambda + d\lambda$ , emitted by an area  $dA$  of a body in time  $dt$  in almost normal directions given by a solid angle  $d\omega^*$ ,

$$\propto d\lambda$$

$$\propto dA$$

$$\propto dt$$

$$\propto d\omega$$

$$\text{i.e., } dQ_\lambda = e_\lambda d\lambda dA dt d\omega \quad (7.1)$$

where  $e_\lambda$  is called the emissive power of the body for wavelengths between  $\lambda$  and  $\lambda + d\lambda$ .

If, on the other hand,  $dQ_\lambda$  is the amount of radiation of wavelengths between  $\lambda$  and  $\lambda + d\lambda$  falling on unit area of a body and a fraction  $a_\lambda dQ_\lambda$  is absorbed by the body, then  $a_\lambda$  is called the absorptive power of the body for these wavelengths. For a black body  $a_\lambda = 1$  for all wavelengths, and this is exactly how a black body is defined.

### 7.3 Temperature Radiation

When the radiation emitted by a body depends only on its temperature, it is called *temperature radiation*. In fact, there are various other ways in which matter may emit radiant energy, e.g., by electrical discharge through gases, by chemical action in flames, by phosphorescence and fluorescence, etc. In this chapter, however, we shall be concerned with temperature radiation only and discuss the thermodynamics of this type of radiation.

\* All directions included in a cone are specified by a quantity (called solid angle)  $d\omega = (\text{normal section of cone})/(\text{distance of normal section from vertex})^2 = r^2 \sin \theta d\theta d\phi/r^2$  [See Fig. 2.2(a)] =  $\sin \theta d\theta d\phi$ .

In this section, we shall prove that the density of radiation of a given wavelength  $\lambda$  in a hollow enclosure at a given temperature depends only on the temperature, and not on the nature of the walls or of any bodies that may exist inside the enclosure.

Suppose, we have two hollow enclosures  $A$  and  $B$  made of different materials at the same temperature  $T$ . Initially  $A$  and  $B$  are isolated from each other and the density of radiation of wavelengths, say, between  $\lambda$  and  $\lambda + d\lambda$  is greater in  $A$  than in  $B$ . Let us now set up communication between  $A$  and  $B$  through a screen (or plate) which is transparent only to radiation of wavelengths between  $\lambda$  and  $\lambda + d\lambda$ . Then, there will be a net gain of energy by  $B$  from  $A$  through the screen\* and, therefore,  $A$  will fall in temperature and  $B$  will rise in temperature. This difference in temperature can be used by a Carnot engine to produce work till the two bodies are brought to the same temperature. But then again, there will be a net flow of energy from  $A$  to  $B$  through the screen, as according to our assumption, the density of radiation of wavelengths between  $\lambda$  and  $\lambda + d\lambda$  is greater in  $A$  than in  $B$ . Hence, the difference in temperature between  $A$  and  $B$  can again be utilised by the engine to convert heat into work. This process may be repeated as often as we please. But this is all contrary to the second law of thermodynamics, because no work can be produced from bodies originally at the same temperature. Hence, we conclude that *the density of radiation of wavelengths, say, between  $\lambda$  and  $\lambda + d\lambda$  in a hollow enclosure at temperature  $T$  depends only on  $T$ , and not on the nature of the walls or of any bodies existing inside the enclosure*. This means that in all hollow enclosures at the same temperature, the distribution of radiant energy among the different wavelengths in any unit volume of space is the same and, so also is the total radiant energy per unit volume. Thus the radiation inside a hollow enclosure depends only on temperature and is, therefore, temperature radiation.

#### 7.4 Kirchhoff's Law

Let us take a hollow enclosure at a certain temperature  $T$ . It is such that there cannot be exchange of energy in any form through the walls between inside and outside. Suppose, a small body  $A$  with different parts having different emissive and absorptive powers, is placed within the enclosure. We shall prove here now that whatever be the initial temperature of  $A$ , it will ultimately attain the temperature of the enclosure in the equilibrium state. Suppose, in the equilibrium state, the temperature of  $A$  is different from that of the enclosure. This difference in temperature can be used by a Carnot engine to produce work till  $A$  and the enclosure are brought to the same temperature. But, then again the temperature of  $A$  will become different from that of enclosure, as according to our assumption, this corresponds to the state of equilibrium. Hence, this difference in temperature can again be utilised by the engine to convert heat into work. This process may be repeated and an indefinite amount of work may be obtained by converting the heat of a single body without maintaining a second body at a lower temperature. But this is all contrary to the second law of thermodynamics. Hence, we conclude that *in the equilibrium state,  $A$  acquires the same temperature as that of the hollow enclosure*. A corollary to this conclusion is this : *Since the different parts of  $A$  have different coefficients of absorption, the radiation travelling inside the enclosure in different directions must be identical in quality and quantity, i.e., must be isotropic so that the total energy absorbed by it in any position or orientation may be equal to the total energy emitted by it which is, by Prevost's law, independent of its position or orientation*.

Now, we proceed to derive Kirchhoff's law. Suppose, a body of emissive power  $e_\lambda$  and absorptive power  $a_\lambda$  is placed inside the hollow enclosure at a large distance from the walls.

\*This happens because, due to higher density of radiation of wavelengths between  $\lambda$  and  $\lambda + d\lambda$ , more of this radiation falls on the  $A$ -side of the screen than on the  $B$ -side.

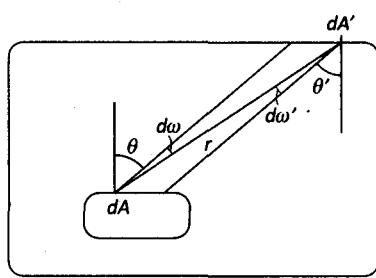


Fig. 7.1: Hollow enclosure

Then, from (7.1) the amount of energy radiated per unit time by an area  $dA$  of the body is (See Fig. 7.1)

$$\begin{aligned}
 &= \int \int e_\lambda d\lambda dA \cos \theta d\omega \\
 &= \int_0^{2\pi} \int_{0(\phi)}^{\pi/2} \int_{0(\lambda)}^{\infty} e_\lambda d\lambda dA \cos \theta d\phi \quad (\because d\omega = \sin \theta d\phi)^* \\
 &= \pi dA \int_0^{\infty} e_\lambda d\lambda.
 \end{aligned}$$

considering all wavelengths and all directions. In the first step above, we have taken  $dA \cos \theta$  instead of  $dA$  as in (7.1), because here  $dA \cos \theta$ , and not  $dA$ , is normal to the radiation in directions included in solid angle  $d\omega$ .

Then, the total amount of energy radiated by the whole body per unit time is

$$\begin{aligned}
 &= \sum \pi dA \int_0^{\infty} e_\lambda d\lambda \\
 &= \left( \sum dA \right) \pi \int_0^{\infty} e_\lambda d\lambda,
 \end{aligned} \tag{7.2}$$

because we have already assumed that the emissive power for any  $\lambda$  is the same for every part of the body.

On the other hand, the amount of energy of wavelengths between  $\lambda$  and  $\lambda + d\lambda$  emitted per unit time by an area  $dA'$  of the enclosure and incident on  $dA$  of the body is, from (7.1) (See Fig. 7.1)

$$\begin{aligned}
 &= E_\lambda d\lambda dA' \cos \theta' d\omega' \\
 &= E_\lambda d\lambda dA' \cos \theta' \frac{dA \cos \theta}{r^2} \quad (r = \text{distance between } dA \text{ and } dA') \\
 &= E_\lambda d\lambda dA \cos \theta \frac{dA' \cos \theta'}{r^2} \\
 &= E_\lambda d\lambda dA \cos \theta d\omega.
 \end{aligned}$$

Out of this incident energy, the amount absorbed per unit time by  $dA$  is

$$= a_\lambda E_\lambda d\lambda dA \cos \theta d\omega,$$

where  $E_\lambda$  is the emissive power of the enclosure. Then, the total energy absorbed by  $dA$  per unit time is

$$\begin{aligned}
 &= \int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} a_\lambda E_\lambda d\lambda dA \cos \theta \sin \theta d\theta d\phi \\
 &= \pi dA \int_0^{\infty} a_\lambda E_\lambda d\lambda.
 \end{aligned}$$

Therefore, the total amount of radiation absorbed by the whole body per unit time is

$$= \sum \pi dA \int_0^{\infty} a_\lambda E_\lambda d\lambda$$

\*See footnote under section 7.2.

$$= \left( \sum dA \right) \pi \int_0^{\infty} a_{\lambda} E_{\lambda} d\lambda \quad (7.3)$$

because we have also assumed that the absorptive power for any  $\lambda$  is the same for every part of the body. Equating (7.2) and (7.3) for the equilibrium state, we obtain

$$\left( \sum dA \right) \pi \int_0^{\infty} e_{\lambda} d\lambda = \left( \sum dA \right) \pi \int_0^{\infty} a_{\lambda} E_{\lambda} d\lambda. \quad (7.4)$$

Now, if, say, a particular wavelength  $\lambda$  is absorbed by the body more than is emitted, then according to (7.4), it can absorb all other wavelengths less than it emits them. This means that in the enclosure the density of  $\lambda$  will be continuously decreasing while that of all other wavelengths will be continuously increasing. Thus, the character of radiation in the enclosure will be steadily changing and the equilibrium will never be established. So, in order that the equilibrium state is set up and maintained\*,  $E_{\lambda}$  must steadily increase or the emissive powers, for other wavelengths, of the enclosure must decrease. But by Prevost's law, the emissive power of the enclosure should be independent of the body. Hence, from (7.4), we must have, for each wavelength  $\lambda$ ,

$$e_{\lambda} = a_{\lambda} E_{\lambda}. \quad (7.5)$$

Now, if we place the body in another hollow enclosure maintained at the same temperature but with a different shape and nature of the walls, then we shall have similar to (7.5)

$$e'_{\lambda} = a'_{\lambda} E'_{\lambda}, \quad (7.6)$$

where  $E'_{\lambda}$  is the emissive power of this enclosure. Comparing (7.5) and (7.6),

$$E_{\lambda} = E'_{\lambda}.$$

Thus the emissive power, for any wavelength  $\lambda$ , of all hollow enclosures maintained at the same temperature is the same.

Now, if we place a perfectly black body inside a hollow enclosure, from (7.5) we find, since  $a_{\lambda} = 1$  in this case,

$$e_{\lambda} = E_{\lambda}. \quad (7.7)$$

Hence, the emissive power of a hollow enclosure is the same as that of a black body at the same temperature. Then, from (7.5) we have

$$\frac{e_{\lambda}}{a_{\lambda}} = E_{\lambda} = \text{emissive power of a black body.} \quad (7.8)$$

This means that *the ratio of the emissive power to the absorptive power of a body at a certain temperature is a constant and is equal to the emissive power of a perfectly black body at the same temperature*. This is Kirchhoff's law. Although we have proved the law here for bodies in a hollow enclosure, it is equally true for any body under any conditions since the emissive and absorptive powers of a body depend on its physical nature and not on the surroundings.

Kirchhoff's law (7.8) has got two important aspects—qualitative and quantitative. Qualitatively, if a body emits radiation of certain wavelengths, it must also absorb the same kinds of radiation when they fall on it. Quantitatively, the law states that the ratio of the left-hand side of (7.8) is the same for all bodies at the same temperature. Kirchhoff's law has wide applications to Astrophysics and Spectroscopy.

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\*It is found from experiments that the character of radiation inside a hollow enclosure at a definite temperature is quite definite and steady. See later sections of this chapter.

## 7.5 Black Body

In the preceding section it has been shown that the emissive power,  $E_\lambda$ , of the walls of a hollow enclosure is equal to that of a perfectly black body. Let us try to understand this, because the material of which the walls may be composed, may have emissive power  $e_\lambda$  different from  $E_\lambda$  and absorptive power  $a_\lambda \neq 1$ . Now, the radiation inside a hollow enclosure is made up of repeated reflections at the walls such that at each reflection some radiation is absorbed. If  $r_\lambda$  is the reflecting power of the walls, then the total radiation coming into the hollow space per unit time on direct emission, single reflection, double reflection, etc. is\* by (7.2)

$$\begin{aligned}
 &= \left( \sum dA \right) \pi \int_0^\infty e_\lambda d\lambda + \left( \sum dA \right) \pi \int_0^\infty r_\lambda e_\lambda d\lambda \\
 &\quad + \left( \sum dA \right) \pi \int_0^\infty r_\lambda^2 e_\lambda d\lambda + \dots \quad (dA = \text{surface element of the wall}) \\
 &= \left( \sum dA \right) \pi \int_0^\infty (e_\lambda + r_\lambda e_\lambda + r_\lambda^2 e_\lambda + \dots) d\lambda \\
 &= \left( \sum dA \right) \pi \int_0^\infty \frac{e_\lambda}{1 - r_\lambda} d\lambda \\
 &= \left( \sum dA \right) \pi \int_0^\infty \frac{e_\lambda}{a_\lambda}, \quad [\because 1 - r_\lambda = a_\lambda, \text{ assuming no transmission to take place through} \\
 &\quad \text{the wall}] \\
 &= \left( \sum dA \right) \pi \int_0^\infty E_\lambda d\lambda. \quad [\text{from (7.8)}] \tag{7.9}
 \end{aligned}$$

Thus, we find that due to repeated reflections (with partial absorption at each reflection), the hollow enclosure behaves like a perfectly black body. It should be evident that no particular part of the walls of the enclosure alone behaves like a black body, but all the walls together contribute to the black-body character of the hollow enclosure. In fact, the emissive and absorptive power of different parts of the walls remain dependent only on temperature by Prevost's law.

Thus, it is clear that an enclosure maintained at a constant temperature becomes filled with radiation characteristic of a black body. This radiation is usually called *black-body radiation* or *full radiation*. Now, if a sufficiently small hole is made in the wall, the *hole* will behave like a perfectly black body. Because, in the first place the radiation emerging out of the hole will be almost same as the radiation from a perfectly black body, and in the second place any radiation incident on the hole passes inside the hollow enclosure and is reflected so many times on the walls before it again reaches the hole that it is completely absorbed. In practice, the walls are usually blackened so that one reflection alone is sufficient to absorb practically all the radiation. It should, however, be remembered that theoretically this blackening is not at all essential. In accurate work, a correction has to be made for the lack of blackness due to the finite size of the hole\*\*.

A black body designed by Fery has a conical projection  $P$  opposite the hole  $O$  [Fig. 7.2(a)]. The projection is to prevent direct emission of radiation or direct reflection of radiation from the surface opposite  $O$ , otherwise the body would not be perfectly black.

\*Saha and Srivastava, *A Treatise on Heat* P. 633 (1958).

\*\*Wien and Lummer, *Wied. Ann.*, **56**, P. 451 (1895); Buckley *Phil. Mag.*, **6**, P. 447 (1928); for a hole in the shape of a slit see Liebmann, *Zeits. f. Techn. Phys.*, **12**, P. 433 (1931).

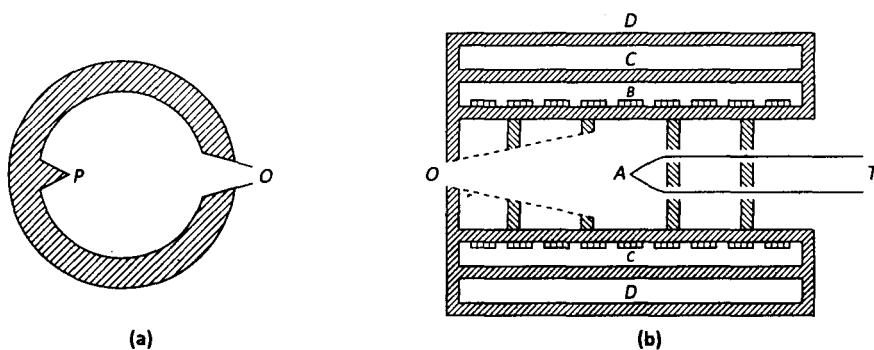


Fig. 7.2: (a) Fery's black body and (b) Wien's black body

However, a commonly used form of the black body [Fig. 7.2(b)], due to Wien, consists of a hollow cylindrical metallic chamber  $A$  made of brass or platinum depending on the range of temperature it is meant for. It is blackened inside and is heated electrically by passing current through thin platinum foil  $B$  wound over  $A$ . The cylinder is surrounded by coaxial heat-resisting porcelain tubes  $C, D$ . The temperature is determined by the thermo-element  $T$ . The radiation passes through a number of limiting diaphragms and finally passes through the hole  $O$ . The diaphragms considerably reduce the radiation from outside coming in to disturb the temperature of the hollow chamber  $A$ .

**Exercise 1.** Prove Kirchhoff's law with two infinitely extended slabs of different materials facing each other parallel such that the faces further away from each other are impervious to heat\*.

**Solution :** Let the two slabs be  $A$  and  $B$ . Let  $e_1, a_1$  denote the radiating power and absorbing power of  $A$ , and  $e_2, a_2$  the radiating power and absorbing power of  $B$ . Since the slabs are parallel and of infinite extensions, the radiation from each will be normal to its surface and, therefore, will fall normally on the other.

Consider first  $e_1$ , emitted by  $A$ . Out of  $e_1$ ,  $a_2e_1$  is absorbed by  $B$ ,  $(1 - a_2)e_1$  reflected. Of the reflected energy,  $(1 - a_2)a_1e_1$  is absorbed by  $A$ ,  $(1 - a_2)(1 - a_1)e_1$  reflected. Of this again,  $(1 - a_2)(1 - a_1)a_2e_1$  is absorbed by  $B$ ,  $(1 - a_2)^2(1 - a_1)e_1$  reflected, and so on. Then, the total quantity absorbed by  $A$  per unit area per unit time is

$$\begin{aligned} &= (1 - a_2)a_1e_1 + (1 - a_2)^2(1 - a_1)a_1e_1 + (1 - a_2)^3(1 - a_1)^2a_1e_1 + \dots \\ &= \frac{(1 - a_2)a_1e_1}{1 - (1 - a_1)(1 - a_2)}. \end{aligned} \quad (7.10)$$

The quantity of radiation absorbed by  $B$  per unit area per unit time is

$$\begin{aligned} &= (a_2e_1) + (1 - a_1)(1 - a_2)a_2e_1 + (1 - a_1)^2(1 - a_2)^2a_2e_1 + \dots \\ &= \frac{a_2e_1}{1 - (1 - a_1)(1 - a_2)}. \end{aligned} \quad (7.11)$$

In (7.11) if we just interchange the suffixes 1 and 2, then we obtain the energy absorbed per unit area of  $A$  out of  $e_2$  radiated by  $B$  as

$$\frac{a_1e_2}{1 - (1 - a_1)(1 - a_2)}. \quad (7.12)$$

\*Kirchhoff gave this proof before he gave the rigorous proof. See Houstoun, R. A., *A Treatise on Light*, Pp. 478-9, (1945).

Hence, the total quantity of energy absorbed by  $A$  per unit area per unit time is, from (7.10) and (7.12),

$$\frac{(1-a_2)a_1e_1}{1-(1-a_1)(1-a_2)} + \frac{a_1e_2}{1-(1-a_1)(1-a_2)} = \frac{(1-a_2)a_1e_1 + a_1e_2}{a_1 + a_2 - a_1a_2}. \quad (7.13)$$

This must be equal to  $e_1$ . Hence,

$$e_1 = \frac{(1-a_2)a_1e_1 + a_1e_2}{a_1 + a_2 - a_1a_2} \quad \text{or,} \quad \frac{e_1}{a_1} = \frac{e_2}{a_2} = e_2, \quad (7.14)$$

if, say, the radiating surface of  $B$  is black, i.e.,  $a_2 = 1$ . This is Kirchhoff's law.

**Exercise 2.** Assuming the sun to be a flat body of infinitely large thickness and extension, prove that the sun radiates like a black body.

**Solution :** Divide the sun into a very large number of parallel layers of equal thickness. Let  $e, a$  be the radiating power and absorbing power of a single layer. Then, the total radiation emitted per unit area per unit time normally from a flat face is

$$\begin{aligned} &= e \text{ (emitted by the first layer on the flat face)} \\ &+ (1-a)e \text{ (emitted by the second layer and transmitted through the first layer)} \\ &+ (1-a)^2e \text{ (emitted by the third layer and transmitted through the first and second layers)} \\ &+ \dots \\ &= \frac{e}{1-(1-a)} = \frac{e}{a} = \text{radiating power of a black body by Kirchhoff's law.} \end{aligned}$$

In respect of absorption of radiation also, this body behaves like a black body, because it can absorb any radiation incident on it owing to the great thickness.

## 7.6 Pressure of Radiation

**Maxwell's Theory :** Maxwell showed in 1870 on the basis of his electromagnetic theory that electromagnetic radiation should exert on a surface pressure equal to the energy-density for a *parallel incident beam*\*. Then, if  $I$  is the intensity of a parallel beam of radiation, then it is equal, by the usual definition, to the energy passing normally through unit area per unit time and hence is contained in a cylinder of unit cross section and of length equal to  $c$ , the velocity of radiation. The density of radiation is, therefore,  $I/c$  so that the pressure exerted on a surface held normal to the parallel beam is

$$P = \frac{I}{c}. \quad (7.15)$$

It has been thoroughly established that the electromagnetic radiation possesses all the properties such as reflection, refraction, etc.—ascribed to other kinds of radiation like light and heat. Hence, it is considered that all kinds of radiation are electromagnetic in nature, but differ from one another only in wavelength. Then, like electromagnetic radiation, light and heat radiations also shall exert pressure when incident on a surface. This, in fact, puts on a sound basis Kepler's belief that as a comet approaches the sun, its tail is always turned away from the sun due to the pressure of solar radiation.

**Bartoli's Thermodynamic Proof for Radiation Pressure :** Bartoli proved by elegant thermodynamic reasoning, shortly after Maxwell, that thermal radiation should exert pressure. Let us take a cylinder (Fig. 7.3) fitted at the two ends with two perfectly conducting black

\*See, for example, Jeans, J., *Mathematical Theory of Electricity and Magnetism*, P. 538 (1963).

plates  $A$  and  $B$  such that  $A$  is maintained at temperature  $T_1$  and  $B$  at  $T_2$  ( $T_1 < T_2$ ).  $X$  and  $Y$  are two perfectly reflecting diaphragms,  $X$  being provided with a valve. At the beginning, the valve in  $X$  is open so that the whole space between  $A$  and  $Y$  is filled with radiation in equilibrium with the black body  $A$  at temperature  $T_1$ . On the other hand, the space between  $Y$  and  $B$  is filled with radiation in equilibrium with the black body  $B$  at temperature  $T_2$ . Now, the valve in  $X$  is closed and  $X$  is moved to a position  $X'$  so that the density of radiation between  $X'$  and  $Y$  is greater than that between  $Y$  and  $B$ . Next,  $Y$  is pulled aside by holding  $Z$  so that there is now communication of radiation between the space  $X'Y$  and the space  $YB$ . Evidently, the whole space  $X'B$  contains now radiation of density higher than that can be in equilibrium with the black body  $B$  maintained at  $T_2$ . So some radiation will be absorbed by  $B$  till the former (i.e., initial) density is restored. Now, this radiation absorbed by  $B$  was actually emitted by  $A$ . Hence, we find that some heat has, in effect, been transferred from a colder to a hotter body and this process can be repeated as often as we please. But, by the second law of thermodynamics (Clausius' statement), this is impossible without any external agency doing work. Hence, in moving  $X$  to the position  $X'$ , work will have to be done, and evidently this must be performed against pressure exerted by radiation on  $X$ .

Although we thus establish by thermodynamic reasoning that radiation exerts pressure, its magnitude, however, cannot be calculated thermodynamically.

**Quantum Theory :** The quantum theory, first propounded by Planck, will be introduced in Chapter 8 and also certain aspects of this theory will be the subject-matter in the last two chapters of this book. According to this idea, briefly, a beam of radiation is just a stream of quanta or photons, each of energy  $h\nu$  ( $h$  is called Planck's constant and  $\nu$  is the frequency of radiation) and of velocity  $c$  so that a photon possesses momentum  $= h\nu/c^*$ , according to the theory of relativity. Hence, as such a stream of photons hits a surface, it must exert pressure.

**Experiments on Radiation Pressure :** The theory of experimental determination of radiation pressure is basically the following. Let  $P$  be the pressure due to radiation on a disc of area  $A$  of a suspended vane. Let the disc be at a distance  $r$  from the axis (i.e., the suspension fibre). Then, the moment applied to the vane is  $PAr$ . If, due to this moment, the vane rotates through an angle  $\phi$ , then the restoring moment applied by the suspension will be  $\alpha\phi$ , where  $\alpha$  is the restoring moment per unit twist of the suspension. Hence, we must have

$$PAr = \alpha\phi \quad \text{or,} \quad P = \frac{\alpha}{Ar}\phi. \quad (7.16)$$

If the moment of inertia of the suspended system is known, then  $\alpha$  can be determined from the period of free angular oscillations of the system. Then knowing all quantities of the right-hand side,  $P$  can be calculated. This value of  $P$  has to be compared with the theoretical value  $I/c$  in (7.15),  $I$  is found by allowing the same radiation to fall on a suitable blackened body and noting its rise of temperature by some thermoelement.

However, for long years the chief difficulty, in these experiments, was the *radiometer* or *gas action* : the side of the disc on which radiation falls gets heated so that the gas pressure on that side increases and this increase in gas pressure masks the radiation pressure. Lebedew of Moscow made the first successful attempt in 1900 to determine radiation pressure by eliminating

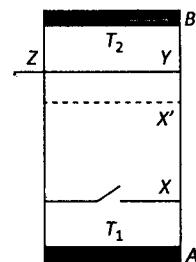


Fig. 7.3: Bartoli's cylinder

\* A. H. Compton was the first to use and experimentally establish this expression for photon momentum. See, Compton, A. H., Phys. Rev. XXI, Pp. 483, 715 (1923); XXII, P. 409 (1923). See also Compton and Allison, *X-rays in Theory and Experiment*, Pp. 204-7 (1949).

gas action. He was followed shortly afterwards by Nichols and Hull\* who further reduced in their experiment the effect of gas action. We shall discuss their experiment here.

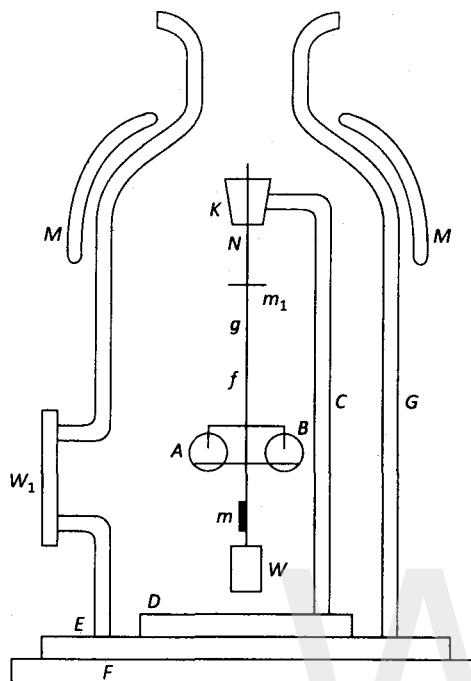


Fig. 7.4: Nichols-Hull arrangement

The arrangement used by Nichols and Hull is shown in Fig. 7.4,  $G$  is a glass vessel (with window  $W_1$ ) 25 cm high and 11 cm in diameter enclosing the whole suspended system. It stands on a glass plate  $E$  which is again supported by a metal plate  $F$ .  $C$  is a bent glass tube standing on a brass plate  $D$  and holding the whole suspended system.  $N$  is a fine steel needle passing through the support  $K$ .  $m_1$  is a light bar magnet.  $g$  is a fine glass thread and  $f$  a fine quartz fibre 3 cm long.  $A$  and  $B$  are two thin glass discs, each silvered on one side only.  $m$  is a small mirror which gives, by lamp-and-scale arrangement, the rotation of the vane  $AB$ . The weight  $W$  keeps the suspension taut. The circular magnets  $M$  outside  $G$  act on  $m_1$  and provide a control on the suspended system. The vessel is evacuated with a mercury pump (not shown) and the pressure is measured with a McLeod gauge (not shown).

The disc ( $A$  or  $B$ ) which is illuminated receives radiation on both the glass and silvered surfaces successively. However, as the beam of light is first passed through a number of lenses and glass plates,

it loses that part which heats glass. Hence, whether the glass surface or the silvered surface is illuminated, it is the silvered surface that gets heated. So, when the radiation is incident on the silvered surface, the radiation pressure and the radiometer or gas action assist each other. But the pressure of radiation falling on the silvered surface and that of radiation incident on the glass surface are in opposition to each other. Thus, the gas action can be found out. Nichols and Hull found that at 16 mm of Hg pressure in the glass vessel  $G$ , the gas action was minimum and they used this pressure for their experiment. They further minimised the effect of gas action by using very short exposures and noting down the "ballistic" deflections. Because, while the action of light pressure is instantaneous, the action of gas pressure takes much longer time.

Poynting and Barlow in 1904 measured tangential pressure of radiation by allowing light to fall at an angle of  $45^\circ$  on a suspended system.

In all these experiments, the results were found to agree with Maxwell's prediction.

**Exercise 1.** Find the pressure exerted by solar radiation falling normally on a black surface, the intensity being  $= 1.75 \times 10^6 \text{ ergs/cm}^2 \cdot \text{sec}$ .

$$\text{Solution : From (7.15), } P = \frac{I}{c} = \frac{1.75 \times 10^6 \text{ ergs/cm}^2 \text{ sec}}{3 \times 10^{10} \text{ cm/sec}} = 5.8 \times 10^{-5} \text{ dynes/sq cm.}$$

Evidently, the pressure is extremely small.

**Exercise 2.** Compare radiation pressure with gravitational attraction due to the sun on a small body.

\*Nichols and Hull, Proc. Amer. Acad., 38 (1903); see also Wood, R. W., Physical Optics.

**Solution :** Let the small body be with a perfectly black surface, a radius  $r$ , a density  $\rho$  and at a particular temperature throughout. If it is exposed to solar radiation of intensity  $I$ , then the force acting on it due to radiation pressure is

$$F_R = \frac{\pi r^2 I}{c}. \quad (7.17)$$

If  $g$  be the acceleration due to gravity towards the sun, then the gravitational force experienced by the body is

$$F_G = \frac{3}{4} \pi r^3 \rho g. \quad (7.18)$$

Hence,  $\frac{F_R}{F_G} = \frac{\frac{3}{4} I}{rc\rho g}.$  (7.19)

If the body be at a distance equal to that of the earth from the sun, then  $I = 1.75 \times 10^6 \text{ ergs/cm}^2 \text{ sec}$ ,  $g = 0.59 \text{ cm/sec}^2$  so that with  $\rho = 1 \text{ gm/cc}$ , we can calculate the value of  $r$  for which  $F_R = F_G$ . It is, from (7.19),

$$r = \frac{3}{4} \frac{I}{c\rho g} = \frac{3}{4} \frac{1.75 \times 10^6 \text{ ergs/cm}^2 \text{ sec}}{3 \times 10^{10} \text{ cm/sec} \times 1 \text{ gm/cc} \times 0.59 \text{ cm/sec}^2} = 7400 \text{ \AA.}$$

That is, the diameter of the body which must be about double the wavelength of red light for  $F_R$  to be equal to  $F_G$ , if, however, we assume that the surface of such a small body can absorb radiation.

## 7.7 Pressure of Diffuse Radiation

Radiation in a hollow enclosure at a uniform temperature is diffuse (i.e., travelling in all possible directions). We now proceed to calculate the pressure of diffuse radiation.

Let us imagine an area  $dA$  in the hollow space. Then, the radiation passing through this area at an angle  $\theta$  through a solid angle  $d\omega$  in time  $dt$  will be

$$\propto dA \cos \theta$$

$$\propto d\omega$$

$$\propto dt$$

i.e. will be equal to  $K dA \cos \theta d\omega dt$ , (7.20)

where  $dA \cos \theta$  is the area through which this radiation passes normally. Here, the constant  $K$  is called the *specific intensity of radiation*. Then, the total radiation passing through  $dA$  from one side to the other in time  $dt$  is, from (7.20),

$$\begin{aligned} &= \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi/2} K dA \cos \theta \sin \theta d\theta d\phi \\ &= \pi K dA dt. \end{aligned} \quad (7.21)$$

Hence,  $\pi K$  is the radiation passing through unit area from one side to the other in unit time. Since the walls of the hollow enclosure behave like the surface of a black body (See sections 7.4 and 7.5) and also since  $\pi K$  amount of radiation will be incident on every unit area of the walls in unit time, it is evident that  $\pi K$  is the energy absorbed by every unit area per unit time. Therefore, under equilibrium condition,  $\pi K$  should also be the energy emitted in unit time by unit area of the walls and hence, also by unit area of a black body at the same temperature.

Now, we find the energy within a small volume  $v$  in the hollow enclosure. With this volume at the centre, draw a large sphere of radius  $r$  (Fig. 7.5). Then,

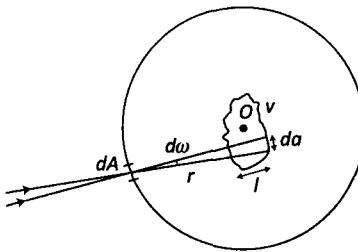


Fig. 7.5

any radiation passing normally through the surface of this sphere must also pass through  $v$ . Now, any radiation passing normally through an area  $dA$  on the sphere through a solid angle  $d\omega$  will traverse a length  $l$  of  $v$  in time  $l/c$ . Then, the radiation, by (7.20),

$$KdAd\omega \cdot \frac{l}{c} = KdA \cdot \frac{da}{r^2} \cdot \frac{l}{c} \quad (7.22)$$

( $da$  = cross section of cone in  $v$ )

passing normally through  $dA$  with a solid angle  $d\omega$  ( $= \frac{da}{r^2}$ ) in time  $l/c$  will be the amount contained in  $v$  at any instant.

Then, summing over all such cones to cover the whole volume  $v$ , we obtain from (7.22) the radiation passing through  $dA$  and contained in  $v$  equal to

$$\sum KdA \cdot \frac{da}{r^2} \cdot \frac{l}{c} = \frac{KdA}{cr^2} \left( \sum da \cdot l \right) = \frac{KdA}{cr^2} v. \quad (7.23)$$

This expression is further integrated over the whole sphere to obtain the total energy contained in  $v$  at any instant. This is,

$$\int \frac{KdA}{cr^2} v = \frac{4\pi K}{c} v. \quad (7.24)$$

Hence, the energy density within the hollow enclosure is

$$E = \frac{4\pi K}{c} v \quad (7.25)$$

so that the energy emitted in unit time by unit area by a black body is

$$\pi K = \frac{cE}{4}. \quad (7.26)$$

Let us now take an area  $dA$  on the wall of the hollow enclosure. If a hemisphere is drawn with  $dA$  at the centre (Fig. 7.6), then any radiation passing normally through the hemisphere must fall on  $dA$ . Then, the radiation passing per unit time normally through  $dA'$  of the hemisphere through solid angle  $d\omega$  and falling per unit time on  $dA$  at an angle  $\theta$  is, by (7.20),

$$\begin{aligned} &= KdA'd\omega' = KdA' \cdot \frac{dA \cos \theta}{r^2} \\ &= KdA \cos \theta \frac{dA'}{r^2} = KdA \cos \theta d\omega. \end{aligned} \quad (7.27)$$

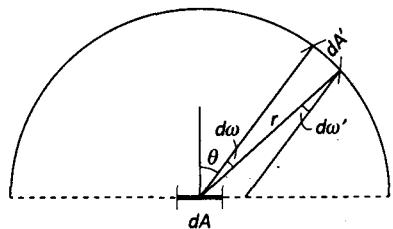


Fig. 7.6

Then, the radiation falling on unit area in unit time at an angle  $\theta$  is

$$K \cos \theta d\omega. \quad (7.28)$$

This radiation will be almost a parallel beam so that the radiation pressure acting on  $dA$  at an angle  $\theta$  is, by (7.15),

$$\frac{K \cos \theta d\omega}{c}. \quad (7.29)$$

Then, the normal pressure on  $dA$  is

$$\left( \frac{K \cos \theta d\omega}{c} \right) \cos \theta$$

so that the total normal pressure, considering radiation incident from all possible directions on  $dA$ , is

$$\begin{aligned} &= \int \frac{K}{c} \cos^2 \theta d\omega = \frac{K}{c} \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi/2} \cos^2 \theta \sin \theta d\theta d\phi \\ &= \frac{1}{3} \frac{2\pi K}{c}. \end{aligned} \quad (7.30)$$

Since  $dA$ , an area of the wall of the hollow enclosure, behaves like a black surface, as much radiation will be incident on it and absorbed by it per unit time as will be emitted during the same time. Then, the pressure due to incident radiation will be added to the recoil pressure due to the emitted radiation, and hence the total pressure\* is, from (7.30),

$$P = 2 \times \left( \frac{1}{3} \cdot \frac{2\pi K}{c} \right) = \frac{E}{3}. \quad [\text{from (7.25)}] \quad (7.31)$$

## 7.8 Stefan-Boltzmann Law

Stefan, on an analysis of the experimental results of Tyndall and of Dulong and Petit stated in 1879 that the total radiation emitted by a heated body is proportional to the fourth power of its absolute temperature. Boltzmann\*\*, however, showed from thermodynamic calculations in 1884 that the law holds strictly in the case of a black body. For this reason, the law is often referred to as Stefan-Boltzmann law. It is also sometimes called Stefan's law.

Now, like a gas, radiation has both energy and pressure. Also as in the case of a gas, the radiation pressure depends upon energy density [according to (7.31)] which again is a function of temperature only (See section 7.3). So it is tempting to apply thermodynamic laws to radiation also.

Suppose, we have radiation in a chamber  $A$  (Fig. 7.7) with perfectly reflecting walls and with a perfectly reflecting piston  $B$  so that no exchange of heat takes place between radiation and the walls, and the thermal capacity of the walls does not come into calculation at all. There is, however, in the chamber a small speck of matter (so small that its thermal capacity may be neglected compared to that of radiation) by means of which heat from outside can reach the radiation, when required. Now, if the speck of matter is at temperature  $T$ , then the radiation will correspond to this temperature.

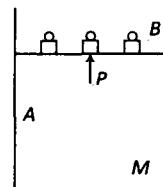


Fig. 7.7

Let an amount of heat  $dQ$  enter the chamber from outside and also at the same time let the volume  $V$  of the chamber change by  $dV$  (by removal of weights) so that the temperature  $T$  and energy density  $E$  both change infinitesimally. All this change, evidently neither isothermal nor adiabatic, is considered to be reversible. Then, by the first law of thermodynamics,

$$dQ = dU + PdV = d(EV) + PdV = (E + P)dV + VdE. \quad (7.32)$$

\*If the surface is perfectly reflecting, then also the total pressure is the same, because as much radiation will be incident as will be reflected. There will be recoil pressure at reflection.

\*\*Boltzmann, *Wied. Ann.*, 22, p. 291 (1884). He conceived of an ether engine to perform a Carnot cycle assuming the radiation energy to be contained in ether just as energy is contained in the working substance of a Carnot engine. We shall, however, apply directly thermodynamic laws to radiation with some argument.

Now, by the second law of thermodynamics, the change in entropy of the radiation is

$$\begin{aligned} dS &= \frac{dQ}{T} = \left( \frac{E + P}{T} \right) dV + \frac{V}{T} dE \\ &= \left( \frac{4E}{3T} \right) dV + \left( \frac{V}{T} \frac{dE}{dT} \right) dT. \quad [\text{from (7.31)}] \end{aligned}$$

Since  $dS$  is a total differential,

$$\begin{aligned} \left[ \frac{d}{dT} \left( \frac{4E}{3T} \right) \right]_V &= \left[ \frac{d}{dV} \left( \frac{V}{T} \frac{dE}{dT} \right) \right]_T \\ \text{or, } \frac{4}{3T} \frac{dE}{dT} - \frac{4}{3} \frac{E}{T^2} &= \frac{1}{T} \frac{dE}{dT}, \end{aligned} \quad (7.33)$$

since  $\frac{dE}{dT}$  is independent of  $V$ ,  $E$  being a function of  $T$  only. (7.33) gives

$$\frac{dE}{E} = 4 \frac{dT}{T}.$$

On integration,

$$\log_e E = 4 \log_e T + \log_e a \text{ (a constant)}$$

$$\text{or, } E = aT^4. \quad (7.34)$$

Then, from (7.26) and (7.34), the radiation emitted in unit time by unit area of a black body is

$$H = \pi K = \frac{ac}{4} T^4 = \sigma T^4, \quad (7.35)$$

where  $\sigma (= \frac{ac}{4})$  is called Stefan's constant. (7.35) represents Stefan-Boltzmann law. From a measurement of  $\sigma$  and the known value of  $c$ , the value of  $a$  can be deduced. Then, from (7.34),  $E$ , the density of total radiation in an enclosure at any temperature  $T$ , can be determined.

Stefan-Boltzmann law (7.35) may also be put in another form : *If a black body at  $T$  is surrounded by another black body at  $T_0$  ( $T > T_0$ ), the amount of energy lost by unit area of the former to the latter per unit time is*

$$H = \sigma(T^4 - T_0^4). \quad (7.36)$$

**Exercise : Newton's Law of Cooling :** Show, from the Stefan-Boltzmann law, that the rate of cooling of a body is proportional to the difference between its temperature and that of the surroundings, provided this difference is very small.

**Solution :** From (7.36),

$$\begin{aligned} H &= \sigma(T - T_0)(T^3 + T^2 T_0 + T T_0^2 + T_0^3) \\ &\approx \sigma 4T_0^3(T - T_0) \quad (\text{assuming that } T - T_0 \text{ is small}) \\ &= A(T - T_0) \quad (\text{where } A = 4\sigma T_0^3). \end{aligned} \quad (7.37)$$

It is evident that Newton's law of cooling is strictly valid for a black body in black surroundings.

## 7.9 Verification of Stefan-Boltzmann Law and Determination of $\sigma$

A large number of investigators tested experimentally this law. We shall, however, discuss here the experiment conducted by Coblentz\*. Let us first consider the principle of the method.

The essential parts of the apparatus are shown in Fig. 7.8. From  $AB$ , the black-body radiator maintained at a high temperature, radiation passes through a small aperture  $CD$  in the screen  $XY$  and falls on the black-body receiver  $EF$ . As the diagram shows, every point of the receiver  $EF$  will receive radiation from some or other part of the radiator  $AB$ . For instance,  $P$  will receive radiation from the area  $LM$  of the radiator. Let  $A_1$  be the area of  $CD$  and  $A_2$  that of  $LM$ . Also let  $D$  be the distance between  $AB$  and  $EF$  and  $d$  that between  $CD$  and  $EF$ . We shall assume that the radiation from a point on  $AB$  falls almost normally on any point of  $EF$ . If  $d\omega$  is the solid angle subtended by an area  $dA$  at  $P$  at any point on the area  $A_2$ , then the radiation received by  $dA$  per unit time from  $A_2$  is by (7.20)\*\*

$$KA_2 d\omega \quad (7.38)$$

(7.38), on simplification, comes to

$$KA_2 \frac{dA}{D^2} = KdA \frac{A_2}{D^2}. \quad (7.39)$$

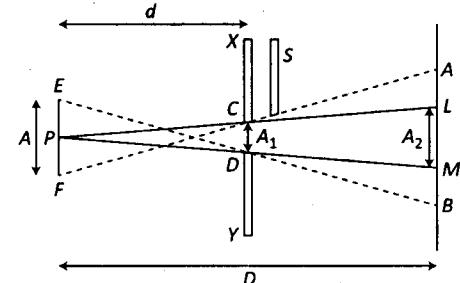


Fig. 7.8: Coblentz's experiment

If, however, the radiator were situated in the plane of the screen, then the radiation from the exposed area equal to  $CD$ , i.e.,  $A_1$ , would have reached the area  $dA$ . This radiation reaching  $dA$  per unit time would be

$$KdA \frac{A_1}{d^2}. \quad (7.40)$$

But, by geometry,

$$\frac{A_2}{D^2} = \frac{A_1}{d^2}. \quad (7.41)$$

Then, we conclude from (7.39) and (7.40) that on account of (7.41), the radiation at  $P$  from the area  $LM$  is the same as the radiation from a surface of the size of  $CD$  situated in the plane of the screen.

The experiment consists in measuring  $Q$  the difference between  $Q_1$  the energy received per unit time by the receiver when  $CD$  is open and  $Q_2$  the energy received per unit time by the receiver when  $CD$  is closed with a blackened water-cooled shutter  $S$ . Let  $T_2$  be the temperature of the radiator and  $T_1$  that of the shutter. Then, from what has been stated just above, from (7.39), (7.40) and (7.41),

$$Q_1 = K_1 A \frac{A_2}{D^2} = K_1 A \frac{A_1}{d^2}, \quad (7.42)$$

where  $A$  is the area of the receiver  $EF$  and when  $CD$  is closed, the receiver receives radiation from the blackened shutter  $S$ . This is, from above,

$$Q_2 = K_2 A \frac{A_1}{d^2}. \quad (7.43)$$

\*Coblentz, *A Dict. of App. Phys.*, 4, P. 541 (1923).

\*\*Because, in fact,  $AB$  is the hole of a black body chamber, we apply (7.20) here. But, since the hole behaves like a black surface, (7.20) applies also to a black surface.

Here,  $K_2$  and  $K_1$  are the specific intensities of radiation from the radiator and the shutter respectively. Hence, using (7.35),

$$Q = \frac{\sigma(T_1^4 - T_2^4)AA_1}{\pi d^2}. \quad (7.44)$$

It should be remembered that according to the calculation carried out, (7.44) is strictly accurate only if the areas which are involved here for emission and absorption of radiation are small compared to the distances between them. In practice, however, this is only approximately satisfied, and therefore, small corrections are necessary to be made on this score.

The temperature  $T_2$  of the shutter was determined, in Coblentz's experiment, by a mercury thermometer placed in the water circulating through it. Although the shutter was not a perfectly black body, it did not matter much because  $T_2^4$  was very small compared with  $T_1^4$  in (7.44).

The radiator consisted of three coaxial porcelain cylinders [similar to Fig. 7.2(b)]. The innermost and the middle tube were wound with platinum ribbons through which current was passed to heat the system. The temperature  $T_1$  of the actual radiating cavity [similar to A in Fig. 7.2(b)] was determined by a thermocouple.

The receiver consisted of a strip of manganin blackened with lamp-black or platinum-black. A thermopile, consisting of a number of thermo-elements of bismuth and silver, was placed behind, but close to, the central part of the manganin receiving surface. The thermopile was heated by radiation from the manganin surface. When exposed to radiation from the radiator, the temperature of the manganin strip increased and it produced a steady deflection in the thermopile galvanometer. Next, when  $CD$  was closed by the shutter, the manganin was heated electrically till the same steady deflection was produced.  $Q$  in (7.44) was obtained by measuring the electrical energy supplied.

A blackened manganin strip does not completely absorb all the radiation incident on it—so a correction is to be made for this.

$Q$  was found to be proportional to  $(T_1^4 - T_2^4)$  which means verification of the Stefan-Boltzmann law.

Coblentz obtained the value  $5.72 \times 10^{-5}$  erg · cm<sup>-2</sup> · sec<sup>-1</sup> · deg<sup>-4</sup> for  $\sigma$ .

Hoare\* also found a similar value for  $\sigma$  by a method similar to that of Coblentz, but using a Callendar radio-balance as receiver.

## 7.10 Black-body Radiation under Adiabatic Change

Suppose, we have black radiation at temperature  $T_1$  in an enclosure with walls perfectly, but diffusely, reflecting\*\*. We allow the enclosure to expand adiabatically by a small amount so that the energy density now corresponds to a lower temperature  $T_2$ . During this expansion the radiation will remain isotropic because of diffuse reflection from the walls. But we may have altered, let us suppose, the quality of radiation so that it is no longer black radiation. Now, we introduce a small speck of matter of negligible heat capacity at  $T_2$  into the enclosure so that the radiation will be rendered black again at temperature  $T_2$  without change in total energy. This (i.e., the role played by the speck of matter) is, however, an irreversible process and, therefore, involves an increase of entropy† of radiation. Next keeping the speck of matter in the enclosure, we compress it adiabatically to the original volume and then we remove the speck of matter.

\* Hoare, F.E., *Phil. Mag.*, **28**, P. 828 (1928).

\*\* This means that the walls are made up of a very large number of very small perfectly reflecting mirrors whereas surfaces are oriented in random directions.

† Hoare, F.E., *A Textbook of Thermodynamics*, P. 239 (1952).

The work now done will be the same as before as the pressure depends only on the energy density. Because of the presence of the speck of matter, the black radiation at  $T_2$  has thus returned to the original state at  $T_1$  so that its entropy and energy must now be the same as at the beginning. But it has been stated that the role played by the speck of matter has caused an increase of entropy of radiation. This is, therefore, contrary to the physical condition. So we must conclude that black radiation remains black under adiabatic changes (i.e., expansion and compression) also.

Now, in an adiabatic change,  $dQ = 0$  and, therefore, from (7.32),

$$0 = d(EV) + \frac{E}{3}dV,$$

which, on integration, gives

$$EV^{4/3} = \text{constant.} \quad (7.45)$$

From (7.34) and (7.45), we obtain

$$VT^3 = \text{constant} \quad (7.46)$$

under an adiabatic change.

## 7.11 Distribution of Energy in Black-body Radiation : Wien's Law

Till now we have considered only the total radiation emitted by a black body and have not dealt with the distribution of energy among the different wavelengths in black radiation. We shall take up this problem now.

Let us consider black radiation contained in a spherical cavity of radius  $r$  with walls perfectly, but diffusely reflecting, i.e., with walls containing randomly oriented perfectly reflecting small mirrors (as in the preceding section). If the sphere is allowed to expand continuously with a *small* velocity  $u$  ( $u \ll c$ ), the radiation will undergo a *reversible* (See the preceding section) adiabatic expansion. Further, at each reflection from the moving walls each wavelength of the radiation will be changed. According to the well-known Doppler principle<sup>§</sup>, the changed wavelength  $\lambda'$  is related to the original wavelength  $\lambda$  by

$$\lambda' = \lambda \left( \frac{c + u \cos \alpha}{c - u \cos \alpha} \right) = \lambda \left( 1 + \frac{2u}{c} \cos \alpha \right), \quad (7.47)$$

where  $\alpha$  is the angle of incidence at the wall receding at velocity  $u$  ( $\ll c$ ) parallel to itself.

We now calculate the change of wavelength when a monochromatic ray is reflected at one of the randomly oriented small mirrors contained in the walls of the spherical cavity [Fig. 7.9(a)]. Let the normal to the mirror  $AB$  make angle  $\beta$  with the radius  $OP$  of the sphere and  $\alpha$ , as above, the angle of incidence. Then, if  $u$  is the velocity with which the radius of the sphere increases,  $u \cos \beta$  is the velocity of the small mirror parallel to itself in the direction of its normal. In the figure,  $A'B'$  is the position of  $AB$  at some later instant. Hence, from (7.47), taking  $u \cos \beta$  in place of  $u$  in the present case,

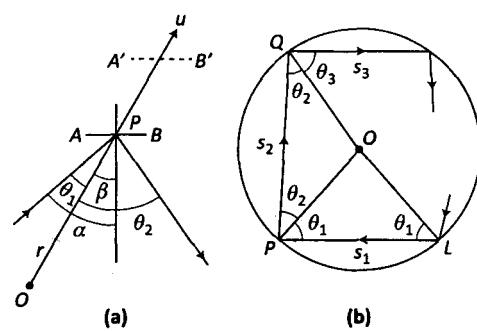


Fig. 7.9

<sup>§</sup>See, for example, Wood, A., *Acoustics*, P. 324 (1947).

$$\lambda' = \lambda \left( 1 + \frac{2u \cos \alpha \cos \beta}{c} \right). \quad (7.48)$$

If  $\theta_1, \theta_2$  are the angles made by the incident and reflected rays respectively with the radius  $OP$  of the sphere, then from the figure,

$$\begin{aligned} \cos \theta_1 + \cos \theta_2 &= 2 \cos\left(\frac{\theta_1 + \theta_2}{2}\right) \cdot \cos\left(\frac{\theta_2 - \theta_1}{2}\right) \\ &= 2 \cos \alpha \cos \beta \end{aligned} \quad (7.49)$$

since  $\theta_1 + \theta_2 = 2\alpha$  and  $\theta_2 - \beta = \alpha = \theta_1 + \beta$  i.e.,  $\theta_2 - \theta_1 = 2\beta$ . Thus, from (7.48) and (7.49),

$$\lambda' = \lambda \left\{ 1 + \frac{u}{c} (\cos \theta_1 + \cos \theta_2) \right\}. \quad (7.50)$$

If the ray starts from the point  $L$  at  $t = 0$  and  $s_1, s_2, s_3, \dots, s_n$  are the lengths of the chords over which it travels between successive reflections in unit time [Fig. 7.9(b)], then

$$c = s_1 + s_2 + s_3 + \dots + s_n. \quad (7.51)$$

From the figure,

$$s_1 = 2r \cos \theta_1, \quad s_2 = 2r \cos \theta_2, \text{ etc.} \quad (7.52)$$

Then, after the first reflection at  $P$ , the wavelength  $\lambda$  is changed to

$$\lambda' = \lambda \left( 1 + \frac{u}{c} \cdot \frac{s_1 + s_2}{2r} \right) \quad [\text{from (7.50) and (7.52)}] \quad (7.53)$$

and after  $n$  successive reflections, this is

$$\lambda' = \lambda \left( 1 + \frac{u}{c} \frac{s_1 + s_2}{2r} \right) \left( 1 + \frac{u}{c} \frac{s_2 + s_3}{2r} \right) \dots \left( 1 + \frac{u}{c} \frac{s_n + s_{n+1}}{2r} \right). \quad (7.54)$$

During  $n$  successive reflections, the sphere is expanding at velocity  $u$  so that we cannot, strictly speaking, write  $r$  in all the successive factors of the right-hand side of (7.54). But, because we have assumed  $u \ll c$ ,  $r$  will be changing very slowly. Again, since  $u$  is  $\ll c$ , (7.54) may be simplified to the form :

$$\begin{aligned} \lambda' &= \lambda \left( 1 + \frac{u}{c} \frac{s_1 + 2s_2 + 2s_3 + \dots + 2s_n + s_{n+1}}{2r} \right) \\ &= \lambda \left\{ 1 + \frac{u}{cr} \left( s_1 + s_2 + s_3 + \dots + s_n - \frac{1}{2} \overline{s_1 - s_{n+1}} \right) \right\} \\ &= \lambda \left\{ 1 + \frac{u}{cr} \left( c - \frac{1}{2} \overline{s_1 - s_{n+1}} \right) \right\}, \quad \text{using (7.51)} \\ &= \lambda \left( 1 + \frac{u}{r} \right), \quad \text{neglecting } \frac{1}{2} \overline{s_1 - s_{n+1}} \text{ compared to } c. \end{aligned} \quad (7.55)$$

Hence, the change of wavelength in unit time is

$$\frac{\lambda' - \lambda}{1} = \frac{d\lambda}{dt} = \frac{u}{r} \lambda$$

or, writing  $u = \frac{dr}{dt}$ ,  $\frac{d\lambda}{dt} = \frac{dr}{dt} \frac{\lambda}{r}$   
i.e.,  $\frac{d\lambda}{\lambda} = \frac{dr}{r}$ .

On integration,

$$\int_{\lambda}^{\lambda'} \frac{d\lambda}{\lambda} = \int_r^{r'} \frac{dr}{r} \quad \text{or} \quad \log_e \left( \frac{\lambda'}{\lambda} \right) = \log_e \left( \frac{r'}{r} \right)$$

$$\text{i.e., } \frac{\lambda}{r} = \frac{\lambda'}{r'}, \quad (7.56)$$

where  $\lambda$  and  $\lambda'$  are the wavelengths of the particular ray under our consideration corresponding to radii  $r$  and  $r'$  respectively. Instead of  $\lambda$ , if we consider  $\lambda + d\lambda$ , then (7.56) gives

$$\frac{\lambda + d\lambda}{r} = \frac{\lambda' + d\lambda'}{r'} \quad (7.57)$$

$$\text{i.e., } \frac{d\lambda}{r} = \frac{d\lambda'}{r'} \quad [\text{from (7.56)}]$$

(7.57) gives how  $d\lambda$  changes to  $d\lambda'$  as  $r$  changes to  $r'$ .

Since we are considering a spherical enclosure, (7.45) and (7.46) give respectively

$$Er^4 = E'r'^4 \quad (7.58)$$

$$\text{and } Tr = T'r'. \quad (7.59)$$

Multiplying (7.56) by (7.59),

$$T\lambda = T'\lambda'. \quad (7.60)$$

This means that as the radiation of a particular wavelength  $\lambda$  at  $T$  is adiabatically changed to  $\lambda'$  at  $T'$ . The product  $T\lambda$  is equal to the product  $T'\lambda'$  under the changed condition, i.e.,

$$T\lambda = \text{constant} \quad (7.61)$$

under adiabatic change of radiation.

It is evident from (7.56) that if the enclosure expands adiabatically, any change that takes place in a particular wavelength is quite independent of the presence or absence of other wavelengths. We can, therefore, assume for a moment that this is the only wavelength present in the enclosure. Then, applying this assumption to the radiation of wavelengths between  $\lambda$  and  $\lambda + d\lambda$ , we obtain from (7.58)

$$E_\lambda d\lambda r^4 = E'_\lambda d\lambda' r'^4, \quad (7.62)$$

where  $E_\lambda d\lambda$  is the energy density of black radiation for this range of wavelengths. Now, using (7.57) and (7.59) in (7.62),

$$\frac{E_\lambda}{T^5} = \frac{E'_\lambda}{T'^5} \quad (7.63)$$

$$\text{i.e., } \frac{E_\lambda}{T^5} = \text{constant} \quad (7.64)$$

under adiabatic change of black radiation. From (7.61), under the same adiabatic change also, we have

$$f(T\lambda) = \text{constant}. \quad (7.65)$$

Then, we can combine (7.64) and (7.65) (since these equations represent collateral conditions)

$$\frac{E_\lambda}{T^5} = \text{constant}$$

i.e.,  $E_\lambda = \text{constant} \cdot T^5 f(\lambda T) = AT^5 f(\lambda T)$ , (say). (7.66)

This is Wien's law\*.

The law may be put in another form\*\* using (7.61).

$$E_\lambda = \frac{B}{\lambda^5} f(\lambda T), \quad (7.67)$$

where  $B$  is a constant.

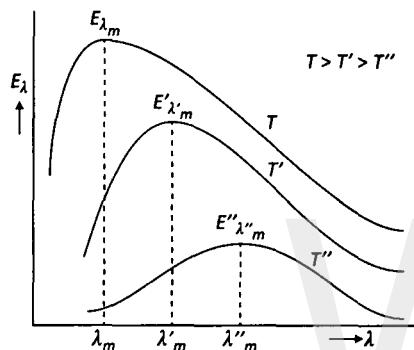


Fig. 7.10:  $E_\lambda$ - $\lambda$  curves

If the curve given by (7.67) has a maximum  $E_{\lambda_m}$  at a wavelength  $\lambda_m$ , then from (7.64),

$$\frac{E_{\lambda_m}}{T^5} = \text{constant}$$

i.e.,  $\frac{E_{\lambda_m}}{E'_{\lambda'_m}} = \left(\frac{T}{T'}\right)^5$ . (7.68)

Similarly, from (7.60),

$$T\lambda_m = T'\lambda'_m = b \text{ (a constant).} \quad (7.69)$$

This is known as Wien's *displacement law*<sup>†</sup>. Fig. 7.10 shows the implications of (7.68) and (7.69).

## 7.12 Evaluation of $f(\lambda T)$

In this section, we shall present some attempts to evaluate  $f(\lambda T)$  so that we may obtain Wien's law (7.67) in a complete form.

(a) **Wien's Radiation Formula** : Let us first discuss Wien's attempt<sup>‡</sup>. He assumed that the radiation in a hollow enclosure is emitted and absorbed by some (gaseous) particles and that the kinetic energy of each particle is proportional to the frequency of radiation emitted by it, i.e., inversely proportional to the wavelength of emitted radiation. Then,

$$\text{kinetic energy } \epsilon = \frac{\alpha}{\lambda}, \quad (7.70)$$

where  $\alpha$  is a constant.

Wien also assumed that Maxwell's distribution law applies to these particles so that the total number of particles having energy between  $\epsilon$  and  $\epsilon + d\epsilon$  is, from (2.29), (2.34) and (2.35)<sup>§</sup>,

\*Instead of combining (7.64) and (7.65), we could combine (7.60) and (7.64) also, one might think. But Wien adopted the general procedure to obtain a general formula. See Smith, R. A., *Thermodynamics*, P. 102 (1952).

\*\*Wien, *Berl. Ber.* P. 55 (1893); *Wied. Ann.*, **52**, P. 132 (1894).

<sup>†</sup>Some authors (e.g., Saha and Srivastava, Roberts and Miller) have called (7.67) Wien's displacement law, while others (e.g., Hoare, Smith) have given this name to (7.69). The present author prefers to line up with the second group of authors.

<sup>‡</sup>Wien, *Ann. d. Phys.* **58**, P. 662 (1896).

<sup>§</sup>In Maxwell's law, put  $\frac{1}{2}mc^2 = \epsilon$  so that  $c^2 d\epsilon = \frac{(2\epsilon)^{\frac{1}{2}}}{m^{\frac{3}{2}}} d\epsilon$ .

$$dN_\epsilon = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}} e^{-\frac{\epsilon}{kT}} \epsilon^{\frac{1}{2}} d\epsilon$$

i.e.,  $dN_\epsilon = \text{constant} \cdot P(\lambda) e^{-\frac{\epsilon}{kT}} d\lambda$ , (7.71)

where we have used (7.6.1) and (7.70) and have expressed the quantity involving  $\lambda$  as  $P(\lambda)$ .

He further assumed that the energy density of radiation of wavelengths between  $\lambda$  as  $\lambda + d\lambda$  is proportional to the number of particles emitting this radiation. Thus,

$$E_\lambda d\lambda \propto dN_\epsilon$$

or,  $E_\lambda d\lambda = Q(\lambda) dN_\epsilon = \text{constant} \cdot Q(\lambda) P(\lambda) e^{-\alpha/k\lambda T} d\lambda$ , (7.72)

where  $Q(\lambda)$  is the energy density for  $dN_\epsilon = 1$  in the wavelength range under consideration.

Now, comparing (7.67) and (7.72), we find that constant  $Q(\lambda) \cdot P(\lambda) = \frac{B}{\lambda^5}$  and  $f(\lambda T) = e^{-\alpha/k\lambda T}$ . Thus,

$$E_\lambda d\lambda = \frac{B}{\lambda^5} e^{-\alpha/k\lambda T} d\lambda = \frac{B}{\lambda^5} e^{-C/\lambda T} d\lambda, \quad (7.73)$$

where  $C = \alpha/k$ . This is known as Wien's *radiation formula*. This formula should, however, be carefully distinguished from Wien's law (7.67) which is rigorously true. (7.73) is only approximate and has limited applications.

**(b) Rayleigh-Jeans Formula :** In order to derive this formula, we require knowledge of the number of modes of vibration that can be set up in an elastic medium. It is well known that a finite stretched string can vibrate in one segment or loop—and this is called fundamental vibration. It can also vibrate in two, three, ... segments or loops with frequencies respectively two, three, ... times that of the fundamental vibration. All these are different modes of stationary vibration of the string.

Now, we can extend these considerations to the various modes of stationary vibration in an elastic continuous medium. Suppose, a plane wave of wavelength  $\lambda$  is moving normally between two parallel boundaries separated by distance  $l$  [Fig. 7.11(a)]. Then, if there are  $n_l$  nodal planes between the boundaries, it is evident from the figure that\*

$$l = n_l \cdot \frac{\lambda}{2}. \quad (7.74)$$

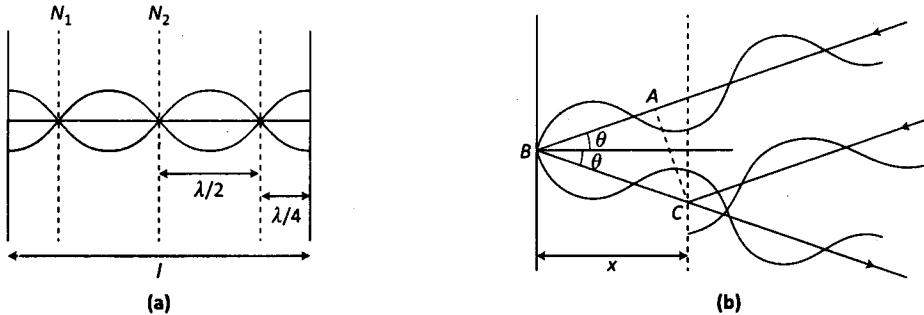


Fig. 7.11

But if the plane wave so moves that it makes an angle  $\theta$  with the normal to the boundaries [Fig. 7.11(b)], then for a nodal plane—at a distance  $x$  from the boundary at  $B$ —to pass through

\*In case of change of phase on reflection, we must consider the loops in place of nodes.

$C$  due to interference between the direct and the reflected waves, we must have the path difference

$$AB + BC = (2n + 1) \frac{\lambda}{2}$$

$$\text{i.e., } BC(\cos 2\theta + 1) = \frac{x}{\cos \theta} (\cos 2\theta + 1) = (2n + 1) \frac{\lambda}{2}. \quad (7.75)$$

If the next nodal plane occurs at a distance  $x'$ , then we shall have

$$\frac{x'}{\cos \theta} (\cos 2\theta + 1) = (2n + 1 + 1) \frac{\lambda}{2} \quad (7.76)$$

Subtracting (7.75) from (7.76), we obtain the distance between successive nodal planes in this case equal to

$$x' - x = \frac{\lambda}{2 \cos \theta} \quad (7.77)$$

so that the distance of the first nodal plane from either boundary is  $\frac{\lambda}{4 \cos \theta}$ . Then, if  $n_1$  is the total number of nodal planes produced in the stationary vibration set up between the boundaries, we have

$$l = n_1 \cdot \frac{\lambda}{2 \cos \theta}, \quad \text{i.e. } l \cos \theta = n_1 \cdot \frac{\lambda}{2}. \quad (7.78)$$

Now, let the plane wave move within the medium in a rectangular box of length  $l$ , breadth  $b$  and height  $h$  so that it makes angles  $\theta, \phi, \psi$  with the faces parallel to  $l, b$  and  $h$  respectively. If there are  $n_1, n_2, n_3$  nodal planes parallel to the first, second and third pairs of faces respectively, we have from (7.78),

$$l \cos \theta = n_1 \cdot \frac{\lambda}{2}, \quad b \cos \phi = n_2 \cdot \frac{\lambda}{2}, \quad h \cos \psi = n_3 \cdot \frac{\lambda}{2}. \quad (7.79)$$

Combining these three equations,

$$\frac{n_1^2}{l^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{h^2} = \frac{4}{\lambda^2} \quad (7.80)$$

since  $\cos^2 \theta + \cos^2 \phi + \cos^2 \psi = 1^*$ . If  $c$  is the velocity of the wave in the medium and  $\nu$  the frequency, then (7.80) becomes

$$\frac{n_1^2}{l^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{h^2} = \frac{4\nu^2}{c^2}$$

$$\text{or, } \left( \frac{n_1 c}{2l} \right)^2 + \left( \frac{n_2 c}{2b} \right)^2 + \left( \frac{n_3 c}{2h} \right)^2 = \nu^2. \quad (7.81)$$

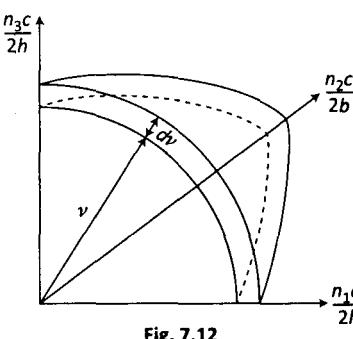


Fig. 7.12

This equation represents a certain mode of stationary vibration within the box of frequency  $\nu$  corresponding to a particular set of positive integral values of  $n_1, n_2, n_3$ . For the same frequency  $\nu$ , there will be different modes of stationary vibration possible corresponding to different sets of positive integral values of  $n_1, n_2, n_3$  satisfying (7.81). Let us see how many modes of stationary vibration are allowed if waves of frequencies between  $\nu$  and  $\nu + d\nu$  move within the box. For this purpose, we have three rectangular axes  $\frac{n_1 c}{2l}, \frac{n_2 c}{2b}, \frac{n_3 c}{2h}$  (Fig. 7.12). Since  $n_1, n_2, n_3$  take on only integral values, the units along the three axes are respectively

\*Take an  $xyz$ -coordinate system. Let  $r$  be a length from the origin making angles  $\theta, \phi, \psi$  with  $x$ -,  $y$ - and  $z$ -axes respectively. Then,  $r^2 = x^2 + y^2 + z^2 = r^2 (\cos^2 \theta + \cos^2 \phi + \cos^2 \psi)$ . Hence,  $\cos^2 \theta + \cos^2 \phi + \cos^2 \psi = 1$ .

$\frac{c}{2l}$ ,  $\frac{c}{2b}$  and  $\frac{c}{2h}$  so that in this three-dimensional space an elementary box or unit box has the volume  $\frac{c^3}{8lbh}$  and corresponds to a point in this space. Then, since we have only to consider the positive values of  $n_1$ ,  $n_2$ ,  $n_3$ , the required number of modes is the number of points lying in one octant between spheres of radii  $\nu$  and  $\nu + d\nu$  (See figure). This is

$$\frac{1}{8} \frac{(4\pi\nu^2 d\nu)}{\frac{c^3}{8lbh}} = \frac{4\pi\nu^2 d\nu}{c^3} V, \quad (7.82)$$

where  $V = lbh$ . Hence, the number of modes of stationary vibration per unit volume of the medium for waves of frequencies  $\nu$  and  $\nu + d\nu$  is\*

$$\frac{4\pi\nu^2 d\nu}{c^3}. \quad (7.83)$$

In term of  $\lambda$ , this number will be

$$\frac{4\pi d\lambda}{\lambda^4} \quad (7.84)$$

since  $\nu = c/\lambda$  and  $d\nu = -\frac{c}{\lambda^2} d\lambda$ . Weyl\* has shown that this result holds for a medium of any shape.

Rayleigh and Jeans assumed radiation—as was usual in those times—as a transverse electromagnetic wave propagating through ether. Then, any vibration for radiation propagating in any direction can be resolved into two independent vibrations. Thus, the number of modes of stationary vibration per unit volume for radiation in a hollow enclosure of frequencies between  $\nu$  and  $\nu + d\nu$  is, from (7.83),

$$2 \times \frac{4\pi\nu^2 d\nu}{c^3} = \frac{8\pi\nu^2 d\nu}{c^3}. \quad (7.85)$$

In the terms of  $\lambda$  this is

$$\frac{8\pi d\lambda}{\lambda^4}. \quad (7.86)$$

Now, as has been explained in sections 2.11 and 2.12, the vibration of an atom can be resolved into three independent vibrations along three independent axes and since the total average energy associated with the vibration of the atom is  $6 \times \frac{1}{2}kT = 3kT$ , the average energy involved in each independent vibration is  $kT$ .

Now, taking  $kT$  also as the average energy associated with each mode of stationary vibration for radiation in a hollow enclosure, we obtain the energy per unit volume of the enclosure for wavelengths between  $\lambda$  and  $\lambda + d\lambda$  as

$$\frac{8\pi kT d\lambda}{\lambda^4}. \quad (7.87)$$

This is the well-known Rayleigh-Jeans formula.

### 7.13 Experimental Study of Black-body Radiation

Wien's theoretical results (7.68), (7.69) and (7.73) and Rayleigh-Jeans formula (7.87) should be subjected to experimental test to estimate their validity in respect of black-body radiation. For this purpose, we describe here in simplified form, a typical arrangement\*\* (called spectroradiometer) for studying the spectrum of black radiation.

\*See Weyl, *Math. Ann.* 71, P. 441 (1911). Born proved the same result for a crystalline body.

\*\*See Coblenz, *A Dict. of App. Phys.*, 4, P. 554 (1923).

$B$  is the black body from which radiation is focussed by the concave mirror  $C_1$ , on reflection at plane mirror  $M_1$ , on the collimator slit  $S_1$ .  $S_1$  being at the focus of the collimating concave mirror  $C_2$ , this mirror delivers a parallel beam of radiation, on reflection at plane mirror  $M_2$ , to the prism  $P$  which may be made of quartz, rock salt, etc., depending on the wavelengths to be studied (because the prism must be transparent to the wavelengths under study). The spectrum produced by  $P$  (at minimum deviation) is focussed by the concave mirror  $C_3$  on the slit which allows a narrow band of wavelengths to pass to the receiver  $R$ , a bolometer (i.e., a resistance thermometer) or a thermopile. All the plane and concave mirrors are silvered on their front surfaces to reduce absorption.

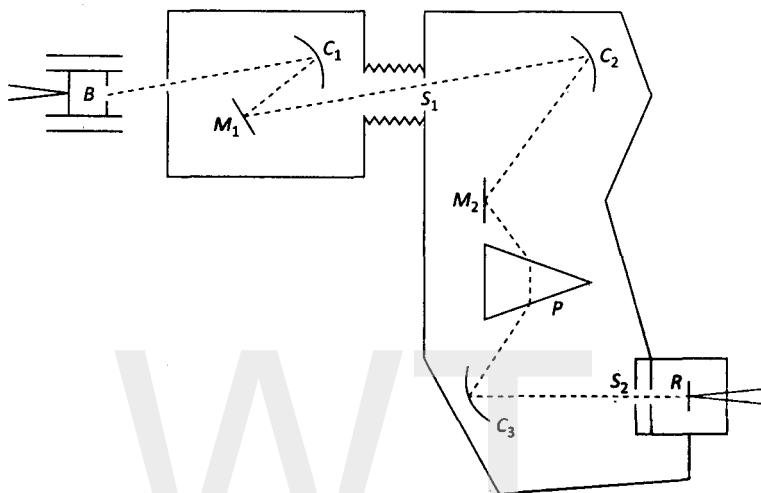


Fig. 7.13: Coblenz's apparatus

By rotating  $C_3$  about a vertical axis, the different parts of the spectrum are thrown on the slit  $S_2$ , but the prism is simultaneously also turned to keep the selected rays always at minimum deviation. As successive parts of the spectrum pass across the receiver, the deflections of the galvanometer connected to it give the relative value of the energy reaching the receiver. The wavelength incident on the receiver is determined from the position of the prism.

As the prism rotates, the range of wavelengths included within the area covered by the slit  $S_2$  varies in a manner depending on the dispersive power of the prism in that part of the spectrum. Hence, a correction must be applied to all the readings of the receiver. Allowance must also be made for absorption by the prism which affects the different parts of the spectrum to different extents. In fact, corrections for this purpose can be calculated from a series of subsidiary experiments at selected parts of the spectrum allowing them to pass through different thicknesses of the prism-materials. Also, corrections for absorption in the air or any other gas filling the apparatus are deduced in the same manner by varying pressure.

The nature of the  $E_\lambda - \lambda$  curve is shown in Fig. 7.10. Lummer and Pringsheim\* showed that Wien's results (7.68) and (7.69) are quite valid. They gave the value of  $b$  equal to  $0.294 \text{ cm} \cdot \text{degree}$  and that of  $E_{\lambda_m} T^{-5}$  to be  $2.188 \times 10^{-14} \text{ ergs} \cdot \text{degree}$ . This gives us a simple method of finding the temperature of all radiating bodies including heavenly bodies. Thus, taking the average value of  $\lambda_m = 4748 \text{ \AA}$  for the sun,  $T$  is found to be  $\frac{0.294 \text{ cm} \cdot \text{degree}}{4738 \times 10^{-8} \text{ cm}} = 6204 \text{ K}$ . Similarly, with  $\lambda_m = 14\mu = 14 \times 10^{-4} \text{ cm}$  for the moon,  $T = 210 \text{ K}$ .

\* Verh. d. D. Phys. Ges., 1, P. 213 (1899).

Paschen, working with short waves, verified Wien's formula (7.73), but Lummer and Pringsheim, working with long wavelengths and at high temperatures, found the formula to fail in the long wavelength region. Again, Lummer and Kurlbaum found that when  $\lambda$  was large, Rayleigh-Jeans formula agreed with experimental results. But the formula was found to fail in the short-wavelength region.

Thus we come to a critical point. No single formula holds for both the long-wavelength and the short-wavelength region of the black-body radiation. We find, therefore, that thermodynamics cannot lead us any further. We shall see in the next chapter how Planck brought in a new idea to get over the crisis in classical physics.

**Exercise 1.** Derive Stefan-Boltzmann law from Wien's radiation formula (7.73).

**Solution :** From (7.26), (7.35) and (7.73),

$$\begin{aligned} H = \pi K &= \frac{cE}{4} = \frac{c}{4} \int_0^\infty E_\lambda d\lambda = \frac{c}{4} \int_0^\infty \frac{B}{\lambda^5} e^{-C/\lambda T} \\ &= \frac{cB}{4} T^4 \int_0^\infty x^3 e^{-Cx} dx, \quad \text{where } x = \frac{1}{\lambda T} \\ &= \frac{3cB}{2C^4} T^4, \quad \text{on integration by parts.} \end{aligned}$$

This is the required result.

**Exercise 2.** Deduce Wien's displacement law (7.69) from his radiation formula (7.73).

**Solution :** (7.73) may be put in the form :

$$\log_e E_\lambda = \log_e B - 5 \log_e \lambda - \frac{C}{\lambda T}.$$

For maximum value of  $E_\lambda$ ,  $\frac{dE_\lambda}{d\lambda} = 0$  so that we have from the above equation :

$$-\frac{5}{\lambda_m} + \frac{C}{\lambda_m^2 T} = 0, \quad \text{i.e., } \lambda_m T = \frac{C}{5} \text{ (a constant).}$$

**Exercise 3.** Use the result of Exercise 2 to show that the maximum value of  $E_\lambda$  varies as  $T^5$ .

**Exercise 4.** The total radiation from platinum varies as the fifth power of the absolute temperature. Show that the formula  $E_\lambda d\lambda = \frac{B}{\lambda^5} e^{-C/\lambda T} d\lambda$  satisfies this requirement and also that this formula gives relatively less radiation in the infrared than is done by the formula (7.73) for the black body.

## 7.14 Measurement of Very High Temperatures : Radiation Pyrometry

Temperature may be measured by gas thermometers up to the order of 1000 °C. Beyond this, it is customary to use thermocouples. But these are also unsuitable for some purposes, and in any case cannot be used beyond the melting point of platinum. This is exactly where radiation pyrometry finds its use. Besides, the radiation pyrometer need not be raised to the temperature of the hot body or placed in contact with it. But it suffers from a serious drawback. The laws on which radiation pyrometry is based hold for perfectly black bodies, whereas no actual radiating surface is perfectly black though many may be approximately so.

There are three distinct methods available for measurement of temperatures :

**(1) Displacement Law Method :** The radiation from the source is dispersed into a spectrum by means of a prism, and a bolometer is moved across the spectrum to determine

$\lambda_m$ , the wavelength of maximum emission. Since  $\lambda_m T = 0.294 \text{ cm} \cdot \text{degree}$ ,  $T$  can be evaluated. Mention of this method has already been made in the preceding section for measurement of temperatures of the sun and the moon.

**(2) Total Radiation Method :** This method uses Stefan-Boltzmann law (7.35). The most convenient form of *total radiation pyrometer* is the one designed by Fény (Fig. 7.14). Radiation from a source enters through the aperture  $AA$  and is incident on the concave mirror  $M$ , usually

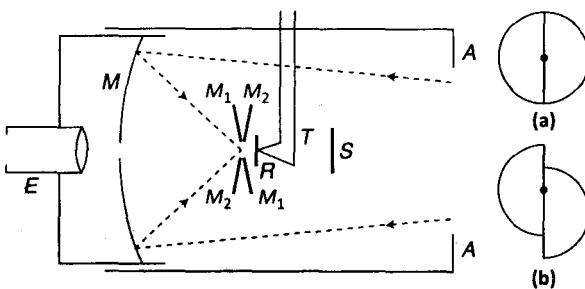


Fig. 7.14: Total radiation pyrometer

of copper plated with nickel or gold. The mirror can be moved backward and forward so as to throw the image on a small blackened receiving surface  $R$ . To the back of  $R$  is attached one junction of a thermocouple  $T$  which is connected to a sensitive milli-voltmeter (not shown) calibrated to give directly the temperature of the source of radiation.  $S$  protects  $R$  from radiation directly falling on it.

In order to enable the observer to tell whether focussing is accurate, a pair of semicircular mirrors  $M_1M_1$  and  $M_2M_2$  inclined to each other at about  $5^\circ$  and with an opening of about  $0.15 \text{ cm}$  at the centre is placed just in front of  $R$ . When the position of  $M$  is such that it focusses the image of the source of the surfaces of  $M_1M_1$  and  $M_2M_2$ , the two halves of the image seen through the eyepiece  $E$  appear undisplaced [See figure (a)] relative to each other. If, however, the position of  $M$  is not correct, the two halves of the image appear relatively displaced [See figure (b)].

In the actual use of the apparatus, it is so arranged that the image of the source formed by  $M$  is always slightly larger than the opening at the centre of the pair of mirrors  $M_1M_1$  and  $M_2M_2$ . In that case, the central part (equal to the area of the opening) of the image of the source will always fall on  $R$  and the thermocouple will measure just the intensity of the image. We shall now show how from this intensity we obtain the temperature of the source. If  $s$  be the area of the source and  $A$  that of the mirror  $M$  then, by (7.38) the radiation incident on  $M$  per unit time is

$$K s d\omega = K s \frac{A}{u^2}, \quad (7.88)$$

where  $u$  is the distance of the source from  $M$ . Evidently, this is also the radiation falling on the image of area, say,  $s'$ . Now, if  $v$  be distance of the image from  $M$ , then

$$\frac{s'}{s} = \frac{v^2}{u^2}. \quad (7.88a)$$

Then, radiation falling on unit area of the image per unit time per unit solid angle is, from (7.88) and (7.88a),

$$K s \frac{A}{u^2} / s' \frac{A}{v^2} = K. \quad (7.89)$$

Hence, emission per unit area of image per unit time is

$$\pi K = \sigma T^4, \quad [\text{from (7.35)}] \quad (7.90)$$

where  $T$  is the temperature of the source. This is how the intensity of the image is related to  $T$ . Then, if  $T_0$  be the temperature of  $R$ , the e.m.f. of the thermocouple will be given by

$$E = k(T^4 - T_0^4). \quad (7.91)$$

It is, however, observed that the index on  $T$  is not 4 exactly but varies from 3.8 to 4.2 due to the following reasons :

- (i) The e.m.f. of the thermocouple is not strictly proportional to the difference between the fourth power of temperature of the hot and the cold junction. When the temperature of the hot junction (i.e., of  $R$ ) is about  $80^\circ$  above that of the surroundings, this causes appreciable deviation.
- (ii) Stray reflections from the walls produce disturbances on  $R$ .
- (iii) The rate of loss of heat from  $R$  is not strictly proportional to its temperature excess.
- (iv) The readings of the millivoltmeter are subject to error.
- (v) Conduction of heat from the hot to the cold junction produces a temperature rise in the cold junction.

Because of this departure from the fourth power law, the pyrometer is calibrated by using radiations from a black body [of the type shown in Fig. 7.2(b)] at different temperatures which are measured accurately by a standard thermocouple. In this way, the millivoltmeter may be calibrated in degrees directly.

This directly calibrated millivoltmeter has a drawback. It is useful only within the range of calibration. The range of the instrument may, however, be extended beyond the maximum calibration temperature by the use of a rotating sector (Fig. 7.15). It is a circular opaque disc from which a sector subtending an angle  $\theta$  at the centre is cut off. It is rotated about the axis of the pyrometer tube in the path of the incident radiation so that only a fraction of the radiation enters the pyrometer during each revolution. If  $T'$  is the temperature now indicated by the millivoltmeter, then  $T$ , the actual temperature of the source, is given by (7.90) :

$$\sigma T'^4 = \frac{\theta}{360} \times \sigma T^4, \quad \text{i.e., } T'^4 = \frac{\theta}{360} T^4. \quad (7.92)$$

Taking  $\theta = 4^\circ$  and  $T' = 1500$  K, we find

$$T = 1500 \left( \frac{360}{4} \right)^{\frac{1}{4}} \text{ K} = 1500(90)^{\frac{1}{4}} \text{ K} = 3080 \text{ K}.$$

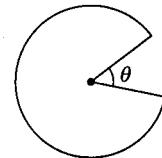


Fig. 7.15: Rotating sector

Thus, if the maximum range is 1500 K, it is extended to 3080 K with  $\theta = 4^\circ$ .

**(3) Distribution Law Method :** In this case, Wien's law (7.73) is usually used\* and the instrument is called the *optical pyrometer*. In this case, the intensity of radiation from a source in a small range of wavelengths between  $\lambda$  and  $\lambda + d\lambda$  is compared with the intensity of emission of the same colour from a standard lamp. If  $e_\lambda^s$  denotes the intensity of emission of  $\lambda$  from a source at temperature  $T^s$  and  $e_\lambda^l$  that of the standard lamp at  $T^l$ , then from (7.73),

$$e_\lambda^s = \frac{D}{\lambda^5} e^{-C/\lambda T^s}, \quad e_\lambda^l = \frac{D}{\lambda^5} e^{-C/\lambda T^l}$$

since emission of a certain wavelength  $\lambda$  from the hole (i.e., the black body) in a hollow enclosure is proportional to the energy density of the same wavelength inside it according to (7.26). Hence,

$$\log_e \left( \frac{e_\lambda^s}{e_\lambda^l} \right) = \frac{C}{\lambda} \left( \frac{1}{T^l} - \frac{1}{T^s} \right). \quad (7.93)$$

\*This is applicable when  $\lambda T$  is small. The law applicable under all conditions is the one given by Planck and discussed in the next chapter.

We shall employ this formula in the disappearing filament type of optical pyrometer here (Fig. 7.16). This was first devised by Morse and later improved by Holborn and Kurlbaum, and by Mendenhall and Forsythe. It is essentially a telescope with a lamp  $L$  in the position usually occupied by cross-wires. The lamp filament and the image of the source (produced at the same position) are viewed through a red glass filter  $G$  and the eyepiece  $E$ . By means of the rheostat  $R$ , the current is adjusted until the brightness of the filament exactly matches the image of the source. It is evident that when this matching occurs, the emissive powers of the image of the source and the filament in the wavelength range transmitted by the red filter glass  $G$  are equal.

Then, by (7.90),

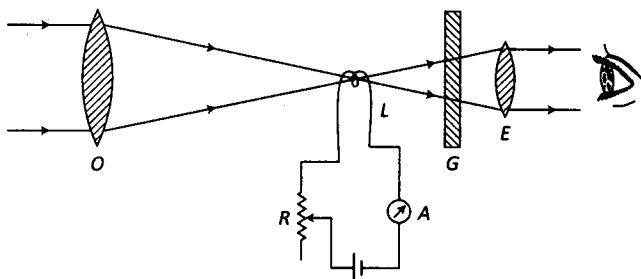


Fig. 7.16: Disappearing filament-type pyrometer

$$e_{\lambda}^l = e_{\lambda}^{im} = e_{\lambda}^s, \quad (7.94)$$

where  $e_{\lambda}^{im}$  is the emissive power of the image for the transmitted red colour. Then, from (7.93) and (7.94),

$$\log_e \left( \frac{e_{\lambda}^s}{e_{\lambda}^l} \right) = 0 = \frac{C}{\lambda} \left( \frac{1}{T^l} - \frac{1}{T^s} \right). \quad (7.95)$$

If  $T^l$  is known,  $T^s$  is found out using (7.95). In practice, the ammeter  $A$  is calibrated by using radiations from a furnace whose temperature is measured by a standard thermocouple.

To extend the range beyond the maximum point of calibration, a rotating sector of the type shown in Fig. 7.15 is employed. With this sector rotating between the source and the pyrometer, the filament current is adjusted till the matching is obtained. Now, if  $T^{s'}$  is the temperature now indicated by the ammeter and  $T^s$  the actual temperature of the source, then since the corresponding emissive power are related by

$$e_{\lambda}^{s'} = \frac{\theta}{360^\circ} e_{\lambda}^s$$

we have

$$\log_e \left( \frac{e_{\lambda}^s}{e_{\lambda}^{s'}} \right) = \log_e \left( \frac{360^\circ}{\theta} \right) = \frac{C}{\lambda} \left( \frac{1}{T^{s'}} - \frac{1}{T^s} \right). \quad (7.96)$$

On the other hand, we have now in place of (7.95)

$$\log_e \left( \frac{e_{\lambda}^{s'}}{e_{\lambda}^l} \right) = 0 = \frac{C}{\lambda} \left( \frac{1}{T^l} - \frac{1}{T^{s'}} \right). \quad (7.97)$$

Thus, from (7.96) and (7.97),  $T^s$  can be found out provided all the constants involved are known. In this way, the upper limit of the range of the pyrometer is further pushed up.

## PROBLEMS

- Two bodies  $A$  and  $B$  are kept in an evacuated vessel maintained at a temperature of  $27^\circ\text{C}$ . The temperature of  $A$  is  $527^\circ\text{C}$  and that of  $B$  is  $127^\circ\text{C}$ . Compare the rates at which heat is lost from  $A$  and  $B$ . [Gau.U.]

2. What do you understand by the 'solar constant'? Show how we can know the temperature of the sun on the basis of the Stefan-Boltzmann law with a knowledge of the following data : Solar constant = 2 cal/sq. cm/min, radius of the sun =  $4.33 \times 10^5$  miles, distance of the earth from the sun =  $9.28 \times 10^7$  miles and  $\sigma = 5.72 \times 10^{-5}$  C.G.S. unit.

**Solution :** The *solar constant* is defined as the amount of energy which is absorbed *per minute* by one square centimetre of a perfectly black surface held at right angles to the sun's rays, and placed at the mean distance of the earth from the sun in the absence of the atmosphere. The mean value of the solar constant obtained by an instrument, called the *pyroheliometer*, has been found to be 1.937 cal/sq. cm/min. It is, however, very probable that this quantity is not really a constant and varies with astronomical conditions.

Here we shall assume the sun to be a black body. If  $E$  = energy emitted per sq. cm per sec at the surface of the sun,  $S$  = energy received per sq. cm per sec on the earth,  $r$  = radius of the sun,  $R$  = mean distance of the earth from the sun, then we may write

$$4\pi r^2 E = 4\pi R^2 S, \text{ i.e., } E = \frac{R^2 S}{r^2}.$$

If  $T$  is the black body temperature of the sun, then  $E = \sigma T^4$  and hence,

$$\sigma T^4 = R^2 S / r^2, \text{ i.e. } T^4 = \frac{R^2 S}{\sigma r^2}.$$

Here,  $S = 2 \text{ cal/sq. cm/min} = \frac{2 \times 4.2 \times 10^7}{60} \text{ ergs/sq. cm/sec} = 1.4 \times 10^6 \text{ ergs/sq. cm/sec.}$

$$\text{Then } T = \left[ \left( \frac{9.28 \times 10^7}{4.33 \times 10^5} \right)^2 \times \left( \frac{1.4 \times 10^6}{5.72 \times 10^{-5}} \right) \right]^{\frac{1}{4}} \text{ K} = 5786 \text{ K.}$$

3. Find the temperature of the sun on the basis of Wien's displacement law with the following data :  $\lambda_m T = 0.290 \text{ cm} \cdot \text{degree}$  and  $\lambda_m = 4580 \times 10^{-8} \text{ cm.}$
4. If the solar constant is 2 cal/sq. cm/min and the conductivity of the earth's crust is 0.003, what must the temperature gradient in the ground be so that the heat escaping from the surface may be just balanced by the heat received from the sun?
5. 'Bodies absorb the radiation that they may emit'. Discuss this statement.
6. Show with the help of theoretical reasoning that good reflectors are poor emitters.
7. If the pressure of diffuse radiation is  $\nu$  times the energy density, then show that the Stefan-Boltzmann law is of the form :

$$E = \sigma T^{(\nu+1)/\nu}$$

and that Wien's law is of the form :

$$E_\lambda = \frac{1}{\lambda^{3\nu+4}} f(\lambda^{3\nu} T).$$

## Chapter 8

# Quantum Theory of Radiation and Specific Heats

### 8.1 Planck's Law

We have seen in the last chapter (section 7.13) that Wien's radiation formula and the Rayleigh-Jeans equation cannot explain the spectrum of black-body radiation for all values of  $\lambda$  and  $T$ . We shall discuss in this section how Planck got over the crisis by introducing a novel idea.

Planck\* assumed that there are electrical oscillators in the walls of a hollow enclosure which oscillate and emit radiation of frequency  $\nu$ . The energy radiated per second by an oscillator is given by\*\*

$$\Delta\epsilon = \frac{2e^2}{3mc^2}(2\pi\nu)^2\bar{\epsilon}. \quad (8.1)$$

where  $e$ ,  $m$  are the charge and mass and  $\bar{\epsilon}$  the average energy of an oscillator associated with  $\nu$ -radiation. On the other hand, the work done on the oscillator per second by radiation (i.e., energy supplied to the oscillator per sec by radiation) in the enclosure of energy density  $E_\nu$  is\*\*

$$\Delta W = \frac{\pi e^2}{3m}E_\nu. \quad (8.2)$$

In the case of equilibrium, the two quantities must be equal. Hence, from (8.1) and (8.2),

$$E_\nu = \frac{8\pi\nu^2}{c^3}\bar{\epsilon}. \quad (8.3)$$

Now, applying Maxwell-Boltzmann law (2.153) to all the  $\nu$ -oscillators as usual we find

$$\bar{\epsilon} = \frac{\int_0^\infty n_\epsilon \epsilon d\epsilon}{\int_0^\infty n_\epsilon d\epsilon} = \frac{\int_0^\infty \epsilon e^{-\epsilon/kT} d\epsilon}{\int_0^\infty e^{-\epsilon/kT} d\epsilon} = kT, \text{ on integration of the numerator by parts.}$$

If we put this value of  $\bar{\epsilon}$  in (8.3), we obtain just the Rayleigh-Jeans equation. So Planck put forward the bold idea that the energy of an oscillator cannot have all values from 0 to  $\infty$  but any of the values (called *quanta*)  $0, \epsilon_0, 2\epsilon_0, 3\epsilon_0, \dots, r\epsilon_0 \dots$  so that it emits and absorbs energy of any of these values.

Now, if we apply the Maxwell-Boltzmann law,  $n_r = n_0 e^{-r\epsilon_0/kT}$ , we obtain

$$\bar{\epsilon} = \frac{\sum_{r=0}^{r=\infty} n_r r \epsilon_0}{\sum_{r=0}^{r=\infty} n_r}, \text{ where } n_r \text{ is the number of oscillators each having energy } r\epsilon_0$$

\*Planck, *Ann. d. Phys.* 4, P. 556 (1901).

\*\*For deduction, see Born, M., *Atomic Physics*, Pp. 151, 424-27 (1963).

$$\begin{aligned}
 & \sum_{r=0}^{r=\infty} r\epsilon_0 e^{-r\epsilon_0/kT} \\
 & = \frac{\sum_{r=0}^{r=\infty} r\epsilon_0 e^{-r\epsilon_0/kT}}{\sum_{r=0}^{r=\infty} e^{-r\epsilon_0/kT}} = -\frac{d}{d\beta} \log_e \sum_{r=0}^{\infty} e^{-\beta r\epsilon_0}, \text{ where } \beta = \frac{1}{kT} \\
 & = -\frac{d}{d\beta} \log_e \frac{1}{1 - e^{-\beta\epsilon_0}} = \frac{\epsilon_0 e^{-\beta\epsilon_0}}{1 - e^{-\beta\epsilon_0}} \\
 & = \frac{\epsilon_0}{e^{\beta\epsilon_0} - 1} = \frac{\epsilon_0}{e^{\epsilon_0/kT} - 1}.
 \end{aligned} \tag{8.4}$$

Then, from (8.3) and (8.4),

$$E_{\nu} d\nu = \frac{8\pi\nu^2}{c^3} \frac{\epsilon_0}{e^{\epsilon_0/kT} - 1}. \tag{8.5}$$

Now, in Wien's law which has been rigorously deduced from thermodynamics,  $T$  occurs in the combination  $\lambda T$  only. So, to achieve consistency with that law, Planck assumed

$$\epsilon_0 = \frac{hc}{\lambda} = h\nu, \tag{8.6}$$

where  $h$  is a universal constant known as *Planck's constant*.

Then, from (8.5) and (8.6), we obtain,

$$E_{\nu} d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1} \tag{8.7}$$

or, in terms of  $\lambda$ ,

$$E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}. \tag{8.8}$$

(8.7) and (8.8) are the two forms in which Planck's law is given.

## 8.2 Some Deductions from Planck's Law

The correctness of Planck's law is strengthened by the fact that a number of radiation laws, which have been found to be true under specific conditions, can be deduced from it.

**(a) Wien's Radiation Formula :** It has been shown in the last chapter (section 7.13) that Wien's radiation formula is valid for short wavelengths. In fact since for small  $\lambda T$ ,  $e^{hc/\lambda kT}$  is  $\gg 1$ , we obtain from (8.8)

$$E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda. \tag{8.9}$$

This is identical with Wien's formula (7.73) of the last chapter. We also find the values of the constants  $B$ ,  $C$  of that equation. They are

$$B = 8\pi hc \quad \text{and} \quad C = \frac{hc}{k}. \tag{8.10}$$

**(b) Rayleigh-Jeans Equation :** This equation, which holds for large wavelengths, is obtained from (8.8) by taking  $\lambda T$  large. Thus,

$$E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{(1 + \frac{hc}{\lambda kT} + \dots) - 1} d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda.$$

(c) **Stefan-Boltzmann Law :** From (8.8), the total energy density is

$$\begin{aligned}
 E &= \int_0^\infty E_\lambda d\lambda = 8\pi hc \int_0^\infty \frac{1}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} d\lambda \\
 &= \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}, \text{ where } x = \frac{hc}{\lambda kT} \\
 &= \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^\infty x^3 e^{-x} (1 + e^{-x} + e^{-2x} + \dots) dx \\
 &= \frac{8\pi k^4 T^4}{h^3 c^3} 6 \left( \frac{1}{1^4} + \frac{1}{2^4} + \frac{1}{3^4} + \dots \right), \text{ on integrating term by term} \\
 &= \frac{8\pi k^4 T^4}{h^3 c^3} \cdot 6 \cdot \frac{\pi^4}{90} \\
 &= \frac{8}{15} \frac{\pi^5 k^4}{h^3 c^3} T^4. \tag{8.11}
 \end{aligned}$$

Hence, from (7.26) and (7.35) of the preceding chapter and (8.11),

$$H = \pi K = \frac{c}{4} E = \frac{2}{15} \frac{\pi^5 k^4}{h^3 c^2} T^4 \tag{8.12}$$

$$\text{so that } \sigma \text{ (Stefan's constant)} = \frac{2}{15} \frac{\pi^5 k^4}{h^3 c^2}. \tag{8.13}$$

Then, with  $\sigma = 5.735 \times 10^{-5} \text{ erg} \cdot \text{cm}^{-2} \cdot \text{deg}^{-4} \cdot \text{sec}^{-1}$ ,  $k = 1.376 \times 10^{-16} \text{ erg} \cdot \text{deg}^{-1}$  and  $c = 3 \times 10^{10} \text{ cm} \cdot \text{sec}^{-1}$ , we obtain  $h = 6.568 \times 10^{-27} \text{ erg} \cdot \text{sec}$ .

(d) **Wien's Displacement Law :** The wavelength  $\lambda_m$  corresponding to the maximum of  $E_\lambda$  is obtained from the equation :

$$\left. \frac{dE_\lambda}{d\lambda} \right|_{\lambda=\lambda_m} = 0.$$

Now carrying out differentiation of (8.8) accordingly and putting

$$\frac{hc}{k\lambda_m T} = x. \tag{8.14}$$

$$e^{-x} + \frac{x}{5} - 1 = 0.$$

The solution of this transcendental equation is

$$x = 4.9651 \tag{8.15}$$

so that from (8.14) and (8.15),

$$\lambda_m T = \frac{hc}{4.9651 k} = \frac{C}{4.9651} = b. \quad [\text{from (8.10)}] \tag{8.16}$$

This is Wien's displacement law.

### 8.3 Experimental Test of Planck's Law\*

From (8.8) and (8.10), we can write Planck's law in the form :

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{C/\lambda T} - 1}. \quad (8.17)$$

According to Planck's theory  $C (= \frac{hc}{k})$  is an absolute constant. Then, it is evident that Planck's law is amply verified, if  $C$  is found to be a constant for all values of  $\lambda$  and  $T$ . The basic principle of the experimental arrangement has been explained in section 7.13 of the last chapter and has been shown in Fig. 7.13. Two important methods have been developed to establish the constancy of  $C$  : (a) *Isothermal Method* and (2) *Isochromatic Method*.

(a) **Isothermal Method** : In this method, the intensity of radiation in different parts of the spectrum is measured at constant temperature (Fig. 7.10). There are, however, two ways of obtaining  $C$  from these measurements. One of the two ways is to find  $\lambda_m$  corresponding to the maximum emission of energy at  $T$  and to calculate  $C$  from (8.16), i.e., from

$$C = 4.9651\lambda_m T.$$

But it is, in actual practice, difficult to locate  $\lambda_m$  exactly from the rounded top of the energy distribution curve. Paschen\*\* and Coblentz†, therefore, used a different method, "method of equal ordinates", to find  $C$ . A line is drawn parallel to  $\lambda$ -axis intersecting the curve at two points  $\lambda_1$  and  $\lambda_2$ . From (8.17), we have

$$e_1 = \left( \frac{8\pi hc}{\lambda_1^5} \frac{1}{e^{C/\lambda_1 T} - 1} \right), \quad e_2 = \left( \frac{8\pi hc}{\lambda_2^5} \frac{1}{e^{C/\lambda_2 T} - 1} \right) \quad (8.18)$$

so that we obtain, since  $e_1 = e_2$ ,

$$\frac{\frac{C}{T}}{\frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1}} = 5 \log_e \frac{\lambda_2}{\lambda_1} - \log_e \left[ \frac{(1 - e^{-\frac{C}{\lambda_1 T}})}{(1 - e^{-\frac{C}{\lambda_2 T}})} \right] \quad (8.19)$$

At first an approximate value of  $C$  is put on the right-hand side of (8.19) and then the method of successive approximation is used to find out the value of  $C$ . The constancy of  $C$  has been observed, for different pairs of  $\lambda_1$ ,  $\lambda_2$ , within limits of experimental errors. Coblentz obtained for  $C$  the value 1.4339 cm · degree.

(c) **Isochromatic Method** : The above method suffers from the drawback that the different parts of the spectrum are absorbed to different extents during their passage through the prism of the experimental arrangement. In the isochromatic method, the emissions from a black body at different temperatures are compared for the same wavelength. In this case, the same wavelength passes through the prism at different temperatures and is, therefore, absorbed in the same proportion at all temperatures. Then, corresponding to (8.18), we have in this case for the same  $\lambda$ ,

$$e_1 = \left( \frac{8\pi hc}{\lambda^5} \frac{1}{e^{C/\lambda T_1} - 1} \right), \quad e_2 = \left( \frac{8\pi hc}{\lambda^5} \frac{1}{e^{C/\lambda T_2} - 1} \right) \quad (8.20)$$

\*See Coblentz, *A Dict. of App. Phys.*, 4, P. 554 (1923)

\*\*Paschen, *Sitzber. Akad. Wiss. Berlin*, XXI, Pp. 403, 959 (1899). He applied the method to Wien's radiation formula.

†Coblentz, *Bur. Stand. Bul.*, X, P. 7, (1913), XIII, P. 459 (1916)

$$\text{so that } \frac{C}{\lambda T_1 T_2} = \log_e \left( \frac{e_2}{e_1} \right) - \log_e \left[ \frac{(1 - e^{-\frac{C}{\lambda T_1}})}{(1 - e^{-\frac{C}{\lambda T_2}})} \right] \quad (8.21)$$

$C$  is calculated from (8.21) as explained in the case of (8.19). Warburg\* established the constancy of  $C$  by this method using quartz prism.

From a study of the results obtained from different methods, Wensel\*\* has suggested for  $C$  the value 1.436 cm · degree.

In 1919, Nernst and Wulf suggested that (8.4) should be taken in the form :

$$\bar{\epsilon} = \frac{\epsilon_0}{e^{\epsilon_0/kT} - 1} (1 - \alpha) = \frac{h\nu}{e^{h\nu/kT} - 1} (1 - \alpha)$$

(where  $\alpha$  is a small variable fraction) to fit the results of earlier experiments better. This led Rubens and Michel (1921) to undertake a thorough redetermination of  $C$  to test the validity of the suggestion. They used a series of black bodies and covered the entire range of temperatures from  $-180^\circ\text{C}$  to  $1900^\circ\text{C}$  and established beyond doubt the constancy of  $C$  and set at naught Nernst and Wulf's hypothesis.

#### 8.4 Quantisation of Black-body Radiation

The success of Planck's law gives strong support to the quantum theory introduced by him. But his deduction is unsatisfactory because of the fact that it is based partly on the laws of classical physics and partly on the new quantum idea. It should be noticed that in deducing (8.1)–(8.3) the classical law of absorption and emission of radiation by an electrical oscillator have been employed whereas the quantum idea, i.e., the idea of discrete energy values of an oscillator, has been used to calculate  $\bar{\epsilon}$  in (8.4).

One may ask, is it not possible to avoid the classical part of the deduction, i.e., the deduction of (8.1)–(8.3)? The immediate suggestion may be to adopt the method of Rayleigh and Jeans explained in the preceding chapter. We have seen there that all modes of stationary vibration are not possible for radiation in a hollow enclosure. We have calculated the number of discrete modes of vibration per unit volume for radiation of frequencies between  $\nu$  and  $\nu + d\nu$ . It is

$$\frac{8\pi\nu^2 d\nu}{c^3}. \quad (8.22)$$

If now we assume that each mode of vibration behaves like a Planck oscillator with the mean energy

$$\frac{h\nu}{e^{h\nu/kT} - 1} \quad (8.23)$$

instead of  $kT$  as adopted in Rayleigh-Jeans equation, then from (8.22) and (8.23), we obtain Planck's formula :

$$E_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1} \quad [8.7]$$

But there is a serious difficulty associated with this method of deduction. It should be remembered that in order to derive (8.23), an oscillator is assumed to possess any of the discrete energy values  $0, h\nu, 2h\nu, \dots, rh\nu$ . Now if we extend this idea to the different modes of stationary vibration of radiation of frequency  $\nu$ , the  $r$ th mode of vibration will have energy

\*Warburg, Hupka and Müller, *Zs. Instrk.*, XXXII, P. 134 (1912).

\*\*Wensel, *Bull. Res. Bur. Stand.*, 22, P. 375 (1939).

$\nu h$ . On the other hand, according to Einstein's photoelectric theory\*—the validity of which has been established beyond doubt—radiation of frequency  $\nu$  in a chamber consists of photons (light-quanta) each moving about with energy  $\nu h$ . How to reconcile these two pictures? We should, no doubt, abandon the former ad-hoc picture in favour of the well-established latter. In fact, S. N. Bose (1923) assumed the black radiation in a hollow enclosure to consist of photons in molecular chaos and obtained the law of distribution of energy among the photons on the basis of a new statistics (Bose statistics). This is, so far, the best deduction of Planck's law. We shall take up this subject in section 10.7.

## 8.5 Einstein's Theory of Specific Heats of Solids

It has been pointed out at the end of section 2.12 that the classical theory fails to explain why the atomic heat of a solid element decreases at low temperatures and tends to zero at absolute zero. The success of quantum theory in explaining the spectrum of black radiation and the phenomenon of photoelectricity prompted Einstein\*\* to apply the theory also to this problem.

Einstein made the simplest assumptions that the atoms in an elementary solid all vibrate independently and that each atom behaves as a Planck oscillator with common frequency  $\nu$ . Then, the average energy associated with each of the three independent vibrations of an atom should be taken as

$$\frac{h\nu}{e^{h\nu/kT} - 1} \quad [8.23]$$

instead of  $kT$  (see end of section 7.12) so that the total energy of a gram-atom of the solid is (since the vibration of an atom can be resolved into three independent vibrations)

$$U = 3 \times N \times \frac{h\nu}{e^{h\nu/kT} - 1}. \quad (8.24)$$

$$\text{Hence, } C_v = \frac{dU}{dT} = 3R \frac{x^2 e^x}{(e^x - 1)^2} \equiv 3RE(x). \quad (8.25)$$

where  $x = h\nu/kT$  and  $E(x)$  is called Einstein function. For large  $T$ , i.e., for  $T \rightarrow \infty$ ,  $x \rightarrow 0$  so that (8.25) gives under this condition :

$$C_v \approx 3R. \quad (8.26)$$

This is exactly the Dulong-Petit law. On the other hand, for  $T \rightarrow 0$ ,  $x \rightarrow \infty$  so that (8.25) gives,

$$C_v \approx 3Rx^2 e^{-x} = 3R \left( \frac{h\nu}{kT} \right)^2 e^{-\frac{h\nu}{kT}}. \quad (8.27)$$

It is experimentally observed that  $C_v$  varies as  $T^3$  at low temperatures while according to (8.27)  $C_v$  diminishes more rapidly at low temperatures. Thus, Einstein's theory fails at low temperatures and should, therefore, be suitably modified.

## 8.6 Debye's Theory of Specific Heats of Solids†

Although Einstein was the first to make an attempt in the right direction, the assumptions on which he based his calculations are, according to Debye, not correct. He argued that atoms

\* Einstein, A., *Ann. d. Phys.*, **17**, P. 132 (1905).

\*\* Einstein, A., *Ann. d. Phys.*, **22**, Pp. 180, 800 (1907).

† Debye, *Ann. d. Phys.*, **39**, P. 789 (1912).

in a solid are strongly bound together so that they cannot perform undisturbed vibrations independently of one another. Secondly, all atoms cannot vibrate with a single common frequency  $\nu$ . Because, due to atomic vibrations, elastic waves, transverse as well as longitudinal, are set up in the body with different frequencies. Then, according to the discussion in section 7.12 in the preceding chapter, the number of modes of stationary vibration in a volume  $V$  of a gram-atom of the solid for frequencies between  $\nu$  and  $\nu + d\nu$  is

$$\frac{4\pi\nu^2 d\nu}{c_l^3} \quad (8.28)$$

for longitudinal wave ( $c_l$  being its velocity) and is

$$2 \times \frac{4\pi\nu^2 d\nu}{c_t^3} V \quad (8.29)$$

for transverse wave ( $c_t$  being its velocity) since a transverse wave is capable of being broken up into two independent transverse waves. Hence, the total number of modes of independent vibration—both longitudinal and transverse—in the solid for frequencies between  $\nu$  and  $\nu + d\nu$  is

$$4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu. \quad (8.30)$$

Since each atom possesses only three independent modes of vibration, we must have for a gram-atom containing  $N$  atoms, from (8.30),

$$3N = 4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \int_0^{\nu_m} \nu^2 d\nu. \quad (8.31)$$

The upper limit of integration on the right-hand side is taken as finite ( $\nu_m$ ), and not infinite, because the left-hand side is finite. From (8.31),

$$4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) = \frac{9N}{\nu_m^3}. \quad (8.32)$$

Now, taking (8.23) as the average energy associated with each independent mode of vibration of the body, the total energy is, from (8.30) and (8.32),

$$U = \int_0^{\nu_m} \frac{h\nu}{e^{h\nu/kT} - 1} \times 4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu.$$

$$\text{Hence, } C_v = \left( \frac{dU}{dT} \right)_V = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{\frac{h^2\nu^4}{kT^2} e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} d\nu = \frac{9R}{x_m^3} \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (8.33)$$

$$\text{where } x = \frac{h\nu}{kT} \quad \text{and} \quad x_m = \frac{h\nu_m}{kT} \quad (8.34)$$

On integration of (8.33) by parts,

$$C_v = 3R \left\{ \frac{12}{x_m^3} \int_0^{x_m} \frac{x^3}{e^x - 1} dx - \frac{3x_m}{e^{x_m} - 1} \right\} \equiv 3RD(x_m). \quad (8.36)$$

This is Debye's equation.

The expression within only brackets is known as Debye function  $D(x_m)$ . It has been calculated by Debye for values of  $x_m$  from 0 to  $\infty$ . We shall, however, consider here two extreme cases.

(a) For high temperatures, i.e., for  $T \rightarrow \infty$ , both  $x$  and  $x_m \rightarrow 0$  so that

$$\underset{x_m \rightarrow 0}{\text{Lt}} \int_0^{x_m} \frac{x^3}{e^x - 1} dx = \underset{x_m \rightarrow 0}{\text{Lt}} \int_0^{x_m} x^2 dx = \underset{x_m \rightarrow 0}{\text{Lt}} \frac{x_m^3}{3} = 0 \quad (8.37)$$

and  $\underset{x_m \rightarrow 0}{\text{Lt}} \frac{3x_m}{e^{x_m} - 1} = 3$ . (8.38)

Thus, from (8.36)–(8.38),

$$C_v = 3R. \quad (8.39)$$

This is exactly the Dulong-Petit law.

(b) For low temperatures, i.e., for  $T \rightarrow 0$ ,  $x \rightarrow \infty$  so that since  $x$  is zero for  $\nu = 0$  from (8.34) at low temperatures,

$$\underset{x_m \rightarrow \infty}{\text{Lt}} \int_0^{x_m} \frac{x^3}{e^x - 1} dx = \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \quad [\text{See (8.11)}] \quad (8.40)$$

and  $\underset{x_m \rightarrow \infty}{\text{Lt}} \frac{3x_m}{e^{x_m} - 1} = 0$ . (8.41)

Then, from (8.36), (8.40) and (8.41),

$$C_v = \frac{12}{5} \frac{R\pi^4}{T_m^3} T^3. \quad (8.42)$$

where  $T_m = \frac{\hbar\nu_m}{k}$ . (8.43)

This is Debye's  $T^3$ -law. This law shows that  $C_v$  is proportional to  $T^3$  at low temperatures.

## 8.7 Comparison of Debye's Equation with Experiment

Writing (8.36) in the form :

$$C_v = 3RD(x_m) = 3RD\left(\frac{T_m}{T}\right) \quad (8.44)$$

it is evident that if we plot  $C_v$  against  $\frac{1}{x_m} (= \frac{T}{T_m})$ , we shall get a curve which will be same for all isotropic bodies. Schrödinger\* showed that this is fairly true for a number of simple substances (e.g., Ag, Pb, Hg, Zn, Cu, Ca, C, Fe, Al, Na, etc.) (Fig. 8.1.).

For this purpose, however, the value of  $T_m$  for each substance must be known. If the value of  $C_v$  is experimentally known at a temperature  $T$ , then corresponding to that value  $x_m$  is found from (8.44), with the aid of Debye's table for the values of  $D(x_m)$  for  $x_m$  from 0 to  $\infty$ . Finally, from the value of  $x_m$  with the aid of (8.35)

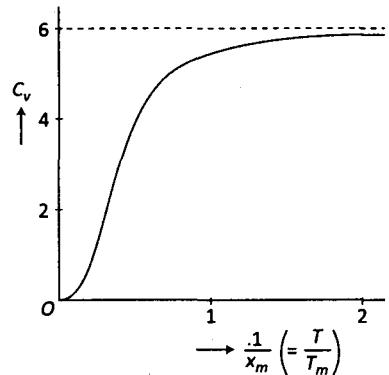


Fig. 8.1

\*Schrödinger, E., *Phys. Zeits.*, **20**, pp. 420, 450, 474, 497, 523 (1919).

and (8.43)  $T_m$  is obtained. For each substance that value of  $T_m$  has, however, been adopted here which fits best the experimental relationship between  $C_v$  and  $T$ .

It is also evident from (8.44) that any two different substances, say, Cu and Fe, will have the same value of  $C_v$  at two different temperatures  $T'$  and  $T''$  since they have got different values for  $T_m$  (Fig. 8.2). The relationship between  $T'$  and  $T''$  for the same value of  $C_v$  is

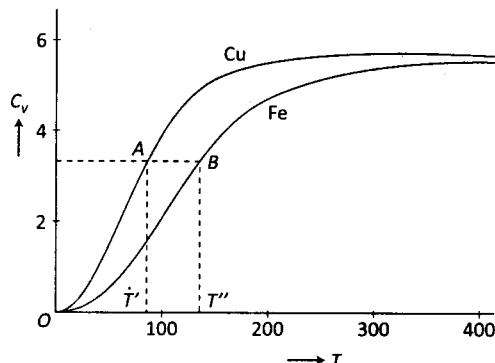


Fig. 8.2:  $C_v$ - $T$  curves

$$\frac{T'}{T'_m} = \frac{T''}{T''_m}, \quad \text{i.e., } T'' = T' \frac{T''_m}{T'_m}, \quad (8.45)$$

where  $T'_m$ ,  $T''_m$  are the characteristic Debye temperatures of Cu and Fe respectively. If  $C_v$  for Cu is known at any temperature  $T'$ , then from (8.45) the corresponding temperature  $T''$  for Fe is found. Thus, from the  $C_v$ - $T$  curve for Cu the  $C_v$ - $T$  curve for Fe can be drawn (as has been shown in Fig. 8.2).  $C_v$ , therefore, obeys a law of corresponding states.

We have mentioned above a method to determine  $T_m$  for a substance.  $T_m$  may also be obtained from the  $T^3$  law (8.42) with a knowledge of  $C_v$  at some low temperature  $T$ . But we can also calculate  $T_m$  independently (without any knowledge of  $C_v$ ) from the elastic constants of the substance. From (8.32) and (8.35),

$$T_m = \frac{h}{k} \left[ \frac{9N}{4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)} \right]^{1/3}. \quad (8.46)$$

Now the values of  $c_l$  and  $c_t$  are given by

$$c_l = \sqrt{\frac{K + \frac{4}{3}\eta}{\rho}} \quad \text{and} \quad c_t = \sqrt{\frac{\eta}{\rho}}, \quad (8.47)$$

where  $\eta$  and  $K$  are respectively the rigidity and the bulk modulus and  $\rho$  the density of the substance. Then, from (8.46) and (8.47),

$$T_m = \frac{h}{k} \left( \frac{9N}{4\pi V} \right)^{1/3} \rho^{1/2} \left[ \frac{1}{(K + \frac{4}{3}\eta)^{3/2}} + \frac{2}{\eta^{3/2}} \right]^{1/3}. \quad (8.48)$$

Schrödinger calculated the values of  $T_m$  from the specific heat data as well as from the elastic constants and found for a number of substances (e.g., Pb, Cd, Ag, Cu, Al, Fe, etc.) that the agreement is only fair but not quite satisfactory. He, however, adopted the values of elastic constants at ordinary temperatures. Now, since the elastic constants vary with temperature one may think that a better agreement may be obtained if the values at low temperatures are used. But Eucken\* has shown that the agreement using these values is considerably worse.

Finally we come to the discussion of the  $T^3$ -law (8.42). Schrödinger studied the validity of this law thoroughly for some substances (e.g., Pb, Cd, Ag, KCl, NaCl, Al, CaF<sub>2</sub>, FeS<sub>2</sub>, etc.).

\*Eucken, Verh. d. dents. phys. Ges., 15, P. 571 (1913).

He found that the law is true for  $\text{CaF}_2^*$  and  $\text{FeS}_2^*$  over a temperature range  $T_m/25$  to  $T_m/12$ , i.e., about 20–40 K and 26–54 K respectively. But he observed that  $T_m$  is 474 K for  $\text{CaF}_2$  and 645 K for  $\text{FeS}_2$  from specific heat data whereas it is 510 K for  $\text{CaF}_2$  and 696 K for  $\text{FeS}_2$  from measurements of elastic constants at ordinary temperatures. The discrepancy is increased considerably if low temperature values of elastic constants are used.

On the other hand, for aluminium the  $T^3$ -law is not valid in the range 19–35 K, the value of  $C_v/T^3$  changing by about 25% in this range. For  $\text{NaCl}$  the value of  $C_v/T^3$  changes by about 20% in the temperature range 10–20 K whereas for lithium it changes by about 30% in the temperature range 15–30 K. Silver and zinc also show similar divergences in the value of  $C_v/T^3$  for temperatures less than 20 K.

Thus Debye's theory is seriously in error with regard to the temperatures at which it predicts the  $T^3$ -region to begin\*\*. We shall see in the following section that a  $T^3$ -region can exist at very much lower temperatures than suggested by Debye's theory. Thus, although this theory describes experimental results for a large number of substances at higher temperatures, it is not satisfactory at low temperatures.

## 8.8 Born's Theory of Specific Heats of Solids

Several modifications of Debye's theory were suggested. We shall discuss here only the work of Born<sup>†</sup>.

We shall first discuss lattice vibrations in terms of a simple model due originally to Born and Kármán<sup>‡</sup>. This case can be easily solved and possesses many features common to lattice vibrations in solids. At the end of this treatment, we shall develop Born's theory.

The simple model due to Born and Kármán consists of a chain of two different types of particles occupying alternate positions (i.e., a diatomic chain) [Fig. 8.3(a)]. When the particles are in equilibrium, the separation between neighbours is  $a/2$  so that then successive particles of the same kind are separated by  $a$ . It is



Fig. 8.3

assumed that forces act only between immediate neighbours and follow Hooke's law. Then regarding the chain as an elastic string, we can calculate Young's modulus  $Y$  of the string. When the string is subjected to a uniform tension so that  $a/2$  becomes  $\frac{a}{2} + x$ , the tension is, by Hooke's law,  $\mu x$  where  $\mu$  is Hooke's constant between unlike neighbours. The corresponding elastic strain (extension per unit length) is  $x/\frac{a}{2}$  so that Young's modulus is

$$Y = \frac{\mu x}{x/\frac{a}{2}} = \frac{1}{2} a \mu. \quad (8.49)$$

The chain is evidently a linear (i.e., one-dimension) lattice with two unlike particles in each cell. We shall assume that the particles vibrate along the length of the chain. Let  $x_l, x'_l$  denote the displacements at any instant of the two particles in the  $l$ th cell. Then, the equations of motion are

\*For a compound, the atomic heat  $C_v$  is found by dividing the molecular heat by the number of atoms in a molecule.

\*\*Eucken and Werth, *Z. anorg. chem.*, **188**, P. 152 (1930); Blackman, *Reports on Progress in Physics*, **8**, P. 11 (1941).

<sup>†</sup>Born and Huang, *Dynamical Theory of Crystal Lattices*, Pp. 55–82 (1954); Seitz, *The Modern Theory of Solids*, Pp. 112–125 (1940).

<sup>‡</sup>Born and Kármán, *Phys. Zeits.*, **13**, P. 297 (1912).

$$\left. \begin{aligned} m \frac{d^2 x_l}{dt^2} &= \mu[(x'_l - x_l) - (x_l - x'_{l-1})] \\ m' \frac{d^2 x'_l}{dt^2} &= \mu[(x_{l+1} - x'_l) - (x'_l - x_l)] \end{aligned} \right\} \quad (8.50)$$

where  $m, m'$  are the masses of the particles. Due to the vibration of the particles of the chain, waves will be set up. Let us, therefore, make the substitution :

$$\left. \begin{aligned} x_l &= Ae^{i2\pi\eta l - i\omega t} \\ x'_l &= Be^{i2\pi\eta l - i\omega t} \end{aligned} \right\} \quad (8.51)$$

These represent progressive wave solutions with  $\omega/2\pi (= \nu)$  as the frequency and with  $|a/\eta|$  as the wavelength\*. Then, from (8.50) and (8.51),

$$\left. \begin{aligned} (m\omega^2 - 2\mu)A + \mu(1 + e^{-2\pi i\eta})B &= 0 \\ \mu(1 + e^{2\pi i\eta})A + (m'\omega^2 - 2\mu)B &= 0 \end{aligned} \right\} \quad (8.52)$$

These linear homogeneous equations are soluble only if

$$\begin{vmatrix} m\omega^2 - 2\mu & \mu(1 + e^{2\pi i\eta}) \\ \mu(1 + e^{2\pi i\eta}) & m'\omega^2 - 2\mu \end{vmatrix} = 0.$$

The roots of this equation are

$$\omega^2 = \left\{ \frac{\mu}{mm'} [(m + m') - \sqrt{(m + m')^2 - 4mm' \sin^2 \pi\eta}] \right. \quad (8.53)$$

$$\left. \frac{\mu}{mm'} [(m + m') + \sqrt{(m + m')^2 - 4mm' \sin^2 \pi\eta}] \right. \quad (8.54)$$

Substituting these values of  $\omega^2$  in (8.52), we obtain the corresponding amplitude ratios :

$$\frac{A}{B} = \left\{ \frac{-m'(1 + e^{2\pi i\eta})}{(m - m') - \sqrt{(m + m')^2 - 4mm' \sin^2 \pi\eta}} \right. \quad (8.55)$$

$$\left. \frac{-m'(1 + e^{2\pi i\eta})}{(m - m') + \sqrt{(m + m')^2 - 4mm' \sin^2 \pi\eta}} \right. \quad (8.56)$$

As usual we can take the real part of the complex solution to represent the actual amplitude ratio.

Now, it is evident from (8.51) that although the solution with  $+\eta$  is quite distinct from that with  $-\eta$ , according to (8.53) and (8.54)  $\omega$  will be same in either case. Thus we find that there are exactly two real modes of vibration for each given value of  $\eta$  according to these two equations.

The solutions for  $\omega^2$  and  $A/B$  show that they are periodic functions of  $\eta$  with period equal to 1. We can thus obtain all the distinct solutions if we restrict  $\eta$  to the unit range given by

$$-\frac{1}{2} \leq \eta < \frac{1}{2}. \quad (8.57)$$

\*That is,  $\eta$  is related to wavelength  $\lambda$  by  $\lambda = |a/\eta|$ . The reason will be clear presently.

This restriction on the range of  $\eta$  is quite plausible. As  $|a/\eta|$  is the wavelength, according to (8.57), the smallest permissible wavelength is  $2a$  [Fig. 8.3(b)]. Because, waves with a shorter wavelength do not correspond to any distinct vibrations in the chain. Herein lies, in fact, the justification for a maximum wave number, i.e., minimum wavelength to be adopted in Debye's theory.

According to (8.53) and (8.54),  $\omega$  has been plotted against  $\eta$  [for the range indicated by (8.57)] for different mass ratios  $\sigma = m'/m$  in Fig. 8.4. Let us first consider the curves for (8.53). Expanding (8.53) in a Taylor series with respect to  $\eta$  and taking  $\eta \rightarrow 0$ , we obtain

$$\omega^2 = \left( \frac{2\pi^2 \mu}{m + m'} \right) \eta^2$$

$$\text{or, } \omega = \left[ \frac{\mu}{2(m + m')} \right]^{\frac{1}{2}} (2\pi\eta). \quad (8.58)$$

Since  $|a/\eta|$  is the wavelength, the velocity for long wavelengths (for  $\eta \rightarrow 0$ ) is, from (8.58),

$$c = \nu\lambda = \frac{\omega}{2\pi} \frac{a}{\eta} = \left[ \frac{\mu}{2(m + m')} \right]^{\frac{1}{2}} a. \quad (8.59)$$

Also it follows from (8.55) that for  $\eta \rightarrow 0$ ,  $A/B \approx 1$ . This means that the two particles in the same cell move practically in unison as a rigid unit.

These long waves can be shown to be identical with longitudinal elastic vibrations in the chain.

For, the velocity of such elastic vibrations is

$$\sqrt{\frac{Y}{\rho}} = \left[ \frac{\mu}{2(m + m')} \right]^{\frac{1}{2}} a \quad (8.60)$$

from (8.49) and with  $\rho = (m + m')/a$ . (8.60) is evidently identical with (8.59). It is for this reason that (8.53) and (8.55) represent (low-frequency) *acoustic* vibrations.

On the other hand, we obtain similarly from (8.54) for  $\eta \rightarrow 0$ ,

$$\omega = \left[ \frac{2(m + m')\mu}{mm'} \right]^{\frac{1}{2}}. \quad (8.61)$$

Also, it follows from (8.56) that for  $\eta \rightarrow 0$ ,

$$\frac{A}{B} = -\frac{m'}{m} \quad \text{or, } Am + Bm' = 0. \quad (8.62)$$

This means that the motions of the two particles in each cell are opposed to one another and the centre of mass of the cell remains stationary. Now, as an analogue to ionic crystals, let us assume that the two particles in each cell are oppositely charged. In that case, the

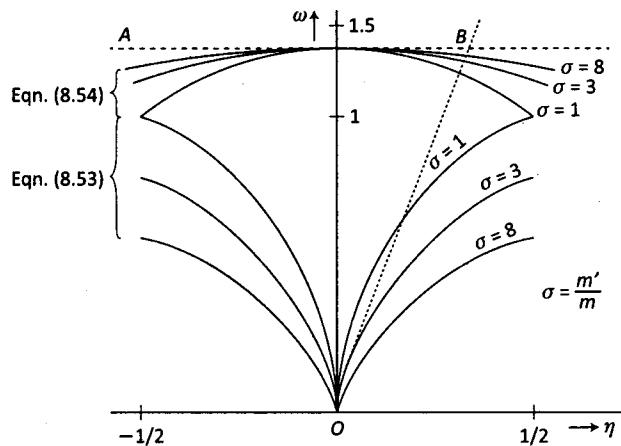


Fig. 8.4

opposed motions of the oppositely charged particles give rise to an oscillating dipole so that these vibrations of long wavelengths are of special importance in considering the interaction of crystals with light. It is for this reason that (8.54) and (8.56) represent (high-frequency) optical vibrations.

Thus, for each value of  $\eta$  there are two modes of vibration—acoustic and optical. Now, in an infinite chain,  $\eta$  can take any value between  $-\frac{1}{2}$  and  $\frac{1}{2}$  so that an infinite number of modes of independent vibration are possible. But we have to deal with a finite bulk of a crystal so that we must find the normal modes of vibration allowed in it. Hence, in the present case, we take a finite chain of, say,  $L$  cells and join the two ends of the chain to form a ring\*. So long as  $L$  is large enough for the curvature of the ring to be negligible, the equations of motion (8.50) remain unaltered if the  $L$ th cell is identified with the cell  $O$ . Thus we have now the condition :

$$x_L = x_0$$

since these displacements refer to the same particle. It follows from this condition that we must have from (8.51)

$$\eta L = h \text{ (an integer).} \quad (8.63)$$

From (8.57) and (8.63),

$$-\frac{1}{2}L \leq h < \frac{1}{2}L. \quad (8.64)$$

Thus, the total number of independent vibrations is  $2L$  equal to the degrees of freedom of the chain since a particle has only one degree of freedom in this case.

The finite ring arrangement adopted here is, in fact, equivalent to the periodic boundary condition which can also be achieved\*\* in the present linear case by adding two additional cells (designated as cell  $O$  and cell  $L+1$ ), one at the beginning and the other at the end of the chain and assuming for the  $L$ th cell and the cell  $O$  the condition

$$x_L = x_0$$

or equivalently for the 1st and the  $(L+1)$ th cell the condition

$$x_1 = x_{L+1}.$$

It has been shown above that the long-wave *acoustic* lattice vibrations are identical with the elastic waves. Now, since Debye's theory takes into account only the elastic waves in the solid, this theory deals with the long-wave acoustic lattice vibrations only represented, according to (8.58), by tangents like  $OB$  shown in Fig. 8.4. Further, the maximum frequency  $\nu$  in Debye's theory follows from the long-wave optical lattice vibrations represented, according to (8.61), by the straight line  $AB$  (Fig. 8.4) which cuts off the tangents like  $OB$  at points such that the total number of vibrational modes are correctly obtained. Thus, Debye's theory represents the lattice vibrations, acoustic as well as optical, in the long wave limit.

Let us now consider a specific example. Suppose, there is a large discrepancy between the masses of the two types of particles. In this case, the frequency of optical vibrations does not vary much (Fig. 8.4) along the curve, i.e., the frequency is confined to a narrow range or is practically constant. Further, these vibrations involve mainly the motion of the light particles, the heavy particles remaining largely stationary. Since the light particles can affect one another only through the motions of the heavy particles, the vibratory motions of the different light

\*Born and Huang, *loc. cit.*

\*\*Seitz, *loc. cit.*

particles are largely independent. Thus, in this case, we can apply Einstein's theory (explained in section 8.5) to describe the optical lattice vibrations. On the other hand, Debye's theory can be applied to describe the acoustic lattice vibrations.

Another interesting example is that the two particles in a cell have equal masses but interact more strongly with one another than with their neighbours. This case is similar to that of a molecular crystal in which *intramolecular* forces are stronger than *intermolecular* forces. If  $\alpha$  is Hooke's constant for interaction between the two particles in a cell,  $\beta$  Hooke's constant for interaction between a particle of one cell and its neighbour in another cell and  $m$  the particle mass, then the equations similar to (8.53) and (8.54) are

$$\omega^2 = \begin{cases} \frac{2(\alpha + \beta) - \sqrt{4(\alpha + \beta)^2 - 16\alpha\beta \sin^2 \pi\eta}}{2m} \\ \frac{2(\alpha + \beta) + \sqrt{4(\alpha + \beta)^2 - 16\alpha\beta \sin^2 \pi\eta}}{2m} \end{cases} \quad (8.65)$$

(8.66)

Now, for  $\alpha \gg \beta$ , we have from (8.65)

$$\omega = 2\sqrt{\frac{\beta}{2m}} |\sin \pi\eta| \quad (8.67)$$

$$\text{or } \omega = \sqrt{\frac{\beta}{2m}} |2\pi\eta| \quad (8.68)$$

for  $\eta \rightarrow 0$  (long waves). In this case the velocity is

$$c = \frac{\omega}{2\pi} \left| \frac{a}{\eta} \right| = a\sqrt{\frac{\beta}{2m}}. \quad (8.69)$$

Let us also calculate independently the velocity of elastic waves for this example. Since  $\alpha$  is  $\gg \beta$ , due to a uniform tension the distance between two particles in a cell will not be affected but  $a$  the distance between the centres of any two neighbouring cells will be changed to  $a + x$  and the tension will be  $\beta x$ . Hence, Young's modulus is

$$Y = \frac{\beta x}{(x/a)} = \beta a. \quad (8.70)$$

Now, here  $\rho = \frac{2m}{a}$  so that the velocity of elastic waves is

$$\sqrt{\frac{Y}{\rho}} = a\sqrt{\frac{\beta}{2m}}. \quad (8.71)$$

This is identical with (8.69). This shows that (8.65) represents acoustic lattice vibrations and also that in this case the two particles in a cell move in unison as a rigid unit. As in the first example, Debye's theory can be applied to describe these vibrations also. Again, for  $\alpha \gg \beta$ , we have from (8.66)

$$\omega = 2\sqrt{\frac{\alpha}{2m}}. \quad (8.72)$$

This evidently represents the (high-frequency) optical lattice vibrations. As in the first example, Einstein's theory can be applied to describe also these vibrations which have a constant frequency.

These simple one-dimensional examples illustrate the background of the postulates Born adopted in his theory of specific heats of solids. Consider an *isotropic* solid containing  $N$  molecules or unit cells each of which consists of  $p$  atoms so that the total number of degrees of freedom is  $3Np$ . Born postulated that out of these, only  $3N$  degrees of freedom that correspond to *intermolecular* (acoustic) vibrations of the  $N$  molecules should be treated by the continuum method, i.e., by Debye's theory. The remaining  $(3p - 3)N$  degrees of freedom represent  $(3p - 3)$  degrees of freedom of each molecule or unit cell. These  $(3p - 3)$  degrees of freedom, in fact, correspond to the *intramolecular* (optical) vibrations of the  $p$  atoms in a molecule or unit cell and, according to Born, should be represented by  $(3p - 3)$  Einstein functions. Born further suggested that since the examination of lattice vibrations leads to a cut-off (i.e., maximum) wave number or a minimum permissible wavelength  $\lambda_m$  it is quite justified to use a cut-off (i.e. maximum) frequency  $\nu_m$  as Debye did. Now, since the longitudinal wave velocity is greater than the velocity of transverse waves, the maximum permissible frequency  $(\nu_m)_l$ , for longitudinal waves is greater than  $(\nu_m)_t$ , for the transverse waves. These are given by

$$c_l = \lambda_m(\nu_m)_l, \quad c_t = \lambda_m(\nu_m)_t. \quad (8.73)$$

Then (8.31) should be replaced by

$$3N = 4\pi V \left[ \frac{1}{c_l^3} \int_0^{\nu=c_l/\lambda_m} \nu^2 d\nu + \frac{2}{c_t^3} \int_0^{\nu=c_t/\lambda_m} \nu^2 d\nu \right]. \quad (8.74)$$

Then, according to Born, the final expression for the specific heat of the solid is, from (8.25) and (8.36),

$$C_v = R[D(x_l) + 2D(x_t)] + R \sum_{i=1}^{3p-3} E(x_i), \quad (8.75)$$

where  $x_l = h(\nu_m)_l/kT$ ,  $x_t = h(\nu_m)_t/kT$  and  $x_i = h\nu_i/kT$ .

For an isotropic monatomic ( $p = 1$ ) solid, (8.75) contains evidently only Debye terms :

$$C_v = R[D(x_l) + 2D(x_t)]. \quad (8.76)$$

For an isotropic diatomic ( $p = 2$ ) solid, (8.75) is reduced to the form :

$$C_v = R[D(x_l) + 2D(x_t)] + R \sum_{i=1}^3 E(x_i). \quad (8.77)$$

Born also suggested that the same method could also be applied in good approximation to *anisotropic* solids. In this case, the three waves of polarisation have different velocities for each direction of propagation. Thus, the limiting frequencies  $(\nu_m)_1$ ,  $(\nu_m)_2$ ,  $(\nu_m)_3$  are now functions of direction. If the direction variables are taken to be the polar angles  $\theta$  and  $\phi$ , then we have from (8.75)

$$C_v = R \sum_{i=1}^3 \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} D(x_i) \frac{\sin \theta d\theta d\phi}{4\pi} + R \sum_{j=1}^{3p-3} E(x_j), \quad (8.78)$$

where  $x_i = h(\nu_m)_i/kT$  and is a function of  $\theta$  and  $\phi$ .

Förstuling\* computed the Debye terms for the cubic salts NaCl, KCl, CaF<sub>2</sub>, and FeS<sub>2</sub> using room-temperature elastic constants. He employed an ingenious expansion method for evaluating

\*Fürstling, K., *Z. Physik*, **3**, P. 9 (1920); *Ann. Physik*, **61**, P. 549 (1920); *Z. Physik*, **8**, P. 251 (1922).

the integrals in (8.78) and found that the result could be expressed approximately in terms of three Debye functions. For the diatomic salts NaCl and KCl, all the three Einstein frequencies ( $j = 1, 2, 3$ ) were taken to be the same, whereas for the triatomic salts CaF<sub>2</sub> and FeS<sub>2</sub>, two sets of three equal frequencies ( $j = 1, 2, \dots, 6$ ) were used. These frequencies were chosen in order to obtain the best fit with the experimental results. The theoretical and experimental values of  $C_v$  for KCl were found to compare well from 70 K to 235 K. The accuracy was also found to be about the same in the case of the other salts.

Now, the contributions from the Einstein terms decrease very rapidly at low temperatures [See, for example, (8.27)] and are negligible below 10 K. Hence, only the Debye terms should be considered below 10 K where they follow the  $T^3$ -law [See, for example, (8.42)]. But since Keesom and Clark found that KCl does not satisfy the  $T^3$ -law below 10 K, it follows that Born's modification of Debye's theory is not free from some of the same drawbacks as the original (i.e., Debye's) theory.

The alkali metal, lithium, is a monatomic solid. So, for this metal the Einstein terms must be omitted from (8.78). Fuchs\* computed by an indirect method the elastic constants of this substance, as these values were not available. Then, he used the computed values of the elastic constants to find the three Debye temperatures  $T_i [= h(\nu_m)_i/k]$  for each direction of propagation and then calculated the specific heat of lithium for different temperatures from (8.78) (omitting the Einstein terms). Next he put these computed values of  $C_v$  on the left-hand side of (8.36) and calculated  $T_m$  at different temperatures. This is shown by curve I in Fig. 8.5. On the other hand, Simon and Swain found from experiment  $C_v$  for lithium at different temperatures and then put the observed values of  $C_v$  on the left-hand side of (8.36) and calculated  $T_m$  at different temperatures. This is shown by curve II in the same figure. It is evident that the agreement between the two curves is far from exact.

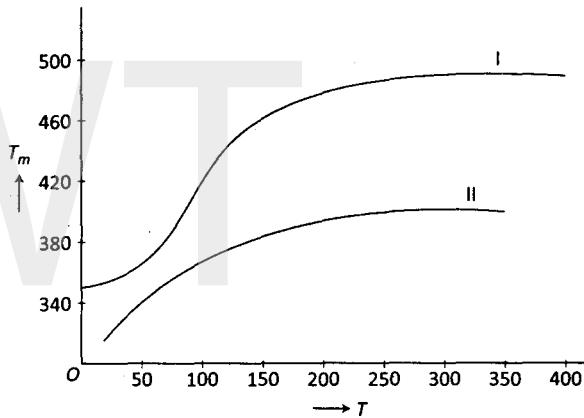


Fig. 8.5

From the above discussion, it is clear that Born's theory also does not provide the right answer to the problem of specific heat of solids. Raman has recently studied the whole subject thoroughly and has put forward a theory purely from the atomistic view-point on the lines of Einstein's theory, rejecting outright the continuum method (i.e., the method based on the identity between the thermal energy and the energy of elastic waves in solids) devised by Debye and followed also by Born in his theory. In the following section, we shall discuss the basic principles of Raman's theory and add some remarks regarding its experimental validity.

## 8.9 Raman's Theory of Specific Heats of Solids\*\*

Although the theories of Debye and Born differ in detail, yet the basic idea in both the theories is the same, namely, that we are dealing here with a boundary value problem in the theory of wave propagation. But actually, the problem is the determination of the modes and frequencies of vibration of the atoms in a crystal about their positions of equilibrium.

\*Fuchs, K., *Proc. Roy. Soc.*, **153**, P. 622 (1936); **157**, P. 444 (1936).

\*\*Raman, C. V., *Proc. Ind. Acad. Soc.*, **43**, Pp. 327-35 (1956); **44**, Pp. 99-102, 153-159, 361-66 (1956).

These modes and frequencies would be determined only by the masses of the atoms and their interactions with the neighbouring atoms. It is, therefore, evident that considerations of wave propagation and boundary conditions are not relevant to the problem.

The untenable character of the theories of Debye and Born may be made clear by a familiar fact of experience. It is the extreme slowness with which heat diffuses through a solid. On the other hand, elastic waves travel through a solid with a velocity of some thousands of metres per second. It is evidently a formidable problem to explain such a difference if one is to identify thermal energy with wave motion as has been done in the theories of Debye and Born. This difficulty, however, disappears if, according to C. V. Raman, the thermal energy is identified with the energy of vibration of atoms in the crystal. The conduction of heat through a solid would, on this view, be the result of an exchange of energy quanta between individual atoms. Such a process would bear no resemblance at all to wave-propagation in the usual sense.

Raman's idea is further strengthened by the fact that the specific heat of a solid tends, with rising temperature, to a limiting value proportional to the number of atoms contained in it (Dulong-Petit law). It is a clear indication that any reasonable theory for explanation of this fact should consider the subject from the atomistic view-point and should be based on a consideration of the normal modes of vibration of the atoms about their mean positions in the lattice structure of the crystal.

Finally, the continuous spectrum of frequencies envisaged by Debye and Born is irreconcilable with the observed spectroscopic behaviour of crystals. The whole body of experimental evidence, in fact, confirms the idea that the atomic vibrations in crystals appear, *for the most part* [It will be clarified from eqn. (A) below], as a set of sharply defined monochromatic frequencies in the spectrum. Thus, Einstein's view of a crystal as an assembly of immense numbers of quantised oscillators having a common set of vibration frequencies seems to be a logical and correct view of the problem. Raman has, therefore, developed and refined Einstein's theory of specific heats keeping in view the actual behaviour of crystals.

**Vibrations of Crystal Structure :** There is a theorem in classical mechanics regarding the small vibrations of a connected system of particles about their positions of equilibrium. This theorem states that *all the possible vibrations of the system are superpositions of its normal modes of vibration in each of which all the particles of the system vibrate with the same frequency and in the same or opposite phases*. Now, Einstein's theory deals with the modes and frequencies of vibration of the *individual oscillators* the total number of which is equal to the number of degrees of freedom of the entire system. Raman has identified the normal modes and frequencies of vibration which are characteristic of the structure of the crystal with those that describe the dynamical behaviour of the *elementary units\** of which the crystal is composed.

Let us first consider a few simple models the behaviour of which will illustrate the principles underlying the general case of the crystal. The simplest model is a stretched string loaded by a series of equidistant particles of equal mass [Fig. 8.6(a)]. It is evident that a mode of oscillation is possible on such a string with successive particles having the same amplitude but opposite phases of vibration. Here all the particles possess the same frequency. Thus it is, according to the above-stated theorem, a normal mode of vibration of the system. Next we consider the case in which the particles on the string are equidistant but have alternately two different masses. It can be easily seen that such a system would have three possible normal modes of vibration with different frequencies [Fig. 8.6(b), (c) and (d)]. In Fig. 8.6(b), successive particles of equal mass have the same amplitude and the same phase, whereas in Fig. 8.6(c) and (d), they have the same amplitude but opposite phases.

\*These elementary units are the supercells defined and described later here.

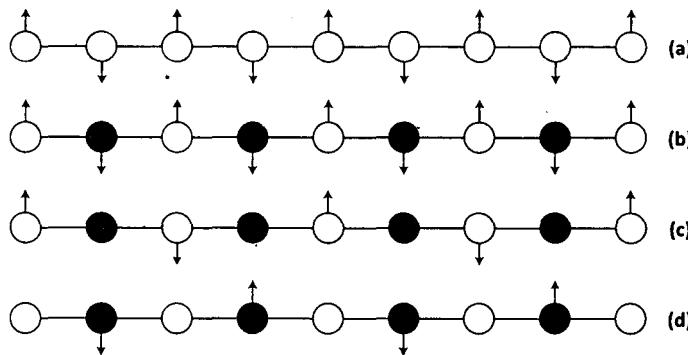


Fig. 8.6

It can be seen on generalisation of these results that a periodic linear lattice with  $p$  particles in each unit cell would have  $(2p - 1)$  normal modes and frequencies of vibration. In  $(p - 1)$  of these modes, the amplitudes and phases of vibration of the corresponding particles in the successive unit cells are the same, whereas in the  $p$  remaining modes they have the same amplitudes but opposite phases. Any disturbance in such a lattice will, in fact, resolve itself into the  $(2p - 1)$  characteristic modes of oscillation with their respective frequencies.

Now we come to study the normal vibrations of crystal structures. The basic principle of a crystal structure is that the structure comes into coincidence with itself following a unit translation\* along any one of the three axes of the lattice. It follows as a natural consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should also possess this property. This can happen in two ways and thus enables us to divide all the normal modes into two distinct classes. In the first class of normal modes, the amplitudes as well as phases of oscillation of the equivalent atoms (in adjacent cells) which come into coincidence following unit translation are identical. In the other class of normal modes the amplitudes of equivalent atoms are the same but the phases are all reversed so that the normal mode remains the same following unit translation. Since these two alternatives are possible for unit translation along each of the three axes of the lattice, we have  $2 \times 2 \times 2$ , i.e., 8 possible situations. In each of these situations, the equations of motion of the  $p$  atoms contained in the unit cell of the structure can be written down in terms of the  $3p$  co-ordinates which determine their displacements. Since the displacements of the equivalent atoms in adjoining cells which interact with the atoms in the cell under consideration are also the same, the  $3p$  equations of the latter contain only  $3p$  independent co-ordinates. They can, therefore, be completely solved giving us  $3p$  solutions for each of the eight possible situations referred to above. Thus we have in all  $24p$  solutions from which the three simple translations must be excluded. Then, there are only  $(24p - 3)$  normal modes of vibration each of which is characterised by a specific frequency. In  $(3p - 3)$  of these modes, the equivalent atoms have the same amplitudes and phases of oscillation in the adjacent cells, whereas in the  $21p$  remaining modes the amplitudes are the same but the phases alternate in adjacent cells along one, two or all the three axes of the lattice.

The  $(24p - 3)$ , i.e.,  $(3 \times 8p - 3)$  normal modes of vibration obtained above may obviously be regarded as the modes of internal vibration of the  $8p$  atoms contained in a *supercell* whose linear dimensions (i.e., length, breadth and height) are twice as large as those of the unit cell containing  $p$  atoms. The omitted 3 degrees of freedom would then represent the 3 degrees of

\*A unit translation is the translation due to which the atoms of one unit cell coincide with the corresponding atoms of an adjacent unit cell.

translatory movement of the whole group of  $8p$  atoms contained in the supercell along the three axes of the crystal lattice. Thus, we find that the structural unit whose dynamical behaviour is representative of the entire crystal is not the unit cell but the supercell which is twice as large in each direction as the unit cell.

Now, following Einstein, we may regard a crystal as an assembly of  $(24p - 3)$  sets of oscillators, each set having its own distinctive frequency of vibration. The number of oscillators in each set is the same as the number of supercells (each containing  $8p$  atoms) contained in the whole crystal. Each set of oscillators forms an assembly in thermal equilibrium the behaviour of which can be described statistically by Maxwell-Boltzmann law. The average energy of an oscillator in each set is given by Einstein's formula (See section 8.5) for the particular frequency. Multiplying this by the number of supercells contained in the whole volume of the crystal, we obtain an expression for the total energy of all the oscillators in that set. Finally, summing over the total energies for all the  $(24p - 3)$  sets of oscillators with their respective frequencies of vibration, we obtain an expression for the thermal energy due to the vibrations of atoms with definite, *discrete* frequencies. This is

$$U_1 = \frac{N}{8} \sum_{r=1}^{24p-3} \frac{h\nu_r}{e^{h\nu_r/kT} - 1}. \quad (\text{A})$$

for a crystal containing  $N$  unit cells.  $N/8$  gives the number of supercells in the whole crystal.

Next, we proceed to consider the 3 omitted degrees of translatory movement of the whole group of  $8p$  atoms contained in a supercell along the three axes of the crystal lattice. Suppose, there are  $S$  supercells (each containing  $8p$  atoms) in the whole crystal. Then, the total number of degrees of atomic freedom is  $S \times 3 \times 8p$ , i.e.,  $24pS$ . Out of these we have already taken account of  $(24p - 3)S$  degrees of freedom. Now, the remaining  $3S$  degrees of atomic freedom is also the number of degrees of freedom of translation of the  $S$  supercells contained in the crystal. Any translation of an individual supercell would necessarily set up forces tending to displace neighbouring supercells. This results in oscillatory movements of volume-elements of larger dimensions than the supercell in question. The larger such a volume-element is, the lower would be the lower limit of frequencies of vibration. Evidently the smallest volume-element set into vibration in this manner is a supercell. Thus, we find that the translations of the individual supercells must be associated with a whole series of frequencies lying between zero (for a very big volume-element) and an upper limit which is equal to the lowest discrete frequency of atomic vibrations in a supercell.

Now we proceed to find the total thermal energy associated with this continuous spectrum of frequencies extending from zero up to an upper limit. For this purpose, consider a volume-element in the crystal which has got the same shape as a supercell but whose dimensions are respectively  $m$  times larger than those of a supercell. Evidently, the volume of each such volume-element is  $m^3$  times that of a supercell so that the total number of such volume-elements in the whole crystal is  $S/m^3$ . The number of degrees of freedom of translation of these volume-elements is then  $3\frac{S}{m^3}$  which we may regard as the number of oscillators with  $\nu$  as the lowest frequency of internal vibration. By the principle of dynamical similarity, we may write,

$$\nu = \frac{k}{m},$$

where  $k$  is a constant. Then,  $\frac{3S\nu^3}{k^3}$  is the number of oscillators with  $\nu$  as the lowest frequency of internal vibration. Now, if we take a *slightly* larger volume-element, say,  $(m + dm)$  times larger in dimensions than a supercell, then for this case the corresponding number of oscillators is

$\frac{3S(\nu - d\nu)^3}{k^3}$  with  $(\nu - d\nu)$  lowest frequency of internal vibration. Hence, the number of oscillators with the lowest frequencies lying between  $\nu$  and  $\nu - d\nu$  is

$$\frac{3S}{k^3} \{ \nu^3 - (\nu - d\nu)^3 \}, \text{ i.e., } \frac{9S}{k^3} \nu^2 d\nu = \frac{9S\nu^2 d\nu}{\nu_l^3},$$

where  $\nu_l$  is the value of  $\nu$  for  $m = 1$  (i.e., for a supercell) and is, therefore, equal to  $k$ . Multiplying this number by the Einstein formula (See section 8.5) for the average energy of an oscillator and integrating from 0 to  $\nu_l$  (since  $\nu_l$  is the lowest frequency of atomic vibrations in a supercell), we obtain the total thermal energy associated with the  $3S$  degrees of freedom. This is

$$U_2 = \int_0^{\nu_l} \frac{h\nu}{e^{h\nu/kT} - 1} \times \frac{9S\nu^2}{\nu_l^3} d\nu = \frac{9N}{8\nu_l^3} \int_0^{\nu_l} \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1}, \quad (\text{B})$$

since  $\frac{N}{8} = S$  for a crystal containing  $N$  unit cells.

**Raman's Formula :** Now, adding  $U_1$  and  $U_2$  we obtain the expression for the total thermal energy of the crystal as

$$U = U_1 + U_2 = \frac{N}{8} \left[ \sum_{r=1}^{24p-3} \frac{h\nu_r}{e^{h\nu_r/kT} - 1} + \frac{9}{\nu_l^3} \int_0^{\nu_l} \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1} \right]. \quad (8.79)$$

Evidently  $\nu_1$ , the lowest frequency in the summation term, is the same as  $\nu_l$ , the upper limit in the integral form. However, on differentiating  $U$  with respect to  $T$ , we obtain

$$C_v = \left( \frac{dU}{dT} \right)_V = \frac{N}{8} \frac{d}{dT} \left[ \sum_{r=1}^{24p-3} \frac{h\nu_r}{e^{h\nu_r/kT} - 1} + \frac{9}{\nu_l^3} \int_0^{\nu_l} \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1} \right]. \quad (8.80)$$

Raman\* first tested (8.80) for diamond. He computed theoretically  $C_v$  for diamond in the temperature range between 15 K and 1100 K, making use of the nine spectroscopically determined vibration frequencies of the diamond structure as well as their known degeneracies and also taking the lowest of these nine frequencies as the upper limit for the integral term in (8.80). He compared the theoretical results with the experimental observations of De Sorbo\*\* for the range 15 K to 300 K and of Magnus and Hodler† for the range 300 K to 1100 K. The agreement was found highly satisfactory.

Later, Raman‡ again compared the theoretical values with the latest available experimental data for diamond and obtained a striking overall agreement over the whole of the temperature range from 0 K to 1000 K.

He also evaluated the specific heats of the four metals—aluminium, copper, silver and lead in terms of the four characteristic frequencies of each of them determined from their elastic constants§. He found good agreement between the theoretical and experimental values in the lower part of the temperature range but observed slight deviations in the upper part. He attributed these deviations to the anharmonicity of atomic oscillators at higher temperatures.

\*Raman, C. V., *Proc. Ind. Acad. Soc.*, **44**, Pp. 160–4 (1956).

\*\*De Sorbo, W. J., *J. Chem. Phys.*, **21**, P. 876 (1953).

†Magnus and Holder, *Ann. d. Phys.*, **80**, P. 808 (1926).

‡Raman, C. V., *Proc. Ind. Acad. Soc.*, **46**, Pp. 323–332 (1957).

§Raman, C. V., *Proc. Ind. Acad. Soc.*, **45**, Pp. 7–14, 59–64 (1957).

## 8.10 Quantum Theory of Specific Heats of Diatomic Gases

The average translational kinetic energy of a diatomic gas molecule, according to the law of equipartition of energy (See section 2.12), is  $\frac{3}{2}kT$  so that the total translational kinetic energy of a gram-molecule is

$$U_t = \frac{3}{2}kT \times N = \frac{3}{2}RT$$

and the specific heat at constant volume is

$$(C_v)_t = \left( \frac{dU_t}{dT} \right)_V = \frac{3}{2}R. \quad (8.81)$$

A diatomic gas molecule is capable of rotation about any axis perpendicular to the line joining the two atoms. This gives rise to two degrees of freedom (See section 2.11). The total energy associated with rotation for a gram-molecule of a diatomic gas is, therefore,

$$U_r = 2 \times \frac{1}{2}kT \times N = RT$$

and the contribution to specific heat on this account is

$$(C_v)_r = R. \quad (8.82)$$

Finally, each atom of a diatomic molecule is also capable of vibration with respect to the other along only the line joining the two atoms. This also gives rise to two degrees of freedom—one due to the kinetic energy and the other due to the potential energy of one atom vibrating with respect to the other. Thus, the total energy associated with vibration for a gram-molecule is

$$U_v = 2 \times \frac{1}{2}kT \times N = RT$$

and the contribution to specific heat on this account is

$$(C_v)_v = R. \quad (8.83)$$

The total specific heat of a diatomic gas should, therefore, according to the classical theory, be

$$C_v = (C_v)_t + (C_v)_r + (C_v)_v = \frac{3}{2}R + R + R = \frac{7}{2}R. \quad (8.84)$$

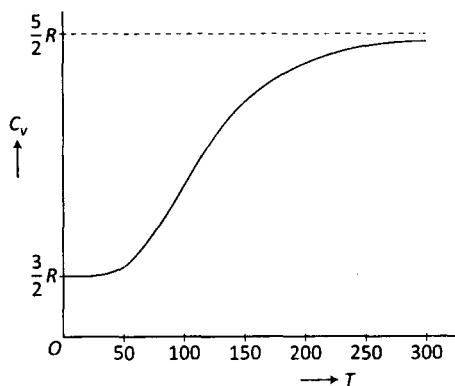


Fig. 8.7

But Eucken\* has shown for hydrogen that  $C_v$  is rather less than  $\frac{5}{2}R$  even at room temperatures and goes gradually down to  $\frac{3}{2}R$  at about 60 K (Fig. 8.7). This shows that (8.84) is not followed at all by hydrogen, because according to (8.84)  $C_v$  may be  $\frac{3}{2}R$  (in absence of rotation and vibration), or  $\frac{5}{2}R$  (if rotation is excited)\*\*, or  $\frac{7}{2}R$  (if both rotation and vibration are also excited). Ehrenfest was the first to point out that the difficulty might be overcome if the quantum theory is applied to the rotational and vibrational motions of the molecules.

We shall, however, first consider the rotational motion of diatomic molecules in the light of quantum

\*Eucken, Berl. Ber., P. 141 (1912).

\*\*It will be seen later in this section that rotation is *Molecular* excited than vibration.

theory. According to the quantum mechanics, the characteristic energy values of a rotating diatomic molecule is\*

$$E_j = \frac{\hbar^2}{8\pi^2 I} j(j+1), \quad (8.85)$$

where  $j = 0, 1, 2, 3, \dots$ ,  $\hbar$  = Planck's constant, and  $I$  = moment of inertia of the molecule about an axis perpendicular to its own axis of symmetry. The angular momentum of the molecule is given by  $\frac{\hbar}{2\pi}\sqrt{j(j+1)}$  ( $= I\omega$ ) in magnitude and is represented vectorially by  $\vec{j}$  along the axis of rotation. Now, if a magnetic field is applied, this axis can lie at an angle  $\theta$  with the field such that

$$m = j \cos \theta = j, j-1, \dots -j-1, -j. \quad (8.86)$$

Thus, altogether  $(2j+1)$  orientations of the molecule with respect to the field are possible. In other words, a diatomic molecule having energy  $E_j$  can stay in any of these  $(2j+1)$  states with respect to a magnetic field. Hence,  $(2j+1)$  gives a measure of the probability of the existence i.e., the statistical weight of a  $j$ -molecule. Then, by a generalisation of Maxwell-Boltzmann law\*\*, the number of molecules having energy  $E_j$  is

$$N_j = N_0(2j+1)e^{-E_j/kT}, \quad (8.87)$$

where  $N_0$  is the number of molecules having zero rotational energy ( $j = 0$ ).

We can now find the average rotational energy of a molecule. It is, from (8.87),

$$\overline{E}_r = \frac{\sum N_j E_j}{\sum N_j} = \frac{\sum E_j (2j+1) e^{-E_j/kT}}{\sum (2j+1) e^{-E_j/kT}}. \quad (8.88)$$

Let us put

$$F_r = \sum (2j+1) e^{-E_j/kT}, \quad (8.89)$$

where  $F_r$  is called the *rotational partition function*. From (8.89),

$$\frac{dF_r}{dT} = \frac{1}{kT^2} \sum E_j (2j+1) e^{-E_j/kT} \quad (8.90)$$

so that from (8.88), (8.89) and (8.89),

$$\overline{E}_r = kT^2 \frac{d}{dT} (\log_e F_r). \quad (8.91)$$

It is therefore evident that

$$(C_v)_r = \left( \frac{dU_r}{dT} \right)_V = N \frac{d\overline{E}_r}{dT} = R \frac{d}{dT} \left( T^2 \frac{d \log_e F_r}{dT} \right) \quad (8.92)$$

$$= Rx^2 \frac{d^2}{dx^2} \log_e F_r, \quad (8.93)$$

$$\text{where } x = \frac{\hbar^2}{8\pi^2 I k T} = \frac{T_r}{T} \text{ (say).} \quad (8.94)$$

In the low temperature region ( $T \ll T_r$ ) (8.89) shows that from (8.85) and (8.94),  $F_r = 1$ . Hence, from (8.92), for  $T \ll T_r$ ,  $(C_v)_r$  tends to vanish.

\*See, for example, Pauling, L., and Wilson, E. B., *Introduction to Quantum Mechanics* (1935).

\*\*See equation (9.13) under section 9.3.

On the other hand, in the high temperature region ( $T \gg T_r$ ), the terms in (8.89) corresponding to successive values of  $j$  differ so little that the summation may be replaced by integration. Thus, from (8.85), (8.89) and (8.94),

$$\begin{aligned} F_r &= \int_0^\infty (2j+1)e^{-\frac{T_r j(j+1)}{T}} dj = \int_0^\infty e^{-\frac{T_r j(j+1)}{T}} d\{j(j+1)\} \\ &= \left[ -\frac{T}{T_r} e^{-\frac{T_r j(j+1)}{T}} \right]_0^\infty = \frac{T}{T_r}. \end{aligned} \quad (8.95)$$

Hence, from (8.92) and (8.95), for  $T \gg T_r$ ,

$$(C_v)_r = R. \quad (8.96)$$

But, although (8.92) shows that  $(C_v)_r$ , the contribution of rotation to specific heat, gradually increases from zero value at low temperatures ( $T \ll T_r$ ) to  $R$  at high temperatures ( $T \gg T_r$ ), it is found to fail completely to explain Eucken's curve shown in Fig. 8.7, when the value of  $I (= 0.464 \times 10^{-40} \text{ gm} \cdot \text{cm}^2)$  obtained by T. Hori\* from spectroscopic analysis of molecular hydrogen gas is used in (8.92).

The explanation is provided by spectroscopic studies of gases. It is observed\*\*, as first pointed by Dennison†, that *homonuclear* gases like  $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{N}_2$ , etc. may be regarded as *mixtures of two modifications—a symmetrical modification* with  $j = 0, 2, 4, 6, \dots$  and an antisymmetrical modification with  $j = 1, 3, 5, 7, \dots$ . The statistical weights (i.e., the probabilities of existence) of the symmetrical and antisymmetrical modifications are found to be respectively  $s(2s+1)$  and  $(2s+1)(s+1)$  for gases like  $\text{H}_2$  with nuclear spin  $s = \text{a half-integral number}$  and are found to be respectively  $(2s+1)(s+1)$  and  $s(2s+1)$  for gases like  $\text{D}_2$  and  $\text{N}_2$  with nuclear spin  $s = \text{an integral number}$ . The modification with the greater statistical weight is usually called the *ortho-modification* and that with the smaller weight the *para-modification*. For gases with  $s = \frac{1}{2}$ , such as  $\text{H}_2$ , the ortho-modification (antisymmetrical) has the statistical weight 3 and has the nuclear spins parallel to each other while the para-modification (symmetrical) has the statistical weight 1 and has the nuclear spins antiparallel to each other. On the other hand, for gases with  $s = 1$ , such as  $\text{D}_2$  and  $\text{N}_2$ , the ortho-modification (symmetrical) has the statistical weight 6 while the para-modification (antisymmetrical) has the statistical weight 3.

Thus, we have to introduce two partition functions for the symmetrical and antisymmetrical modifications of the same gas :

$$F_{sr} = \sum_{j=0,2,4,\dots} (2j+1)e^{-E_j/kT} \quad (8.97)$$

$$F_{ar} = \sum_{j=1,3,5,\dots} (2j+1)e^{-E_j/kT}. \quad (8.98)$$

Now, if  $(C_v)_{sr}$  and  $(C_v)_{ar}$  are the rotational specific heats of a gram-molecule of the symmetrical modification and a gram-molecule of the anti-symmetrical modification respectively of a homo-nuclear gas, then from (8.93),

\*Hori, T., *Zeit. f. Phys.*, **44**, P. 834 (1927).

\*\*Herzberg, G., *Molecular Spectra and Molecular Structure, I. Spectra of diatomic Molecules*, Pp. 130–140 (1961).

†Dennison, D. M. *Proc. Roy. Soc.*, **115**, P. 483 (1927).

$$(C_v)_{sr} = Rx^2 \frac{d^2}{dx^2} \log_e F_{sr} \quad (8.99)$$

$$(C_v)_{ar} = Rx^2 \frac{d^2}{dx^2} \log_e F_{ar}. \quad (8.100)$$

First we consider the case of a homonuclear gas like H<sub>2</sub> with half-integral nuclear spin. For this case, on the basis (as explained above) that the gas is a mixture of  $s(2s + 1)$  parts of the symmetrical (para) modification and  $(2s + 1)(s + 1)$  parts of the antisymmetrical (ortho) modification,  $(C_v)_r$  is given by

$$\begin{aligned} (C_v)_r &= \frac{s(2s + 1)}{s(s + 1) + (2s + 1)(s + 1)} (C_v)_{sr} + \frac{(2s + 1)(s + 1)}{s(2s + 1) + (2s + 1)(s + 1)} (C_v)_{ar} \\ &= \frac{s}{2s + 1} (C_v)_{sr} + \frac{s + 1}{2s + 1} (C_v)_{ar}. \end{aligned} \quad (8.101)$$

For H<sub>2</sub> with  $s = \frac{1}{2}$ , that is

$$(C_v)_r = \frac{1}{4} (C_v)_{sr} + \frac{3}{4} (C_v)_{ar}. \quad (8.102)$$

The calculated values of  $(C_v)_{sr}$  from (8.89), of  $(C_v)_{ar}$  from (8.100) and finally of  $(C_v)_r$  from (8.102) for H<sub>2</sub> are plotted against  $T$  in Fig. 8.8. The curve I gives the variation of  $(C_v)_{sr}$  with  $T$  and the curve III represents the variation of  $(C_v)_{ar}$  with  $T$ . From I and III, the II for  $(C_v)_r$  has been drawn. It is found that it agrees quite satisfactorily with the experimental observation of Eucken represented in Fig. 8.7.

Next we consider the case of a homonuclear gas like D<sub>2</sub> and N<sub>2</sub> with integral nuclear spin. For this case, on the basis that the gas is a mixture of  $(2s + 1)(s + 1)$  parts of the symmetrical (ortho) modification and  $s(2s + 1)$  parts of the anti-symmetrical (para) modification,  $(C_v)_r$  is given by

$$\begin{aligned} (C_v)_r &= \frac{(2s + 1)(s + 1)}{s(2s + 1) + (2s + 1)(s + 1)} (C_v)_{sr} + \frac{s(2s + 1)}{s(2s + 1) + (2s + 1)(s + 1)} (C_v)_{ar} \\ &= \frac{s + 1}{2s + 1} (C_V)_{sr} + \frac{s}{2s + 1} (C_V)_{ar}. \end{aligned} \quad (8.103)$$

For D<sub>2</sub>, N<sub>2</sub>, etc. with  $s = 1$ , this is

$$(C_V)_r = \frac{2}{3} (C_V)_{sr} + \frac{1}{3} (C_V)_{ar}. \quad (8.104)$$

It is evident from (8.99), (8.100), (8.101) and (8.103) that  $(C_v)_r$  is a function of  $x$ , i.e.,

$$(C_v)_r = f(x). \quad (8.105)$$

Also it is evident from (8.94) that  $I$  and  $T$  occur in  $x$  only as the product  $IT$  in the denominator. Then, the larger the value of  $I$ , the lower is the temperature at which  $(C_v)_r$  becomes

effectively equal to  $R$ . Thus it is that in the case of all diatomic molecules which contain no hydrogen atom, on account of large values of  $I$ ,  $(C_v)_r = R$  at very low temperatures. So the calculation of the rotational specific heats for such molecules is not of much practical interest. For these cases, we have, therefore, to consider only the contribution to specific heat due to vibration.

According to quantum mechanics, the energy of a harmonic oscillator may have any of the following values\* :

$$\frac{1}{2}h\nu, \quad \left(1 + \frac{1}{2}\right)h\nu, \dots, \left(n + \frac{1}{2}\right)h\nu, \quad (8.106)$$

where  $\nu$  is the fundamental frequency and  $n$  is any integral number. So when a diatomic molecule is excited to its characteristic vibrations, it can have any of these energy-values. Let us now calculate the total energy of the whole system due to vibration. If  $N_n$  is the number of molecules with  $(n + \frac{1}{2})h\nu$ , then from Maxwell-Boltzmann law\*\*,

$$N_n = Ae^{-(n+\frac{1}{2})h\nu/kT}. \quad (8.107)$$

For  $n = 0$

$$N_0 = Ae^{-\frac{1}{2}h\nu/kT} \quad (8.108)$$

is the number with energy  $\frac{1}{2}h\nu$ . Then, combining (8.107) and (8.108),

$$N_n = N_0 e^{-nh\nu/kT}. \quad (8.109)$$

Then the total energy is

$$\begin{aligned} U_v &= \sum_{n=0}^{\infty} N_n \left(n + \frac{1}{2}\right) h\nu = \frac{1}{2}h\nu \sum_{n=0}^{\infty} N_n + N_0 \sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT} \\ &= \frac{1}{2}Nh\nu + N_0 \sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}. \end{aligned} \quad (8.110)$$

Let us put

$$F = \sum_{n=0}^{\infty} e^{-nh\nu/kT} = 1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots = \frac{1}{1 - e^{-h\nu/kT}},$$

where  $F$  is called the *vibrational partition function*. If  $h\nu/kT$  is put equal to  $y$ , then

$$F = \sum_{n=0}^{\infty} e^{-ny} = \frac{1}{1 - e^{-y}} \quad (8.111)$$

$$\text{with } \frac{dF}{dy} = - \sum_{n=0}^{\infty} ne^{-ny}. \quad (8.112)$$

Hence, from (8.110) and (8.112),

$$\begin{aligned} U_v &= \frac{1}{2}Nh\nu - N_0 h\nu \frac{dF}{dy} = \frac{1}{2}Nh\nu - \frac{N_0 h\nu F}{F} \frac{dF}{dy} \\ &= \frac{1}{2}Nh\nu - Nh\nu \frac{d}{dy} \log_e F \quad [\text{from (8.109) and (8.111)}] \end{aligned}$$

\*See, for example, Pauling and Wilson, *loc. cit.*

\*\*See equation (9.13) under section 9.3.

On differentiation of  $U_v$  with respect to  $T$ , we obtain  $(C_v)_v$  :

$$\begin{aligned} (C_v)_v &= \frac{dU_v}{dT} = -N h \nu \frac{d}{dT} \left( \frac{d}{dy} \log_e F \right) = -N h \nu \left( \frac{d^2}{dy^2} \log_e F \right) \frac{dy}{dT} \\ &= N k \left( \frac{h \nu}{kT} \right)^2 \frac{d^2}{dy^2} \log_e F = R y^2 \frac{d^2}{dy^2} \log_e F = R \frac{y^2 e^y}{(e^y - 1)^2} \\ &\equiv RE(y), \quad [\text{from (8.111)}] \end{aligned} \quad (8.113)$$

where  $E(y)$  is the Einstein function. Writing  $\frac{h \nu}{k} = T_v$ , (8.113) takes the form :

$$(C_v)_v = RE \left( \frac{T_v}{T} \right) \quad (8.114)$$

$\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  are the best examples for application of (8.114). For these gases,  $I$  being large,  $C_r = R$  even at low temperatures so that

$$C_v = \frac{5}{2}R + RE \left( \frac{T_v}{T} \right). \quad (8.115)$$

Since  $C_p - C_v = R$ , from (8.115),

$$C_p - \frac{7}{2}R = (C_v)_v = RE \left( \frac{T_v}{T} \right). \quad (8.116)$$

From the experimental values of  $C_p$  of  $\text{Cl}_2$  for different temperatures it is found from (8.116) that  $T_v$  should be taken as = 810. This gives  $\nu = 1.695 \times 10^{13} \text{ sec}^{-1}$  so that the wave number is  $= \frac{\nu}{c} = \frac{1.695 \times 10^{13} \text{ sec}^{-1}}{3 \times 10^{10} \text{ cm sec}^{-1}} = 565 \text{ cm}^{-1}$ . In the spectroscopic analysis of  $\text{Cl}_2$  by Kuhn and Elliot\*, this wave number has actually been obtained.

If  $\nu$  for a diatomic gas is known, the value of  $(C_v)_v$  at any temperature can be calculated from (8.114).

For  $T \rightarrow \infty$ ,  $y \rightarrow 0$  so that (8.114) gives under this condition

$$(C_v)_v = R \quad (8.117)$$

## 8.11 Transformation of Symmetrical and Anti-Symmetrical Modifications

There is a law\*\* in spectroscopy which states that *for homonuclear molecules with non-zero nuclear spin, the probability of transition from the symmetrical to the antisymmetrical or vice versa is very small though not zero*. Thus, it may take months, if not years, before such a molecule goes from a symmetrical to antisymmetrical state or vice versa.

In the case of  $\text{H}_2$ , it is possible to transform, by virtue of the above law, the antisymmetrical modification into the symmetrical modification and thus obtain the whole gas in the symmetrical state. When the gas (in which the normal ratio of the symmetrical modification to the antisymmetrical modification is 1 : 3) is cooled to a very low temperature (temperature of liquid hydrogen), by the above law the symmetrical molecules will go over to the lowest rotational state  $j = 0$  while the antisymmetrical molecules will go to the lowest antisymmetrical state

\*Kuhn and Elliot, *Proc. Roy. Soc.*, **123**, P. 629.

\*\*Herzberg, G., *loc. cit.*

$j = 1$ . Now, if the gas is kept for a sufficiently long time (many weeks or months) at the low temperature, even the molecules that were at first in the state  $j = 1$  will eventually go into the lowest state  $j = 0$  of the symmetric system since the probability of transition is, in fact, *small but not zero*. So we have now all the molecules in the symmetrical state. If the gas is now allowed to warm up again to the normal temperatures, the molecules at first can go from the  $j = 0$  state to the higher symmetric levels but not to the antisymmetric levels (owing to the above law). This means that *for some time* we have only the symmetrical (para) modification in the system at normal temperatures because *after a long time* there may be some transitions from the symmetrical to the antisymmetrical state (by the above law).

Bonhoeffer and Harteck\* and independently Eucken and Hiller\*\* were the first to conduct experiments on hydrogen and indeed confirmed the above theoretical predictions. Bonhoeffer and Harteck, however, made the important discovery that if ordinary hydrogen is passed over activated charcoal placed in a low temperature bath (liquid air), it is easily converted into the symmetrical (para) modification to the extent of 50%, but the conversion is 99.8% if a temperature 20 K is used so that it is necessary to keep hydrogen at low temperature for weeks or months. That actually only one modification (symmetrical) was present after it was raised to normal temperatures was shown in the first place by observations of the heat conductivity and heat capacity (which differ from those of the normal gas by an amount which can be predicted<sup>†</sup>) and in the second place by spectroscopic observations.

So far, apart from  $H_2$ , the symmetrical (ortho) modification of  $D_2$  has been produced<sup>‡</sup> by applying to deuterium the method described above for production of the symmetrical (para) hydrogen. For  $N_2$ , a temperature of less than 1 K would be necessary to obtain an appreciable amount of only one modification.

## PROBLEMS

1. Take the value  $h\nu/k$  for carbon to be 1302 and show from Einstein's equation for specific heats that the value of  $C_v$  is 3.331 at 479.1 K, 4.082 at 600 K and 5.181 at 1000 K.
2. Take  $h\nu_m/k$  for copper to be 286 and show from Debye's equation for specific heats that the value of  $C_v$  is 5.937 at 1144 K, 4.913 at 143 K and 0.058 at 14.3 K.

\*Bonhoeffer, K. F., Harteck, P., *Z. Physik. Chem.*, **B4**, P. 113 (1929).

\*\*Eucken, A. and Hiller, K., *Z. Physik. Chem.*, **B4**, P. 114 (1929).

<sup>†</sup>Herzberg, G., *loc. cit.*, P. 470.

<sup>‡</sup>Clausius, K. and Bartholomé, E., *Z. Electrochem.*, **40**, P. 524 (1934); Forkas, A. and L. and Harteck, P., *Proc. Roy. Soc.*, **144**, P. 481 (1934).

# Chapter 9

## Classical Statistics

### 9.1 Scope of Statistics

The science of statistics is applied to study a system containing a large number of elements such that it is impossible or sometimes meaningless to know the state or behaviour of individual elements at any particular instant. Classical statistics, the subject-matter of this chapter, was, in fact, devised for the treatment of complicated systems containing so large a number of molecules that it would be too hard to try to calculate the precise behaviour of the individual molecules as a function of time by the methods of ordinary mechanical laws. For example, if the positions and velocities of all the molecules in a gas are known at some initial moment, it should be possible, in principle, to determine the future behaviour of all of them by applying ordinary mechanical laws. But, because of the presence of a very large number of molecules in the gas, the calculations involving them would be insuperably difficult. Besides, in actual practice, the positions and velocities of the gas molecules cannot at all be known. Nevertheless, a system, such as a gas containing so many molecules, exhibits definite *macroscopic* properties which are, in fact, traceable to the laws of ordinary mechanics although the practical application of these laws in detail to the individual elements (i.e., molecules) of the system would be simply out of the question. The statistical method, however, makes it possible to obtain information regarding these properties of the system without any detailed knowledge of the characteristics of the individual elements of the system.

### 9.2 Phase Space (or $\mu$ -space) and Probability of Distribution

Let us consider a system containing a large number of *weakly interacting* (i.e., perfect) gas molecules. We propose to find the probability of the gas being in a certain *macroscopic* state. We take  $N$  as the total number of *similar* molecules composing the system and  $r$  as the number of degrees of freedom due to translation, rotation, vibration, etc. for each molecule. We denote by  $q_1, q_2, \dots, q_r$  the coordinates and by  $p_1, p_2, \dots, p_r$  the corresponding momenta of a single molecule. These  $2r$  quantities specify completely the molecule. For clarity, one may as well have the following set of coordinates and momenta :

$$x, y, z, q_4, \dots, q_r; \quad p_x, p_y, p_z, p_4, \dots, p_r$$

where  $x, y, z$  have replaced  $q_1, q_2, q_3$  and are the Cartesian coordinates for the centre of gravity of the molecule,  $p_x, p_y, p_z$  have replaced  $p_1, p_2, p_3$  and are the corresponding components of translational momentum of the molecule, and the remaining coordinates and momenta refer to the internal configuration and motion (e.g., rotation and vibration) of the molecule. We may imagine a *conceptual* euclidean space with  $2r$  rectilinear axes, one for each of the  $r$  coordinates and  $r$  momenta, such a space is called *phase space* or  $\mu$ -space,  $\mu$  (i.e.,  $m$ ) standing for *molecule*. The state of each molecule of the system at any instate represented by a point in this  $\mu$ -space.

For statistical purposes, we are, however, not interested, as explained in the preceding section, in the precise states of the molecules of a system but rather in the various small ranges

in which their coordinates and momenta might fall. Now, the coordinates of a molecule may lie between  $q_1$  and  $q_1 + dq_1$ ,  $q_2$  and  $q_2 + dq_2$  and so on, and its momenta may lie between  $p_1$  and  $p_1 + dp_1$ ,  $p_2$  and  $p_2 + dp_2$  and so on. These ranges correspond to an *elementary region* in  $\mu$ -space of volume

$$dV_\mu = dq_1 dq_2 \cdots dq_r dp_1 dp_2 \cdots dp_r. \quad (9.1)$$

We may thus consider the whole  $\mu$ -space as divided into a *number of equal elementary regions corresponding to different ranges*. We can label these elementary regions by integers 1, 2, 3, ...,  $s$  .... Out of the  $N$  molecules under consideration, some will be in the 1st elementary region, some in the 2nd, and so on, at any instant. Let us, therefore, take up the following distribution

$$N_1, N_2, N_3, \dots, N_s \dots, \quad (9.2)$$

where  $N_1$  is the number of molecules in the 1st elementary region,  $N_2$  the number in the second elementary region, and so on. The total number of arrangements (called *microscopic complexions or states*) corresponding to the same distribution (i.e., the same *macroscopic state*) is

$$G = \frac{N!}{N_1! N_2! \cdots N_s! \cdots}, \quad (9.3)$$

since arrangements of molecules in the same elementary region do not change the microscopic complexion. Here  $N = N_1 + N_2 + \cdots + N_s + \cdots$ .

In deducing (9.3) we have made the tacit assumption that the probability of a molecule being in any elementary region is the same, i.e., all the elementary regions have the same *a priori* probability. *The reason is provided by Liouville's theorem* (See Appendix 3) according to which the probability of a molecule being in any elementary region in the  $\mu$ -space is proportional to the volume of that region. Now, *since all the elementary regions in our case have the same volume*, they all have got the same *a priori* probability, i.e., the probability of a molecule being in any elementary region is the same.

Obviously,  $P$ , the probability of obtaining the distribution (9.2), would be proportional to  $G$  the number of ways in which this distribution can be realised\*. Hence, from (9.3),

$$P = \text{constant} \times \frac{N!}{N_1! N_2! \cdots N_s! \cdots}, \quad (9.4)$$

where the 'constant' would have the same value irrespective of the distribution considered.

### 9.3 Distribution of Maximum Probability and Maxwell-Boltzmann Law

The most probable distribution of  $N$  molecules among the different elementary regions in the  $\mu$ -space, is obtained from the conditions under which  $P$ , as given in (9.4), becomes maximum. For this purpose, it is convenient to express the condition of maximum probability in the form :

$$d(\log_e P) = 0. \quad (9.5)$$

Now, from (9.4),

$$\log_e P = \log_e N! - \sum_s \log_e N_s! + \text{constant}. \quad (9.6)$$

In problems of ordinary interest the total number of molecules  $N$  is very large and also the number of molecules  $N_s$  in the most of the occupied elementary regions  $s$  can be taken as

\*See Tolman, R.C., *Principles of Statistical Mechanics*, P. 78 (1962).

large compared with unity. Under this condition, we can apply Stirling's approximation for the factorials of large numbers (See the box at the end of this chapter) :

$$\log_e x! = x \log_e x - x. \quad (9.7)$$

Hence, from (9.6) and (9.7),

$$\log_e P = N \log_e N - \sum_s N_s \log_e N_s + \text{constant}, \quad (9.8)$$

remembering that  $\sum_s N_s$  is equal to  $N$ . Then, from (9.5) and (9.8), since  $N$  is a fixed number,

$$d(\log_e P) = -d \left( \sum_s N_s \log_e N_s \right) = 0, \quad \text{i.e.,} \quad \sum_s (\log_e N_s + 1) dN_s = 0. \quad (9.9)$$

Now, the above variations  $dN_s$  in the number of molecules  $N_s$  in the various states  $s$  cannot be carried out arbitrarily. We must take note of two subsidiary conditions. First, the total number of molecules is fixed so that

$$dN = \sum_s dN_s = 0. \quad (9.10)$$

Secondly, the total energy  $U$  of the system has to remain constant so that

$$dU = \sum_s \epsilon_s dN_s = 0, \quad (9.11)$$

where  $\epsilon_s$  is the energy of a molecule when in the  $s$ th elementary region.

(9.9), (9.10) and (9.11) represent the conditions which must be satisfied simultaneously for the system of maximum probability. Now, using Lagrange's method of undetermined multipliers, i.e., multiplying (9.10) and (9.11) by the undetermined constants  $\alpha$  and  $\beta$  respectively and adding to (9.9) we obtain

$$\sum_s (\log_e N_s + \alpha + \beta \epsilon_s) dN_s = 0. \quad (9.12)$$

Now, since  $dN_s$ 's are *arbitrary* variations, the coefficient of each must vanish :

$$\log_e N_s + \alpha + \beta \epsilon_s = 0, \quad \text{i.e.,} \quad N_s = e^{-\alpha-\beta\epsilon_s} = e^{-\alpha} e^{-\beta\epsilon_s}. \quad (9.13)$$

This is the *most probable* number of molecules in the  $s$ th elementary region of the  $\mu$ -space. This result, which gives the *most probable distribution* of molecules among the different states for a system in a *macroscopically steady condition* is called the *Maxwell-Boltzmann law* and was first given by Boltzmann in 1896.

It should be noted that in deriving the Maxwell-Boltzmann law, no restriction has been made as to the nature of the energy, i.e., translational, rotational, vibrational, etc. The law, therefore, holds for the distribution, among molecules, of any form of energy which has a constant value for the given system.

Before closing this section, we should call attention to the following approximations and assumptions made in our derivation.

- (1) We have used the Stirling approximation for the factorials  $N_s!$  and also considered the numbers  $N_s$  as continuous variables. As remarked earlier in this section, the introduction of these approximations has no serious consequences in the treatment of systems of ordinary interest containing a large number of molecules.

- (2) We have also assumed that the molecules are distinguishable [See (9.3)] from one another.
- (3) Finally, we have neglected intermolecular forces so that the law holds for perfect gases only.

## 9.4 Maxwell-Boltzmann Law for a Mixture of Gases

Now we consider the law of most probable distribution for a system containing a mixture of gases. We denote by  $N, N', N'', \dots$  the total numbers of molecules of different kinds in the systems and specify a certain distribution by  $N_s, N'_p, N''_t, \dots$  as the numbers of molecules of these different kinds in the *various (equal) elementary regions s, p, t ...* of the  $\mu$ -space. As shown in section 9.2, the probability  $P$  of obtaining the given distribution is

$$P = \text{constant} \times \frac{N!}{N_1!N_2!\cdots N_s! \cdots} \cdot \frac{N'!}{N'_1!N'_2!\cdots N'_p! \cdots} \cdot \frac{N''!}{N''_1!N''_2!\cdots N''_t! \cdots} \cdots \quad (9.14)$$

$$\text{or, } \log_e P = \left( N \log_e N - \sum_s N_s \log_e N_s \right) + \left( N' \log_e N' - \sum_p N'_p \log_e N'_p \right) + \cdots + \text{constant}, \quad (9.15)$$

using Stirling's approximation (9.7).

Then, the condition for the maximum probability is

$$\sum_s (\log_e N_s + 1) dN_s + \sum_p (\log_e N'_p + 1) dN'_p + \cdots = 0. \quad (9.16)$$

Since the total numbers of molecules of different kinds remain constant,

$$\sum_s dN_s = 0 \quad (9.17)$$

$$\sum_p dN'_p = 0 \quad (9.18)$$

Further, since the total energy of the system has a definite value  $U$ ,

$$dU = \sum_s \epsilon_s dN_s + \sum_p \epsilon_p dN'_p + \cdots = 0. \quad (9.19)$$

Combining (9.16), (9.17), (9.18) ... and (9.19) by the method of undetermined multipliers  $\alpha, \alpha', \alpha'', \dots$  and  $\beta$ , we obtain

$$\begin{aligned} \sum_s (\log_e N_s + \alpha + \beta \epsilon_s) dN_s + \sum_p (\log_e N'_p + \alpha' + \beta \epsilon'_p) dN'_p \\ + \sum_t (\log_e N''_t + \alpha'' + \beta \epsilon_t) dN''_t + \cdots = 0. \end{aligned} \quad (9.20)$$

Now, since  $dN'_s, dN'_p, dN''_t$ , etc. are arbitrary variations, the coefficient of each must vanish. Hence, (9.20) gives

$$\begin{aligned} N_s &= e^{-\alpha} e^{-\beta \epsilon_s} \\ N'_p &= e^{-\alpha'} e^{-\beta \epsilon_p} \\ N''_t &= e^{-\alpha''} e^{-\beta \epsilon_t} \\ &\dots \\ &\dots \end{aligned} \quad (9.21)$$

These are the most probable numbers of molecules of different kinds in the different elementary regions of the  $\mu$ -space. It is evident that each kind of molecules follows the same form of the Maxwell-Boltzmann law.

It is evident from (9.21) that although the constant  $\alpha$  varies from one kind of molecules to another,  $\beta$  is the same for all kinds of gases in the system.

## 9.5 Evaluation of $\alpha$ and $\beta$

The Maxwell-Boltzmann law may be written in a form which expresses the relationship between the number of molecules in any elementary region of the  $\mu$ -space, the volume of that elementary region and the total number of molecules in the system.

For this purpose, we introduce a new constant  $C$  such that

$$e^{-\alpha} = NC dq_1 dq_2 \dots dp_r, \quad (9.22)$$

where  $N$  is the total number of molecules in the system and  $dq_1, \dots, dp_r$  is the volume in the  $\mu$ -space of the different (*equal*) elementary regions into which we have divided that space. Now, denoting by  $dN$  the number of molecules in the  $s$ th elementary region and supposing that  $dq_1 \dots dp_r$  refers to that region, we obtain from (9.22) the Maxwell-Boltzmann law (9.13) in the following form :

$$dN = N C e^{-\beta \epsilon} dq_1 \dots dp_r. \quad (9.23)$$

Integrating for all possible values of the coordinates and momenta, we have from (9.23)

$$N = \int dN = NC \int \dots \int e^{-\beta \epsilon} dq_1 \dots dp_r \quad (9.24)$$

so that  $C = \frac{1}{\int \dots \int e^{-\beta \epsilon} dq_1 \dots dp_r}. \quad (9.25)$

This integration can be carried out and, the value of  $C$  and hence of  $\alpha$  determined if we know how the energy  $\epsilon$  of a molecule is related to its coordinates and momenta.

We can solve the problem easily for a simple case, viz., for a perfect monatomic gas contained in a vessel of volume  $V$ . For this case in the Cartesian system, we have from (9.25)

$$\frac{1}{C} = \int \dots \int e^{-\beta \epsilon} dx dy dz dp_x dp_y dp_z = V \iiint e^{-\beta \epsilon} dp_x dp_y dp_z, \quad (9.26)$$

where  $V = \iiint dx dy dz = \text{volume of the vessel}. \quad (9.27)$

Since the system is a perfect monatomic gas, it can have  $\epsilon$  only as the translational kinetic energy per molecule :

$$\epsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2), \quad (9.28)$$

where  $m$  is the mass of each molecule. Combining (9.26) and (9.28),

$$\begin{aligned} \frac{1}{C} &= V \int_{-\infty}^{\infty} e^{-\beta p_x^2/2m} dp_x \int_{-\infty}^{\infty} e^{-\beta p_y^2/2m} dp_y \int_{-\infty}^{\infty} e^{-\beta p_z^2/2m} dp_z \\ &= V \left( \frac{2\pi m}{\beta} \right)^{3/2} \quad (\text{See Appendix 1}) \end{aligned} \quad (9.29)$$

Again, the total energy  $U$  may be expressed as

$$\begin{aligned}
 U &= \int \epsilon dN \\
 &= NC \int \cdots \int \epsilon e^{-\beta \epsilon} dx dy dz dp_x dp_y dp_z \quad [\text{from (9.23) for this case}] \\
 &= \frac{NVC}{2m} \iiint_{-\infty}^{\infty} (p_x^2 + p_y^2 + p_z^2) e^{-\beta(p_x^2 + p_y^2 + p_z^2)/2m} dp_x dp_y dp_z \quad [\text{from (9.27) and (9.28)}] \\
 &= \frac{NVC}{2m} \int_{-\infty}^{\infty} e^{-\beta p_x^2/2m} p_x^2 dp_x \int_{-\infty}^{\infty} e^{-\beta p_y^2/2m} p_y^2 dp_y \int_{-\infty}^{\infty} e^{-\beta p_z^2/2m} p_z^2 dp_z \\
 &= \frac{NVC}{2m} \cdot \frac{3m}{\beta} \left( \frac{2\pi m}{\beta} \right)^{3/2} \quad [\text{See Appendix 1}] \\
 &= \frac{3N}{2\beta}. \tag{9.30}
 \end{aligned}$$

Let us suppose that we have under consideration a gram-molecule of the gas. Then, we know from experiment that

$$U = \frac{3}{2}RT = N \times \frac{3}{2}kT. \tag{9.31}$$

Comparison of (9.30) and (9.31) show that

$$\beta = \frac{1}{kT}. \tag{9.32}$$

Then, substituting for  $\beta$  from (9.32) in (9.29),

$$C = \frac{1}{(2\pi mkT)^{3/2}V}. \tag{9.33}$$

Now, although the expression for  $C$  given by (9.33) holds for a perfect *monatomic* gas, the expression for  $\beta$  given by (9.32) holds for all kinds of gases. To see this, suppose that one of the constituents of a mixture of gases is monatomic. Then, for this monatomic gas,  $\beta$  is  $1/kT$  as given by (9.32). But, according to the last paragraph of the preceding section,  $\beta$  is same for all kinds of gases in the system. Hence, we conclude that  $\beta$  is  $1/kT$  irrespective of the nature of the molecules concerned.

## 9.6 Maxwell's Law of Distribution of Velocities

Maxwell's law deals with the distribution of translational velocities, i.e., translational kinetic energies among the molecules of a system. To obtain this law, we write (9.23) in the form :

$$dN = NC e^{-\beta \epsilon} dx dy dz q_4 \cdots q_r dp_x dp_y dp_z dp_4 \cdots dp_r, \tag{9.34}$$

where  $x, y, z$  have replaced  $q_1, q_2, q_3$  and are the Cartesian coordinates for the centre of gravity a molecule with respect to axes fixed relative to the containing vessel,  $p_x, p_y, p_z$  have replaced  $p_1, p_2, p_3$  and are the corresponding components of momentum, and the remaining coordinates and momenta refer to the internal configuration and motion (e.g., rotation and vibration) of the molecule.

We may write  $\epsilon$  in the general form

$$\epsilon = \epsilon(x, y, z) + \frac{1}{2}m(u^2 + v^2 + w^2) + \epsilon(q_4 \cdots q_r p_4 \cdots p_r), \quad (9.35)$$

where  $\epsilon(x, y, z)$  is the *potential energy* of a molecule due to any (constant) external (not intermolecular) field of force present,  $\frac{1}{2}m(u^2 + v^2 + w^2)$  the *kinetic energy* due to the momenta  $p_x, p_y, p_z$  and  $\epsilon(q_4 \cdots q_r p_4 \cdots p_r)$  the *internal energy* associated with the remaining coordinates and momenta. Then, from (9.34) and (9.35),

$$dN = NCm^3 e^{-\frac{\epsilon(x, y, z) + \frac{1}{2}m(u^2 + v^2 + w^2) + \epsilon(q_4 \cdots p_r)}{kT}} \times dx dy dz dq_4 \cdots dq_r du dv dw dp_4 \cdots dp_r, \quad (9.36)$$

since  $p_x = mu, p_y = mv, p_z = mw$ .

Now, to obtain the distribution of velocities among the molecules we integrate (9.36) over all possible values of  $x, y, z$  and of the *internal* coordinates and momenta  $q_4 \cdots q_r p_4 \cdots p_r$ . Then, we shall obtain an expression of the form :

$$dN = N A e^{-\frac{1}{2}m(u^2 + v^2 + w^2)/kT} du dv dw, \quad (9.37)$$

$$\text{where } A = Cm^3 \int \cdots \int e^{-\frac{\epsilon(x, y, z) + \epsilon(q_4 \cdots p_r)}{kT}} dx dy dz dq_4 \cdots dp_r. \quad (9.38)$$

But the value of  $A$  may be readily obtained by integrating (9.37) over all possible values of,  $u, v, w$ . Thus, from (9.37)

$$\begin{aligned} N = \int dN &= NA \int_{-\infty}^{\infty} e^{-\frac{1}{2}mu^2/kT} du \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv^2/kT} dv \int_{-\infty}^{\infty} e^{-\frac{1}{2}mw^2/kT} dw \\ &= NA \left( \frac{2\pi kT}{m} \right)^{3/2} \quad (\text{See Appendix 1}) \end{aligned}$$

$$\text{Hence, } A = \left( \frac{m}{2\pi kT} \right)^{3/2} \quad (9.39)$$

From (9.37) and (9.39),

$$dN = N \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}m(u^2 + v^2 + w^2)/kT} du dv dw. \quad (9.40)$$

This is Maxwell's law. Evidently it is a special form of the more general Maxwell-Boltzmann law (9.13) [or (9.23)]. (9.40) may be put in another form in terms of spherical polar coordinates  $c, \theta, \phi$ , where  $c^2 = u^2 + v^2 + w^2$ . In terms of these coordinates

$$du dv dw = c^2 dc \sin \theta d\theta d\phi.$$

Then, from (9.40), we obtain

$$dN_{c\theta\phi} = N \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mc^2/kT} c^2 dc \sin \theta d\theta d\phi.$$

On integration for all directions,

$$dN_c = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mc^2/kT} c^2 dc. \quad (9.41)$$

## 9.7 Principle of Equipartition of Energy

The mean energy of a molecule in a system is

$$\begin{aligned}\bar{\epsilon} &= \frac{\int \epsilon dN}{\int dN} = \frac{NC \int \cdots \int \epsilon e^{-\epsilon/kT} dq_1 \cdots dp_r}{N} \quad [\text{from (9.23) and (9.32)}] \\ &= \frac{\int \cdots \int \epsilon e^{-\epsilon/kT} dq_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon/kT} dq_1 \cdots dp_r} \quad [\text{from (9.25) and (9.32)}].\end{aligned}\quad (9.42)$$

This can be evaluated if we know how  $\epsilon$  is related to the coordinates and momenta. The problem becomes much simplified, however, when we can express the energy  $\epsilon$  of a molecule as a sum of terms such that one or more of these terms depend only on a *single variable* out of the total set of coordinates and momenta  $q_1 \cdots q_r p_1 \cdots p_r$ . For example, if we have

$$\epsilon = \epsilon(p_1) + \epsilon(q_1 \cdots q_r p_2 \cdots p_r), \quad (9.43)$$

where the momentum  $p_1$  occurs only in a single term, then the mean energy associated with this variable is, from (9.42),

$$\begin{aligned}\overline{\epsilon(p_1)} &= \frac{\int \cdots \int \epsilon(p_1) e^{-\epsilon(p_1)/kT} e^{-\epsilon(q_1 \cdots q_r p_2 \cdots p_r)/kT} dq_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon(p_1)/kT} e^{-\epsilon(q_1 \cdots q_r p_2 \cdots p_r)/kT} dq_1 \cdots dp_r} \\ &= \frac{\int \epsilon(p_1) e^{-\epsilon(p_1)/kT} dp_1 \int \cdots \int e^{-\epsilon(q_1 \cdots q_r p_2 \cdots p_r)/kT} dq_1 \cdots dq_r dp_2 \cdots dp_r}{\int e^{-\epsilon(p_1)/kT} dp_1 \int \cdots \int e^{-\epsilon(q_1 \cdots q_r p_2 \cdots p_r)/kT} dq_1 \cdots dq_r dp_2 \cdots dp_r} \\ &= \frac{\int \epsilon(p_1) e^{-\epsilon(p_1)/kT} dp_1}{\int e^{-\epsilon(p_1)/kT} dp_1}.\end{aligned}\quad (9.44)$$

Now, it frequently happens that  $\epsilon(p_1)$  can be expressed as a *quadratic function* of  $p_1$ . Thus,

$$\epsilon(p_1) = ap_1^2, \quad (9.45)$$

where  $a$  is a constant. In fact, if  $p_1$  is translational momentum, then

$$\epsilon(p_1) = \frac{p_1^2}{2m}, \quad (9.46)$$

where  $m$  is the mass of the molecule. Or, if  $p_1$  is rotational (i.e., angular) momentum, then

$$\epsilon(p_1) = \frac{p_1^2}{2I}, \quad (9.47)$$

where  $I$  is the moment of inertia of the molecule about the axis of rotation. Hence, from (9.44) and (9.45),

$$\overline{\epsilon(p_1)} = \frac{\int_{-\infty}^{\infty} ap_1^2 e^{-ap_1^2/kT} dp_1}{\int_{-\infty}^{\infty} e^{-ap_1^2/kT} dp_1} = \frac{1}{2}kT. \quad (\text{See Appendix 1}) \quad (9.48)$$

If, instead of (9.43), we take

$$\epsilon = \epsilon(q_1) + \epsilon(q_2 \cdots q_r p_1 \cdot p_r) \quad (9.49)$$

then, preceding as before, we shall obtain, instead of (9.44),

$$\overline{\epsilon(q_1)} = \frac{\int \epsilon(q_1) e^{-\epsilon(q_1)/kT} dq_1}{\int e^{-\epsilon(q_1)/kT} dq_1}. \quad (9.50)$$

Now, it also often happens that  $\epsilon(q_1)$  can be expressed as a *quadratic function* of  $q_1$ . Thus,

$$\epsilon(q_1) = bq_1^2, \quad (9.51)$$

where  $b$  is a constant. In fact, for small oscillation the potential energy of a particle vibrating along  $q_1$ -axis is of the form :

$$\epsilon(q_1) = \frac{1}{2}\mu q_1^2, \quad (9.52)$$

where  $\mu$  is a constant. Hence, from (9.50) and (9.51), we also obtain

$$\epsilon(q_1) = \frac{1}{2}kT. \quad (9.53)$$

Now, the total energy of a particle vibrating along  $q_1$ -axis is

$$\frac{p_1^2}{2m} + \frac{1}{2}\mu q_1^2, \quad (9.54)$$

where the first term is the vibrational kinetic energy and the second term is the potential energy. It follows, therefore, that the average energy of the vibrating particle is

$$\frac{1}{2}kT + \frac{1}{2}kT = kT.$$

From all the above discussion, it is evident that the average energy associated with each *single variable, coordinate or momentum*, which contributes a *quadratic term* to the total energy, is  $\frac{1}{2}kT$  for a molecule. This result is ordinarily called the *principle of equipartition of energy*.

This principle has, however, limited applications. It holds for radiation only in the long-wavelength region (Rayleigh-Jeans law) and for the specific heats of solids only at ordinary and high temperatures (Dulong-Petit law). It also fails to explain the variation of specific heats of gases. Besides, if the energy  $\epsilon$  is not an exact quadratic function of the associated coordinate or momentum, then also this principle fails. For example, if the vibration along an axis is not strictly harmonic in character, then the potential energy is given not by (9.52) but by

$$\epsilon(q_1) = \frac{1}{2}\mu q_1^2 + vq_1^3 + \gamma q_1^4 + \dots$$

It is obvious that from (9.50),  $\overline{\epsilon(q_1)}$  will not be  $\frac{1}{2}kT$  now. Tolman\* has derived a considerably more general form of equipartition principle which applies under wider circumstances and reduces to the equipartition of energy in the case of  $\epsilon(p)$  [or  $\epsilon(q)$ ] being an exact quadratic function of  $p$  (or  $q$ ).

### Stirling's Formula

$$\log_e n! = \log_e 1 + \log_e 2 + \cdots + \log_e x + \cdots \log_e n$$

$$\text{and } \log_e n^n = \log_e n + \log_e n + \cdots + \log_e n + \cdots \log_e n$$

$$\text{Hence, } \log_e \left( \frac{n!}{n^n} \right) = \log_e \frac{1}{n} + \log_e \frac{2}{n} + \cdots + \log_e \frac{x}{n} + \cdots + \log_e \frac{n}{n} = \sum_n (\log_e x - \log_e n).$$

The summation may be replaced, though not rigorously, by integration as follows :

$$\int_1^n (\log_e x - \log_e n) dx = [x \log_e x - x]_1^n + [x \log_e n]_1^n = -(n-1) + \log_e n.$$

$$\text{Hence, } \log_e n! = n(\log_e n - 1) + \log_e n + 1.$$

For large  $n$ , the last terms may be left out so that we obtain

$$\log_e n! = n(\log_e n - 1).$$

This is Stirling's formula.

## PROBLEM

1. Show, on the basis of classical statistics, that the pressure of a gas is given by  $P = \frac{N}{V}kT$ .

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\*Tolman, R. C., *Phys. Rev.*, **11**, P. 261 (1918).

# Chapter 10

## Quantum Statistics

### 10.1 Quantum Phase Space

We divide the phase space ( $\mu$ -space) into elementary regions so that the volume of an elementary region for particles existing anywhere in the containing vessel of volume  $V$  and having energy between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  is (from section 9.2)

$$(\Delta V_\mu)_k = \left( \int dV_\mu \right)_k = \iiint_0^V dx dy dz \int_{\epsilon_k}^{\epsilon_k + \Delta\epsilon_k} \cdots \int dq_4 \cdots dq_r dp_x dp_y dp_z dp_4 \cdots dp_r \quad (10.1)$$

$$= V \int_{\epsilon_k}^{\epsilon_k + \Delta\epsilon_k} \cdots \int dq_4 \cdots dq_r dp_x dp_y dp_z dp_4 \cdots dp_r. \quad (10.2)$$

It is an *intrinsic character* of quantum theory, in contrast to classical physics, that the state of a particle (a material particle or a light particle, i.e., photon) of the system cannot be represented by just a point in the  $\mu$ -space. According to quantum theory, if the position of a particle moving along, say,  $x$ -axis is found from measurement to lie between  $x$  and  $x + dx$ , then its momentum will be found from measurement to be between  $p_x$  and  $p_x + dp_x$  such that the product of  $dx$  and  $dp_x$ , the *uncertainties* in measurement (as they are called), is of the order of  $h$  (Planck's constant)\*, i.e.,

$$dx dp_x \sim h. \quad (10.3)$$

Now, applying this principle, usually called the *uncertainty principle* of Heisenberg, to all the coordinates and momenta of a particle of the system, we obtain\*\*

$$dx dp_x \sim h, dy dp_x \sim h, dz dp_z \sim h, dq_4 dp_4 \sim h, \dots dq_r dp_r \sim h.$$

Thus, the product representing the uncertainty in defining the position (i.e., state) of a particle in  $\mu$ -space is

$$(dx dp_x)(dy dp_y) \cdots (dq_r dp_r) \sim h^r. \quad (10.4)$$

It follows from (10.4) that the position (i.e., state) of a particle in  $\mu$ -space cannot be more exactly defined than by a phase volume  $h^r$ ; the most that we can assert in this regard is that the state of the particle lies within a phase volume  $h^r$  in  $\mu$ -space. So we may say that the volume

\*This may be explained briefly in the following way. The resolving power of a microscope depends on the wavelength of light used in such a manner that the shorter the wavelength used, the smaller may be the size of the observable object. Hence, the uncertainty in the position of a particle is of the order of the wavelength  $\lambda$  of the light used. Now, since the light, i.e., the photon with which the particle is observed enters the microscope on being scattered by the particle, i.e., on colliding with the particle, an uncertainty enters into the momentum of the particle. This uncertainty is naturally of the order of the momentum  $h/\lambda (= h\nu/c)$  of the photon. Evidently, the product of these two uncertainties is of the order of  $\lambda \times \frac{h}{\lambda} = h$  (See, for example, Wilson, H. A., *The Mysteries of the Atom*, P. 133 (1934).

\*\*Landau, L. D. and Lifshitz, E. M., *Quantum Mechanics*, P. 185 (1958).

of phase space occupied by a particle is  $h^r$ . Thus, in order to define the position (i.e., state) of a particle in  $\mu$ -space, we have to divide up the whole phase-space into *elementary cells*, each of volume  $h^r$ . Then, the number of elementary cells at the disposal of particles having energy between  $\epsilon_k$ , and  $\epsilon_k + \Delta\epsilon_k$  is, from (10.2),

$$g_k = \left( V \int_{\epsilon_k}^{\epsilon_k + \Delta\epsilon_k} \cdots \int dq_4 \cdots dq_r dp_x dp_y dp_z dp_4 \cdots dp_r \right) / h^r. \quad (10.5)$$

It is evident from above that a particular phase cell in  $\mu$ -space corresponds to a particular state of the particle which occupies it. Thus, the total number of states in the energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  is  $g_k$  given by (10.5). But if the particles have got intrinsic angular momentum, i.e., spin  $s$ , then a particle in a phase cell may exist in any of the  $(2s+1)$  spin-states which are specified by  $s, s-1, \dots, -s-1, -s^*$  (See eqn. (8.86) of section 8.10). Then, the total number of distinct states in the energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  is  $(2s+1)$  times the total number of phase cells in this energy range. For this case, therefore, the total number of distinct states in the energy range  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  is, from (10.5),

$$g_k = \left\{ (2s+1)V \int_{\epsilon_k}^{\epsilon_k + \Delta\epsilon_k} \cdots \int dq_4 \cdots dq_r dp_x dp_y dp_z dp_4 \cdots dp_r \right\} / h^r. \quad (10.6)$$

If the particles are monatomic so that they have got only translational kinetic energy, then (10.6) is reduced to the form :

$$g_k = \left\{ (2s+1)V \int_{\epsilon_k}^{\epsilon_k + \Delta\epsilon_k} \int dp_x dp_y dp_z \right\} / h^3 \quad (10.6')$$

$$= \left\{ (2s+1)V \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} \int_{p_k}^{p_k + \Delta p_k} p_k^2 dp_k \sin \theta d\theta d\phi \right\} / h^3 \quad (10.6'')$$

in terms of spherical polar coordinates  $p_k$ ,  $\theta$  and  $\phi$ . Here  $\epsilon_k = p_k^2/2m$ ,  $m$  being the particle-mass. Evidently\*\*

$$g_k = \frac{4\pi(2s+1)V}{h^3} p_k^2 \Delta p_k \quad (10.7)$$

$$= \frac{4\sqrt{2}\pi(2s+1)V(m)^{3/2} \epsilon_k^{1/2} \Delta\epsilon_k}{h^3}. \quad (10.8)$$

This is the total number of states in the energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  for monatomic particles having spin  $s$ .

Now, it is evident from above that the phase space (i.e.,  $\mu$ -space) with which we have acquired familiarity in this section so far can accommodate in the energy range between, for example,  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  the  $g_k$  states given by (10.5) and not by the  $g_k$  states given by (10.6), the number of which is  $(2s+1)$  times larger. So we may conceive of a *generalised phase space* and divide it into elementary regions such that the number of cells states in the  $k$ th elementary region, say, corresponding to the energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  is given by (10.6) or,

\*The case is a bit different with photons. See section 10.7.

\*\*Since the range of integration of  $p_k$  is very small,  $\int_{p_k}^{p_k + \Delta p_k} p_k^2 dp_p = p_k^2 \int_{p_k}^{p_k + \Delta p_k} dp_k = p_k^2 \Delta p_k$ .

for monatomic particles, by (10.8). Evidently, this generalised phase space will be reduced to the familiar phase space (or  $\mu$ -space) in the case of particles with zero spin ( $s = 0$ ). We shall, however, deal with the generalised phase space in this chapter.

## 10.2 Probability of Distribution in Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac Statistics

In this section we shall calculate the probability of distribution of particles among the different states in different energy ranges in each of the three statistics : (a) Maxwell-Boltzmann, (b) Bose-Einstein and (c) Fermi-Dirac.

**(a) Maxwell-Boltzmann Statistics\*** : Let us take a system of  $N$  (weakly interacting) similar particles (i.e., particles of the same kind). In Maxwell-Boltzmann statistics, they are, however, considered as *distinguishable* from one another (see end of section 9.3). We take up a distribution  $N_1, N_2, \dots, N_k, \dots$  where, for example,  $N_k$  is the number of particles in the energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$ . We first find the number of ways in which  $N$  particles can be divided into these groups and distributed among the different elementary regions of the generalised phase space (defined in the preceding section). This is (as in section 9.2)

$$\frac{N!}{N_1! N_2! \cdots N_k! \cdots}. \quad (10.9)$$

Again, in each elementary region of the generalised phase space  $N_k$  particles may be distributed among the  $g_k$  cells, i.e., states. In this statistics, there is no restriction as to the number of particles that may be put in each cell (or state). So this is a problem of permutation with repetition and the number of ways in which  $N_k$  particles may be distributed among  $g_k$  cells (or states) is  $g_k^{n_k}$ . Then the total number of ways in which the distribution may be realised is, from (10.9),

$$G = \frac{N!}{N_1! N_2! \cdots N_k! \cdots} \times g_1^{N_1} \cdot g_2^{N_2} \cdots g_k^{N_k} \cdots = N! \prod_k \frac{g_k^{N_k}}{N_k!}. \quad (10.10)$$

Hence, the probability of this distribution is (See section 9.2)

$$P = \text{constant} \cdot N! \prod_k \frac{g_k^{N_k}}{N_k!}. \quad (10.11)$$

**(b) Bose-Einstein Statistics** : S. N. Bose\*\* (1923) originally devised this statistics for photons and derived Planck's radiation formula in a very elegant manner (This will be taken up in section 10.7). Einstein† extended this statistics to real gases. This statistics is called *Bose-Einstein statistics* (or just *Bose statistics*) and is applicable to photons, gravitons, nuclei containing an even number of nucleons (i.e., protons and neutrons), prendo-scalar mesons (i.e.,  $\pi$ -mesons,  $K$ -mesons, etc.), vector mesons (i.e.,  $\rho$ -mesons,  $K^*$ -mesons, etc.) and tensor mesons. In fact, these particles are usually called *bosons* after Bose and possess integral spins.

Let us take a system of  $N$  (weakly interacting) similar particles (i.e., particles of the same kind). In Bose-Einstein statistics, they are considered as indistinguishable. We take up a distribution  $N_1, N_2, \dots, N_k, \dots$  where, for example,  $N_K$  is the number of particles in the

\*See Tolman, R. C., *Principles of Statistical Mechanics*, Pp. 368-9 (1962); Glasstone, S. *Theoretical Chemistry*, P. 312 (1961).

\*\*Bose, S. N., *Zeits. f. Physik.*, **26**, P. 178 (1924).

†Einstein, A., *Berl. Ber.*, P. 261 (1924); *ibid*, P. 18 (1925).

energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$ . Now, since the particles are indistinguishable, the number of ways in which  $N$  particles can be divided into these groups and distributed among the different elementary regions of the generalised phase space is just 1. Let us, therefore, see how in each elementary region of the generalised phase space  $N_k$  particles may be distributed among the  $g_k$  cells or states. In this statistics, as Bose assumed, there is no restriction as to the number of particles that may be put in each cell (i.e., state). This problem can be solved in a simple manner\* with the help of the following array :

$$Z_1 a_1 a_2 Z_2 a_3 Z_3 a_4 a_5 a_6 Z_4 Z_5 a_7 \dots,$$

where  $Z_1$  is cell number 1,  $Z_2$  cell number 2, etc. and  $a_1$  is particle number 1,  $a_2$  particle number 2, etc. The meaning of the array is that particles 1, 2 are in cell 1, particle 3 is in cell 2, particles 4, 5, 6 are in cell 3, no particle is in cell 4, etc. In short the particles contained in a cell are indicated on the right-hand side of the cell concerned. We have in the array the total number of terms equal to  $g_k + N_k$  for the  $k$ th elementary region of the generalised phase space. Evidently, all possible distributions of  $N_k$  among  $g_k$  cells (i.e., states) may be obtained by keeping  $Z_1$  fixed and permitting the remaining  $(g_k + N_k - 1)$  terms among themselves. The number of these permutations, i.e., distributions, is  $(g_k + N_k - 1)!$ . But these permutations include also permutations of the cells among themselves which are  $(g_k - 1)!$  in number and also include permutations of the *indistinguishable* particles among themselves which are  $N_k!$  in number. These permutations are immaterial and we reject them. Hence, the total number of distributions of  $N_k$  particles among  $g_k$  cells (or states) is

$$\frac{(g_k + N_k - 1)!}{(g_k - 1)! N_k!}. \quad (10.12)$$

Thus, the total number of ways in which the given distribution  $N_1, N_2, \dots, N_k, \dots$  (involving distributions of  $N_1$  particles among  $g_1$  cells,  $N_2$  particles among  $g_2$  cells,  $\dots, N_k$  particles among  $g_k$  cells  $\dots$ ) may be realised is, from (10.12),

$$G = 1 \times \frac{(g_1 + N_1 - 1)!}{(g_1 - 1)! N_1!} \cdot \frac{(g_2 + N_2 - 1)!}{(g_2 - 1)! N_2!} \cdots \frac{(g_k + N_k - 1)!}{(g_k - 1)! N_k!} \cdots = \prod_k \frac{(g_k + N_k - 1)!}{(g_k - 1)! N_k!}. \quad (10.13)$$

Hence, the probability of this distribution is

$$P = \text{constant} \cdot \prod_k \frac{(g_k + N_k - 1)!}{(g_k - 1)! N_k!}. \quad (10.14)$$

**(c) Fermi-Dirac Statistics :** Fermi\*\* devised this statistics on the basis of *Pauli's principle* which states that *no two electrons in an atom can be in the same state*. Dirac† provided the quantum-mechanical basis to this statistics. This statistics is called *Fermi-Dirac statistics* (or just *Fermi statistics*) and is applicable to electrons, protons, neutrons, nuclei containing an odd number of nucleons (i.e., protons and neutrons), hyperons, etc. In fact these particles are usually called *fermions* after Fermi and possess half-integral spins.

As before, we take a system of  $N$  (weakly interacting) similar particles. In Fermi-Dirac statistics also, they are considered as indistinguishable. We consider a distribution  $N_1, N_2, \dots, N_k, \dots$  where, for example,  $N_k$  is the number of particles in the energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$ . Now, since the particles are indistinguishable, the number of ways in which

\*Born, M., *Atomic Physics*, Pp. 274-5 (1963).

\*\*Fermi, E., *Atti Lincei*, (6), **3**, P. 145 (1926); *Zeit. f. Phys.*, **36**, P. 902 (1926).

†Dirac, P. A. M., *Proc. Roy. Soc.*, **112A**, P. 661 (1926).

$N$  particles can be divided into these groups and distributed among the different elementary regions of the generalised phase-space is just 1. Let us, therefore, see how in each elementary region of the generalised phase space  $N_k$  particles may be distributed among the  $g_k$  cells or states. In this statistics, however, it is considered on the basis of Paul's principle that only one particle, or no particle at all, can be accommodated in a cell (or state). This problem can be easily\* solved with the help of the following array :

$$Z_1 a_1 Z_2 a_2 Z_3 Z_4 a_3 Z_5 Z_6 a_4 \dots,$$

where  $Z_1$  is cell number 1,  $Z_2$  cell number 2, etc. and  $a_1$  is particle number 1,  $a_2$  particle number 2, etc. The meaning of the array is that particle 1 is in cell 1, particle 2 in cell 2, no particle in cell 3, particle 3 in cell 4, etc. Briefly, the particle contained in a cell is on the right-hand side of the cell concerned. We have in the array the total number of terms equal to  $g_k + N_k$  for the  $k$ th elementary region of the generalised phase-space. Evidently, all possible distributions of  $N_k$  among  $g_k$  cells (i.e., states) may be obtained by keeping  $a_1, a_2, \dots, a_k$  fixed and permuting  $Z_1, Z_2, \dots, Z_k, \dots$  among themselves. The number of these permutations, i.e., distributions, is  $g_k!$ . But these permutations include also permutations of  $(g_k - N_k)$  empty cells among themselves which are  $(g_k - N_k)!$  in number and also include the permutations of the  $N_k$  cells occupied by the  $N_k$  indistinguishable particles among themselves (i.e., cells) which (i.e., permutations) are  $N_k!$  in number. These permutations are immaterial and we reject them. Hence, the total number of distributions of  $N_k$  particles among  $g_k$  cells (or states) is, in this case,

$$\frac{g_k!}{(g_k - N_k)!N_k!}. \quad (10.15)$$

Thus, the total number of ways in which the given distribution  $N_1, N_2, \dots, N_k, \dots$  (involving distributions of  $N_1$  particles among  $g_1$  cells,  $N_2$  particles among  $g_2$  cells  $\dots$   $N_k$  particles among  $g_k$  cells  $\dots$ ) may be realised is, from (10.15),

$$G = 1 \times \frac{g_1!}{(g_1 - N_1)!N_1!} \cdot \frac{g_2!}{(g_2 - N_2)!N_2!} \cdots \frac{g_k!}{(g_k - N_k)!N_k!} \cdots = \prod_k \frac{g_k!}{(g_k - N_k)!N_k!}. \quad (10.16)$$

Hence, the probability of this distribution is

$$P = \text{constant} \cdot \prod_k \frac{g_k!}{(g_k - N_k)!N_k!}. \quad (10.17)$$

**Exercise :** Show that for  $g_k \gg N_k$ , (10.14) (B-E statistics) and (10.17) (F-D statistics) reduce to (10.11) (M-B statistics). But why for  $g_k \gg N_k$ ?

### 10.3 Distributions of Maximum Probability in Three Statistics

Assuming that  $N, N_k, g_k$  and also  $g_k - N_k$  are large compared with unity, we can apply Stirling's approximation (See the box at the end of Chapter 9) and obtain the following results :

For Maxwell-Boltzmann statistics from (10.11),

$$\log_e P = N \log_e N + \sum_k \{N_k \log_e g_k - N_k \log_e N_k\} + \text{constant}. \quad (10.18)$$

For Bose-Einstein statistics from (10.14),

$$\log_e P = \sum_k \{(N_k + g_k) \log_e (N_k + g_k) - N_k \log_e N_k - g_k \log_e g_k\} + \text{constant} \quad (10.19)$$

\*Born, M., loc. cit, P. 280.

For Fermi-Dirac statistics from (10.17),

$$\log_e P = \sum_k \{(N_k - g_k) \log_e(g_k - N_k) - N_k \log_e N_k + g_k \log_e g_k\} + \text{constant}. \quad (10.20)$$

Since the condition of maximum probability may be expressed in the form :

$$d(\log_e P) = 0, \quad (10.21)$$

we obtain respectively from (10.18), (10.19) and (10.20) (since  $N$  is a fixed number)

$$\sum_k \{\log_e N_k - \log_e g_k + 1\} dN_k = 0 \quad (10.22)$$

$$\sum_k \{\log_e N_k - \log_e(N_k + g_k)\} dN_k = 0 \quad (10.23)$$

$$\sum_k \{\log_e N_k - \log_e(g_k - N_k)\} dN_k = 0. \quad (10.24)$$

The two subsidiary conditions that must also be satisfied at the same time are

$$dN = \sum dN_k = 0 \quad (10.25)$$

for  $N$  the total number of particles in the system and

$$dU = \sum \epsilon_k dN_k = 0 \quad (10.26)$$

for  $U$  is the constant total energy of the system.

Multiplying (10.25) by  $\alpha$  and (10.26) by  $\beta$  and adding them to (10.22), (10.23) and (10.24), we obtain respectively

$$\sum_k \{\log_e(N_k/g_k) + \alpha + \beta\epsilon_k\} dN_k = 0 \quad (10.27)$$

$$\sum_k \left\{ \log_e \frac{N_k}{N_k + g_k} + \alpha + \beta\epsilon_k \right\} dN_k = 0 \quad (10.28)$$

$$\sum_k \left\{ \log_e \frac{N_k}{g_k - N_k} + \alpha + \beta\epsilon_k \right\} dN_k = 0, \quad (10.29)$$

where  $\alpha$  and  $\beta$  are undetermined constants. Since  $dN_k$ 's are arbitrary variations the coefficients of  $dN_k$ 's in each of the above equations are zero. Hence, the most probable distribution in the *Maxwell-Boltzmann* case is, from (10.27),

$$N_k = \frac{g_k}{e^{\alpha+\beta\epsilon_k}}. \quad (10.30)$$

The same in the *Bose-Einstein* case is, from (10.28),

$$N_k = \frac{g_k}{e^{\alpha+\beta\epsilon_k} - 1}. \quad (10.31)$$

Also the most probable distribution in the *Fermi-Dirac* case is, from (10.29),

$$N_k = \frac{g_k}{e^{\alpha+\beta\epsilon_k} + 1}. \quad (10.32)$$

It is evident from (10.31) and (10.32) that when  $g_k \gg N_k$ ,  $e^{\alpha+\beta\epsilon_k}$  becomes very large compared with unity. In that case the Bose-Einstein law (10.31) and the Fermi-Dirac law (10.32) are reduced to the Maxwell-Boltzmann law (10.30). This happens, i.e.,  $g_k$  becomes  $\gg N_k$ , when the temperature is too low or the pressure is too high\*. It follows, therefore, that for all conditions under which normal gases exist, the Maxwell-Boltzmann law (10.30) may be applied to describe their behaviour. But there are a limited number of cases where the Maxwell-Boltzmann law is not at all applicable : radiation (i.e., photons) in a chamber and liquid helium II must be studied under Bose-Einstein statistics and *electron gas* in metals under Fermi-Dirac statistics. These cases will, however, be taken up in due course in this chapter.

## 10.4 Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac Laws for Gas Mixtures

It is not difficult to see that the foregoing treatments of Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics can be applied to systems containing large numbers of different kinds of weakly interacting particles, say,  $N'$  particles of one kind,  $N''$  particles of another kind and so on. We specify a certain distribution by  $N'_k$ ,  $N''_l$ ,  $N'''_m$ , ... as the numbers of particles of different kinds in the  $g_k$ ,  $g_l$ ,  $g_m$ , ... states respectively in the various elementary regions  $k$ ,  $l$ ,  $m$ , ... of the generalised phase space. The probability of this distribution is evidently given by the product

$$P = P' P'' P''' \dots , \quad (10.33)$$

where  $P'$ ,  $P''$ ,  $P'''$ , ... are respectively the distribution probabilities associated with the particles of different kinds which are  $N'$ ,  $N''$ ,  $N'''$ , ... in number.  $P'$  is given by (10.11) or (10.14) or (10.17) depending on the statistics followed by the  $N'$  particles, similarly  $P''$  is also given by (10.11) or (10.14) or (10.17) according to the statistics obeyed by the  $N''$  particles, and so on. Taking logarithm of both sides of (10.33),

$$\log_e P = \log_e P' + \log_e P'' + \log_e P''' + \dots \quad (10.34)$$

The condition of maximum probability is given by

$$-d(\log_e P) = -d(\log_e P') - d(\log_e P'') - d(\log_e P''') - \dots = 0$$

$$\text{i.e., } -\sum_k \frac{d(\log_e P')}{dN'_k} dN'_k - \sum_l \frac{d(\log_e P'')}{dN''_l} dN''_l - \dots = 0 \quad (10.35)$$

since, as shown by (10.18), (10.19) and (10.20),  $P'$  is a function of  $N'_1$ ,  $N'_2$ , ...,  $N'_k$ , ...,  $P''$  is a function of  $N''_1$ ,  $N''_2$ , ...,  $N''_l$ , ... and so forth.

The subsidiary conditions to be satisfied are

$$dN' = \sum_k dN'_k = 0 \quad (10.36)$$

$$dN'' = \sum_l dN''_l = 0 \quad (10.37)$$

.....

$$dU = \sum_k \epsilon_k dN'_k + \sum_l \epsilon_l dN''_l + \dots = 0, \quad (10.38)$$

where  $U$  is the constant total energy of the whole system.

\*See sections 10.8 and 10.9.

Multiplying (10.36), (10.37) ... by  $\alpha'$ ,  $\alpha''$ , ... and (10.38) by  $\beta$  and adding 4o (10.35), we obtain

$$\sum_k \left\{ -\frac{d(\log_e P')}{dN'_k} + \alpha' + \beta\epsilon_k \right\} dN'_k + \sum_l \left\{ -\frac{d(\log_e P'')}{dN''_l} + \alpha'' + \beta\epsilon_l \right\} dN''_l + \dots = 0, \quad (10.39)$$

where  $\alpha'$ ,  $\alpha''$ , ... and  $\beta$  are undetermined constants. Since  $dN'_k$ ,  $dN''_l$ , ... are arbitrary variations the coefficients of  $dN'_k$ ,  $dN''_l$ , ... are each zero. Thus,

$$-\frac{d(\log_e P')}{dN'_k} + \alpha' + \beta\epsilon_k = 0 \quad (10.40)$$

$$-\frac{d(\log_e P'')}{dN''_l} + \alpha'' + \beta\epsilon_l = 0 \quad (10.41)$$

.....  
.....

From (10.40), we obtain

$$N'_k = \frac{g_k}{e^{\alpha' + \beta\epsilon_k} + \gamma}, \quad (10.42)$$

where  $\gamma$  is 0, -1 or +1 according as  $\log_e P'$  is given by (10.18) (Maxwell-Boltzmann statistics) or by (10.19) (Bose-Einstein statistics) or by (10.20) (Fermi-Dirac statistics). From (10.41) also we obtain a similar equation :

$$N''_l = \frac{g_k}{e^{\alpha'' + \beta\epsilon_l} + \gamma} \quad (10.43)$$

and so forth.

It is evident from (10.42), (10.43) ... that although the constant  $\alpha$  varies from one kind of particles to another,  $\beta$  is the same for all kinds of particles in the system.

## 10.5 Evaluation of $\alpha$ and $\beta$

We may write (10.30), (10.31) and (10.32) in the form :

$$N_k = \frac{g_k}{e^{\alpha + \beta\epsilon_k} + \gamma}, \quad (10.44)$$

where  $\gamma$  is 0 for (10.30), -1 for (10.31) and +1 for (10.32).

**(a) Value of  $\alpha$  :** Summing up for all particles, we have from (10.44)

$$N = \sum_k \frac{g_k}{e^{\alpha + \beta\epsilon_k} + \gamma}. \quad (10.45)$$

In order to find  $\alpha$  or  $e^\alpha$ , this equation will have to be solved. This equation, however, takes a simple form for  $\gamma = 0$  (Maxwell-Boltzmann case) or for  $e^{\alpha + \beta\epsilon_k} \gg \mp 1$  (Bose-Einstein or Fermi-Dirac case). Then, we have from (10.45),

$$e^\alpha = \frac{1}{N} \sum_R g_k e^{-\beta\epsilon_k}. \quad (10.46)$$

This equation, it may be noted, is the quantum analogue of the classical equation (9.25) under section 9.5 which gives the equivalent constant  $C$  there. Some solutions of (10.46) will be given in this and the following section.

It should be pointed out that in general, no simple explicit solution of (10.45) is available for  $\gamma = \mp 1$  (Bose-Einstein or Fermi-Dirac case) to find  $\alpha$ . For this purpose, special methods of treatment have been devised. These methods will be discussed in sections 10.8 and 10.9.

**(b) Value of  $\beta$**  : Let us consider a system containing a spinless ( $s = 0$ ), perfect (i.e., weakly interacting), monatomic gas and obeying Maxwell-Boltzmann statistics. For this gas, from (10.8),

$$g_k = \frac{4\sqrt{2}\pi V(m)^{\frac{3}{2}}\epsilon_k^{\frac{1}{2}}\Delta\epsilon_k}{h^3}. \quad (10.47)$$

Now, putting this value of  $g_k$  in (10.30) and writing the equation [i.e., (10.30)] in a differential form, we obtain

$$dN = \frac{4\sqrt{2}\pi V(m)^{\frac{3}{2}}}{h^3} e^{-\alpha} e^{-\beta\epsilon} \epsilon^{\frac{1}{2}} d\epsilon \quad (10.48)$$

$$= Ae^{-\beta\epsilon} \epsilon^{\frac{1}{2}} d\epsilon, \text{ (say).} \quad (10.49)$$

$$\text{Hence, } N = \int dN = A \int_0^\infty e^{-\beta\epsilon} \epsilon^{\frac{1}{2}} d\epsilon = A \left(\frac{1}{\beta}\right)^{\frac{3}{2}} \sqrt{\pi}/2. \quad (\text{See Appendix 1}) \quad (10.50)$$

$$\text{Therefore, } A = \frac{2N\beta^{\frac{3}{2}}}{\sqrt{\pi}}. \quad (10.51)$$

The total energy  $U$  of the system is, from (10.49),

$$U = \int \epsilon dN = A \int_0^\infty \epsilon e^{-\beta\epsilon} \epsilon^{\frac{3}{2}} d\epsilon = A \left(\frac{1}{\beta}\right)^{\frac{5}{2}} \frac{3\sqrt{\pi}}{4}. \quad (\text{See Appendix 1}) \quad (10.52)$$

Supposing that we have taken a gram-molecule of the gas, we have from experiment

$$U = \frac{3}{2}RT = N \times \frac{3}{2}kT. \quad (10.53)$$

We then obtain from (10.51), (10.52) and (10.53),

$$\beta = \frac{1}{kT}. \quad (10.54)$$

The expression of  $\beta$  given by (10.54) for a spinless, perfect, monatomic gas also holds for all kinds of gases. To see this, suppose that one of the constituents of a mixture of gases is spinless, perfect and monatomic and obeys Maxwell-Boltzmann statistics. Then, for this constituent  $\beta$  is  $1/kT$  as given by (10.54). But according to the last paragraph of the preceding section,  $\beta$  is the same for all kinds of gases in the system. Hence, we conclude that  $\beta$  is  $1/kT$  irrespective of the nature of the molecules concerned.

Further, substituting for  $\beta$  from (10.54) in (10.51),

$$A = \frac{2N}{\sqrt{\pi}(kT)^{\frac{3}{2}}}. \quad (10.55)$$

Then, from (10.48), (10.49) and (10.55),

$$e^\alpha = \frac{V(2\pi mkT)^{\frac{3}{2}}}{Nh^3}, \quad (10.56)$$

for a spinless, perfect, monatomic gas.

## 10.6 Maxwell's Law from Maxwell-Boltzmann Statistics

Let us consider a system containing a perfect gas and obeying Maxwell-Boltzmann statistics. For this gas, we obtain from (10.6), (10.30) and (10.54), the equation in differential form :

$$\begin{aligned} dN &= \frac{(2s+1)V e^{-\alpha} e^{-\epsilon/kT}}{h^r} dq_4 \cdots dq_r dp_x dp_y dp_z dp_4 \cdots dp_r \\ &= \frac{(2s+1)V e^{-\alpha}}{h^r} e^{-\frac{[\epsilon(p_x, p_y, p_z) + \epsilon(q_4 \cdots p_r)]}{kT}} dq_4 \cdots dq_r dp_x dp_y dp_z dp_4 \cdots dp_r. \end{aligned} \quad (10.57)$$

To obtain Maxwell's law, we integrate (10.57) over  $p_x, p_y, p_z$  from  $\epsilon(p_x, p_y, p_z)$  to  $\epsilon + d\epsilon$  and over all possible values of other coordinates and momenta since we are now interested only in translational kinetic energy. Then, we obtain an expression of the form :

$$dN = \frac{(2s+1)V}{h^r} B e^{-\alpha} \iiint_{\epsilon}^{\epsilon+d\epsilon} e^{-\epsilon/kT} dp_x dp_y dp_z, \quad (10.58)$$

where  $B = \int \cdots \int e^{-\epsilon(q_4 \cdots p_r)/kT} dq_4 \cdots dq_r dp_4 \cdots dp_r.$  (10.59)

Since  $\epsilon(p_x, p_y, p_z) = p^2/2m$  ( $m$  being the molecular mass), we have from (10.58) in terms of spherical polar coordinates  $p, \theta, \phi,$

$$\begin{aligned} dN &= \frac{(2s+1)V}{h^r} B e^{-\alpha} \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi} \int_p^{p+dp} e^{-\epsilon/kT} p^2 dp \sin \theta d\theta d\phi \\ &= \frac{(2s+1)V}{h^r} B e^{-\alpha} 4\pi e^{-\epsilon/kT} p^2 dp \\ &= \frac{4\sqrt{2}\pi(2s+1)V m^{3/2}}{h^r} B e^{-\alpha} e^{-\epsilon/kT} \epsilon^{\frac{1}{2}} d\epsilon. \end{aligned} \quad (10.60)$$

Hence,  $N = \int dN = \frac{4\sqrt{2}\pi(2s+1)V m^{3/2}}{h^r} B e^{-\alpha} \int_0^\infty e^{-\epsilon/kT} \epsilon^{\frac{1}{2}} d\epsilon$   
 $= \frac{4\sqrt{2}\pi(2s+1)V m^{\frac{3}{2}}}{h^r} B e^{-\alpha} (kT)^{\frac{3}{2}} \frac{\sqrt{\pi}}{2}. \quad (\text{See Appendix 1})$  (10.61)

Therefore, from (10.61),

$$e^\alpha = \frac{(2s+1)(2\pi mkT)^{\frac{3}{2}} V B}{N h^r} \quad (10.62)$$

for a perfect gas with spin  $s.$  If, however, the gas is perfect and monatomic, then (10.57) is reduced to the form :

$$dN = \frac{(2s+1)V e^{-\alpha}}{h^3} e^{-\epsilon/kT} dp_x dp_y dp_z. \quad (10.63)$$

Proceeding as above, (10.63) gives

$$e^\alpha = \frac{(2s+1)(2\pi mkT)^{\frac{3}{2}} V}{N h^3} \quad (10.64)$$

for a perfect monatomic gas with spin  $s.$

However, substituting for  $e^\alpha$  from (10.62) in (10.60),

$$dN = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}} e^{-\epsilon/kT} \epsilon^{\frac{1}{2}} d\epsilon. \quad (10.65)$$

This is Maxwell's law. This may be put in another form by putting  $\epsilon = \frac{1}{2}mc^2$  :

$$dN_c = 4\pi N \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{1}{2}mc^2/kT} c^2 dc. \quad (10.66)$$

Since Maxwell's law which comes from classical statistics (See section 9.6) also comes from Maxwell-Boltzmann statistics, it is evident that both the statistics are equivalent.

The total energy of the system containing a gram-molecule of the gas is, from (10.65),

$$U = \int \epsilon dN = \frac{2\pi N}{(\pi kT)^{\frac{3}{2}}} \int_0^\infty e^{-\epsilon/kT} \epsilon^{\frac{3}{2}} d\epsilon = \frac{3}{2} NkT \quad (\text{See Appendix 1}) \quad (10.67)$$

$$= \frac{3}{2} RT. \quad (10.68)$$

The pressure  $P$  of the perfect gas is given by (See section 2.3)

$$P = \frac{1}{3} \sum m n_k c_k^2 = \frac{2}{3} \sum n_k \epsilon_k = \frac{2}{3} \frac{U}{V}, \quad (10.68)$$

where  $n_k$  is the number of molecules per unit volume, each having translational velocity  $c_k$  and energy  $\epsilon_k$ .

## 10.7 Bose's Deduction of Planck's Law

S. N. Bose\* (1923) conceived that a black body chamber might be supposed to be full of photons in thermal equilibrium. The problem of finding the distribution of energy among the different frequencies  $\nu$  (or wavelengths  $\lambda$ ) is then reduced to that of finding the numbers of photons possessing different energies  $h\nu$  (i.e.,  $\epsilon$ ) in a black-body chamber at temperature  $T$ .

In this treatment, however, one important point must be noted. Although the energy of the system remains constant at a definite temperature  $T$ , the total number of photons in the system is not a constant but a variable quantity. Since photons do not interact with one another\*\*, the presence of some matter, however little, is in general necessary to enable thermal equilibrium to be set up in the radiation. The mechanism which brings about the establishment of equilibrium is the emission and absorption of photons by the matter. This process also goes on after the equilibrium has been set up. Hence, the subsidiary condition (10.25) is not applicable to photons and, therefore, the term involving the constant  $\alpha$  does not enter into the present treatment. So we have in this case, instead of (10.31),

$$N_k = \frac{g_k}{e^{\epsilon_k/kT} - 1}, \quad (10.69)$$

taking  $\beta$  as equal to  $1/kT$ .

We consider photons as monatomic particles so that we obtain, from (10.7) and (10.69), the equation in differential form :

$$dN = \frac{4\pi \cdot 2 \cdot V}{h^3} \frac{p^2 dp}{e^{\epsilon/kT} - 1}, \quad (10.70)$$

\*Bose, S. N., Zeits. f. Physik, **26**, 178 (1924).

\*\*Landau, L. D., and Lifshitz, E. M., *Statistical Physics*, Pp. 171-2 (1959).

where we have replaced  $(2s + 1)$  by 2. A photon, because of its spin being 1, should have 3 (i.e.,  $+1, 0, -1$ ) possible spin-states, but it exists only in any of the two spin-state or states of polarisation (as sometimes called)  $+1$  (with spin-vector parallel to its momentum, i.e., to its direction of motion) and  $-1$  (with spin-vector anti-parallel, i.e., opposite to its momentum), and the 0 spin-state does not occur\*.

Putting  $p$  (photon momentum) equal to  $h\nu/c$  and  $\epsilon$  equal to  $h\nu$ , we have from (10.70)

$$dn_\nu = \frac{dN}{V} = \frac{8\pi\nu^2 d\nu}{c^3(e^{h\nu/kT} - 1)}, \quad (10.71)$$

where  $dn_\nu$  is the number of photons per unit volume of the black-body chamber having energy between  $h\nu$  and  $h(\nu + d\nu)$ . If both sides of (10.71) are multiplied by  $h\nu$ , we obtain the energy density  $E_\nu d\nu (= h\nu dn_\nu)$  in the frequency range between  $\nu$  and  $\nu + d\nu$ .

$$E_\nu d\nu = \frac{8\pi h\nu^3 d\nu}{c^3(e^{h\nu/kT} - 1)}. \quad (10.72)$$

This is Planck's radiation law.

## 10.8 Application of Bose-Einstein Statistics to Gases : Bose-Einstein Condensation

We shall consider a system containing a perfect (i.e., weakly interacting) monatomic gas. Then, from (10.8) and (10.31), we have the equation in differential form :

$$dN = \frac{4\sqrt{2\pi}(2s+1)V m^{\frac{3}{2}} \epsilon^{\frac{1}{2}} d\epsilon}{h^3(e^\alpha e^{\epsilon/kT} - 1)}. \quad (10.73)$$

$$\text{Now, writing } Q = \frac{(2s+1)(2\pi mkT)^{\frac{3}{2}} V}{h^3} \quad (10.74)$$

$$D = e^\alpha \quad (10.75)$$

$$x = \frac{\epsilon}{kT} \quad (10.76)$$

we obtain from (10.73)

$$dN = \frac{2Q}{\sqrt{\pi}} \frac{x^{\frac{1}{2}} dx}{De^x - 1}. \quad (10.77)$$

On integration,

$$N = \frac{2Q}{\sqrt{\pi}} \int_0^\infty \frac{x^{\frac{1}{2}} dx}{De^x - 1}. \quad (10.78)$$

The total (translational) energy of the system is

$$U = \int \epsilon dN = \frac{2kTQ}{\sqrt{\pi}} \int_0^\infty \frac{x^{\frac{3}{2}} dx}{De^x - 1}. \quad (10.79)$$

We shall only have to consider the positive values of  $\alpha$  and hence the values of  $D > 1$ . Because, if  $\alpha$  is negative and hence  $D$  is  $< 1$ , it is evident from (10.31) that at sufficiently low values of  $\epsilon_k$ ,  $N_k$  may become negative which is unphysical. It is, therefore, clear that the

\* It is a characteristic of mass-less particles, such as photons and neutrinos, that they have got only spin-states parallel or antiparallel to their momentum. See Roman, P., *Theory of Elementary Particles*, Pp. 232, 360 (1961).

*limiting value* of  $D$  is 1. However, for  $D > 1$ , the evaluation of the integrals in (10.78) and (10.79) becomes much simplified. In this case, we can write :

$$\frac{1}{(De^x - 1)} = \frac{e^{-x}}{D} \left( 1 + \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} + \dots \right).$$

This is a converging series and will converge more rapidly for  $\alpha \gg 1$ , i.e., for  $D \gg 1$ . Then, from (10.78),

$$\begin{aligned} N &= \frac{2Q}{D\sqrt{\pi}} \int_0^\infty \left[ e^{-x} x^{\frac{1}{2}} dx + \frac{e^{-2x} x^{\frac{1}{2}} dx}{D} + \dots \right] \\ &= \frac{Q}{D} \left( 1 + \frac{1}{2^{\frac{3}{2}} D} + \frac{1}{3^{\frac{3}{2}} D^2} + \dots \right). \end{aligned} \quad (10.80)$$

This may be put in the form :

$$D = \frac{Q}{N} \left( 1 + \frac{1}{2^{\frac{3}{2}} D} + \frac{1}{3^{\frac{3}{2}} D^2} + \dots \right). \quad (10.81)$$

Now, from (10.79),

$$\begin{aligned} U &= \frac{2kTQ}{D\sqrt{\pi}} \int_0^\infty \left[ e^{-x} x^{\frac{3}{2}} dx + \frac{e^{-2x} x^{\frac{3}{2}} dx}{D} + \dots \right] \\ &= \frac{3kTQ}{2D} \left( 1 + \frac{1}{2^{\frac{5}{2}} D} + \frac{1}{3^{\frac{5}{2}} D^2} + \dots \right). \end{aligned} \quad (10.82)$$

On substituting for  $D$  from (10.81) in (10.82),

$$\begin{aligned} U &= \frac{3}{2} N k T \left( 1 + \frac{1}{2^{\frac{5}{2}} D} + \frac{1}{3^{\frac{5}{2}} D} + \dots \right) \left( 1 + \frac{1}{2^{\frac{3}{2}} D} + \frac{1}{3^{\frac{3}{2}} D^2} + \dots \right)^{-1} \\ &= \frac{3}{2} R T \left( 1 - \frac{1}{2^{\frac{5}{2}} D} - \frac{1}{3^{\frac{5}{2}} D^2} - \dots \right) \end{aligned} \quad (10.83)$$

for a gram-molecule of gas. When  $D$  (i.e.,  $e^\alpha$ ) is sufficiently large so that  $e^{\alpha+\beta\epsilon_k}$  is  $\gg 1$ , the Bose-Einstein law (10.31) is reduced to the classical Maxwell-Boltzmann law (10.30). In that case,  $D$  is given by (10.64) for a perfect monatomic gas. Comparing (10.64) and (10.74), this value of  $D$  is  $Q/N$ . If, as a first approximation, this classical value of  $D$  is put in (10.83), we have

$$U = \frac{3}{2} R T \left\{ 1 - \frac{1}{2^{\frac{5}{2}}} \left( \frac{N}{Q} \right) - \frac{1}{3^{\frac{5}{2}}} \left( \frac{N}{Q} \right)^2 - \dots \right\}. \quad (10.84)$$

The pressure  $P$  of the perfect gas is, as shown in (10.68), given by

$$P = \frac{2}{3} \frac{U}{V} = \frac{RT}{V} \left( 1 - \frac{1}{2^{\frac{5}{2}} D} - \frac{1}{3^{\frac{5}{2}} D^2} - \dots \right). \quad [\text{from (10.83)}] \quad (10.85)$$

If, as a first approximation, the classical value of  $D$  is put in (10.85), then

$$P = \frac{RT}{V} \left\{ 1 - \frac{1}{2^{\frac{5}{2}}} \left( \frac{N}{Q} \right) - \frac{1}{3^{\frac{5}{2}}} \left( \frac{N}{Q} \right)^2 - \dots \right\}. \quad (10.86)$$

Comparing (10.83) with (10.67) and (10.85) with (10.68) it is found that the energy (translational) and the pressure of a perfect (i.e., weakly interacting) Bose-Einstein gas are different from those of a perfect Maxwell-Boltzmann gas. These deviations of a Bose-Einstein gas from the behaviour of a classical Maxwell-Boltzmann gas are usually referred to as *degeneration*. It is evident from (10.83) and (10.85) that this degeneration depends on  $D$ . The degree of degeneration of a particular gas, i.e., how far it behaves like a Bose-Einstein gas and, therefore, deviates from the behaviour of a classical Maxwell-Boltzmann gas may be approximately estimated by taking  $D$  equal to the classical value (10.64), i.e.,

$$D \approx \frac{Q}{N} = \frac{(2s+1)(2\pi mkT)^{\frac{3}{2}}}{h^3(N/V)}. \quad (10.87)$$

Since (10.83) and (10.85) show that for small values of  $D$  (but  $> 1$ ) the degree of degeneration is large, it is clear from (10.87) that a gas may *degenerate* into a Bose-Einstein gas if its mass  $m$  is small, the temperature  $T$  low and the density  $N/V$  or pressure high.

Let us consider now some cases in the light of the ideas developed here.

**(a) Hydrogen :** It is evident from above that the lightest gas, hydrogen, though diatomic, should act as a Bose-Einstein gas. Let us estimate the deviation of this gas from the ideal classical behaviour when it degenerates into the Bose-Einstein state. The lowest temperature at which it can exist in the gaseous state at atmospheric pressure is 20.38 K (boiling-point at atmos. pr.). We, therefore, calculate  $D$  at this temperature. With  $N = 6.02 \times 10^{23}$ ,  $h = 6.62 \times 10^{-27}$  erg · sec,  $m = 2 \times 1.67 \times 10^{-24}$  gm,  $k = 1.38 \times 10^{-16}$  erg K<sup>-1</sup>,  $V = 1400$  cc and  $s = 0$ , we obtain  $1/D = 0.84 \times 10^{-2}$ . Hence, (10.86) gives

$$P = \frac{RT}{V}(1 - 1.49 \times 10^{-3}). \quad (10.88)$$

Thus, the extent of degeneration of hydrogen gas, i.e.,  $1.49 \times 10^{-3}$ , is very small and is, in fact, much smaller than the ordinary departure from the classical behaviour due to intermolecular forces. Hence, it is impossible to detect the effect of this degeneration. At very low temperatures and high densities, the deviations of Bose-Einstein gases from the classical behaviour of perfect gases would of course become important but would be very much masked by the strong intermolecular forces under these conditions.

**(b) Helium :** Next we consider helium which is the second lightest (next to hydrogen) gas and can exist in the gaseous state at much lower temperatures. In fact, the boiling point of helium at atmospheric pressure is 4.240 K. Then, with  $V = 345$  cc and  $m = 4 \times 1.67 \times 10^{-24}$  gm and the above data, we have at this temperature  $1/D = 0.134$ . Then, (10.86) gives

$$P = \frac{RT}{V}(1 - 0.02). \quad (10.89)$$

Thus, the extent of degeneration of helium gas, though higher than that of hydrogen gas, is not very large in itself. It is only 2% at the boiling point. Yet, the reality of Bose-Einstein degeneration of helium can be seen\* from the following discussion.

The behaviour of helium gas is represented by a Kammerlingh Onnes type of equation :

$$P = \frac{RT}{V} \left\{ 1 + \frac{B(T)}{V} \right\}. \quad (10.90)$$

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\*This has not, in fact, been proved quite convincingly so far. See, for discussion, Saha and Srivastava, *A Treatise on Heat*, P. 753 (1958).

Beth and Uhlenbeck\* have shown that if at very low temperatures (e.g., 4.240 K at  $P = 77.6$  cm of Hg to 2.050 K at  $P = 2.8$  cm of Hg), the contribution due to the van der Waals term  $\frac{1}{V} (b - \frac{a}{RT})$  (See (3.69) of section 3.8) is added to that due to the Bose-Einstein degeneration term  $\frac{1}{2\pi} \left( \frac{N}{Q} \right)$  [See (10.86)], then their sum comes out to be approximately equal to the experimental value of the term  $\frac{B(T)}{V}$  of (10.90). Thus, it is apparent that helium undergoes Bose-Einstein degeneration under these conditions.

We have discussed above two cases of *slight degeneration*. Now we shall consider an *extreme or limiting case of Bose-Einstein degeneration* ( $D \rightarrow 1$ ).

(c) **Liquid Helium II** : (10.84) and (10.86) show that the energy (translational) and pressure of a perfect Bose-Einstein gas are lower than those of a perfect classical gas under the same temperature and volume. The reason for this can be seen from (10.73). At the higher energy cells or states when  $De^{\epsilon/kT}$  is  $\gg 1$ , the gas behaves like a Maxwell-Boltzmann gas. Therefore, if a gas is to behave like a Bose-Einstein gas,  $De^{\epsilon/kT}$  must not be too large in comparison with 1. This means that a Bose-Einstein gas will have a tendency to exist in the lower energy cells or states than does a classical gas under the same conditions of temperature and volume. This explains the comparatively low kinetic energy and hence, also the comparatively low pressure of a Bose-Einstein gas.

Now, in view of this comparatively low pressure of a Bose-Einstein gas, one may say that there arises an *effective attraction* between the particles when the gas follows Bose-Einstein statistics at very low temperatures and high density<sup>††</sup>. Evidently, this effect should be particularly marked under the condition of *extreme degeneration* when  $D$  tends to unity as this is the smallest value for  $D$  as explained earlier in this section. Under this condition, a *phenomenon analogous to condensation called Bose-Einstein condensation*, though not due to intermolecular attraction, might occur<sup>††</sup>. London<sup>†</sup> has, therefore, suggested that due to this sort of condensation, liquid helium I is converted into liquid helium II at  $\lambda$ -point (See section 6.16 and Appendix-8) and that the peculiar properties of liquid helium II which can exist down to the absolute zero (provided the pressure does not exceed 25 atmospheres) (See Fig. 10.1) are due to its behaviour as an extremely degenerate ( $D \rightarrow 1$ ) Bose-Einstein gas.

He II begins to acquire the property of superfluidity at  $\lambda$ -point and becomes completely superfluid at absolute zero. Superfluidity means absence of viscosity.

Under the limiting condition  $D = 1$  we have<sup>§</sup>, from (10.74) and (10.78) with  $s = 0$ ,

$$N = \frac{2(2\pi mkT)^{\frac{3}{2}} V}{\sqrt{\pi h^3}} \int_0^\infty \frac{x^{\frac{1}{2}} dx}{e^x - 1} \quad (10.91)$$

\*Beth and Uhlenbeck, *Physica*, **4**, P. 915 (1937).

<sup>†</sup>Saha and Srivastava, *A Treatise on Heat*, P. 526 (1958).

<sup>††</sup>Landau, L. D., and Lifshitz, E. M., *loc. cit.*, P. 159.

<sup>†</sup>London, *Phys. Rev.*, **54**, P. 947 (1938); *J Phys. Chem.*, **43**, P. 49 (1939).

<sup>§</sup>Schrödinger, E., *Statistical Thermodynamics* P. 76 (1948).

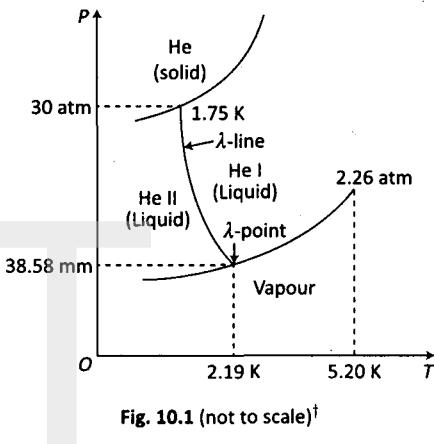


Fig. 10.1 (not to scale)<sup>†</sup>

$$\begin{aligned}
 &= \frac{2(2\pi mkT)^{\frac{3}{2}}V}{\sqrt{\pi}h^3} \left( \frac{\sqrt{\pi}}{2} \times 2.612 \right) \text{ (on evaluation of integral)} \\
 &= \frac{(2\pi mkT)^{\frac{3}{2}}V}{h^3} \times 2.612.
 \end{aligned}$$

This gives  $T = \left( \frac{N}{2.612V} \right)^{\frac{2}{3}} \frac{h^2}{2\pi mk} \approx 3.12 \text{ K},$  (10.92)

where we have put  $V = 27.4 \text{ cc}$  at the  $\lambda$ -point of helium. This theoretical value for the  $\lambda$ -point is not far removed from the experimental value of  $2.18 \text{ K}$  (See section 6.16).

It may be argued that although (10.91) holds for a gas for which interaction between particles is completely disregarded, yet it is applied here to the liquid state for which the interaction cannot be ignored. But it has been pointed out above that liquid helium II, in fact, possesses high zero-point energy (i.e., high energy even down to absolute zero) and can exist down to absolute zero (provided the pressure does not exceed 25 atmospheres under which it gets solidified (See Fig. 10.1)). Thus, the liquid helium particles move about like gas molecules and, therefore, the gas equation (10.91) may not be so inappropriate for liquid helium as one might imagine.

Now we calculate the energy and pressure under the limiting condition  $D = 1^*$ . From (10.79), the energy is, for  $D = 1$ ,

$$\begin{aligned}
 U &= \frac{2kTQ}{\sqrt{\pi}} \int_0^\infty \frac{x^{\frac{3}{2}}dx}{e^x - 1} = \frac{2kTQ}{\sqrt{\pi}} \left( \frac{3\sqrt{\pi}}{4} \times 1.34 \right) \text{ (on evaluation of integral)} \\
 &= \frac{2.01k^{\frac{5}{2}}T^{\frac{5}{2}}(2\pi m)^{\frac{3}{2}}V}{h^3}.
 \end{aligned}$$

from (10.74) with  $s = 0$  for helium. Hence,

$$C_v = \left( \frac{dU}{dT} \right)_V = \frac{10.05k^{\frac{5}{2}}T^{\frac{3}{2}}(2\pi m)^{\frac{3}{2}}V}{2h^3}.$$

This shows that  $U$  and  $C_v$  both become zero at absolute zero under the limiting condition  $D = 1$ .

The pressure is given by

$$P = \frac{2U}{3V} = \frac{4.02k^{\frac{5}{2}}T^{\frac{5}{2}}(2\pi m)^{\frac{3}{2}}}{3h^3}.$$

Thus, the pressure under the limiting condition is independent of volume and depends only on temperature. If, therefore, we compress the system, its particles will gradually go to the zero-energy state. Conversely, upon expansion the particles will come out of the zero-energy state until there are none left. If expansion continues further, the pressure will begin to decrease (as it happens to a gas (See above)).

## 10.9 Application of Fermi-Dirac Statistics to Gases

We consider a system containing a perfect (i.e., weakly interacting) monatomic gas. Then, from (10.8) and (10.32), we have the equation in differential form :

\*Komparreyets, A. S., *Theoretical Physics*, P. 497 (1961); Mayer, J. F. and Mayer, M. G. *Statistical Mechanics*, Pp. 422, 423, 426 (1940).

$$dN = \frac{4\sqrt{2}\pi(2s+1)Vm^{\frac{3}{2}}}{h^3} \frac{\epsilon^{\frac{1}{2}}d\epsilon}{e^\alpha e^{\epsilon/kT} + 1}. \quad (10.93)$$

Writing as before,

$$Q = \frac{(2s+1)(2\pi mkT)^{\frac{3}{2}}V}{h^3} \quad (10.94)$$

$$D = e^\alpha \quad (10.95)$$

$$x = \frac{\epsilon}{kT}, \quad (10.96)$$

we obtain from (10.93)

$$dN = \frac{2Q}{\sqrt{\pi}} \frac{x^{\frac{1}{2}}dx}{De^x + 1}. \quad (10.97)$$

On integrating,

$$N = \frac{2Q}{\sqrt{\pi}} \int_0^\infty \frac{x^{\frac{1}{2}}dx}{De^x + 1}. \quad (10.98)$$

The total (translational) energy of the system is

$$U = \int \epsilon dN = \frac{2kTQ}{\sqrt{\pi}} \int_0^\infty \frac{x^{\frac{3}{2}}dx}{De^x + 1}. \quad (10.99)$$

We can consider here both positive and negative values of  $\alpha$ , because, as is evident from (10.32), we do not face any unphysical situation here for negative values of  $\alpha$  as we do in the case of Bose-Einstein statistics. We shall discuss the cases for positive and negative values of  $\alpha$  separately.

**(a) Slight Fermi-Dirac Degeneration :** If  $\alpha$  is positive so that  $D$  is  $> 1$ , then the condition is referred to as *slight degeneration* of a gas into the Fermi-Dirac character. For this case, we can write :

$$\frac{1}{(De^x + 1)} = \frac{e^{-x}}{D} \left( 1 - \frac{e^{-x}}{D} + \frac{e^{-2x}}{D^2} - \dots \right).$$

This is a converging series and converges more rapidly for  $\alpha \gg 1$ , i.e.,  $D \gg 1$ .

Proceeding as in the preceding section, we can write from (10.98) :

$$N = \frac{Q}{D} \left( 1 - \frac{1}{2^{\frac{3}{2}}D} + \frac{1}{3^{\frac{3}{2}}D^2} - \dots \right) \quad (10.100)$$

$$\text{so that } D = \frac{Q}{N} \left( 1 - \frac{1}{2^{\frac{3}{2}}D} + \frac{1}{3^{\frac{3}{2}}D^2} - \dots \right). \quad (10.100a)$$

Also proceeding as in the preceding section, we have from (10.100) [See (10.83)]

$$U = \frac{3kTQ}{2D} \left( 1 - \frac{1}{2^{\frac{5}{2}}D} + \frac{1}{3^{\frac{5}{2}}D^2} - \dots \right) = \frac{3}{2}RT \left( 1 + \frac{1}{2^{\frac{5}{2}}D} - \frac{1}{3^{\frac{5}{2}}D^2} + \dots \right) \quad (10.101)$$

for a gram-molecule of the gas. If, as a first approximation the classical value of  $D$ , i.e.,  $Q/N$  [See (10.87)] is put in (10.101), we have

$$U = \frac{3}{2}RT \left\{ 1 + \frac{1}{2^{\frac{5}{2}}} \left( \frac{N}{Q} \right) - \frac{1}{3^{\frac{5}{2}}} \left( \frac{N}{Q} \right)^2 + \dots \right\}. \quad (10.102)$$

The pressure  $P$  of the perfect gas is, as shown in (10.68), given by

$$P = \frac{2}{3} \frac{U}{V} = \frac{RT}{V} \left( 1 + \frac{1}{2^{\frac{5}{2}} D} - \frac{1}{3^{\frac{5}{2}} D^2} + \dots \right). \quad [\text{from (10.101)}] \quad (10.103)$$

If, as a fast approximation, the classical value of  $D$  is put in (10.103), then

$$P = \frac{RT}{V} \left\{ 1 + \frac{1}{2^{\frac{5}{2}}} \left( \frac{N}{Q} \right) - \frac{1}{3^{\frac{5}{2}}} \left( \frac{N}{Q} \right)^2 + \dots \right\}. \quad (10.104)$$

(10.102) and (10.104) show that the energy (translational) and pressure of a perfect Fermi-Dirac gas are higher than those of a perfect classical gas under the same temperature and volume. In view of this comparatively high pressure of a Fermi-Dirac gas, one may say that there arises an *effective repulsion* between the particles when the gas follows Fermi-Dirac statistics\*.

Since (10.101) and (10.103) show that for small values of  $D$  (but  $> 1$ ) the degree of degeneration is large, it is clear from (10.87) that a gas may degenerate into a Fermi-Dirac gas if its mass  $m$  is small, the temperature  $T$  low and the density  $N/V$  high. But since the deviations of a Fermi-Dirac gas from classical behaviour are almost the same as for a Bose-Einstein gas, it is evident that it is hardly possible to observe them even with heavy hydrogen (i.e., deuterium gas), the lightest gas that should follow Fermi-Dirac statistics.

**(b) Extreme Fermi-Dirac Degeneration :** If  $\alpha$  is negative and large so that  $D \ll 1$ , then the condition is referred to as *extreme degeneration* and a gas under this condition is called an *extremely degenerate Fermi-Dirac gas*. In the case of the interiors of stars\*\* and in the case of the conduction electrons—which can be treated in first approximation as an *electron gas*—in a metal, we have high density ( $N/V$ ) and low particle mass ( $m$ ), so that even at the high temperatures of stellar interiors and at the ordinary temperatures for metals the condition of extreme degeneration ( $D \ll 1$ ) is satisfied [See (10.87)]. We shall now develop the theory for these cases.

When  $\alpha$  is negative, Sommerfeld<sup>†</sup> has shown by an approximate treatment that we can write :

$$\int_0^\infty \frac{x^{\frac{1}{2}} dx}{e^{\alpha+x} + 1} = \frac{2(-\alpha)^{\frac{3}{2}}}{3} \left[ 1 + 2 \left\{ \frac{\left(\frac{3}{2}\right)\left(\frac{1}{2}\right)c_2}{\alpha^2} + \frac{\left(\frac{3}{2}\right)\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)c_4}{\alpha^4} + \dots \right\} \right] \quad (10.105)$$

$$\text{and } \int_0^\infty \frac{x^{\frac{3}{2}} dx}{e^{\alpha+x} + 1} = \frac{2(-\alpha)^{\frac{5}{2}}}{5} \left[ 1 + 2 \left\{ \frac{\left(\frac{5}{2}\right)\left(\frac{3}{2}\right)c_2}{\alpha^2} + \frac{\left(\frac{5}{2}\right)\left(\frac{3}{2}\right)\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)c_4}{\alpha^4} + \dots \right\} \right], \quad (10.106)$$

where the constants  $c_2, c_4, \dots$  have the values

$$c_\nu = 1 - \frac{1}{2^\nu} + \frac{1}{3^\nu} - \frac{1}{4^\nu} + \dots \quad (10.107)$$

(10.105) and (10.106) converge rapidly when  $(-\alpha) \gg 1$ . It should be noted that the approximation employed in obtaining (10.105) and (10.106) involves an error of the order of  $e^\alpha$ . This error becomes too small in the case of extreme degeneration where  $D$ , i.e.,  $e^\alpha \ll 1$ .

\*Landau, L. D., and Lifshitz, E. M., *loc. cit.*, P. 159.

\*\*Fowler, *Monthly Notices*, **87**, P. 114 (1926-7).

†Sommerfeld, *Zeits. f. Phys.*, **47**, P. 1 (1928).

Now, from (10.98) and (10.105), we obtain

$$N = \frac{4Q(-\alpha)^{\frac{3}{2}}}{3\sqrt{\pi}} \left[ 1 + 2 \left\{ \frac{3c_2}{4\alpha^2} + \frac{9c_4}{16\alpha^4} + \dots \right\} \right]$$

or  $\frac{N}{Q} = \frac{4(-\alpha)^{\frac{3}{2}}}{3\sqrt{\pi}} \left[ 1 + 2 \left\{ \frac{3c_2}{4\alpha^2} + \frac{9c_4}{16\alpha^4} + \dots \right\} \right]. \quad (10.108)$

Since we are dealing with extreme degeneration,  $e^\alpha \ll 1$ , i.e.,  $(-\alpha) \gg 1$ . Therefore, we shall retain the series (10.108) up to the second term only :

$$\frac{N}{Q} = \frac{4(-\alpha)^{\frac{3}{2}}}{3\sqrt{\pi}} \left( 1 + \frac{3c_2}{2\alpha^2} \right). \quad (10.109)$$

Now, from (10.107),

$$c_2 = 1 - \frac{1}{2^2} + \frac{1}{3^2} - \frac{1}{4^2} + \dots = \frac{\pi^2}{12}. \quad (10.110)$$

Also, the first-approximation value of  $\alpha$  is given from (10.109) by

$$\frac{N}{Q} \approx \frac{4(-\alpha)^{\frac{3}{2}}}{3\sqrt{\pi}}, \quad \text{i.e.,} \quad -\alpha \approx \left( \frac{3\sqrt{\pi}N}{4Q} \right)^{\frac{2}{3}}. \quad (10.111)$$

Substituting the value of  $c_2$  from (10.110) and the first approximation value of  $\alpha$  from (10.111) in the second term of (10.109),

$$\frac{N}{Q} = \frac{4(-\alpha)^{\frac{3}{2}}}{3\sqrt{\pi}} \left\{ 1 + \frac{3\pi^2}{2 \cdot 12} \left( \frac{4Q}{3\sqrt{\pi}N} \right)^{\frac{4}{3}} \right\}$$

or,  $(-\alpha) = \left( \frac{3\sqrt{\pi}N}{4Q} \right)^{\frac{2}{3}} \left\{ 1 - \frac{\pi^2}{12} \left( \frac{4Q}{3\sqrt{\pi}N} \right)^{\frac{4}{3}} + \dots \right\}. \quad (10.112)$

Now, from (10.109) and (10.106), we obtain

$$U = \frac{4kTQ(-\alpha)^{\frac{5}{2}}}{5\sqrt{\pi}} \left[ 1 + 2 \left\{ \frac{15c_2}{4\alpha^2} - \frac{15c_4}{16\alpha^4} + \dots \right\} \right]$$

$$= \frac{3}{5}RT(-\alpha) \left[ 1 + \frac{3c_2}{2\alpha^2} + \dots \right]^{-1} \left[ 1 + \frac{15c_2}{2\alpha^2} - \dots \right]. \quad (10.113)$$

On putting the value of  $c_2$  from (10.110) in (10.113) and on simplification,

$$U = \frac{3}{5}RT(-\alpha) \left( 1 + \frac{\pi^2}{2\alpha^2} + \dots \right). \quad (10.114)$$

Now, writing for  $(-\alpha)$  the value given by (10.112) and for  $\alpha^2$  in the denominator of the second term the first approximation value of  $(-\alpha)$  given by (10.111), we obtain from (10.114),

$$U = \frac{3}{5}RT \left( \frac{3\sqrt{\pi}N}{4Q} \right)^{\frac{2}{3}} \left\{ 1 - \frac{\pi^2}{12} \left( \frac{4Q}{3\sqrt{\pi}N} \right)^{\frac{4}{3}} + \dots \right\} \left\{ 1 + \frac{\pi^2}{2} \left( \frac{4Q}{3\sqrt{\pi}N} \right)^{\frac{4}{3}} + \dots \right\}$$

$$\begin{aligned}
 &= \frac{3}{5} RT \left( \frac{3\sqrt{\pi}N}{4Q} \right)^{\frac{2}{3}} \left\{ 1 + \frac{5\pi^2}{12} \left( \frac{4Q}{3\sqrt{\pi}N} \right)^{\frac{4}{3}} + \dots \right\} \\
 &= \frac{3}{5} RT \left( \frac{3\sqrt{\pi}N}{4Q} \right)^{\frac{2}{3}} + \frac{\pi^2}{4} RT \left( \frac{4Q}{3\sqrt{\pi}N} \right)^2 + \dots \\
 &= \frac{3Nh^2}{10m} \left\{ \frac{3N}{4\pi V(2s+1)} \right\}^{\frac{2}{3}} + \frac{Nm\pi^2k^2}{2h^2} \left\{ \frac{4\pi V(2s+1)}{3N} \right\}^{\frac{2}{3}} T^2 + \dots
 \end{aligned} \tag{10.115}$$

on substituting the value of  $Q$  from (10.94).

The pressure  $P$  is given, as shown in (10.68), by

$$P = \frac{2}{3} \frac{U}{V} = \frac{Nh^2}{5Vm} \left\{ \frac{3N}{4\pi V(2s+1)} \right\}^{\frac{2}{3}} + \frac{Nm\pi^2k^2}{3h^2V} \left\{ \frac{4\pi V(2s+1)}{3N} \right\}^{\frac{2}{3}} T^2 + \dots \tag{10.116}$$

We see from (10.115) and (10.116) that an extremely degenerate Fermi-Dirac gas would have a residual *zero-point* energy and pressure even at the absolute zero of temperature.

The specific heat (at constant volume) of an extremely degenerate Fermi-Dirac gas at low temperatures would be, from (10.115),

$$C_v = \left( \frac{dU}{dT} \right)_V = \frac{Nm\pi^2k^2}{h^2} \left\{ \frac{4\pi V(2s+1)}{3N} \right\}^{\frac{2}{3}} T. \tag{10.117}$$

Evidently,  $C_v$  would be small for large density ( $N/V$ ) and small particle mass ( $m$ ), i.e., for an extremely degenerate gas.

**(c) Alternative Derivation of Zero-point Energy and Pressure\***— We can also derive independently the expressions for the zero-point (sometimes also called null-point) energy and pressure. For this purpose, it should be noted that under the condition of extreme degeneration there would be a great tendency for most of the gas particles to accumulate in the cells or states of the lowest energy, each particle filling one such cell or state (because no two Fermi-Dirac particles can occupy the same cell or state). Now, the reason\*\* for this tendency can be seen from the law :

$$N_k = \frac{g_k}{e^{\alpha+\beta\epsilon_k} + 1}, \tag{10.118}$$

connecting the number of particles  $N_k$  in the energy range between  $\epsilon_k$  and  $\epsilon_k + \Delta\epsilon_k$  with the number of cells or states  $g_k$  in that range. Under the condition of extreme degeneration, i.e.,  $\alpha$  large and negative (i.e.,  $(-\alpha) \gg 1$ ,  $e^{\alpha+\beta\epsilon_k} \ll 1$  for very low values of  $\epsilon_k$  so that from (10.118),

$$N_k \approx g_k. \tag{10.119}$$

But under the same condition  $e^{\alpha+\beta\epsilon_k}$  is not negligible compared to 1 for high values of  $\epsilon_k$  so that from (10.118)

$$N_k < g_k. \tag{10.120}$$

This leads to the conclusion that the gas particles, under the condition of extreme degeneration, have got a *tendency* to occupy all the low energy states. So, since the total energy of the system

\*Landau, L.D., and Lifshitz, E.M., *loc. cit.*, Pp. 160-1.

\*\*Tolman, R. C., *loc. cit.*, P. 393.

must have the smallest possible value at absolute zero, the gas particles will, as a result of this tendency, occupy all cells or states from zero energy up to some energy  $\epsilon_0$  high enough to include the total number of particles of the system. We shall call this energy  $\epsilon_0$  the limiting energy at absolute zero and shall denote the corresponding limiting momentum by  $p_0$ .

Now, since the number of cells or states in the momentum range between  $p$  and  $p + dp$  is, from (10.7),

$$\frac{4\pi(2s+1)V}{h^3} p^2 dp, \quad (10.121)$$

the total number of particles filling all cells or states with momenta between 0 and  $p_0$  is

$$N = \frac{4\pi(2s+1)V}{h^3} \int_0^{p_0} p^2 dp = \frac{4\pi(2s+1)Vp_0^3}{3h^3} \quad (10.122)$$

so that  $p_0 = \left( \frac{3N}{4\pi(2s+1)V} \right)^{\frac{1}{3}} h.$  (10.123)

Hence, the limiting energy is

$$\epsilon_0 = \frac{p_0^2}{2m} = \frac{h^2}{2m} \left( \frac{3N}{4\pi(2s+1)V} \right)^{\frac{2}{3}}. \quad (10.124)$$

The total energy of the gas at absolute zero (i.e., zero-point energy) is obtained on multiplying by  $p^2/2m (= \epsilon)$  the number of cells or states given by (10.121) and then integrating over all momenta from 0 to  $p_0$ :

$$\begin{aligned} U_0 &= \int_0^{\epsilon_0} \epsilon dN = \int_0^{p_0} \frac{p^2}{2m} \left\{ \frac{4\pi(2s+1)V}{h^3} p^2 dp \right\} = \frac{4\pi(2s+1)Vp_0^5}{10mh^3} \\ &= \frac{3Nh^2}{10m} \left\{ \frac{3N}{4\pi(2s+1)V} \right\}^{\frac{2}{3}}. \quad [\text{from (10.123)}] \end{aligned} \quad (10.125)$$

The zero-point pressure  $P_0$  is

$$P_0 = \frac{2}{3} \frac{U_0}{V} = \frac{Nh^2}{5Vm} \left\{ \frac{3N}{4\pi(2s+1)V} \right\}^{\frac{2}{3}} \quad (10.126)$$

The situation at 0 K is shown by the continuous sharp-cornered line  $ABC$  (Fig. 10.2), since all the cells or states are occupied by the particles from zero energy up to the limiting energy  $\epsilon_0$  called *Fermi energy* at this temperature. The situation at any other (higher) temperature is shown by the curve  $ADE$ . As the temperature rises from 0 K, the particles of the lower energy states (i.e., states deep below  $\epsilon_0$ ) cannot be raised to the adjoining higher energy states which are already occupied. Only the particles in the states near about  $\epsilon_0$  can be raised in the sharp, corner at  $B$  to be rounded off and we obtain the curve  $ADE^*$ .

**(d) Electron Gas in Metals :** The concept of electron gas in metals has been introduced in sections 2.21 and 2.22 and, with the help of this concept, the high thermal and electrical

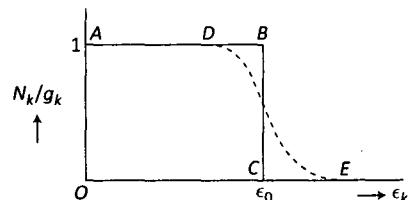


Fig. 10.2: Fermi particles at 0 K

\*Tolman, R.C., loc. cit., P. 393; Born, M., loc. cit., P. 285.

conductivities exhibited by metals and also the Wiedemann-Franz law have been explained there. In fact, we regard the outer valence electrons of the atom of a metal as behaving in first approximation as a *free electron gas* because, to a first approximation, we may neglect the repulsive forces between them owing to the neutralising effect of the positive ions (which are formed after the electrons have left the atoms). However, the classical theory faced difficulty in regard to the explanation of specific heats of metals. To appreciate the difficulty, let us take a gram-atom of a metal containing  $N$  (Avogadro number) atoms. The total energy of vibration of these atoms (i.e., ions) is  $N \times (6 \times \frac{1}{2}kT) = 3RT$ . Assuming that every atom (i.e., ion) contributes one free electron, there are  $N$  free electrons moving about in the metal. The total translational energy of the electron gas is  $N \times (3 \times \frac{1}{2}RT) = 3/2RT$ . Hence, the total energy of the gram-atom is  $(3 + 3/2)RT$  so that  $C_v$  is  $(3 + 3/2)R \approx 9$  cal. But the experimental value, according to the Dulong-Petit law, is 6 cal at ordinary and high temperatures.

The solution of this difficulty is due to Pauli and Sommerfeld (1927) who pointed out that electrons, being subject to Pauli's principle, should be regarded as a Fermi-Dirac gas. To appreciate the importance of this point of view, let us calculate  $D$  and  $\alpha$  for electron gas in a metal, say, silver at ordinary temperature. Assuming that each atom contributes one free electron, there are  $5.9 \times 10^{22}$  electrons per cc. This is  $N/V$ . With  $h = 6.5 \times 10^{-27}$  erg · sec,  $m = 9.0 \times 10^{-28}$  gm,  $k = 1.4 \times 10^{-16}$  erg/K,  $s = \frac{1}{2}$  (for electrons) and  $T = 300$  K, we have, from (10.87),

$$\frac{1}{D} = 2.2 \times 10^3 \quad (10.127)$$

so that  $\alpha = -205$ . (10.128)

Thus, we find that the conduction electrons of a metal must be regarded as a Fermi-Dirac gas in a condition of extreme degeneration.

Now, since the electron gas in metals is an extremely degenerate Fermi-Dirac gas, we can explain why there is negligible contribution by the electron gas to the total specific heat of a metal. According to the last paragraph of the above subsection (c), most of the electrons are unaffected as the temperature rises from 0 K only the electrons in the states near about the limiting energy  $\epsilon_0$  can be raised to the higher energy states. Thus, for not too high temperatures only a vanishingly small fraction of the electrons takes part in the thermal agitation due to the rise of temperature so that the specific heat of electron gas is very small. From (10.117), we find for silver at  $T = 300$  K,

$$C_v \approx 0.046 \text{ cal.} \quad (10.129)$$

But according to classical theory, it should be as large as 3 cal. It is only when high temperatures (say, of the order of  $10^4$  degrees centigrade) are reached that the tight packing of the deeper low-energy states gets loosened gradually and a noticeable contribution by the electron gas to the specific heat of metals is obtained.

**(e) Pauli's Theory of Paramagnetism of Alkali Metals :** The Fermi-Dirac theory also clears up another difficulty faced by the classical theory. Since electrons have magnetic moment it is evident that, according to the classical theory, all the electrons of the free electron gas should orient themselves in the direction of an applied magnetic field and should, therefore, make all metals highly paramagnetic in character. But this is contrary to experience. Pauli\* has, however, brilliantly treated the magnetic properties of alkali metals on the Fermi-Dirac idea that only a small fraction of the electron gas in the *boundary states* (i.e., in the states near

\*Pauli, W., *Zeit. f. Phys.*, **41**, P. 81 (1927).

about the limiting energy  $\epsilon_0$ ) can take part in orientation in an applied magnetic field, because it is only this small number of electrons which possess the advantage of occupying the adjoining unoccupied states of nearly the same energy after orientation in the field.

We shall briefly discuss here Pauli's treatment on the paramagnetism of an alkali metal\*\*. Let us suppose that in the presence of an *extremely weak* magnetic field  $H$ , providing a reference direction, the energy distribution of electron gas in the metal is given by the curve  $ABC$  in Fig. 10.2. The limiting energy  $\epsilon_0$  in this case is, from (10.124),

$$\epsilon_0 = \frac{\hbar^2}{2m} \left\{ \frac{3}{4\pi V} \left( \frac{N}{2} \right) \right\}^{\frac{2}{3}}, \quad (10.130)$$

where  $s = \frac{1}{2}$  for an electron. Since  $2s + 1$  is equal to 2 for an electron, it is evident from section 10.1 that there are two cells or states in the generalised phase space corresponding to the two orientations—parallel ( $+\frac{1}{2}$ ) and anti-parallel ( $-\frac{1}{2}$ ) to the reference field  $H$ —of the electron for the same energy value. It is, therefore, clear that since the metal is ordinarily in an unmagnetised condition, of the  $N$  electrons filling the  $N$  cells or states between zero energy and the limiting energy  $\epsilon_0$ ,  $N/2$  electrons occupy the parallel spin states or cells between zero energy and  $\epsilon_0$  while the other  $N/2$  electrons occupy the anti-parallel spin states or cells between these energy limits. This is schematically shown in Fig. 10.3(a). The upper row consists of cells  $C_1^A, C_2^A, \dots$  representing anti-parallel spin states filled up to the cell  $C_{N/2}^A$  (with energy  $\epsilon_0$ ) and the lower row consists of cells  $C_1^P, C_2^P, \dots$  representing parallel spin-states filled up to the cell  $C_{N/2}^P$  (with energy  $\epsilon_0$ ).

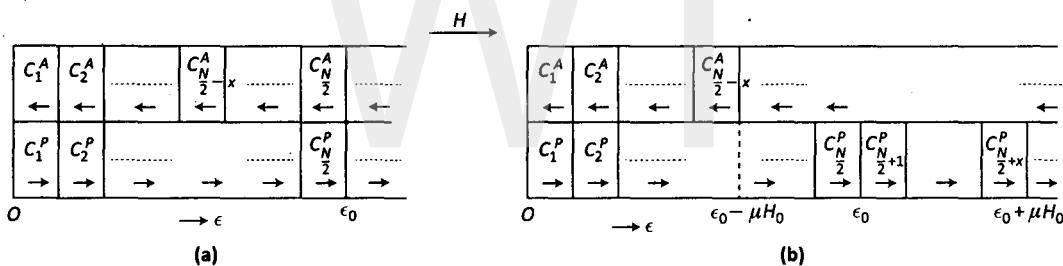


Fig. 10.3: Orientation of electrons in a magnetic field

Now, as the magnetic field  $H$  is slowly strengthened, first the electron occupying the cell  $C_{N/2}^A$  reverses its spin direction and goes from its anti-parallel spin state to a parallel spin state gaining, as a result kinetic energy at the cost of its magnetic potential energy. Since there is no parallel spin state in the upper row, this electron experiences a transition from the cell  $C_{N/2}^A$  to the cell  $C_{N/2+1}^P$  which is just to the right of the cell  $C_{N/2}^P$  and which possesses energy just higher than  $\epsilon_0$  [Fig. 10.3(b)]. With further enhancement of the magnetic field, the electron occupying the cell  $C_{N/2-1}^A$  in the upper row reverses its spin direction and undergoes transition to the cell  $C_{N/2+2}^P$  in the lower row with more kinetic energy than that gained by the first electron. This process continues with electrons coming from lower and still lower energy states of the upper row and occupying higher and still higher energy states in the lower row with the increasing strength of the magnetic field. Finally, by the time the field strength is raised to  $H_0$ , a total number of  $x$  electrons are transferred from the upper row to the lower row. The last electron, in this process, goes from the cell  $C_{N/2-x+1}^A$  of the upper row to the cell  $C_{N/2+x}^A$  of the lower row gaining kinetic energy at the cost of its magnetic potential energy  $= (+\mu h_0) - (-\mu H_0) = 2\mu H_0$ ,

\*\*See also Kompaneets, A. S., *Theoretical Physics*, P. 483 (1961).

$\mu$  being the magnetic moment of an electron (since the magnetic potential energy of the electron with spin antiparallel to  $H_0$  is  $+\mu H_0$  and, with spin parallel to  $H_0$ , is changed to  $-\mu H_0$ ).

Thus, there remain  $\frac{N}{2} - x$  electrons with spins anti-parallel to the field, while  $\frac{N}{2} + x$  have spins parallel to the field. It is evident that the limiting energy of the  $\frac{N}{2} - x$  electrons of the upper row is not given by (10.130) now but by

$$\epsilon_0 - \mu H_0 = \frac{h^2}{2m} \left\{ \frac{3}{4\pi V} \left( \frac{N}{2} - x \right) \right\}^{\frac{2}{3}} \quad (10.131)$$

and also the limiting energy of the  $\frac{N}{2} + x$  electrons of the lower row is given not by (10.130) but by

$$\epsilon_0 + \mu H_0 = \frac{h^2}{2m} \left\{ \frac{3}{4\pi V} \left( \frac{N}{2} + x \right) \right\}^{\frac{2}{3}}. \quad (10.132)$$

Since  $x$  is  $\ll \frac{N}{2}$  according to Fermi-Dirac statistics, we have, by binomial expansion,

$$\left( \frac{N}{2} \pm x \right)^{\frac{2}{3}} = \left( \frac{N}{2} \right)^{\frac{2}{3}} \pm \left( \frac{N}{2} \right)^{\frac{2}{3}} \frac{4x}{3N}. \quad (10.133)$$

Hence, subtracting (10.131) from (10.132) and using (10.133),

$$2\mu H_0 = \frac{h^2}{2m} \left( \frac{3}{4\pi V} \right)^{\frac{2}{3}} 2 \left( \frac{N}{2} \right)^{\frac{2}{3}} \frac{4x}{3N} \quad \text{or, } x = \mu H_0 \frac{6 \text{ Nm}}{h^2} \left( \frac{\pi V}{3N} \right)^{\frac{2}{3}}, \quad (10.134)$$

It is evident from Fig. 10.3(b) that the total magnetic moment of the metal will be due to the  $2x$  electrons in the lower row which have got their magnetic moments unbalanced. Hence, the total magnetic moment of the metal is, from (10.134),

$$M = 2x \cdot \mu = 12\mu^2 H_0 \frac{6 \text{ Nm}}{h^2} \left( \frac{\pi V}{3N} \right)^{2/3}. \quad (10.135)$$

Thus, the volume susceptibility is

$$\chi_V = \left( \frac{M}{V} \right) / H_0 = 12\mu^2 \left( \frac{\pi}{3} \right)^{\frac{2}{3}} \left( \frac{N}{V} \right)^{\frac{1}{3}} \frac{m}{h^2}. \quad (10.136)$$

Since  $\mu = \frac{eh}{4\pi mc}$ , we have from (10.136)

$$\chi_V = 2.209 \times 10^{-14} \times \left( \frac{N}{V} \right)^{\frac{1}{3}}. \quad (10.137)$$

Pauli assumed in the case of alkali metals that each atom contributes one free electron to the electron gas, i.e.,  $N$  is equal to the total number of atoms in the metallic sample. The theoretical values of  $\chi_V$ , for Na and K tallied well with the experimental values. This theory, together with necessary diamagnetic corrections, has been found to give a good account of the magnetic susceptibilities of the alkali metals.

(f) **Thermionic Emission :** We have already discussed thermionic emission in section 6.2. We propose to give here the theory of the phenomenon on the basis of Fermi-Dirac statistics. We already know that within a metal, electrons (i.e., electron gas) can move freely but their escape is prevented by a potential barrier,  $\epsilon^0$  (say)\*. At higher temperatures, however, it may

\*  $\epsilon^0$  is also called *work function* because an electron has to do work equal to  $\epsilon^0$  to be released from a metal surface.

so happen that the energy of an electron becomes greater than  $\epsilon^0$  so that it can escape from the metal. Now, in order to find the thermionic emission of electrons per unit area of a metal surface per second, we have to calculate the number of those electrons striking unit area of the metal surface per second which have got the kinetic energy of their motion normal to the metal surface sufficient to carry them outside. If we take a coordinate system such that the  $x$ -axis is normal to the metal surface, then this means that electrons with kinetic energy  $\frac{1}{2}mu^2 > \epsilon^0$  ( $u = x$ -component of electron velocity) only will be of interest to us in this discussion.

We obtain, from (10.6') (omitting the integrals over  $dp_x dp_y dp_z$ ) and from (10.32), the equation in differential form :

$$dN = \frac{(2s+1)V}{h^3} \frac{dp_x dp_y dp_z}{e^{\alpha e^{\epsilon/kT}} + 1}. \quad (10.138)$$

Here  $dN$  is the number of electrons in a metal of volume  $V$  having the momentum components between  $p_x$ , and  $p_x + dp_x$ ,  $p_y$  and  $p_y + dp_y$ ,  $p_z$  and  $p_z + dp_z$ . From (10.94), (10.111) and (10.124), we find that the approximate value of  $\alpha$  is (since  $s = \frac{1}{2}$  for an electron)

$$\alpha \approx -\frac{\epsilon_0}{kT}. \quad (10.139)$$

Hence, from (10.138) and (10.139),

$$dn = \frac{dN}{V} = \frac{2m^3}{h^3} \frac{dudv dw}{e^{(\epsilon-\epsilon_0)/kT} + 1} \quad (10.140)$$

with  $s = \frac{1}{2}$  for an electron and  $dp_x = mdu$ ,  $dp_y = mdv$  and  $dp_z = mdw$ . Now, integrating (10.140) for all values of  $v$  and  $w$ , we obtain the number of electrons per unit volume having  $x$ -component of velocity between  $u$  and  $u + du$  :

$$dn_x = \frac{2m^3}{h^3} du \int_{-\infty}^{+\infty} \int_{-\infty}^{\infty} \frac{dv dw}{e^{(\epsilon-\epsilon_0)/kT} + 1}. \quad (10.141)$$

If we multiply  $dn_x$  by  $u$ , we obtain the number of electrons hitting unit area of the metal surface per second (since  $x$ -axis is normal to the metal surface) with the  $x$ -component of velocity,  $u$  :

$$udn_x = \frac{2m^3}{h^3} u du \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dv dw}{e^{(\epsilon-\epsilon_0)/kT} + 1}. \quad (10.142)$$

To obtain the number of electrons escaping from unit area of the metal surface per unit time, we shall have to integrate (10.142) over  $u$  from  $\sqrt{2\epsilon^0/m}$  (since an electron must have kinetic energy  $\frac{1}{2}mu^2 > \epsilon^0$  to escape) to  $\infty$ . Thus this number is

$$\nu = \int u ddn_x = \frac{2m^3}{h^3} \int_{\sqrt{\frac{2\epsilon^0}{m}}}^{\infty} u du \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dv dw}{e^{(\epsilon-\epsilon_0)/kT} + 1} \quad (10.143)$$

Finally, multiplying (10.143) by  $e$  (electronic charge), we obtain the thermionic (emission) current :

$$i = \frac{2m^3 e}{h^3} \int_{\sqrt{\frac{2\epsilon^0}{m}}}^{\infty} u du \int_{-\infty}^{\infty} \frac{du dw}{e^{(\epsilon-\epsilon_0)/kT} + 1}. \quad (10.144)$$

Now, in the heated metal ( $\epsilon^0 - \epsilon_0$ ) is always very large compared with  $kT$ ,  $\epsilon^0 - \epsilon_0$  amounting to several electron-volts (1 electron-volt =  $1.6 \times 10^{-12}$  erg) but  $kT$  at 300 K (say) being only about 0.03 electron-volt. Hence, we have always  $e^{(\epsilon-\epsilon_0)/kT} \gg 1$  in the integrand so that we

may neglect +1 in the denominator. Thus, (10.136) gives (since  $\epsilon = \frac{1}{2}m(u^2 + v^2 + w^2)$ ),

$$\begin{aligned} i &= \frac{2m^3 e}{h^3} e^{\epsilon_0/kT} \int_{\sqrt{\frac{2\epsilon_0}{m}}}^{\infty} e^{-\frac{1}{2}mu^2/kT} u du \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv^2/kT} dv \int_{-\infty}^{\infty} e^{-\frac{1}{2}mw^2/kT} dw \\ &= \frac{2m^3 e}{h^3} e^{\epsilon_0/kT} \cdot \frac{kT}{m} e^{-\epsilon_0/kT} \cdot \sqrt{\frac{2\pi kT}{m}} \cdot \sqrt{\frac{2\pi kT}{m}} \quad [\text{See Appendix 1}] \\ &= \frac{4\pi m e k^2 T^2}{h^3} e^{-(\epsilon_0 - \epsilon_0)/kT}. \end{aligned} \quad (10.145)$$

This is of the same form as Richardson's equation (6.17) derived in section 6.2.

If the constant  $4\pi m e k^2/h^3$  is evaluated it is found to be  $120 \text{amp cm}^{-2} \text{deg}^{-2}$ . But, according to experimental observation in a number of reliable cases, the constant should have the value  $60 \text{amp} \cdot \text{cm}^{-2} \text{deg}^{-2}$  approximately. Several explanations have been proposed to account for this discrepancy\*. According to one of these several explanations, it is possible that some of the electrons are reflected at the surface although they may have sufficient energy to escape. This means that (145) should be multiplied by a *transmission coefficient* of about 0.5 to fit in with the experimental observation. But quantum-mechanical calculations indicate that we can have theoretically a transmission coefficient very nearly equal to 1. According to another explanation, the quantity  $(\epsilon^0 - \epsilon_0)$  is not independent of temperature. Such a temperature variation, if not taken into account, would affect the value of the constant.

**Exercise 1 :** Find the number of collisions per second with a wall for an extremely degenerate Fermi-Dirac gas at absolute zero.

**Solution :** Since, at absolute zero, all the cells or states with momenta between 0 and  $p_0$  are filled by particles, the number of particles in the system with momentum components between  $p_x$  and  $p_x + dp_x$ ,  $p_y$  and  $p_y + dp_y$ ,  $p_z$  and  $p_z + dp_z$  is, from (10.6') (omitting integrals over  $dp_x dp_y dp_z$ ),

$$dN = \frac{(2s+1)V}{h^3} dp_x dp_y dp_z \quad \text{or,} \quad dn = \frac{dN}{V} = \frac{(2s+1)}{h^3} p^2 dp \sin \theta d\theta d\phi \quad (10.146)$$

in terms of spherical polar coordinates  $p, \theta, \phi$ , the pole being normal to the wall. The required number of collisions per unit area of the wall per second is obtained by multiplying (10.146) by  $c \cos \theta$  ( $c$  = particle velocity =  $p/m$ ) and integrating over  $\theta$  from 0 to  $\pi/2$ , over  $\phi$  from 0 to  $2\pi$ , and over  $p$  from 0 to  $p_0$ . This is

$$\begin{aligned} &= \frac{(2s+1)}{mh^3} \int_{0(\phi)}^{2\pi} \int_{0(\theta)}^{\pi/2} \int_0^{p_0} p^3 dp \sin \theta \cos \theta d\theta d\phi = \frac{(2s+1)\pi p_0^4}{4mh^3} \\ &= \frac{3hN}{16mV} \left\{ \frac{3N}{4\pi(2s+1)V} \right\}^{\frac{1}{3}}, \quad \text{from (10.123).} \end{aligned} \quad (10.147)$$

**Exercise 2 :** Find the total energy possessed by an extreme relativistic completely degenerate Fermi-Dirac gas at absolute zero.

**Solution :** In this case, the energy of the particles is large compared with  $mc^2$  ( $m$  = rest-mass and  $c$  = velocity of light) so that, in this limit, as is well known,

$$\epsilon = cp. \quad (10.148)$$

\*Mayer, J. E. and Mayer, M. G., *Statistical Mechanics*, P. 393 (1940), or, Glasstone, S., *loc. cit.*, P. 339.

Then, the limiting energy is

$$\epsilon_0 = cp_0 = hc \left\{ \frac{3N}{4\pi(2s+1)V} \right\}^{\frac{1}{3}}, \text{ from (10.123).} \quad (10.149)$$

Hence, the total energy is [See (10.125)]

$$\begin{aligned} U_0 &= \int_0^{\epsilon_0} \epsilon dN = \frac{4\pi(2s+1)Vc}{h^3} \int_0^{p_0} p^3 dp \quad [\text{from (10.121) and (10.140)}] \\ &= \frac{\pi(2s+1)Vcp_0^4}{h^3} = \frac{3Nch}{4} \left\{ \frac{3N}{4\pi(2s+1)V} \right\}^{\frac{1}{3}}. \quad [\text{from (10.123)}] \end{aligned} \quad (10.150)$$

## PROBLEMS

1. Derive entropy (S), free energy (F) and Gibbs' potential (G) in Bose-Einstein and Fermi-Dirac statistics.
2. Find the entropy of a degenerate electron gas.
3. Find the entropy of a degenerate extreme relativistic electron gas. [Lindau & Lifshitz]



## Chapter 11

# Statistical Thermodynamics

### 11.1 Quantum Statistical Definition of Entropy

Statistical thermodynamics deals with the correlation between statistics and thermodynamics. The most convenient approach to the problem is through the concept of entropy. This has, in fact, been initiated already in section 5.21. But, for the purpose of relating thermodynamics to quantum statistics, it is *more satisfactory* to define the entropy of a system in terms of  $G$ , the number of microstates corresponding to a macrostate\* :

$$S = \gamma \log_e G, \quad (11.1)$$

where  $\gamma$  is a constant having the dimensions of energy per degree. Evidently, since  $G$  is a pure number,  $S$  has the dimensions of energy per degree, i.e., of entropy. It will be shown in the following section that by a suitable choice of the value of  $\gamma$ , we can indeed make  $S$  exactly identical with entropy.

If we have two independent systems with  $G_1$ ,  $G_2$  as the numbers of microstates corresponding to their respective macrostates, then the number of microstates for the two systems considered together (but not combined or added together) is

$$G_{12} = G_1 \times G_2 \quad (11.2)$$

and the entropy of the two systems considered together is

$$S_{12} = S_1 + S_2. \quad (11.3)$$

Now, from (11.1) and (11.2), we find

$$S_{12} = \gamma \log_e G_{12} = \gamma \log_e G_1 + \gamma \log_e G_2 = S_1 + S_2 \quad (11.4)$$

so that (11.3) which is a property of entropy, is immediately satisfied.

It should be pointed out that the definition of entropy given by (11.1) is not satisfactory in classical statistics. It has been seen in the preceding chapter that  $G$  involves  $g_k$  which is the number of cells—each of volume  $h^r$ —in a certain energy range in the (generalised) phase space. In classical statistics,  $h$  is absent so that the volume of a phase cell is indeterminate, i.e., can have any arbitrary value. Thus,  $g_k$  and hence  $G$  also become arbitrary. This makes  $S$ , defined by (11.1), quite indefinite and arbitrary in classical statistics.

### 11.2 Choice of $\gamma$ and Identification of $S$

For ordinary gases  $D$ , i.e.,  $e^\alpha$  [approximately given by (10.87) of the last chapter] is large compared with unity so that 1 in the denominators of Bose-Einstein law (10.31) and Fermi-Dirac law (10.32) of the preceding chapter may be dropped. In that case, for both the statistics, from (10.13) and (10.16) of the last chapter,

$$\log_e G = \sum_k (N_k \log_e g_k - N_k \log_e N_k + N_k). \quad (11.5)$$

\*Fermi, E., *Thermodynamics*, P. 141 (1938); Glasstone, S., *loc. cit.*, P. 348; Landau, L. D. and Lifshitz, E. M., *loc. cit.*, P. 22.

on using first Stirling's approximation to (10.13) and (10.16) of the preceding chapter and then the condition  $g_k/N_k \gg 1$ . This can be seen easily as follows. From (10.13) of the preceding chapter using Stirling's approximation,

$$\begin{aligned}\log_e G &= \sum_k \{(N_k + g_k) \log_e(N_k + g_k) - N_k \log_e N_k - g_k \log_e g_k\} \\ &= \sum_k \left\{ N_k \log_e \left( 1 + \frac{g_k}{N_k} \right) + g_k \log_e \left( 1 + \frac{N_k}{g_k} \right) \right\} \\ &= \sum_k \left\{ N_k \log_e \left( \frac{g_k}{N_k} \right) + g_k \left( \frac{N_k}{g_k} \right) \right\},\end{aligned}$$

since  $g_k/N_k \gg 1$ . This can be written in the form :

$$\log_e G = \sum_k (N_k \log_e g_k - N_k \log_e N_k + N_k). \quad (11.6)$$

This is the same as (11.5). Now, from (10.16) of the preceding chapter, using Stirling's approximation

$$\begin{aligned}\log_e G &= \sum_k \{(N_k - g_k) \log_e(g_k - N_k) - N_k \log_e N_k + g_k \log_e g_k\} \\ &= \sum_k \left\{ N_k \log_e \left( \frac{g_k}{N_k} - 1 \right) - g_k \log_e \left( 1 - \frac{N_k}{g_k} \right) \right\} \\ &= \sum_k \left\{ N_k \log_e \left( \frac{g_k}{N_k} \right) - g_k \left( -\frac{N_k}{g_k} \right) \right\},\end{aligned}$$

since  $g_k/N_k \gg 1$ . This can be put in the form :

$$\log_e G = \sum_k (N_k \log_e g_k - N_k \log_e N_k + N_k). \quad (11.7)$$

This is the same as (11.5).

Under this condition, as stated above, (10.31) and (10.32) of the preceding chapter give

$$N_k = \frac{g_k}{e^{\alpha+\beta\epsilon_k}} \quad (11.8)$$

so that  $\log_e g_k = \log_e N_k + (\alpha + \beta\epsilon_k)$ . (11.9)

Hence, from (11.1), (11.5) and (11.9),

$$S = \sum_k \gamma N_k (\alpha + \beta\epsilon_k + 1) = \gamma N \alpha + \gamma \beta U + \gamma N, \quad (11.10)$$

since  $\sum_k N_k = N$  and  $\sum_k N_k \epsilon_k = U$ .

Now, for definiteness, let us consider a monatomic perfect gas. Now, since  $\beta$  is  $1/kT$  and  $U$  is  $\frac{3}{2}NkT$  in both the statistics for such a gas under the condition  $D \gg 1$  [See (10.84) and (10.101) of the preceding chapter], we have

$$\beta = \frac{3N}{2U}. \quad (11.11)$$

Then, from (11.10) and (11.11),

$$S = \gamma N \alpha + \frac{5}{2} \gamma N. \quad (11.12)$$

From (10.87) of the last chapter putting  $\frac{1}{\beta}$  in place of  $kT$ , we have

$$e^\alpha = D = \frac{(2s+1)}{Nh^3} \left( \frac{2\pi m}{\beta} \right)^{3/2} V = \frac{(2s+1)}{Nh^3} \left( \frac{4\pi m U}{3N} \right)^{3/2} V, \quad [\text{from (11.11)}] \quad (11.13)$$

Taking logarithms of both sides of (11.13),

$$\alpha = \log_e \left\{ \frac{(2s+1)}{Nh^3} \left( \frac{4\pi m U}{3N} \right)^{3/2} V \right\}. \quad (11.14)$$

Thus (11.12) and (11.14) give

$$S = \gamma N \log_e \left\{ \frac{(2s+1)}{Nh^3} \left( \frac{4\pi m U}{3N} \right)^{3/2} V \right\} + \frac{5}{2} \gamma N. \quad (11.15)$$

Now, from (11.15) we obtain

$$\left( \frac{dS}{dU} \right)_V = \frac{3\gamma N}{2U} \quad \text{and} \quad \left( \frac{dS}{dV} \right)_U = \frac{\gamma N}{V}. \quad (11.16)$$

But, we already know from thermodynamics [See (6.37) of section 6.6] that the change of entropy of the system is given by

$$dS = \frac{1}{T} dU + \frac{P}{T} dV. \quad (11.17)$$

From this equation, we find easily

$$\left( \frac{dS}{dU} \right)_V = \frac{1}{T} = \frac{k}{kT} = \frac{3Nk}{2U} \quad (11.18)$$

and  $\left( \frac{dS}{dV} \right)_U = \frac{P}{T} = \frac{Nk}{V}$ . (11.19)

Now, comparing (11.16) with (11.18) and (11.19), we find that  $S$  given by (11.1) will be identical with entropy represented by (11.17) if  $\gamma$  is taken as the same as  $k$ . So if we write (11.1) in the form :

$$S = k \log G, \quad (11.20)$$

then this  $S$  will represent the entropy of the system. (11.20), therefore, gives the *quantum statistical definition of entropy* and provides a very significant approach to thermodynamics from statistics.

### 11.3 Sackur-Tetrode Equation

Taking  $\gamma = k$ , we have, from (11.15), the entropy of a gram-molecule of a monatomic gas :

$$\begin{aligned} S &= kN \log_e \left\{ \frac{(2s+1)}{Nh^3} \left( \frac{4\pi m U}{3N} \right)^{3/2} V \right\} + \frac{5}{2} kN \\ &= R \log_e \left\{ \frac{2s+1}{Nh^3} \left( \frac{4\pi m U}{3N} \right)^{3/2} V \right\} + \frac{5}{2} R \end{aligned}$$

$$= R \log_e \left\{ \frac{(2s+1)V}{Nh^3} (2\pi mkT)^{3/2} \right\} + \frac{5}{2}R, \quad (11.21)$$

since  $U = \frac{3}{2}RT = \frac{3}{2}kNT$ .

(11.21) is a form of the Sackur-Tetrode equation\* for the entropy of a gram-molecule of a monatomic gas. Since we have neglected gas degeneration in all calculations above, we may put  $PV = RT$  so that (11.21) gives

$$S = R \log_e \left\{ \frac{(2s+1)}{Nh^3} (2\pi mkT)^{3/2} \frac{RT}{P} \right\} + \frac{5}{2}R. \quad (11.22)$$

Gibbs' function for the monatomic gas is given by

$$\begin{aligned} G &= U + PV - TS = \frac{3}{2}RT + RT - TS = \frac{5}{2}RT - TS \\ &= -RT \log_e \left\{ \frac{(2s+1)}{Nh^3} (2\pi mkT)^{3/2} \cdot \frac{RT}{P} \right\}. \quad [\text{from (11.22)}] \end{aligned} \quad (11.23)$$

The free (or available) energy function for the gas is given by

$$F = U - TS \quad (11.24)$$

$$\begin{aligned} &= G - PV = G - RT \\ &= -RT \log_e \left\{ \frac{(2s+1)}{Nh^3} (2\pi mkT)^{3/2} \cdot \frac{RT}{P} \right\} - RT. \quad [\text{from (11.23)}] \end{aligned} \quad (11.25)$$

We shall now make use of the ideas of this section for some problems in the following sections.

**Exercise :** Calculate the entropy of a gram-molecule of (monatomic) mercury vapour. The boiling point of mercury is 630 K at normal atmospheric pressure.

**Hints :** Use Sackur-Tetrode equation (11.22) with  $h = 6.55 \times 10^{-27}$  C.G.S. unit,  $N = 6.03 \times 10^{23}$  and  $m = 200.6$  atomic mass units and  $s = 0$ . **[Ans.  $191 \times 10^7$  C.G.S. unit]**

## 11.4 Electron Vapour in Metal Cavity

We shall obtain here an expression\*\* for the density of electron vapour in equilibrium with a hot metal cavity. Since the density of electrons in the vapour state is very small, the system will approach classical behaviour [See (10.87) of the last chapter] so that we can justifiably apply here the expressions for thermodynamical functions of the preceding section.

Let  $\nu$  be the number of gram-molecules of electron gas inside the cavity of volume  $V$ . The total energy of the whole gas is

$$U = \nu \left( W_0 + \frac{3}{2}RT \right), \quad (11.26)$$

where  $W_0$  is the potential energy of a gram-molecule of electron gas acquired in leaving the metal surface and  $\frac{3}{2}RT$  the kinetic energy of a gram-molecule of the gas in the cavity. Evidently  $W_0$  is the energy needed to extract one gram-molecule of electrons from the metal.

\*Sackur, *Ann. Physik.* **40**, P. 67 (1913); Tetrode, *ibid*, **38**, P. 434 (1912); **39**, P. 255 (1913).

\*\*Fermi, E., *Thermodynamics*, P. 154 (1938).

The free energy function of the whole gas is, from (11.21), (11.24) and (11.26),

$$\begin{aligned} F &= U - TS \\ &= \nu \left( W_0 + \frac{3}{2}RT \right) - \nu RT \left[ \log_e \left\{ \frac{(2s+1)}{Nh^3} (2\pi mkT)^{3/2} \frac{V}{\nu} \right\} + \frac{5}{2} \right] \\ &= \nu \left( W_0 + \frac{3}{2}RT \right) - \nu RT \left[ \log_e \left\{ \frac{2(2\pi mk)^{3/2}}{Nh^3} \frac{V}{\nu} \right\} + \frac{5}{2} \right], \end{aligned} \quad (11.27)$$

since  $s = \frac{1}{2}$  for an electron and  $\frac{V}{\nu}$  is, in the present case, the volume of a gram-molecule of electron vapour in the cavity.

Now, since for a system

$$dG = 0 \quad (11.28)$$

in equilibrium condition under constant temperature and pressure [See (6.40) of section 6.6], we have under this condition

$$dF = d(U - TS) = d(U + PV - TS) - d(PV) = dG - d(PV) = 0. \quad (11.29)$$

Then, under the equilibrium condition at constant temperature and pressure for the electron gas in the metal cavity, we find from (11.27) and (11.29)

$$dF = \left\{ \left( W_0 + \frac{3}{2}RT \right) - RT \left[ \log_e \left\{ \frac{2(2\pi mk)^{3/2}}{Nh^3} \right\} + \log_e V - \log_e \nu + \frac{5}{2} \right] + RT \right\} d\nu = 0. \quad (11.30)$$

Now, in the state of equilibrium as many electrons are emitted per unit time as are absorbed by the metal so that  $\nu$ , on the whole, remains fixed. In (11.30)  $d\nu$  means the number of gram-molecules emitted or absorbed in the equilibrium condition under which  $F$  remains constant. Then the coefficient of  $d\nu$  in (11.30) must be zero. Hence,

$$\begin{aligned} W_0 - RT \left[ \log_e \left\{ \frac{2(2\pi mkT)^{3/2}}{Nh^3} \right\} + \log_e \left( \frac{V}{\nu} \right) \right] &= 0, \quad \text{i.e.,} \quad \frac{\nu}{V} = \frac{2(2\pi mkT)^{3/2}}{Nh^3} e^{-W_0/RT} \\ \text{or,} \quad n &= \frac{N\nu}{V} = \frac{2(2\pi mkT)^{3/2}}{h^3} e^{-W_0/RT}. \end{aligned} \quad (11.31)$$

This gives the number of electrons per unit volume in the cavity, since  $N$  is the number of electrons in a gram-molecule of the gas.

Since we have in this case

$$PV = \nu RT, \quad (11.32)$$

we obtain from (11.31)

$$P = 2(2\pi mkT)^{3/2} kTe^{-W_0/RT} \quad (11.33)$$

as the pressure of the gas.

**Exercise :** Find the number of electrons hitting unit area of the metal surface per unit time under equilibrium condition and hence derive an expression for thermionic current.

**Hints :** Use (11.31) (given above) in (2.39) of section 2.6 and utilise (2.36) of the same section. The final expression for thermionic current is

$$i = \frac{4\pi mek^2 T^2}{h^3} e^{-W_0/RT}, \quad (11.34)$$

where  $e$  is the charge of an electron.

## 11.5 Saha's Theory of Thermal Ionization

We shall develop here M. N. Saha's theory of ionisation\* from Sackur-Tetrode equation (11.22)\*\*. This equation can be put in the form :

$$\log_e P = -\frac{S}{R} + \frac{5}{2} + \frac{5}{2} \log_e T + \log_e \left\{ \frac{(2s+1)(2\pi m)^{3/2} k^{5/2}}{h^3} \right\}. \quad (11.35)$$

At sufficiently high temperatures, collisions between gas particles may produce ionisation. When this *thermal ionisation* reaches the state of equilibrium, definite proportions of the total number of gas particles are in the different stages of ionisation, i.e., are singly ionised, doubly ionised, ... etc. The study of thermal ionisation of a monatomic gas is of the greatest interest since at the temperature of thermal ionisation chemical bonds between atoms of gas molecules are usually broken off completely.

We shall, however, consider here the thermal ionisation of a *monovalent* monatomic gas such as an alkali vapour. When this gas is heated to a very high temperature, some of the atoms get ionised, i.e., some of the atoms lose their valency electrons (a monovalent atom possesses just one valency electron) and are changed into ions. Denoting by  $A$ ,  $A^+$  and  $e$  an atom, an ion and an electron respectively, we have the following ionisation reaction :



When the state of equilibrium is reached, a definite proportion of the total number of atoms of the system is in the ionised state and the rest in the neutral state. Thus, the system contains definite proportions of neutral atoms, ions and electrons. In the equilibrium condition, however, ionisation of neutral atoms and recombination of ions and electrons continue to take place, but at an equal rate, so that the proportions of neutral atoms, ions and electrons in the system are unaffected. This process in equilibrium state may be represented by the reversible reaction



Considering the three kinds of particles (atoms, ions and electrons) in the system as three perfect monatomic gases, we obtain, from (11.35), the following expressions for their respective partial pressures :

$$\log_e P_a = -\frac{S_a}{R} + \frac{5}{2} + \frac{5}{2} \log_e T + \log_e \left\{ \frac{(2s_a+1)(2\pi m_a)^{3/2} k^{5/2}}{h^3} \right\} \quad (11.38)$$

$$\log_e P_i = -\frac{S_i}{R} + \frac{5}{2} + \frac{5}{2} \log_e T + \log_e \left\{ \frac{(2s_i+1)(2\pi m_i)^{3/2} k^{5/2}}{h^3} \right\} \quad (11.39)$$

$$\log_e P_e = -\frac{S_e}{R} + \frac{5}{2} + \frac{5}{2} \log_e T + \log_e \left\{ \frac{(2s_e+1)(2\pi m_e)^{3/2} k^{5/2}}{h^3} \right\} \quad (11.40)$$

where the subscripts  $a$ ,  $i$ ,  $e$  represent atoms, ions and electrons respectively. Now, adding (11.39) and (11.40) and subtracting (11.38) from the sum,

$$\log_e \frac{P_i P_e}{P_a} = -\frac{S_i + S_e - S_a}{R} + \frac{5}{2} + \frac{5}{2} \log_e T + \log_e \left\{ \frac{(2s_i+1)(2s_e+1)(2\pi m_e)^{3/2} k^{5/2}}{(2s_a+1)h^3} \right\}, \quad (11.41)$$

\*Saha, M. N., *Phil. Mag.* **40**, Pp. 472-88 (1920).

\*\*Zoos, G., *Theoretical Physics*, Pp. 630, 833 (1956).

where we have taken  $m_a$  and  $m_i$  to be equal. From (6.68) of section 6.8 we may put

$$(S_i + S_e) - S_a = \frac{W_0}{T}, \quad (11.42)$$

where  $W_0$  is the energy needed to ionise all the atoms in a gram-molecule of the neutral gas. Then, from (11.41) and (11.42),

$$\log_e \frac{P_i P_e}{P_a} = -\frac{W_0}{RT} + \frac{5}{2} + \frac{5}{2} \log_e T + \log_e \left\{ \frac{(2s_i + 1)(2s_e + 1)(2\pi m_e)^{3/2} k^{5/2}}{(2s_a + 1)h^3} \right\}. \quad (11.43)$$

Supposing that we had originally started with  $\nu$  gram-molecules of the neutral monatomic gas and had heated it in a confined space  $V$  up to a temperature  $T$  so that  $\alpha$  is the fraction ionised, we have

$$P_i V = \alpha \nu RT, \quad P_e V = \alpha \nu RT, \quad P_a V = (1 - \alpha) \nu RT. \quad (11.44)$$

Hence the total pressure  $P$  in the system at  $T$  is given by

$$PV = (P_a + P_i + P_e)V = (1 + \alpha)\nu RT \quad (11.45)$$

From (11.44) and (11.45),

$$P_i = P_e = \frac{\alpha}{1 + \alpha} P \quad \text{and} \quad P_a = \frac{1 - \alpha}{1 + \alpha} P. \quad (11.46)$$

Substituting for  $P_i$ ,  $P_e$  and  $P_a$  from (11.46) in (11.43),

$$\begin{aligned} \log_e \left( \frac{\alpha^2}{1 - \alpha^2} \right) P &= -\frac{W_0}{RT} + \frac{5}{2} + \frac{5}{2} \log_e T \\ &\quad + \log_e \left\{ \frac{(2s_i + 1)(2s_e + 1)(2\pi m_e)^{3/2} k^{5/2}}{(2s_a + 1)h^3} \right\} \end{aligned} \quad (11.47)$$

Expressing (11.47) in common logarithms,

$$\begin{aligned} \log_{10} \left( \frac{\alpha^2}{1 - \alpha^2} \right) P &= -\frac{W_0}{2.3RT} + \frac{5}{2 \times 2.3} + \frac{5}{2} \log_{10} T \\ &\quad + \log_{10} \left\{ \frac{(2s_i + 1)(2s_e + 1)(2\pi m_e)^{3/2} k^{5/2}}{(2s_a + 1)h^3} \right\}. \end{aligned} \quad (11.48)$$

If  $P$  is expressed in atmospheres and  $W_0$  in calories, (11.48) becomes

$$\begin{aligned} \log_{10} \left( \frac{\alpha^2}{1 - \alpha^2} \right) P &= -\frac{W_0}{2.3RT} + \frac{5}{2 \times 2.3} + \frac{5}{2} \log_{10} T \\ &\quad + \log_{10} \left\{ \frac{(2s_i + 1)(2s_e + 1)(2\pi m_e)^{3/2} k^{5/2}}{(2s_a + 1)h^3} \right\} - \log_{10}(1.013 \times 10^6), \end{aligned} \quad (11.49)$$

since  $1.013 \times 10^6$  is the value of one atmosphere in dynes. For an alkali vapour (e.g., Li, Na, K, Rb or Cs), we have  $s_i = 0$ ,  $s_a = \frac{1}{2}$  so that with  $s_e = \frac{1}{2}$  and putting the values of

$h (= 6.54 \times 10^{-21} \text{ ergs} \cdot \text{s})$ ,  $k (= 1.34 \times 10^{-16} \text{ erg} \cdot \text{K}^{-1})$  and  $m_e$  (mass of an electron), we obtain from (11.49)

$$\log_{10} \left( \frac{\alpha^2}{1 - \alpha^2} \right) P = -\frac{W_0}{2.3RT} + \frac{5}{2} \log_{10} T - 6.459. \quad (11.50)$$

This is the form in which Saha gave his original equation in 1919. (11.50) holds almost rigorously for alkali vapour, but has to be slightly modified\* for alkaline earth metals (e.g., Be, Mg, Ca, Sr or Ba).

Saha's theory opened up a new technique of investigations in a number of fields, viz., astrophysics dealing with the physics of stars and nebulae, electrical conductivity of flames, formation of electrical arcs, formation of the ionosphere, etc.

**Exercise 1.** Find the percentage of ionisation of Na-vapour at 6000 K and at  $10^{-4}$  atmos. The ionisation potential of Na is 5.11 volts.

**Solution :** Corresponding to an ionisation potential of 5.11 volts,  $W_0$  is  $5.11 \times 23040$  calories. Then, with  $R = 1.985 \text{ cal/deg}$ , we have from (11.50)

$$\log_{10} \left( \frac{\alpha^2}{1 - \alpha^2} \right) = 4 - \frac{5.11 \times 23040}{2.3 \times 985 \times 6000} + \frac{5}{2} \log_{10} 6000 - 6.549.$$

Now calculate  $\alpha$  and express it as a percentage.

**Exercise 2.** Calculate the degree of ionisation of Li-vapour at 4000 K at a pressure of 1 cm of mercury. The ionisation potential of Li is 5.37 volts.

## 11.6 Nernst's Theorem

Nernst's theorem states that the entropy of any body vanishes at absolute zero. We shall deduce this theorem here from quantum statistics on the basis of the concept of discrete quantum states\*\*.

The fact that the specific heat  $C_v$  of a body is positive means that the energy is a monotonically increasing function of temperature. Hence, as the temperature falls the energy decreases monotonically so that at the lowest possible temperature, i.e., at absolute zero, the body must be in the state of the lowest possible energy. Considering the energy of the body to be the sum of the energies of the parts into which we may imagine it to be divided, it is evident that for the sum of the energies of the different parts of the body to take the lowest possible value, the energy of each part must be at its lowest possible value.

So we find that any part of the body must be in the lowest quantum state—viz., the ground state—at absolute zero. This means that the probability of any part of the body being in the lowest quantum state at absolute zero is a certainty, i.e., is equal to unity. Thus, the probability of the whole body being in the lowest quantum state is also unity as it is equal to the product of the probabilities of the component parts. Hence, the entropy of the body which is according to quantum statistics, proportional to the logarithm of this probability (See sections 11.1 and 11.2) is zero at absolute zero. This is *Nernst's theorem* and is also called *the third law of thermodynamics*.

It should be pointed out that this theorem cannot be derived from classical statistics since in this statistics the entropy defined as the logarithm of probability of state does not possess any definite value because of arbitrariness in the volume of a phase cell (See end of section 11.1).

\*Saha and Srivastava, *A Treatise on Heat*, P. 815, (1958).

\*\*See Landau and Lifshitz, *Statistical Physics*, Pp. 66-8 (1961).

Now we shall make some deductions from Nernst's theorem. We have

$$C_v = T \left( \frac{dS}{dT} \right)_V = \left[ \frac{dS}{d(\log_e T)} \right]_V. \quad (11.51)$$

As  $T$  tends to zero,  $\log_e T$  tends to  $-\infty$ . But since  $S$  tends to a constant value (i.e., zero) at  $T \rightarrow 0$ . It is evident from (11.51) that  $C_v$  tends to zero at  $T \rightarrow 0$ . We can show in a similar manner also that  $C_p$  tends to zero at  $T \rightarrow 0$ .

Next we have Maxwell's relation (See section 6.6.)

$$\left( \frac{dS}{dP} \right)_T = - \left( \frac{dV}{dP} \right)_P. \quad (11.52)$$

Now, since  $S$  tends to a constant value (i.e., zero) at  $T \rightarrow 0$  under any arbitrary pressure  $P$ , the left-hand side of (11.52) vanishes. This means that  $(\frac{dV}{dP})_P$ , i.e., the coefficient of thermal expansion at  $T \rightarrow 0$  also vanishes. In a similar manner also we can see from Maxwell's relation (See section 6.6.)

$$\left( \frac{dS}{dV} \right)_T = \left( \frac{dP}{dT} \right)_V \quad (11.53)$$

that  $(\frac{dP}{dT})_V$  vanishes at  $T \rightarrow 0$ .

Entropy tends to zero at  $T \rightarrow 0$  following usually the law :

$$S = aT^n, \quad (11.54)$$

where  $a$  is a function of pressure or volume. Then, it is evident from (11.51), (11.52) and (11.53) that  $C_v$ ,  $C_p$ ,  $(\frac{dV}{dT})$  and  $(\frac{dP}{dT})$  should also tend to zero according to the same law (with the same power  $n$ )

Now, we have from thermodynamics (See section 6.9)

$$C_p - C_v = -T \left( \frac{dP}{dV} \right)_T \left( \frac{dV}{dT} \right)_P^2 = - \left( \frac{dP}{dV} \right)_T \left( \frac{da}{dP} \right)_T^2 T^{2n+1}, \quad (11.55)$$

from (11.52) and (11.54). Again, we have at  $T \rightarrow 0$

$$C_p = T \left( \frac{dS}{dT} \right)_P = naT^n. [\text{from (11.54)}] \quad (11.56)$$

Similarly, at  $T \rightarrow 0$

$$C_v = T \left( \frac{dS}{dT} \right)_V = naT^n. [\text{from (11.54)}] \quad (11.57)$$

Thus, we find that  $C_p - C_v$  tends to zero more rapidly than  $C_p$  or  $C_v$  (remembering the fact that  $(\frac{dP}{dT})_V$  in general remains finite at  $T \rightarrow 0$ ).

From  $C_p = T (\frac{dS}{dT})_P$ , we have

$$dS = \frac{C_p}{T} dT \quad (11.58)$$

so that since  $S$  is zero at absolute zero, we obtain

$$S = \int_0^T dS = \int_0^T \frac{C_p}{T} dT. \quad (11.59)$$

Thus, if the specific heat of a body is known over the whole range of temperature from 0 K to  $T$  K, the entropy at  $T$  can be calculated from (11.59).

**Exercise 1.** Show that Debye's theory of specific heats of solids leads to zero entropy for a body at absolute zero.

**Exercise 2.** Investigate if Born's and Raman's theories of specific heats of solids also agree with Nernst's theorem.

## 11.7 Vapour Pressure of a Monatomic Gas

We now consider the problem of calculating the vapour pressure for a monatomic substance. We know from thermodynamics (See section 6.6) that at constant pressure  $P$  and temperature  $T$ , Gibbs's function is unchanged during transformation between the vapour phase and the condensed phase,

$$G_v = G_c$$

$$\text{or, } U_v + PV_v - TS_v = U_c + PV_c - TS_c, \quad (11.60)$$

where the subscripts  $v, c$  represent respectively the vapour and the condensed (i.e., liquid or solid) phase. Neglecting  $V_c$  compared with  $V_v$ ,

$$U_v + PV_v - TS_v = U_c - TS_c. \quad (11.61)$$

All these quantities refer to a gram-molecule of the monatomic substance. Now, since

$$(C_v)_v = \left( \frac{dU_v}{dT} \right)_V \quad \text{or, } U_v - (U_v)_0 = \int_0^T dU_v = \int_0^T (C_v)_v dT$$

$$\text{i.e., } U_v = (U_v)_0 + \int_0^T (C_v)_v dT. \quad (11.62)$$

$$\text{Similarly, } U_c = (U_c)_0 + \int_0^T (C_v)_c dT = (U_c)_0 + \int_0^T (C_p)_c dT, \quad (11.63)$$

since, for a condensed (i.e., liquid or solid) phase,  $(C_p)_c - (C_v)_c$  (= work done against external pressure  $P$  during heating from 0 to  $T$  K) may be neglected\*. Finally,

$$PV_v = RT = \int_0^T RdT. \quad (11.64)$$

Now, using (11.62), (11.63) and (11.64) in (11.61) and substituting for  $S_v$  from Sackur-Tetrode equation (11.35) and for  $S_c$  from (11.59), we have

$$\begin{aligned} (U_v)_0 + \int_0^T \{(C_v)_v + R\} dT + RT \left\{ \log_e P - \frac{5}{2} - \frac{5}{2} \log_e T \right\} \\ - \log_e \left\{ \frac{(2s+1)(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} = (U_c)_0 + \int_0^T (C_p)_c dT - T \int_0^T \frac{(C_p)_c}{T} dT \\ \text{or, } \log_e P = -\frac{\lambda_0}{RT} + \frac{5}{2} \log_e T - \frac{1}{R} \left\{ \int_0^T \frac{(C_p)_c}{T} dT - \frac{1}{T} \int_0^T (C_p)_c dT \right\} \\ + \log_e \left\{ \frac{(2s+1)(2\pi m)^{3/2} k^{5/2}}{h^3} \right\}, \quad (11.65) \end{aligned}$$

\* Joos, G., loc. cit. P. 528.

where we have put

$$\lambda_0 = (U_v)_0 - (U_c)_0 = \text{latent heat of vaporisation at absolute zero} \quad (11.66)$$

$$\text{and } (C_v)_v + R = (C_p)_v = \frac{5}{2}R, \quad (11.67)$$

since the vapour is monatomic.

Expressing (11.65) in common logarithms,

$$\begin{aligned} \log_{10} P &= -\frac{\lambda_0}{2.3RT} + \frac{5}{2} \log_{10} T - \frac{1}{2.3R} \int_0^T \frac{dT}{T^2} \int_0^T (C_p)_c dT \\ &\quad + \log_{10} \left\{ \frac{(2s+1)(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} - \log_{10}(1.013 \times 10^6), \end{aligned} \quad (11.68)$$

where  $P$  is in atmospheres (since  $1.013 \times 10^6$  dynes/sq. cm is equal to 1 atmosphere) and  $\lambda_0$  is in calories

In (11.68), the expression

$$\begin{aligned} \int_0^T \frac{dT}{T^2} \int_0^T (C_p)_c dT &= \left[ -\frac{1}{T} \int_0^T (C_p)_c dT \right]_0^T + \int_0^T \frac{(C_p)_c}{T} dT \text{ (on integration by parts)} \\ &= \int_0^T \frac{(C_p)_c}{T} dT - \frac{1}{T} \int_0^T (C_p)_c dT, \end{aligned} \quad (11.69)$$

since  $\frac{1}{T} \int_0^T (C_p)_c dT$  tends to zero at  $T \rightarrow 0$  [See (11.56)].

Now comparing (11.68) with (6.143) of section 6.14, we find that the chemical constant

$$C = \log_{10} \left\{ \frac{(2s+1)(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} - \log_{10}(1.013 \times 10^6) \quad (11.70)$$

for a monatomic substance.

(11.68) has been tested by a large number of workers for monatomic substances such as Zn, Cd, Hg, Ne, A, Kr, etc. and its validity is established.

**Exercise :** Calculate chemical constants for Zn, Cd, Hg, Ne, A and Kr from (11.70). Take  $s = 0$  for each element.

## PROBLEM

- Explore literature to find how Saha originally derived his equation of thermal ionisation.

# Appendices

## Appendix-1

### Some Useful Integrals

The following definite integrals occur very frequently in the text :

$$1. \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$2. \int_0^{\infty} e^{-ax^2} x dx = \frac{1}{2a}$$

$$3. \int_0^{\infty} e^{-ax^2} x^{2n} dx = \frac{1 \cdot 3 \cdots (2n-1)}{2^{n+1}} \sqrt{\frac{\pi}{a^{2n+1}}}$$

$$4. \int_0^{\infty} e^{-ax^2} x^{2n+1} dx = \frac{n!}{2a^{n+1}}$$

$$5. \int_0^{\infty} e^{-ax} x^{\frac{1}{2}} dx = \left(\frac{1}{a}\right)^{3/2} \frac{\sqrt{\pi}}{2}$$

$$6. \int_0^{\infty} e^{-ax} x^{\frac{3}{2}} dx = \left(\frac{1}{a}\right)^{5/2} \frac{3\sqrt{\pi}}{4}$$

$$7. \int_0^{\infty} x^n e^{-ax} dx = \frac{\Gamma(n+1)}{a^{n+1}} \text{ with } \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \text{ and } \Gamma\left(m + \frac{1}{2}\right) = \frac{1 \cdot 3 \cdot 5 \cdots (2m-1)}{2^m} \sqrt{\pi}.$$

## Appendix-2

### Equivalence of Different Statements of Second Law of Thermodynamics

#### (a) Planck Statement vis-a-vis Clausius Statement\*

Fig. 1 shows an engine  $E$ , which takes heat  $Q_1$  from the source  $S_1$  at a temperature  $T_1$  K converts the whole of it into work,  $W = Q_1$ . This violates the Planck statement. A Carnot refrigerator  $CR$  (i.e., a reverse Carnot engine) takes heat  $Q_2$  from the sink  $S_2$  at a lower temperature  $T_2$  K. Suppose,  $E$  and  $CR$  are coupled together. Then, an amount of work,  $W = Q_1$ , which is available from  $E$  is done on  $CR$  so that a net amount of heat  $Q_2$  is delivered to  $S_1$  at a higher temperature  $T_1$ . The coupled engine, therefore, becomes an engine carrying heat  $Q_2$  from  $S_2$  to  $S_1$  without any work done on the system. Thus the coupled engine violates the Clausius statement.

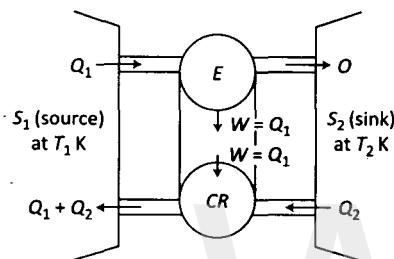


Fig. 1

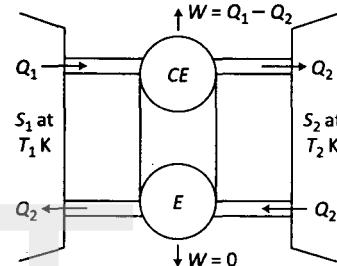


Fig. 2

Fig. 2 shows an engine  $E$ , which takes heat  $Q_2$  from  $S_2$  to  $S_1$  without any work done on it and thus violates the Clausius statement.  $CE$ , a Carnot engine, takes heat  $Q_1$  from  $S_1$ , does work  $W = Q_1 - Q_2$ , and delivers heat  $Q_2$  to  $S_2$ . Now  $E$  is coupled to  $CE$ . The coupled engine takes heat  $= Q_1 - Q_2$  from  $S_1$  and converts the whole of it into work without affecting any other body. This violates the Planck statement.

#### (b) Kelvin Statement vis-a-vis Clausius Statement

Fig. 3 shows an engine  $E$  at the bottom which takes heat  $Q_1$  from  $S_2$ , converts the whole of it into work,  $W = Q_1$  and delivers nothing to  $S_1$  (source). It thus violates the Kelvin statement. There is a Carnot refrigerator  $CR$  at the top. It takes  $Q_2$  from  $S_2$ , requires an amount of work,  $W = Q_1$ , to be done on it so that it may deliver an amount of heat,  $Q_1 + Q_2$ , to  $S_1$ . Therefore, if the two engines are coupled, the coupled engine takes heat,  $Q_1 + Q_2$ , from  $S_2$  and delivers the whole amount of heat to  $S_1$  without any work done on it. This violates the Clausius statement.

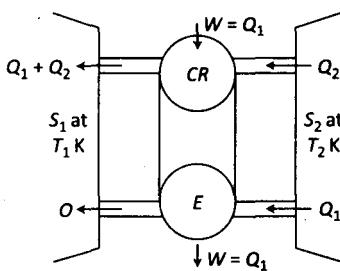


Fig. 3

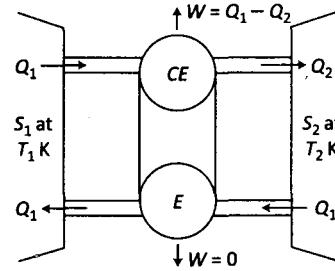


Fig. 4

\*See also Zemansky, M. W., *Heat and Thermodynamics*, Pp. 148-9 (1957).

Fig. 4 shows an engine  $E$  at the bottom which takes heat  $Q_1$  from  $S_2$ , does no work and delivers the whole of heat  $Q_1$  to  $S_1$ , thus violating the Clausius statement. A Carnot engine  $CE$  takes heat  $Q_1$  from  $S_1$ , does an amount of work,  $W = Q_1 - Q_2$ , and delivers heat  $Q_2$  to the sink,  $S_2$ . If  $E$  and  $CE$  are coupled, then the coupled engine takes heat,  $Q_1 - Q_2$ , from the sink and converts the whole of it into work violating the Kelvin statement.

So we see that if one statement of the second law of thermodynamics is violated, then another statement is also violated. We, therefore, say that all the statements of the law are logically equivalent.



## Appendix-3

### Liouville's Theorem\*

Every molecule of a system has a representative point in the phase space or  $\mu$ -space. If we consider a volume-element  $\Delta V_\mu$  in this space, the representative points will enter and leave through the boundary of the element due to molecular movements. Let the position and velocity of a representative point in the  $\mu$ -space be  $(q_1, q_2, q_3, p_1, p_2, p_3)$  and  $(c_1, c_2, c_3, c_4, c_5, c_6)$ . Then choosing a small six-dimensional cube as the volume-element ( $\delta V_\mu$ ), we have

$$\begin{aligned} \operatorname{div} \vec{c} &= \frac{\partial c_1}{\partial q_1} + \frac{\partial c_2}{\partial q_2} + \frac{\partial c_3}{\partial q_3} + \frac{\partial c_4}{\partial q_4} + \frac{\partial c_5}{\partial q_5} + \frac{\partial c_6}{\partial q_6} \\ &= \frac{\partial}{\partial q_1} \left( \frac{dq_1}{dt} \right) + \frac{\partial}{\partial q_2} \left( \frac{dq_2}{dt} \right) + \frac{\partial}{\partial q_3} \left( \frac{dq_3}{dt} \right) + \frac{\partial}{\partial p_1} \left( \frac{dp_1}{dt} \right) + \frac{\partial}{\partial p_2} \left( \frac{dp_2}{dt} \right) + \frac{\partial}{\partial p_3} \left( \frac{dp_3}{dt} \right). \quad (1) \end{aligned}$$

Now, the molecules themselves obey the fundamental laws of mechanics\*\* :

$$\frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k}, \quad \frac{dq_k}{dt} = +\frac{\partial H}{\partial p_k}, \quad (2)$$

where  $H$  is the Hamiltonian. From (2) it follows that

$$\frac{\partial}{\partial p_k} \left( \frac{dp_k}{dt} \right) + \frac{\partial}{\partial q_k} \left( \frac{dq_k}{dt} \right) = -\frac{\partial^2 H}{\partial p_k \partial q_k} + \frac{\partial^2 H}{\partial q_k \partial p_k} = 0. \quad (3)$$

It is evident from (3), putting  $k = 1, 2, 3$ , that the right-hand side of (1) vanishes. Thus

$$\operatorname{div} \vec{c} = 0. \quad (4)$$

This equation is characteristic of the flow of an *incompressible fluid*\*\*. This means that the representative points of the molecules in the phase space behave like an incompressible fluid in this space. Thus, due to the representative points behaving like an incompressible fluid in  $\mu$ -space, all volume-elements of equal size will hold the same number of these points, and the larger the size of a volume-element, the larger is the number of representative points contained in it. In other words, the probability of a molecule being in an elementary region in phase space is proportional to the volume of that region. This is *Liouville's theorem*. This theorem is, however, not limited to a phase space of six dimensions only but holds for any generalised phase space as well.

\*See Joos, G., *Theoretical Physics*, Pp. 576-7 (1956).

\*\*Kar, K. C., *Theoretical Physics*, Vol-I, Pp. 182-4 (1964).

## Appendix-4

### Quantum-Mechanical Basis of Bose-Einstein and Fermi-Dirac Statistics\*

Let us consider a system of  $n$  particles with  $\hat{H}$  as the total Hamiltonian or energy operator. If the particles are identical in all respects, i.e., indistinguishable from one another, then the energy operator  $\hat{H}$  will be invariant under the interchange of any two particles. Let us denote by  $\hat{P}_{kl}$  the interchange operator which interchanges the particles numbered  $k$  and  $l$ . Then, the fact that all the particles of the system are identical may be stated mathematically by the condition that the Hamiltonian  $\hat{H}$  commutes with the interchange operator  $\hat{P}_{kl}$ .

$$\hat{P}_{kl}\hat{H} = \hat{H}\hat{P}_{kl} \quad (1)$$

Again, since  $\hat{P}_{kl}$  commutes with  $\hat{H}$ , the eigenvalues of  $\hat{P}_{kl}$  will be constants of motion.

Let us denote by  $\psi(1, 2, \dots, l, k, \dots, n)$  the eigenfunctions of  $\hat{P}_{kl}$  which must satisfy the equation :

$$\hat{P}_{kl}\psi(1, 2, \dots, l, k, \dots, n) = \lambda\psi(1, 2, \dots, l, k, \dots, n), \quad (2)$$

where  $\lambda$  is the eigenvalue of  $\hat{P}_{kl}$ . On second operation by  $\hat{P}_{kl}$ , we obtain from (2)

$$\hat{P}_{kl}^2\psi(1, 2, \dots, l, k, \dots, n) = \lambda^2\psi(1, 2, \dots, l, k, \dots, n). \quad (3)$$

Again, it is evident from the very definition of the interchange operator that we must have

$$\hat{P}_{kl}\psi(1, 2, \dots, l, k, \dots, n) = \psi(1, 2, \dots, k, l, \dots, n)$$

so that on second operation by  $\hat{P}_{kl}$  the system must return to the original state :

$$\hat{P}_{kl}^2\psi(1, 2, \dots, l, k, \dots, n) = P_{kl}\psi(1, 2, \dots, k, l, \dots, n) = \psi(1, 2, \dots, l, k, \dots, n). \quad (4)$$

Then, comparing (3) and (4),

$$\lambda^2 = 1, \text{ i.e., } \lambda = \pm 1. \quad (5)$$

Thus, the interchange operator  $\hat{P}_{kl}$  has only two eigenvalues  $\pm 1$ . The eigenfunction  $\psi_s(1, 2, \dots, l, k, \dots, n)$  corresponding to  $\lambda = +1$  is called the *symmetric function* and is defined by the equation :

$$\hat{P}_{kl}\psi_s(1, 2, \dots, l, k, \dots, n) = \psi_s(1, 2, \dots, l, k, \dots, n). \quad (6)$$

On the other hand,  $\psi_a(1, 2, \dots, l, k, \dots, n)$  corresponding to the eigenvalue  $\lambda = -1$  is called the *anti-symmetric function* and is defined by the equation :

$$\hat{P}_{kl}\psi_a(1, 2, \dots, l, k, \dots, n) = -\psi_a(1, 2, \dots, l, k, \dots, n). \quad (7)$$

The symmetric or anti-symmetric character of the wavefunctions for a system of identical particles is fixed and does not change at all, since, as explained above, the eigenvalues  $\pm 1$  of  $\hat{P}_{kl}$  are constants of motion. Thus, experiment shows that a system of electrons, protons or neutrons is always described by an anti-symmetric function whereas a system of photons, mesons or  $\alpha$ -particles is always described by a symmetric function.

Let us now study an interesting consequence of the above discussion. Consider, for simplicity, a system of two similar particles—particle 1 in state  $a$  and particle 2 in state  $b$ ,  $a$  and  $b$  describing the complete states of the particles including their spin orientations. Let  $\psi_a(1), \psi_a(2)$  be the

\*See, for example, Davydov, A. S., *Quantum Mechanics*, Pp. 335–39 (1965).

normalised wave functions of the separate particles. If there is no interaction between the particles, then the wave function of the system of the two particles is  $\psi_a(1)\psi_a(2)$ , or (since the particles are identical)  $\psi_b(1)\psi_a(2)$ . From these we form the normalised symmetric and antisymmetric combinations :

$$\psi_s = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)] \quad (8)$$

$$\text{and } \psi_a = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)]. \quad (9)$$

since the *physically acceptable* solutions for the system must be, as explained above, either symmetric or antisymmetric. Evidently, if  $\hat{P}_{12}$  operates on  $\psi_s$  and  $\psi_a$ , the eigenvalues will be respectively +1 and -1. Further, it is clear from (8) and (9) that if both the particles are in the same state, then

$$\psi_s = \frac{1}{\sqrt{2}}[2\psi_a(1)\psi_a(2)] = \sqrt{2}\psi_a(1)\psi_a(2) \quad (10)$$

$$\text{but } \psi_a = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2)] = 0. \quad (11)$$

The significance of these results is that two identical particles in a system represented by symmetric functions may be in the same state whereas two identical particles in a system represented by antisymmetric functions cannot exist in the same state. We may easily generalise this result to systems of  $n$  identical particles. In this case, any number of particles in system represented by symmetric functions may be in the same state. On the other hand, no two particles in a system represented by antisymmetric functions can exist in the same state. This is *Pauli's principle*. The first group of particles (with integral spins) follow Bose-Einstein statistics while the latter (with half-integral spins) follow Fermi-Dirac statistics.

Before we close this subject we must note that the symmetric or anti-symmetric character of the wave functions of a system of identical particles cannot be changed by an external perturbation. In fact, the perturbation energy (i.e, Hamiltonian) must be symmetric with respect to the interchange of a pair of particles (as the particles are identical) so that the perturbation Hamiltonian operator must commute with  $\hat{P}_{kl}$ . Thus, the eigenvalues of  $\hat{P}_{kl}$  remain constants of motion under perturbation also.

## Appendix-5

### Liquefaction of Gases

Gases are liquefied by cooling them to low temperatures. The following are the principal methods for the production of low temperatures :

**(a) Cooling by Freezing Mixtures :** The production of cooling by freezing mixtures has been explained towards the end of section 6.15. By adding common salt ( $\text{NaCl}$ ) to ice, about  $-22^\circ\text{C}$  may be reached while  $\text{CaCl}_2$  and  $\text{KOH}$  added to ice may cool down to  $-55^\circ\text{C}$  and  $-65^\circ\text{C}$  respectively. These temperatures are, in fact, not too low and, therefore, this method is not useful for liquefaction of gases.

**(b) Boiling under Reduced Pressure :** When the pressure over a liquid is sufficiently reduced, it starts boiling. This is called *boiling under reduced pressure*. When this occurs, the liquid takes the latent heat of vaporisation from its surroundings and produces cooling. By reducing the pressure over the liquid it is possible, in this way, to go down to the triple point of the liquid. The normal boiling points of liquid oxygen and liquid hydrogen are respectively  $-182.9^\circ\text{C}$  and  $-252.8^\circ\text{C}$ . By reducing pressure over liquid oxygen and liquid hydrogen one can go down to  $-218.4^\circ\text{C}$  (triple point of oxygen) and  $-259.1^\circ\text{C}$  (triple point of hydrogen) respectively. On the other hand, the normal boiling point of helium is  $-268.9^\circ\text{C}$ , and by allowing it to boil under reduced pressure a temperature of  $-272.3^\circ\text{C}$  has been reached.

**(c) Adiabatic Expansion :** When a gas does work by adiabatic expansion, cooling is produced. We shall see later how this method is utilised in Claude's method for liquefaction of air.

**(d) Joule-Thomson Cooling :** This effect has already been discussed in sections 3.3 and 3.7. We shall see below how this effect is used in the liquefaction of air, hydrogen and helium.

**(e) Adiabatic Demagnetisation :** This has also already been discussed experimentally in section 2.25 and theoretically in section 6.11.

We shall consider here liquefaction of only air, hydrogen and helium.

#### (i) Claude's Method for Liquefaction of Air

Pure and dry air is compressed to a pressure of 40 atmospheres by means of compressors ( $P_1$  and  $P_2$ ) [Fig. 1] and passed through the heat exchanger I where it is cooled to a temperature  $-80^\circ\text{C}$  by the outgoing expanded gas (flowing upward through the tube Y). At X, the gas is divided into two streams. One stream goes to the expansion engine P where it does work by adiabatic expansion to 1 atmosphere (this work being partly used for operating the compressors) and consequently suffers cooling. This cooled gas flows upward through the tube Y and cools the other stream (which is flowing downward through the tube XZ) in the heat exchangers II and I. This highly compressed, cooled, downward stream suffers Joule-Thomson expansion to 1 atmosphere at the throttle valve V and a portion of it liquefies and is collected in the Dewar vessel D. The portion not liquefied passes upward (through the tube Y) through the heat exchangers III,

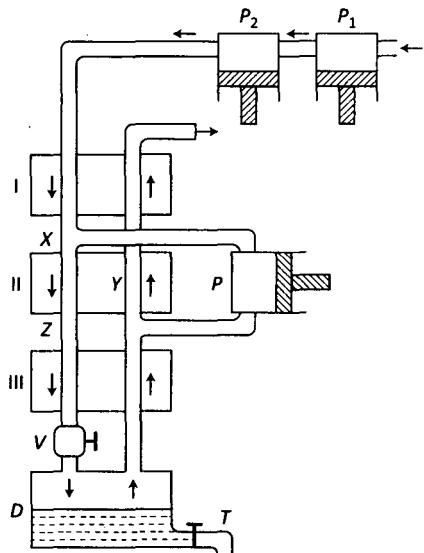


Fig. 1: Air liquefier

II and I and cools the gas flowing downward through the tube  $XZ$ . All the gas that passes out through the tube  $Y$  is again compressed and recirculated through the liquefier.

### (ii) Liquefaction of Hydrogen

It has been explained in section 3.7 that a gas must be precooled below its temperature of inversion before Joule-Thomson expansion so that cooling may be produced after this expansion. Obszewski found experimentally the temperature of inversion of hydrogen to be  $-79^{\circ}\text{C}$ . Now, since hydrogen gas liquefies at  $-252.8^{\circ}\text{C}$  under normal pressure, it is evident that it cannot be liquefied by cooling it just below  $-79^{\circ}\text{C}$  before Joule-Thomson expansion. It has, in fact, been observed that for practical purposes, hydrogen gas must be precooled to about  $-194^{\circ}\text{C}$  at a pressure of 160 atmospheres before undergoing Joule-Thomson expansion.

Hydrogen prepared from zinc and sulphuric acid is compressed to a pressure of 150 atmospheres and passed through a water bath to remove the heat produced during compression. The gas is then passed through caustic potash to deprive it of carbon dioxide and through some dehydrating agent to remove moisture, otherwise these impurities would solidify much before hydrogen liquefies and would choke the tubes.

A schematic diagram of the hydrogen liquefier has been shown here [Fig. 2]. The pure, dry gas enters the tube  $X$  and is cooled, in the final steady state (i.e., when the process has ultimately reached a steady state), to  $-170^{\circ}\text{C}$  by the outgoing cold hydrogen gas. Then, the gas passes successively through the tubes  $Y$  and  $Z$ .  $Y$  is surrounded by liquid air in the chamber  $P$  and  $Z$  is surrounded by liquid air boiling in the chamber  $Q$  under a reduced pressure of 100 mm of Hg. Thus, after passing through the tube  $Z$ , the gas attains a temperature of about  $-200^{\circ}\text{C}$ . Then it enters the tube  $R$  and finally undergoes Joule-Thomson expansion at the valve  $V$ . The cold gas now passes up through the tube  $C$ , round the chambers  $P$  and  $Q$ , back to the compressor. Thus the outgoing cold gas cools the incoming compressed gas. It is found that after a few cycles of this process the temperature of the incoming gas is about  $-250^{\circ}\text{C}$  when it reaches the valve  $V$ . So, after Joule-Thomson expansion at  $V$  now the gas liquefies and is collected in the Dewar vessel  $D$ .

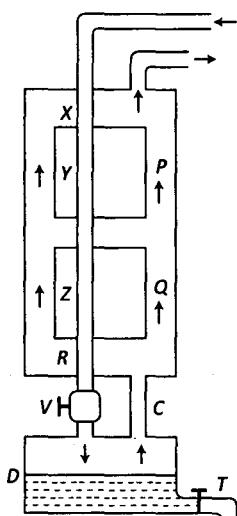


Fig. 2: Hydrogen liquefier

As already indicated, liquid hydrogen boils at  $-252.8^{\circ}\text{C}$  under normal pressure. If it is allowed to boil under reduced pressure it can be frozen to a white solid.

### (iii) Liquefaction of Helium

The inversion temperature of helium is about  $-238^{\circ}\text{C}$ . Now, since at normal pressure helium liquefies at  $-268.9^{\circ}\text{C}$ , it is evident that it cannot be liquefied by cooling it just below  $-238^{\circ}\text{C}$  before Joule-Thomson expansion. Kammerling Onnes was the first to observe (1908) that for practical purposes, helium gas must be precooled to about  $-258^{\circ}\text{C}$  in a bath of liquid hydrogen boiling under reduced pressure before Joule-Thomson expansion.

A schematic diagram of the helium liquefier has been shown here [Fig. 3]. The purified helium gas, compressed to 100 atmospheres and then cooled in a bath, enters the tube  $X$  and is cooled by the outgoing cold helium gas. Then the gas passes through the tube  $Y$  which is surrounded by liquid hydrogen boiling in the chamber  $P$  under reduced pressure.

Thus, it enters the tube  $Z$  and finally undergoes Joule-Thomson expansion at the valve  $V$ . The cold gas now passes up through the tube  $C$ , round the chamber  $P$ , back to the compressor.

Thus, the outgoing cold gas cools the incoming compressed gas. It is found that after a few cycles of this process, the gas is sufficiently cooled when it reaches the valve  $V$ . So, after Joule-Thomson expansion at  $V$  now the gas liquefies and collects in the Dewar vessel  $D$ .

Later, Kapitza applied the method of adiabatic expansion (similar to Claude's method) to liquefy helium. The purified gas was compressed to about 30 atmospheres and then cooled to about  $-208\text{ }^{\circ}\text{C}$  by passing through a liquid nitrogen bath. Then the gas is divided into two streams. One stream passed through the expansion engine and, due to work done in adiabatic expansion, was cooled to  $-263\text{ }^{\circ}\text{C}$ . Then this stream cooled the other stream of the gas proceeding towards the J-T expansion valve. The advantage of this method is that liquid hydrogen is not required here.

Keesom was the first to solidify liquid helium by subjecting it to a very high pressure. He solidified helium by compressing liquid helium to 130 atmospheres in a narrow brass tube which was immersed in a liquid helium bath. Later experiments, however, show that liquid helium solidifies at  $4.20\text{ K}$  at 140 atmospheres but at  $1.10\text{ K}$  at only 23 atmospheres. Solid helium can hardly be distinguished from liquid helium because both possess almost the same refractive index.

Fig. 10.1 (due to Keesom) shows that helium has got two triple points—one at  $A$  ( $1.75\text{ K}$  and 30 atoms) and the other at  $B$  ( $2.19\text{ K}$  and  $38.58\text{ mm of Hg}$ ).  $B$  is called the  $\lambda$ -point [See also section 6.16] and  $AB$  the  $\lambda$ -line.  $A$  is the meeting point of the solid phase, liquid I-phase and liquid II-phase while  $B$  is the meeting point of the liquid I-phase, liquid II-phase and vapour-phase. Thus, unlike other substances, the solid, liquid and gas never exist together. This is a strange behaviour of helium.

It is also found that the gas and the liquid phase continue in equilibrium down to absolute zero, as indicated by the curve  $BY$ .

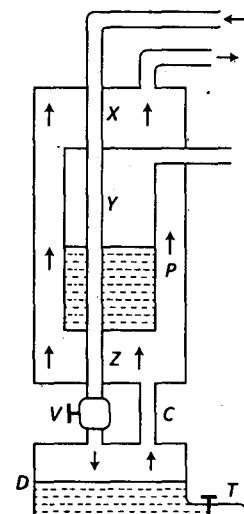
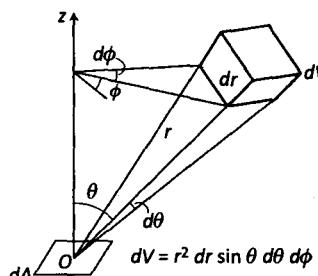


Fig. 3: Helium liquefier

## Appendix-6

### A Rigorous Deduction of Gaseous Viscosity and Conductivity

Let us suppose that a certain property,  $\zeta$ , of each molecule of a gas varies from layer to



**Fig. 1**

layer, each layer being perpendicular to the  $z$ -axis (Fig. 1). The value of  $\zeta$  at the layer passing through  $O$  is  $\zeta_0$ . Then the value of  $\zeta$  at the level of the elementary volume,  $dV$  ( $dV = r^2 dr \sin \theta d\theta d\phi$ ) is

$$\zeta_0 + r \cos \theta \frac{d\zeta}{dz}.$$

Let  $dn_c$  be the number of  $c$ -molecules (i.e., molecules having the speed,  $c$ ) per unit volume inside the volume,  $dV$ . Then the total number of  $c$ -molecules is  $dn_c dV$ . After the collisions  $c$ -molecules spread out in all directions. Some of them will travel a free distance between  $r$  and  $r + dr$  towards the elementary area  $dA$  (at  $O$ ) perpendicular to the  $z$ -axis. Their number will be (See § 2.14)

$$\frac{1}{4\pi} \left( \frac{dA \cos \theta}{r^2} \right) (dn_c dV) \alpha e^{-\alpha r} dr = \frac{1}{4\pi} \frac{dA}{r^2} dn_c (r^2 dr \sin \theta \cos \theta d\theta d\phi) \frac{1}{\lambda} e^{-\frac{r}{\lambda}} \left( \frac{dr}{dt} \right) dt,$$

where  $dt$  = time during which such a molecule travels a distance  $dr$  and  $\alpha = \frac{1}{\lambda}$ ,

$$= \frac{dA}{4\pi} \frac{c}{\lambda} dn_c e^{-\frac{r}{\lambda}} dr dt \sin \theta \cos \theta d\theta d\phi, \quad \text{where } c = \frac{dr}{dt}.$$

This number of  $c$ -molecules will pass through the area  $dA$  in time  $dt$ . They will transport downward an amount of the property,  $\zeta$ ,

$$dT \downarrow = \frac{dA}{4\pi} \frac{c}{\lambda} dn_c e^{-\frac{r}{\lambda}} dr dt \sin \theta \cos \theta d\theta d\phi \left( \zeta_0 + \frac{d\zeta}{dz} r \cos \theta \right) \text{ in time } dt.$$

Similarly, the transport of the property,  $\zeta$ , upward through  $dA$  is

$$dT \uparrow = \frac{dA}{4\pi} \frac{c}{\lambda} dn_c e^{-\frac{r}{\lambda}} dr dt \sin \theta \cos \theta d\theta d\phi \left( \zeta_0 - \frac{d\zeta}{dz} r \cos \theta \right) \text{ in time } dt.$$

Hence, the net downward transport of  $\zeta$  through  $dA$  in time  $dt$  is

$$\begin{aligned} G &= \int_{cr\theta\phi} (dT \downarrow - dT \uparrow) = \frac{2dAdt}{4\pi} \frac{d\zeta}{dz} \int_0^\infty cdn_c \int_0^{\frac{\pi}{2}} \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^\infty \frac{e^{-\frac{r}{\lambda}}}{\lambda} dr \\ &= \frac{1}{3} dAdt \frac{d\zeta}{dz} \frac{1}{\lambda} \int_0^\infty cdn_c \quad \left( \because \int_0^\infty \frac{e^{-\frac{r}{\lambda}}}{\lambda} dr = \frac{1}{\lambda} \right) \\ &= \frac{1}{3} dAdt \frac{d\zeta}{dz} \bar{\lambda} n \bar{c}. \end{aligned} \tag{1}$$

#### Two Particular Cases :

(a)  $\zeta = mv$  (momentum of a gas molecule)

In this case,

$$G \text{ transported downward per second through } dA = \frac{1}{3} dAm \frac{dv}{dz} \bar{\lambda} n \bar{c}. \tag{2}$$

Then,  $\frac{1}{3}dAm\frac{dv}{dz}\bar{\lambda}n\bar{c} = \eta dA\frac{dv}{dz}$ , from the theory of viscosity.

Hence, we have

$$\eta = \frac{1}{3}nm\bar{c}\bar{\lambda} = \frac{1}{3}\rho\bar{c}\bar{\lambda}. \quad (3)$$

This is the result derived in (2.84)

(b)  $\zeta = E$ , thermal energy, so that

$d\zeta = dE = mc_v dT$ , where  $c_v$  = specific heat at constant volume per unit mass.

Then  $\frac{d\zeta}{dz} = \frac{dE}{dz} = mc_v \frac{dT}{dz}$ .

Hence,  $G$  transported downward per second through  $dA$

$$\begin{aligned} &= \frac{1}{3}dA \left( mc_v \frac{dT}{dz} \right) \bar{\lambda}n\bar{c} \\ &= KdA \frac{dT}{dz}, \text{ from the theory of conductivity.} \end{aligned}$$

Hence, we have

$$K = \frac{1}{3}n\bar{c}\bar{\lambda}mc_v = \eta c_v. \quad (4)$$

This is the result derived in (2.94).

## Appendix-7

### Heat Engines\*

#### (a) External Combustion Engine: Steam Engine

A schematic diagram of a simple steam engine is given in Fig. 1. A small fixed mass of water

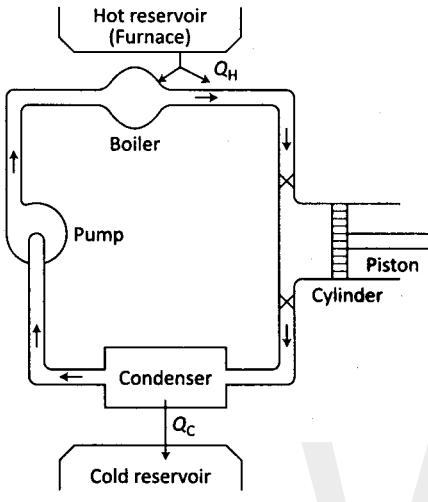


Fig. 1

flows from the condenser, through the boiler, into the expansion chamber (cylinder and piston) and then back to the condenser. The water in the condenser is subjected to a pressure less than the atmospheric pressure and a temperature less than the normal boiling point of water. A pump pushes the water into the boiler where the pressure and the temperature are much higher. Inside the boiler the water is heated to its boiling point and converted into steam at the same pressure. The steam is further heated, i.e., superheated at the same pressure. The superheated steam passes into a cylinder fitted with a movable piston. It then expands adiabatically against the piston until its pressure and temperature are reduced to those of the condenser. Inside the condenser, the steam condenses into water at the initial pressure and temperature, thus completing the cycle. Now a second cycle begins.

It should be recognised that a mathematical analysis of the cyclic operation of the steam engine becomes difficult on account of the occurrence of a few processes like (i) acceleration and turbulence in the steam flow, (ii) friction, (iii) conduction losses and (iv) irreversible heat flow on account of a finite difference of temperature between the furnace and the boiler.

Ignoring these processes we consider a cycle called the *Rankine cycle* shown in Fig. 2. This cycle is composed of the following steps.

- 1 → 2 : Adiabatic compression of water to the pressure of the boiler (with a little change of temperature), the temperature being  $T_C$ .
- 2 → 3 : Heating of water at constant pressure to the boiling point,  $T_B$ .
- 3 → 4 : Vaporizing of water into saturated steam at constant pressure and temperature.
- 4 → 5 : Superheating of steam at constant pressure into superheated steam at temperature  $T_H$ .
- 5 → 6 : Adiabatic expansion of steam into wet steam.
- 6 → 1 : Condensation of steam at constant pressure and temperature,  $T_C$ .

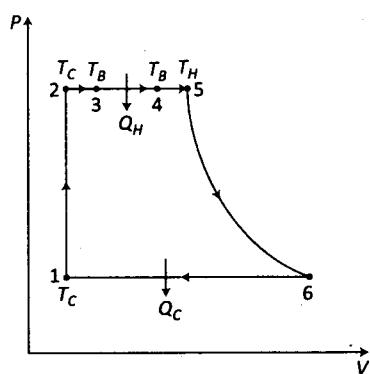


Fig. 2

It has to be noted that during the steps  $2 \rightarrow 3$ ,  $3 \rightarrow 4$  and  $4 \rightarrow 5$ , an amount of heat,  $Q_H$ , enters the system from the hot reservoir (furnace). On the other hand, during the step  $6 \rightarrow 1$ , condensation occurs and an amount of heat,  $Q_C$ , flows out of the system at  $T_C$ .

\*M. W. Zemansky, *Heat and Thermodynamics*, Chapter 7 (1968).

## Efficiency of the Rankine cycle

We start with the expression for enthalpy :  $H = U + PV$ .

On taking differentials,

$$dH = dU + PdV + VdP = dQ + VdP = dQ \text{ at constant pressure.}$$

Then  $H_f - H_i = Q = \text{heat transferred from the initial state, } i, \text{ to the final state, } f.$

Now, in the Rankine cycle, the steps  $2 \rightarrow 3$ ,  $3 \rightarrow 4$  and  $4 \rightarrow 5$  occur at constant pressure. Hence, the heat absorbed during these steps is

$$Q_H = (H_3 - H_2) + (H_4 - H_3) + (H_5 - H_4) = H_5 - H_2. \quad (1)$$

The step  $6 \rightarrow 1$  occurs at constant pressure when the heat rejected is

$$Q_C = -(H_1 - H_6) = H_6 - H_1. \quad (2)$$

Now, the step  $1 \rightarrow 2$  is a case of adiabatic compression so that  $dQ = 0$ . Hence, in this case,

$$H_2 - H_1 = \int_1^2 dH = \int_1^2 VdP = V(P_2 - P_1). \quad (3)$$

Therefore, the efficiency of the cycle is

$$\begin{aligned} \eta &= \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = \frac{(H_5 - H_2) - (H_6 - H_1)}{H_5 - H_2} \\ &= \frac{H_5 - H_6 - (H_2 - H_1)}{H_5 - H_1 - (H_2 - H_1)} = \frac{H_5 - H_6 - (P_2 - P_1)V}{H_5 - H_1 - (P_2 - P_1)V}, \quad \text{using (3)} \end{aligned} \quad (4)$$

$$\approx \frac{H_5 - H_6}{H_5 - H_1}, \quad (5)$$

since, in practice,

$$(H_5 - H_6) \gg (P_2 - P_1)V \quad \text{and} \quad (H_5 - H_1) \gg (P_2 - P_1)V.$$

The steam engine is called an *external combustion engine* since the hot reservoir (furnace) is outside the engine proper.

### (b) Internal Combustion Engines

**(i) Otto cycle :** An *internal combustion engine* is so called because the combustion of fuel occurs inside a cylinder fitted with a piston. The gasoline engine is one such engine fitted with two valves—an admit valve and an exhaust valve. Six processes occur in this engine. Four of them are called strokes because they involve the motion of the piston.

In the *intake stroke*, a mixture of gasoline and air is drawn through the admit valve into the cylinder by the suction stroke of the piston. Then the mixture of gasoline vapour and air is so compressed that the pressure and temperature increase appreciably. This is the *compression stroke*. Next, the combustion of the mixture is caused very rapidly by an electric spark. The combustion products acquire a very high pressure and temperature. The volume, however, remains unchanged because the piston does not move in this process called *explosion*. Thereafter, the hot combustion products expand and push the piston out. This is called the *power or working stroke*. In this process there is a drop in pressure and temperature. At the end of this stroke, the pressure and temperature are still higher than the outside. Now the exhaust valve opens and allows some of the gas to escape till the pressure drops to the atmospheric pressure. In this process called the *valve exhaust*, the piston does not move. Finally the *exhaust*

stroke occurs. Now, the piston pushes almost all the remaining combustion products out of the cylinder by exerting a pressure sufficiently higher than that of the outside.

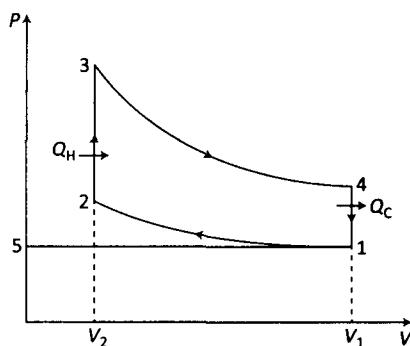


Fig. 3

The operation of the engine described above involves acceleration, friction and heat loss by conduction which render a mathematical analysis difficult. Ignoring these phenomena, we consider a cycle called the *Otto cycle* shown in Fig. 3. The cycle is composed of the following steps. The gas is assumed to behave like an ideal gas.

$5 \rightarrow 1$  : It represents a quasi-static intake at constant pressure equal to the atmospheric pressure,  $P_0$ , and temperature,  $T_1$ .

$1 \rightarrow 2$  : It represents a quasi-static, adiabatic compression from volume  $V_1$  to  $V_2$  and temperature  $T_1$  to  $T_2$ .

$2 \rightarrow 3$  : It represents a quasi-static isochoric (constant-volume) rise of temperature (from  $T_2$  to  $T_3$ ) and pressure. Now the explosion occurs in the engine and there is an absorption of heat,  $Q_H$ , in the system.

$3 \rightarrow 4$  : It represents a quasi-static, adiabatic expansion involving a drop in temperature from  $T_3$  to  $T_4$ .

$4 \rightarrow 1$  : It represents a quasi-static isochoric fall in temperature and pressure. The temperature falls from  $T_4$  to  $T_1$  and there is a rejection of heat,  $Q_C$ , by the engine. The exhaust valve opens and the pressure falls to that of the atmosphere.

$1 \rightarrow 5$  : It represents a quasi-static isobaric exhaust at atmospheric pressure. The volume decreases from  $V_1$  to 0.

It has to be mentioned that in this cycle, the steps  $5 \rightarrow 1$  and  $1 \rightarrow 5$  just cancel each other and need not be taken into consideration.

### Efficiency of the Otto Cycle

We have here

$$Q_H = \text{heat received in the process } 2 \rightarrow 3 = C_v(T_3 - T_2)$$

$$\text{and } Q_C = \text{heat rejected in the process } 4 \rightarrow 1 = C_v(T_4 - T_1),$$

where  $C_v$  is the specific heat at constant volume during these processes.

Hence, the efficiency is

$$\eta = \frac{\text{Heat converted to work}}{\text{Heat absorbed}} = \frac{C_v(T_3 - T_2) - C_v(T_4 - T_1)}{C_v(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2}. \quad (6)$$

Since 1 and 2 are on the same adiabatic,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\text{so that } \frac{T_1}{T_2} = \left( \frac{V_2}{V_1} \right)^{\gamma-1} \quad (7)$$

Also since  $T_3$  and  $T_4$  are on the same adiabatic,

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

$$\text{so that } \frac{T_4}{T_3} = \left( \frac{V_2}{V_1} \right)^{\gamma-1} \quad (8)$$

Hence, from (7) and (8),

$$\left( \frac{V_2}{V_1} \right)^{\gamma-1} = \frac{T_1}{T_2} = \frac{T_4}{T_3} = \frac{T_4 - T_1}{T_3 - T_2}. \quad (9)$$

Therefore, the efficiency from (6) and (9) is

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \left( \frac{V_2}{V_1} \right)^{\gamma-1} = 1 - \left( \frac{1}{\rho} \right)^{\gamma-1}, \quad (10)$$

where  $\rho = \frac{V_1}{V_2}$  = expansion ratio.

**(ii) Diesel cycle :** A diesel engine is also a four-stroke engine. But it has three valves—an air admit valve, a fuel valve and an exhaust valve. In this engine, undesirable effects like chemical combination, friction, acceleration and heat losses occur. Ignoring these effects, we consider in this case a cycle called the *Diesel cycle* shown in Fig. 4. The following are the four strokes :

5 → 1 : This is the *intake stroke* during which the air admit valve is open, the other two being closed. Air is admitted at nearly the atmospheric pressure.

1 → 2 : This is the *compression stroke* during which all the three valves are closed. The air admitted into the cylinder is compressed adiabatically resulting in a high pressure and temperature.

2 → 3 : In this process the air admit valve and the exhaust valve remain closed. The fuel valve is opened at the beginning of the stroke and remains open for a very short time. The air, heated to a high temperature, ignites the fuel as soon as it is admitted into the cylinder. The combustion continues as long as the fuel valve remains open and this is imagined to result in expansion at a constant pressure.

3 → 4 : This is the *power or working stroke*. Due to combustion the gaseous mixture adiabatically expands pushing the piston outward.

4 → 1 : At the end of the working stroke, the pressure drops to the atmospheric value and the exhaust valve opens.

1 → 5 : This is the *scavenging stroke* during which the piston moves inward pushing the spent gases out through the exhaust valve. Thereafter, the engine is ready for the next cycle.

### Efficiency of the Diesel cycle

Refer to Fig. 4. Now,

$$Q_H = \text{heat absorbed} = C_p(T_3 - T_2) \quad (11)$$

$$\text{and } Q_C = \text{heat rejected} = C_v(T_4 - T_1). \quad (12)$$

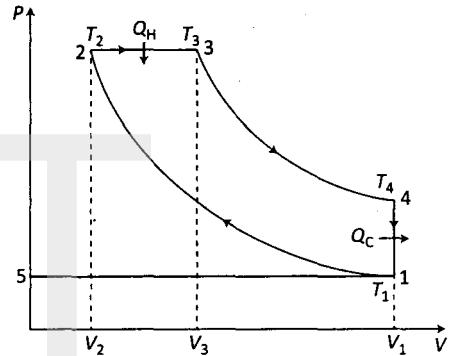


Fig. 4

$$\therefore \eta = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{1}{\gamma} \frac{T_4 - T_1}{T_3 - T_2}, \quad (13)$$

where  $\gamma = \frac{C_p}{C_v}$ .

$$\text{Now, } \frac{V_1}{V_2} = \rho_1 \text{ (say)} \quad \text{and} \quad \frac{V_1}{V_3} = \rho_2 \text{ (say).} \quad (14)$$

$$\text{We write, } \theta = \frac{\rho_1}{\rho_2} = \frac{V_3}{V_2}. \quad (15)$$

Since  $1 \rightarrow 2$  and  $3 \rightarrow 4$  are adiabatic curves,

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = T_1 \rho_1^{\gamma-1} \quad (16)$$

$$\text{and} \quad T_4 = T_3 \left( \frac{V_3}{V_1} \right) = T_3 \left( \frac{1}{\rho_2} \right)^{\gamma-1}. \quad (17)$$

Since the pressure is constant along  $2 \rightarrow 3$ ,

$$\frac{T_3}{T_2} = \frac{V_3}{V_2} = \theta. \quad (18)$$

From (16) and (18),

$$T_3 = T_2 \theta = T_1 \theta \rho_1^{\gamma-1}. \quad (19)$$

From (17) and (18),

$$T_4 = T_3 \left( \frac{1}{\rho_2} \right)^{\gamma-1} = T_1 \theta \rho_1^{\gamma-1} \left( \frac{1}{\rho_2} \right)^{\gamma-1} = T_1 \theta \left( \frac{\rho_1}{\rho_2} \right)^{\gamma-1} = T_1 \theta^\gamma. \quad (20)$$

Hence, from (16), (19) and (20),

$$\eta = 1 - \frac{1}{\gamma} \frac{T_1 \theta^\gamma - T_1}{T_1 \theta \rho_1^{\gamma-1} - T_1 \rho_1^{\gamma-1}} = 1 - \frac{1}{\gamma} \frac{\theta^\gamma - 1}{\theta \rho_1^{\gamma-1} - \rho_1^{\gamma-1}} = 1 - \frac{1}{\gamma} \frac{\theta^\gamma - 1}{(\theta - 1) \rho_1^{\gamma-1}}. \quad (21)$$

## Appendix-8

### Superfluidity\*

#### (a) Liquid Helium II—A Superfluid

Under a pressure of 1 atmosphere helium gas liquefies at 4.215 K. When the temperature of liquid helium in equilibrium with its own vapour is reduced to 2.172 K (called  $\lambda$ -point) it is transformed into liquid helium II. This liquid helium II has some very interesting properties. One of them is that if the temperature of liquid helium II is further reduced, its density diminishes. This means that its volume expansibility is negative. Secondly, the viscosity of liquid helium II is extremely low. Fig. 1 shows how the rate of flow of liquid helium through a fine annulus abruptly rises as the temperature is lowered below the  $\lambda$ -point. Liquid helium II is called a *superfluid* because of its extremely low viscosity.

L. D. Landau and F. London studied the behaviour of liquid helium II intensively. London concluded from his studies that the formation of liquid helium II from liquid helium I at  $\lambda$ -point is a peculiar state of *quantum condensation* called *Bose-Einstein condensation*. However, this phenomenon occurs not in ordinary space but in momentum space where the particles of liquid helium II have zero-point energy and momentum.

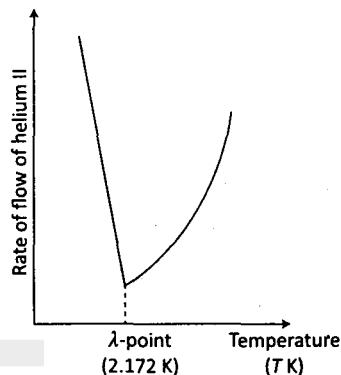


Fig. 1

It is interesting to note that Tisza described Landau's and London's ideas by picturing liquid helium II as a two-fluid model. This picture should, however, not be taken literally. But it appears to be very useful to the experimentalists. According to this picture, liquid helium II is conceived to be a mixture of two liquids—one of them having normal atoms with normal viscosity and the other having superfluid atoms which have zero-point energy and entropy and which are capable of moving through the normal atoms without friction.

The density of liquid helium II,  $\rho$ , is therefore thought to be composed of a normal component with density,  $\rho_n$ , and a superfluid component with density,  $\rho_s$ . Thus, we write the total density in the form :

$$\rho = \rho_n + \rho_s. \quad (1)$$

At  $\lambda$ -point,  $\rho_s = 0$  and so  $\rho = \rho_n$ . As the temperature progressively falls on the lower side of  $\lambda$ -point,  $\rho_n$  decreases and  $\rho_s$  increases. At  $T = 0$ ,  $\rho = \rho_s$  and  $\rho_n = 0$ .

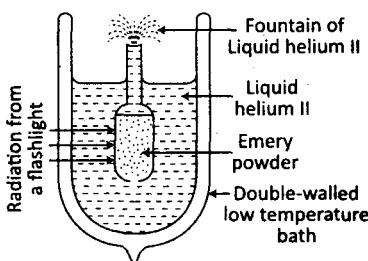


Fig. 2

#### (b) Fountain Effect

A peculiar phenomenon associated with liquid helium II is the *fountain effect*. Fig. 2 shows an apparatus used by Allen and Misener to demonstrate this effect. This liquid helium II between grains of the fine emery powder gets warmed up by the radiation from a flashlight. Consequently, the pressure in the liquid inside the bulb rises and pushes the liquid up producing a fountain.

\*M. W. Zemansky, *Heat and Thermodynamics*, Chapter 15 (1968).

### (c) Creeping Film

Another peculiar phenomenon associated with liquid helium II and discovered by H.K. Onnes

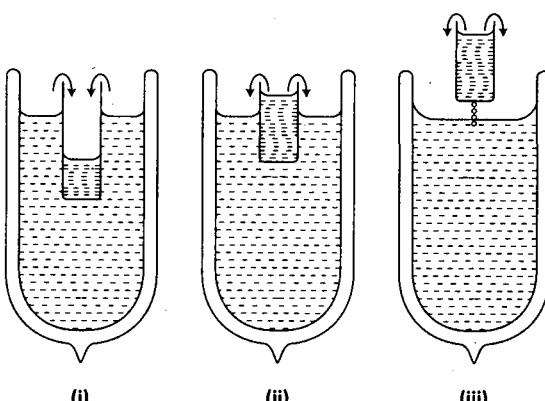


Fig. 3

in 1922 is the fact that the liquid film creeps from a higher to a lower level as shown in Figs. 3(i), (ii) and (iii). In Fig. 3(i), an empty test tube is put into the liquid helium II in a low temperature bath. The liquid film outside the tube creeps up the outer wall and falls into the tube till the liquid levels inside and outside the tube are same. In Fig. 3(ii), the liquid level inside the test tube is higher than that in the bath. Now the liquid film creeps up the inner wall of the tube and drops into the bath till the liquid levels inside and outside the tube are same. In Fig. 3(iii), the liquid film creeps up the inner wall of the tube and drops into the bath till the test tube is completely empty.

### (d) First Sound, Second Sound, Fourth Sound and Third Sound

*First Sound* occurs in liquid helium II when normal and superfluid atoms vibrate together. The propagation of these vibrations involves variations of pressure and density but no variations of temperature. Landau and Tisza independently predicted the occurrence of what they called *second sound*. In second sound, the normal and superfluid atoms vibrate *relative to each other*. These vibrations involve variations of temperature but no variations of pressure and density.

First sound may be produced in liquid helium by a vibrating piston in contact with the liquid. Second sound may be generated by variations in temperature of a paramagnetic salt caused by superposing an alternating magnetic field on a steady field. The speed of second sound was first measured by Peshkov followed by de Klerk, Hudson and Pellam. The formula for the speed of second sound is given by the following formula :

$$v_2 = \sqrt{\frac{\rho_s}{\rho_n} \frac{s^2 T}{c}}, \quad (1)$$

where  $s$  = specific heat capacity of liquid helium II and  $c$  = entropy per unit mass of the liquid.

In 1948 Pellam suggested that a wave might be generated in liquid helium II with only the superfluid atoms undergoing vibrations but with the normal atoms being immobilised in the narrow spaces of a porous material. In 1959, Atkins also arrived at the same view and called this wave *fourth sound*. First and second sound are produced when both normal and superfluid atoms vibrate. When, however normal atoms are damped, first sound reduces to fourth sound, second sound failing to propagate.

The speed of fourth sound is given by the formula

$$v_4 = \left( \frac{\rho_s}{\rho} v_1^2 + \frac{\rho_n}{\rho} v_2^2 \right)^{\frac{1}{2}}, \quad (2)$$

where  $v_1$  = speed of first sound.

In 1959, Atkins predicted the occurrence of a *surface wave\** on liquid helium II and called such a wave *third sound*. He assumed that in this wave the superfluid atoms oscillate whereas the normal atoms remain locked to the wall. This results in oscillation in the thickness of the film. The speed of third sound, found to be in the range of 20 to 500 cm/s, is given by the following formula :

$$v_3^2 = 3 \left( \frac{\rho_n}{\rho} \right) gy, \quad (3)$$

where  $g$  = acceleration due to gravity and  $y$  = height of the film (disturbed by the wave) above the bulk liquid mass.

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\* A surface wave is a wave phenomenon confined to and near the surface of a liquid mass, the liquid further below remaining undisturbed—Newman, F. H. and Searle, V. H. L. *The General Properties of Matter*, p. 391 (1949).

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