EXERCISES

1. Define the co-efficient of :
   (*i*) Volume expansion (*ii*) Isothermal compressibility
   (*iii*) Adiabatic compressibility.
2. Derive the Maxwell relations and explain their importance in thermodynamics.
3. Show that the equation of state of a substance may be written in the form

$$\frac{dv}{v} = -Kdp + \beta dT.$$

4. A substance has the volume expansivity and isothermal compressibility :

$$\beta = \frac{1}{T}\ ;K = \frac{1}{p}$$

   Find the equation of state. $\left[\textbf{Ans. } \frac{pv}{T} = \text{constant}\right]$

5. For a perfect gas, show that the difference in specific heats is

$$c_p - c_v = \frac{R}{T}\ .$$

6. For the following given differential equations,

$$du = Tds - pdv$$

   and $$dh = Tds + vdp$$

   prove that for perfect gas equation,

$$\left(\frac{\partial u}{\partial p}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial h}{\partial p}\right)_T = 0.$$

7. Using the cyclic equation, prove that

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{KT}\cdot$$

8. Prove that the change in entropy is given by

$$ds = \frac{c_v}{T}\left[\frac{KT}{\beta}.dp + \frac{c_p}{\beta v}\right]dv.$$

9. Deduce the following thermodynamic relations :

$$(i)\ \left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p = -c_p\left(\frac{\partial T}{\partial p}\right)_h \qquad (ii)\ \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p.$$

10. Show that for a Van der Waals gas

$$c_p - c_v = \frac{R}{1 - 2a\,(v-b)^2 / RTv^3}\ .$$

11. A gas obeys $p(v - b) = RT$, where b is positive constant. Find the expression for the Joule-Thomson co-efficient of this gas. Could this gas be cooled effectively by throttling ?
12. The pressure on the block of copper of 1 kg is increased from 10 bar to 1000 bar in a reversible process maintaining the temperature constant at 15°C. Determine :
   (*i*) Work done on the copper during the process (*ii*) Change in entropy
   (*iii*) The heat transfer (*iv*) Change in internal energy
   (*v*) $(c_p - c_v)$ for this change of state.
   The following data may be assumed :
   Volume expansivity (β) = 5×10^{-5}/K
   Isothermal compressibility (K) = 8.6×10^{-12} m^2/N
   Specific volume (v) = 0.114×10^{-3} m^3/kg
   [**Ans.** (*i*) – 4.9 J/kg ; (*ii*) – 0.57 J/kg K ; (*iii*) – 164 J/kg ; (*iv*) – 159.1 J/kg ; 9.5 J/kg K]

8

Ideal and Real Gases

8.1. INTRODUCTION

An *'ideal gas'* is defined as a *gas having no forces of intermolecular attraction.* The gases which *follow the gas laws at all ranges of pressures and temperatures* are considered as *"ideal gases".* However, *'real gases' follow these laws at low pressures or high temperatures or both.* This is because the forces of attraction between molecules *tend to be very small* at reduced pressures and elevated temperatures.

An *ideal gas* obeys the law $pv = RT$. The specific heat capacities *are not constant but are functions of temperature.* A *perfect gas* obeys the law $pv = RT$ and has *constant specific heat capacities.*

A perfect gas is well suited to mathematical manipulation and is therefore a most useful model to use for analysis of practical machinery which uses real gases as a working substance.

In *reality there is no ideal or perfect gas.* At a very low pressure and at a very high temperature, real gases like hydrogen, oxygen, nitrogen, helium etc. behave nearly the same way as perfect gases. These gases are called *semi-perfect* or *permanent gases.* The term semi-perfect has the implication that the behaviour of the gases are nearly the same as that of a perfect gas. The term *'permanent'* was used for these gases by earlier chemists who thought that these gases did not change their phase (*i.e.,* did not condense to a liquid state). Hence they are called permanent gases. There is no gas which does not change phase, and there is no permanent gas in the real sense. However, these gases can be changed into a liquid phase only if they are subjected to a great decrease in temperature and increase in pressure.

All gases behave in nearly in a similar way, especially at pressures considerably lower than the critical pressure, and at temperatures above the critical temperature. *The relation between the independent properties, such as pressure, specific volume and temperature for a pure substance* is known as the *'equation of state'.* For engineering calculations, the equation of state for perfect gases can be used for real gases so long as the pressures are well below their critical pressure and the temperatures are above the critical temperature.

8.2. THE EQUATION OF STATE FOR A PERFECT GAS

Boyle's law. It states that *volume of a given mass of a perfect gas varies inversely as the absolute pressure when temperature is constant.*

If p is the absolute pressure of the gas and V is the volume occupied by the gas, then

$$V \propto \frac{1}{p}$$

or pV = Constant, so long as the temperature is constant ...(8.1)

Fig. 8.1 shows the graphical representation of Boyle's law. The curves are rectangular hyperbolas asymptotic to the p-v axis. Each curve corresponds to a different temperature. For any two points on the curve,

$$\frac{p_1}{p_2} = \frac{V_2}{V_1} \qquad ...(8.2)$$

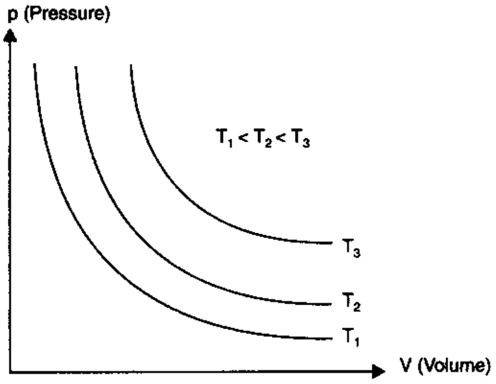


Fig. 8.1. p-V relation of a perfect gas at constant temperature.

Charle's law. It states that *if any gas is heated at constant pressure, its volume changes directly as its absolute temperature.*

In other words, $V \propto T$

or $\frac{V}{T}$ = Constant, so long as pressure is constant ...(8.3)

If a gas changes its volume from V_1 to V_2 and absolute temperature from T_1 to T_2 without any change of pressure, then

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad ...(8.4)$$

Fig. 8.2 gives the graphical representation of Charle's law.

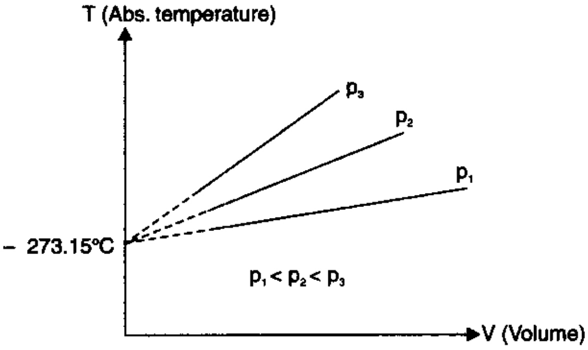


Fig. 8.2. T-v relation of a perfect gas constant pressure.

To derive the *equation of state* for a perfect gas let us consider a *unit mass* of a perfect gas to change its state in the following two successive processes (Fig. 8.3)

(*i*) Process 1-2′ at constant pressure, and

(*ii*) Process 2′-2 at constant temperature.

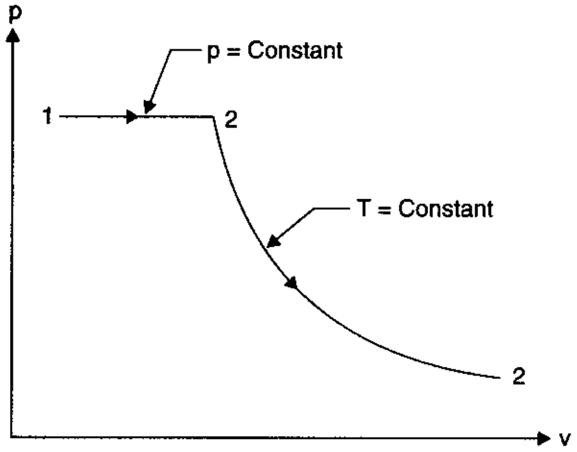


Fig. 8.3. Formulation of equation of state of a perfect gas.

For the *process 1-2′*, applying Charle's law

$$\frac{v_1}{T_1} = \frac{v_2'}{T_2'}$$

and since $T_2' = T_2$, we may write

$$\frac{v_1}{T_1} = \frac{v_2'}{T_2} \qquad \text{...}(i)$$

For the *process 2′-2*, using Boyle's law

$$p_2'v_2' = p_2v_2$$

and since $p_2' = p_1$

$$p_1v_2' = p_2v_2$$

i.e.,

$$v_2' = \frac{p_2v_2}{p_1} \qquad \text{...}(ii)$$

Substituting the value of v_2' from eqn. (*ii*) in eqn. (*i*), we get

$$\frac{v_1}{T_1} = \frac{p_2v_2}{p_1T_2}$$

or

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$$

i.e.,

$$\frac{pv}{T} = \text{constant} \qquad \text{...(8.5)}$$

The magnitude of this constant depends upon the particular gas and it is denoted by R, where R is called the **specific gas constant**. Then

$$\frac{pv}{T} = R$$

The equation of the state for a perfect gas is thus given by the equation

$$pv = RT \qquad ...(8.6)$$

or for m kg, occupying V m^3,

$$pV = mRT \qquad ...(8.7)$$

If the mass is chosen to be numerically equal to the molecular weight of the gas then 1 mole of the gas has been considered, *i.e.*, 1 kg mole of oxygen is 32 kg oxygen, or 1 kg mole of hydrogen is 2 kg hydrogen.

The equation may be written as

$$pV_0 = MRT \qquad ...(8.8)$$

where V_0 = Molar volume, and

M = Molecular weight of the gas.

Avogadro discovered that V_0 *is the same for all gases at the same pressure and temperature* and therefore it may be seen that MR = a constant ; R_0 and thus

$$pV_0 = R_0T \qquad ...(8.9)$$

R_0 is called the **molar or universal gas constant** and its value is **8.3143 kJ/kg mol K.**

If there are n moles present then the ideal gas equation may be written as

$$pV = nR_0T \qquad ...(8.10)$$

where V is the volume occupied by n moles at pressure p and temperature T.

8.3. p-v-T SURFACE OF AN IDEAL GAS

The equation of state of an ideal gas is a relationship between the variables pressure (p), volume (V) and temperature (T). On plotting these variables along three mutually perpendiculars axes, we get a surface which represents the equation of state ($pv = RT$). Such a surface is called *p-v-T surface*. These surfaces represent the fundamental properties of a substance and *provide a tool to study the thermodynamic properties and processes of that substance.* Fig. 8.4 shows a portion of a *p-v-T* surface for an *ideal gas. Each point on this surface represents an equilibrium state and a line on the surface represents a process.* The Fig. 8.4 also shows the constant pressure, constant volume and constant temperature lines.

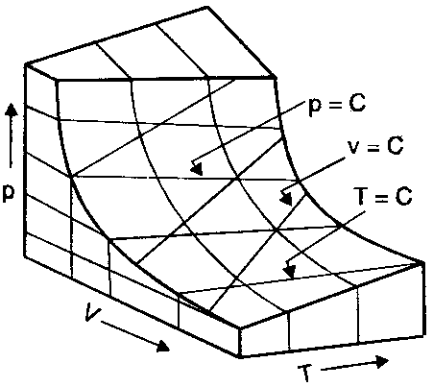


Fig. 8.4

8.4. INTERNAL ENERGY AND ENTHALPY OF A PERFECT GAS

Joule's Law. *Joule's law states that the specific internal energy of a gas depends only on the temperature of the gas and is independent of both pressure and volume.*

i.e., $u = f(T)$

Joule concluded this result from a series of experiments conducted with an apparatus similar to the one shown in Fig. 8.5.

— Two tanks connected by a valve were submerged in a bath of water.

— Initially one tank was evacuated and the other was filled with air under high pressure.

— A thermometer was placed in the water bath.

— After the tank and water had attained the same temperature, the valve between the two tanks was opened to pass air slowly from high pressure tank to the evacuated tank. Time was allowed for equilibrium to be attained.

Joule observed that there was *no change in temperature of water during or after the process.* Since there was no change in the temperature of water, he concluded that there *was no heat transfer between air and water i.e.,* $\delta Q = 0$. And since there was no work during the process, *i.e.,* $\delta W = 0$, from the first law of thermodynamics, $\delta Q = dE + \delta W$, Joule *concluded that change in internal energy of the air is zero, i.e.,* $dE = 0$.

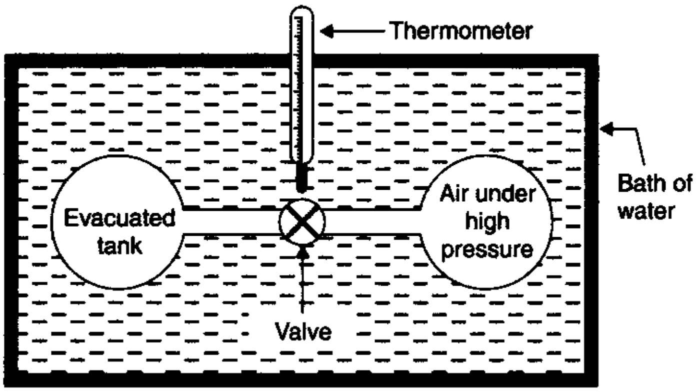


Fig. 8.5. Apparatus for demonstration of Joule's law.

Again, since both pressure and volume changed during the process, he remarked that *internal energy was a function only of temperature ; since during the process temperature did not change, the internal energy remained constant.*

Later on when experiments were conducted with more refined instruments, it was found that there was a *very small change in temperature of water,* indicating that *for real gases internal energy was not a function of temperature alone.* However, at low pressure and high temperature where real gases behave like semi-perfect gases and where the equation of state for a semi-perfect gas, $pv = RT$, is sufficiently accurate, Joule's law holds equally good in that range.

From definition of enthalpy,

$$h = u + pv$$

Also $$pv = RT$$

$\therefore$ $$h = u + RT \qquad ...(8.11)$$

Since u is a function of temperature only, h is a function of temperature,

i.e., $$h = f(T) \qquad ...(8.12)$$

8.5. SPECIFIC HEAT CAPACITIES OF AN IDEAL GAS

The specific heat capacity at constant volume of any substance is defined by

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

It may be seen that as Joule's law for an ideal gas states $u = f(T)$, then

$$c_v = \frac{du}{dT} \qquad \text{...(8.13)}$$

Since $h = u + pv$, Boyle's law, $pV = f(T)$ and Joule's law $u = f(T)$ together show, $h = f(T)$ and by similar argument to the above it may be seen that :

$$c_p = \frac{dh}{dT} \qquad \text{...(8.14)}$$

Further as $h = u + pv$, then $h = u + RT$ and by differentiation

$$\frac{dh}{dT} = \frac{du}{dT} + R$$

Substitution from eqns. (8.13) and (8.14) gives,

$$c_p = c_v + R \quad \text{i.e.,} \quad c_p - c_v = R \qquad \text{...(8.15)}$$

If expressed in terms of molar quantities then eqn. (8.15) becomes

$$C_p - C_v = R_0 \qquad \text{...(8.16)}$$

where C_p and C_v are *molar specific heat capacities.*

Equations for specific heat capacities of ideal gases

Since both u and h are functions of temperature, the equations to c_p and c_v must also be functions of temperature. They are usually expressed in a form :

$$c_p = a + KT + K_1T^2 + K_2\,T^3 \qquad \text{...(8.17)}$$

$$c_v = b + KT + K_1T^2 + K_2T^3 \qquad \text{...(8.18)}$$

where a, b, K, K_1 and K_2 are constants. Values of specific enthalpy etc. are then obtained by integration.

8.6. REAL GASES

It has been observed that when experiments are performed at relatively low pressures and temperatures most of the real gases obey Boyle's and Charle's laws quite closely. But the actual behaviour of real gases at elevated pressures and at low temperatures deviates considerably.

The ideal gas equation $pv = RT$ can be derived analytically using the kinetic theory of gases by making the following **assumptions** :

(*i*) A finite volume of gas contains large number of molecules.

(*ii*) The collision of molecules with one another and with the walls of the container are perfectly elastic.

(*iii*) The molecules are separated by large distances compared to their own dimensions.

(*iv*) The molecules do not exert forces on one another except when they collide.

As long as the above assumptions are valid the behaviour of a real gas approaches closely that of an ideal gas.

8.7. VAN DER WAALS' EQUATION

Van der Waals' equation (for a real gas) may be written as :

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \qquad \text{...[8.19 (a)]}$$

The constants a and b are specific constants and depend upon the type of the fluid considered, 'v' represents the volume per unit mass and R is the gas constant.

If the volume of one mole is considered then the above equation can be written as

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_0 T \qquad \text{...[8.19 (b)]}$$

The units of p, $\bar{v}$, T, R, a and b are as follows :

p (N/m^2), $\bar{v}$ (m^3/kg-mol), T (K) and R = 8314 Nm/kg mol K, a [Nm^4/(kg-mol)^2], b (m^3/kg mol).

Table 8.1. Constants of Van der Waals' Equation

S.No.	*Substance*	*a* *Nm⁴/(kg-mol)²*	*b* *m³/kg-mol*
1.	Hydrogen (H_2)	25105	0.0262
2.	Oxygen (O_2)	139250	0.0314
3.	Carbon dioxide (CO_2)	362850	0.0423
4.	Helium (He)	3417620	0.0228
5.	Air	135522	0.0362
6.	Water (H_2O) vapour	551130	0.0300
7.	Mercury (Hg) vapour	2031940	0.0657

Van der Waals equation was proposed in 1873 for the gaseous and liquid states of a fluid, and accounts qualitatively for many important properties, but quantitatively it fails in many particulars.

The characteristic equation for a perfect gas is obtained by neglecting the finite size of the molecules. If this be taken into account it is obvious that the equation must be modified, for the distance travelled by a molecule between two successive encounters will be less than if the molecules were point spheres. Let the average distance traversed by a molecule between two successive encounters be denoted by λ, the mean free path. In Fig. 8.6 suppose L and M to be the two molecules of diameter 'd' at a distance λ apart. If these molecules were to impinge along the line of centres the path moved over would be less by an amount 'd' than if the molecules were point spheres. Now all the encounters between molecules are not direct, so their mean free paths will be lessened by an amount kd, where k is a fraction. That is, the mean free path is diminished in the ratio $(\lambda - kd) : \lambda$ or $\left(1 - \frac{kd}{\lambda}\right) : 1$.

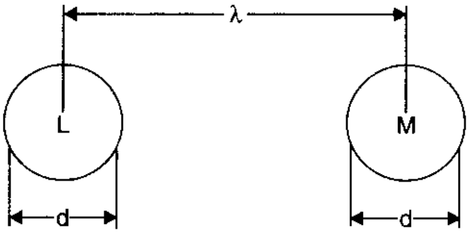


Fig. 8.6

If the mean free path is lessened in this ratio, the encounters per second will be increased in the ratio $1 : 1 - \frac{kd}{\lambda}$. But the pressure of the gas depends upon the encounters per second with the wall of the containing vessel. Hence the new pressure is given by

$$p = \frac{1}{3}\rho \bar{C}^2 \cdot \frac{1}{1 - \frac{kd}{\lambda}} \qquad \text{...(8.20)}$$

(where ρ is the density and $\bar{C}$ is the average velocity).

The mean free path is inversely proportional to the density of the gas, for if the volume were halved, *i.e.,* the density doubled, there would be twice as many molecules in the same space, and therefore any molecule would only have to travel approximately half as far before encountering another molecule. Hence writing v for $\frac{1}{\rho}$ and $\frac{b}{v}$ for $\frac{kd}{\lambda}$ in eqn. (8.20), we get

$$pv\left(1-\frac{b}{v}\right) = \frac{\bar{C}^2}{3} = RT$$

or

$$p(v - b) = RT \qquad \text{...(8.21)}$$

Next consider the *forces of cohesion* which act between a molecule and those surrounding it. When the molecule is sufficiently far removed from the surface of the gas in all directions the resultant of these cohesives forces are equally probable, as the individual forces are varying continuously as the surrounding molecules change their positions. Hence if the resultant is averaged over a sufficient length of time the aggregate force will be nil. *This is not true, however, when the molecule is near the surface.* Let the force from each molecule be resolved into normal and tangential components. All directions for the resultant in the tangential plane are equally likely, but the resultant normal component is most often directed inwards. Averaged over a sufficient length of time the total resultant force will therefore be a normal force always directed inwards. Thus the average effect of the cohesive forces is the same as if there was a permanent field of force acting at and near the surface. This field of force can be regarded as exerting a pressure p_1 over the boundary of the gas. The pressure is proportional to the number of molecules per unit area near the boundary surface and to the normal component of the force. Both of these factors are proportional to the density, so p_1 will be proportional to the square of the density.

i.e.,

$$p_1 = a\rho^2 \qquad \text{...(8.22)}$$

where a is a constant.

Hence the molecules are not deflected by impact alone on reaching the boundary, but as the total result of their impact and of the action of the supposed field of force. That is, their change of momentum may be supposed to be produced by a total pressure $p + p_1$ instead of by the simple pressure p.

Hence eqn. (8.21) now becomes :

$$(p + p_1)(v - b) = RT,$$

or

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

by substitution from p_1 from (8.22) and replacing ρ^2 by $\frac{1}{v^2}$.

Evaluation of constants *a* and *b* :

The general form of the isothermals for carbon dioxide given by Van der Waals' equation is shown in Fig. 8.7. These curves are obtained from the equation,

$$\left(p + \frac{0.00874}{v^2}\right)(v - 0.0023) = \frac{1.00646}{273}\,T \qquad \text{...(8.23)}$$

where the unit of pressure is the atmosphere, and the unit of volume that of the gas at 0°C under one atmosphere pressure.

Van der Waals' equation being a cubic in v has three roots which may be either all real, or two imaginary and one real, as imaginary roots always occur in pairs. In Fig. 8.7, the 40°C isothermal corresponds to the first condition, and the other isothermals to the latter. There is one isothermal where there are three real coincident roots at a point of inflexion. All the isothermals for temperatures higher than that corresponding to the isothermal with three real coincident roots have no horizontal tangent, and all those lower have a maximum and minimum. Consequently this curve is identified with the critical isothermal. The temperature of the critical isothermal is obtained in the following manner. Equation (8.19) may be written

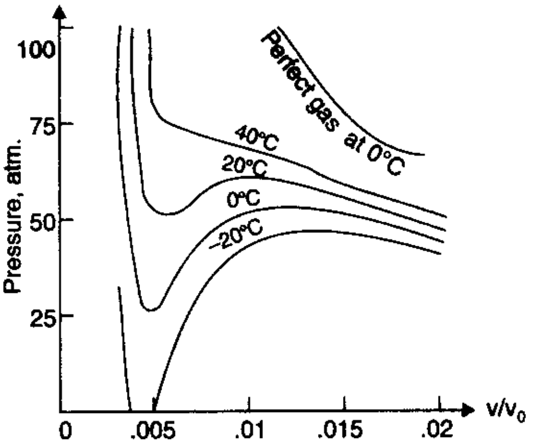


Fig. 8.7. Van der Waals' Isothermal for CO_2.

$$v^3 - \left(b + \frac{RT}{p}\right) v^2 + \frac{av}{p} - \frac{ab}{p} = 0 \qquad ...(8.24)$$

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$$= pv - pb + \frac{a}{v^2} \times v - \frac{a}{v^2} \times b - RT = 0$$

$$= pv - pb + \frac{a}{v} - \frac{ab}{v^2} - RT = 0$$

Multiplying both sides by $\frac{v^2}{p}$, we get

$$pv \times \frac{v^2}{p} - pb \times \frac{v^2}{p} + \frac{a}{v} \times \frac{v^2}{p} - \frac{ab}{v^2} \times \frac{v^2}{p} - \frac{RT}{p} v^2 = 0$$

$$v^3 - \left(b + \frac{RT}{p}\right) v^2 + \frac{av}{p} - \frac{ab}{p} = 0$$

Now at the critical point, as the three roots are equal, the equation must be of the form :

$$(v - v_c)^3 = 0 \qquad ...(8.25)$$

where the suffix c denotes conditions at the critical point. For the critical point equation (8.24) becomes

$$v^3 - \left(b + \frac{RT_c}{p_c}\right) v^2 + \frac{av}{p_c} - \frac{ab}{p_c} = 0 \qquad ...(8.26)$$

Equations (8.25) and (8.26) are identical, hence equating coefficients

$$3v_c = b + \frac{RT_c}{p_c},$$

$$3v_c^2 = \frac{a}{p_c},$$

$$v_c{}^3 = \frac{ab}{p_c},$$

and from these by a simple reduction, we have

$$\left.\begin{aligned} v_c &= 3b \\ p_c &= \frac{a}{27b^2} \\ T_c &= \frac{8}{27} \cdot \frac{a}{bR} \end{aligned}\right\} \qquad \text{...(8.27)}$$

From these equations it follows that *the critical volume, pressure, and temperature are all completely determined by the constants of equation (8.19).*

The equation (8.27) indicates the critical constants for a particular gas and leads to the following results :

The values of a and b are also given by

$$a = 3p_c\, v_c{}^2 = \frac{9}{8}\, RT_c\, v_c = \frac{27}{64} \cdot \frac{R^2T_c^2}{p_c} \qquad \text{...(i)}$$

$$b = \frac{v_c}{3} = \frac{RT_c}{8p_c} \qquad \text{...(ii)}$$

and

$$R = \frac{8}{3}\, \frac{p_c v_c}{T_c} \qquad \text{...(iii)}$$

Using the values of a, b and R in equation (8.23), and substituting in (8.26), we have for carbon dioxide

$$p_c = 61.2 \text{ atmospheres,}$$
$$T_c = 305.3 \text{ K or } 32.2^\circ\text{C}.$$

It is frequently assumed that the approximate agreement between the calculated and experimental values of the critical temperature for carbon dioxide is a sufficient verification of Van der Waals' theory, but the constant b cannot be calculated with the required degree of accuracy from Regnault's experiments to make this an adequate test of the theory.

Also from equations (8.27), we have

$$\frac{p_c v_c}{RT_c} = \frac{3}{8} = 0.375$$

whereas experiment shows that about 0.27 as the average value of this ratio, varying considerably, however, from gas to gas.

The Reduced Equation :

When the pressure, volume and temperature of the fluid are expressed as fractions of the critical pressure, volume and temperature the reduced form of Van der Waals' equation is obtained. Thus, writing

$$p = ep_c = \frac{ea}{27b^2},$$
$$v = nv_c = 3nb,$$
$$T = mT_c = \frac{8}{27} \cdot \frac{ma}{bR}$$

and substituting these values in eqn. (8.19), this reduces to

$$\left(e + \frac{3}{n^2}\right)(3n - 1) = 8m$$

In this *"reduced"* equation the three constants which characterised a particular fluid have disappeared. The equation is accordingly true of any substance which satisfies an equation of the Van der Waals type, and the form of the curves connecting e, n and m is the same for all these substances. Thus we see that two substances, the behaviour of each of which is represented by Van der Waals' equation, will be in corresponding states when the pressure, volume and temperature are the same multiples of their critical values.

This *theorem of corresponding states*, enunciated by Van der Waals, was tested by Amagat and found to be approximately true for a large number of fluids. The theorem of corresponding states is not unique to the equation of Van der Waals. Any equation of state giving a critical point and having not more than three constants will serve equally well to give a reduced equation, in which the constants peculiar to any one fluid disappear, and therefore become the basis of the theorem of corresponding states.

It must be remembered in applying the theorem that the accuracy of results deduced by its aid cannot be greater than the accuracy with which the original equation represents the behaviour of the fluids under consideration.

Amagat's Experiments

As per Amagat's experiments Van der Waals' equation accounts for the variation of the product pv with increasing pressure as follows.

Writing equation (8.19) in the form

$$pv = \frac{RTv}{v - b} - \frac{a}{v},$$

and differentiating with respect to p, keeping T constant, we have

$$\left(\frac{d(pv)}{dp}\right)_T = \left\{\frac{a}{v^2} - \frac{RTb}{(v - b)^2}\right\}\left(\frac{dv}{dp}\right)_T \qquad \text{...(8.28)}$$

Since the condition for a minimum on any isothermal is

$$\left(\frac{d(pv)}{dp}\right)_T = 0,$$

the right-hand side of equation (8.28) must vanish at this point. Now $\left(\frac{dv}{dp}\right)_T$ is *never zero,* so we have as the condition for a *minimum* :

$$\frac{RTb}{(v - b)^2} = \frac{a}{v^2} \quad \text{or} \quad RT \cdot \frac{b}{a} = \left(1 - \frac{b}{v}\right)^2 \qquad \text{...(8.29)}$$

This equation shows that the *volume at which the minimum value of pv occurs on any isothermal gradually increases as the temperature is raised.*

To find the locus of minima the temperature T must be eliminated from equation (8.29) by substitution from the original equation. Thus from equation (8.19)

$$RT = \left(p + \frac{a}{v^2}\right)(v - b),$$

and substituting this in equation (8.28), we have

$$\frac{b}{a}\left(p+\frac{a}{v^2}\right)(v-b)=\left(1-\frac{b}{v}\right)^2,$$

which reduces to $v = b\left(\dfrac{pv^2}{a}+2\right)$

Multiply each side of this equation by p, and put $pv = y$ and $p = x$, and we obtain

$$y = b\left(\frac{y^2}{a}+2x\right) \quad \text{or} \quad y(a-by) = 2abx$$

The above expression gives the locus of minima and is a parabola with axis parallel to the x-axis as shown in Fig. 8.8.

Consider the isothermal which goes through the point A. Here $x = 0$ and $y = \dfrac{a}{b}$.

Writing Van der Waals' equation in terms of x and y, we have

$$\left(1+\frac{ax}{y^2}\right)(y-bx) = RT,$$

and substituting the coordinates of the point A

$$RT = \frac{a}{b}$$

or

$$T = \frac{a}{bR} \qquad \text{...(8.30)}$$

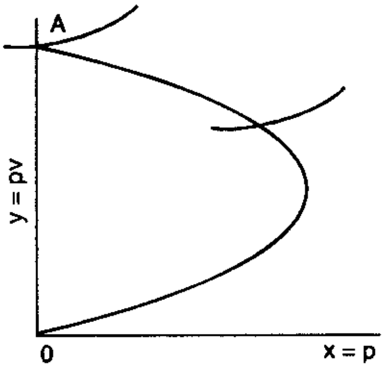


Fig. 8.8

For temperatures above that given by equation (8.30) the minima lie in the region of negative pressure, so an Amagat isothermal for a temperature equal to or greater than $\dfrac{a}{bR}$ will slope upwards along its whole length for increasing values of p, but for a temperature less than $\dfrac{a}{bR}$ the isothermals first dip to a minimum and then rise.

Using the result from equation (8.27)

$$T_c = \frac{8}{27}\,\frac{a}{bR},$$

we see that the limiting temperature for an isothermal to show a *minimum* is

$$T = \frac{27}{8}\,.\,T_c$$

The reason for Amagat finding no dip in the isothermals for hydrogen is now apparent. The critical temperature is 35 K, and therefore the limiting temperature above which minima do not occur is $\dfrac{27}{8} \times 35 = 118.1$ K or – 155°C, and all Amagat's experiments were conducted between 0°C and 100°C.

The Cooling effect :

The most gases show an inversion of the cooling effect at a certain temperature. The equation of Van der Waals indicates at what temperature this occurs.

We have

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \qquad \text{[From eqn. (8.15)]}$$

Keeping p constant and differentiating with respect to T, we get

$$\left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\}\left(\frac{dv}{dT}\right)_p = R$$

or

$$\left(\frac{dv}{dT}\right)_p = \frac{R}{\left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\}}$$

Substituting this value of $\left(\frac{dv}{dT}\right)_p$ in the equation $c_p\mu = T\left(\frac{dv}{dT}\right)_p - v$ (where μ is a measure of cooling effect), we get

$$c_p\mu = \frac{RT}{\left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\}} - v$$

and substituting for RT from equation (8.19) this reduces to

$$c_p\mu = \frac{-bp + \frac{2a}{v} - \frac{3ab}{v^2}}{p - \frac{a}{v^2} + \frac{2ab}{v^3}}$$

The denominator of this expression is *always positive*, since it is $R\left(\frac{dT}{dv}\right)_p$. Hence the cooling effect, μ, is *positive* if

$$bp < \frac{2a}{v} - \frac{3ab}{v^2} \qquad \text{...(8.31)}$$

and *negative* if

$$bp > \frac{2a}{v} - \frac{3ab}{v^2} \qquad \text{...(8.32)}$$

and *inversion occurs* when

$$bp = \frac{2a}{v} - \frac{3ab}{v^2}$$

or

$$p = \frac{a}{b}\left(\frac{2}{v} - \frac{3b}{v^2}\right) \qquad \text{...(8.33)}$$

In order to get the temperature of inversion this equation must be combined with the original equation. Thus

$$\frac{2a}{b}\left(1 - \frac{b}{v}\right)^2 = RT \qquad \text{...(8.34)}$$

Since v is necessarily always greater than b, it will be seen that as v *increases so also does the temperature of inversion.*

The form of curve given by equation (8.33) is shown in Fig. 8.9. The pressure is zero when $v = \frac{3b}{2}$, or infinity. These values of v determine the limiting values of the temperature of inversion, as it is only between these limits that p is positive. Substituting these limits of v in equation (8.34) the limiting values of the temperature of inversion are $\frac{2}{9}\frac{a}{bR}$ and $\frac{2a}{bR}$, or from (8.27), $\frac{3}{4}T_c$ and $\frac{27}{4}T_c$.

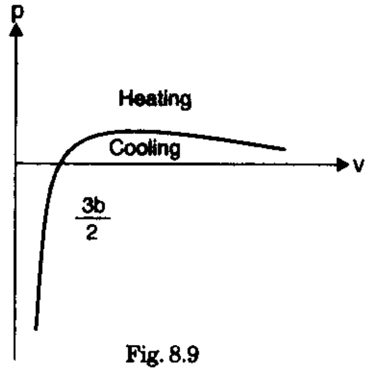


Fig. 8.9

The equation (8.33) being quadratic there are two values of v for a constant value of p at which inversion occurs, as may also be seen by reference to Fig. 8.9. Consequently by equation (8.34) there are two temperatures for a constant value of p at which inversion occurs. As the temperature increases through the lower of these values the change is from a heating to a cooling effect, and as it increases through the higher of these values the change is from a cooling to a heating effect.

The inversion will occur when the maximum value of p is $\frac{a}{3b^2}$, when $v = 3b$. For any value of p less than this there is a cooling effect provided the condition of the substance is represented by a point inside the area enclosed by the curve and the axis of volume, Fig. 8.9, and for any greater value of p there is a heating effect as indicated by equations (8.31) and (8.32) respectively.

Let us take the case of *hydrogen*. In the experiments of Joule and Thomson the pressure used was 4.7 atmospheres. The critical temperature and pressure are 35 K and 15 atmospheres. From equation (8.33) we can find the values of $\frac{b}{v}$ corresponding to the pressure used by Joule and Thomson, and by substitution in equation (8.34) find the two temperatures at which inversion occurs at this pressure. Equation (8.33) can be written as :

$$p = 27p_c\left[2\frac{b}{v} - 3\left(\frac{b}{v}\right)^2\right]$$

Hence
$$\frac{b}{v} = \frac{2 \pm \sqrt{4 - \frac{12p}{27\,p_c}}}{6} = 0.6608 \text{ or } 0.0058$$

by substitution of the above values for p and p_c.

Writing equation (8.34) in the form

$$T = \frac{27}{4}\,T_c\left(1 - \frac{b}{v}\right)^2,$$

we have by substitution for $\frac{b}{v}$: T = 233.5 K or 27.2 K that is, below – 245.9°C there would be a *heating effect*, between – 245.9°C and – 39.6°C *a cooling effect*, and above – 39.6°C a heating effect. Thus **Van der Waals' equation qualitatively accounts for the heating effect observed at ordinary temperatures.**

Limitations of Van der Waals' Equation

Van der Waals' equation under actual condition becomes *invalid* as discussed below :

- The values of a and b (which are assumed to be constant) are found to vary with temperature. Thus the results obtained from the equation are *incorrect when the variation of a and b is large with respect to temperature.*
- The equation is *not accurate enough in the critical region* and it is also obvious from its derivation.

8.8. VIRIAL EQUATION OF STATE

The virial (a Latin word used for force which refers to interaction forces between molecules) equation of state may be expressed as follows :

$$\frac{pv}{RT} = A_0 + A_1p + A_2p^2 + A_3p^3 + ... \qquad ...(8.35)$$

or

$$\frac{pv}{RT} = B_0 + \frac{B_1}{v} + \frac{B_2}{v^2} + \frac{B_3}{v^3} + ... \qquad ...(8.36)$$

where $A_0, A_1, ...$ and $B_0, B_1, ...$ are called the *virial co-efficients which are functions of temperature only.*

- The virial equation can be used only for gases at low and medium densities.
- The *advantage* of virial equation is that the *virial co-efficients can be determined from experimental p-v-T data.*

8.9. BEATTIE-BRIDGEMAN EQUATION

Beattie-Bridgeman equation is expressed as follows :

$$p = \frac{R_0T(1-e)}{(\bar{v})^2}(\bar{v}+B) - \frac{A}{(\bar{v})^2} \qquad ...(8.37)$$

where p = pressure

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right)$$

$$B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

and $e = \frac{c}{\bar{v}T^3}$

The factors A_0, a, B_0, b and c are constants whose values for different gases are given in Table 8.2.

- This equation is normally used for substances at pressures less than critical pressure.
- The equation is accurate enough when the volumes involved are greater than twice the critical volume.
- The equation fits the data of fourteen gases down to the critical point and over a wide range of pressure within ± 0.5% error. However, it is *inaccurate near critical point.*

Table 8.2. Constants of the Beattie-Bridgeman Equation of State

Gas	A_0	a	B_0	b	$c \times 10^{-4}$
Hydrogen (H_2)	20.0117	−0.00506	0.02096	−0.04359	0.0504
Oxygen (O_2)	151.0857	0.02562	0.04624	0.004208	4.80
Carbon dioxide (CO_2)	507.2836	0.07132	0.10476	0.07235	66.0
Helium (He)	2.1886	0.05984	0.01400	0.0	0.0040
Air	131.8441	0.01931	0.04611	−0.001101	4.34
Nitrogen	136.2315	0.02617	0.05046	−0.00691	4.20
Argon	130.7802	0.02328	0.03931	0.0	5.99

8.10. REDUCED PROPERTIES

The ratios of pressure, temperature and specific volume of a real gas to the corresponding critical values are called the **reduced properties.**

$$p_r = \frac{p}{p_c}\ ,\ T_r = \frac{T}{T_c}\ ,\ v_r = \frac{v}{v_c} \qquad \text{...(8.38)}$$

Table 8.3. Critical Constants

Substance	*Pressure (p_c) bar*	*Temperature (T_c) K*
Air	37.69	132.5
Argon	48.64	151.0
Carbon dioxide	73.86	304.2
Carbon monoxide	34.96	133.0
Helium	2.29	5.3
Hydrogen	12.97	33.3
Nitrogen	33.94	126.2
Oxygen	50.76	154.8
Water	228.59	647.15
Ethane	48.84	305.5
Ethylene	51.17	282.4
Methane	46.41	191.1
Propane	42.55	370.0

Table 8.4. Properties of Gases

Gas	*Molecular weight (M)*	c_p *(kJ/kg K)*	c_v *(kJ/kg K)*	$R = c_p - c_v$ *(kJ/kg K)*	$\gamma = \frac{c_p}{c_v}$	$Z_c = \frac{p_c \bar{v}}{R_0 T_c}$
Air	28.97	1.005	0.718	0.287	1.4	0.284
Oxygen	32	0.920	0.660	0.260	1.4	0.307
Nitrogen	28	1.046	0.754	0.292	1.39	0.291
Hydrogen	2	14.40	10.40	4.0	1.38	0.304
Carbon monoxide	28	1.046	0.754	0.292	1.39	—

Carbon dioxide	44	0.840	0.650	0.190	1.3	0.274
Water	18	—	—	0.462	—	0.230
Methane	16	2.22	1.70	0.520	1.3	—
Sulphur dioxide	64	0.796	0.67	0.126	1.19	0.268
Ammonia	17	—	—	0.488	—	—

8.11. LAW OF CORRESPONDING STATES

If any two gases have equal values of reduced pressure and reduced temperature, then they have same values of reduced volume ; i.e., $v_R = f(T_r, p_r)$ *for all gases and the function is the same.*

This law is most accurate in the *vicinity of the critical point.*

8.12. COMPRESSIBILITY CHART

The *compressibility factor* (Z) of any gas is a function of only two properties, usually temperature and pressure, so that $Z = f(T_r, p_r)$ except near the critical point. The value of Z for any real gas may be less or more than unity, depending on pressure and temperature conditions of the gas.

The general compressibility chart is plotted with Z versus p_r for various values of T_r. This is constructed by plotting the known data of one or more gases and can be used for any gas. Such a chart is shown in Fig. 8.10. This chart gives best results for the regions well removed from the critical state for all gases.

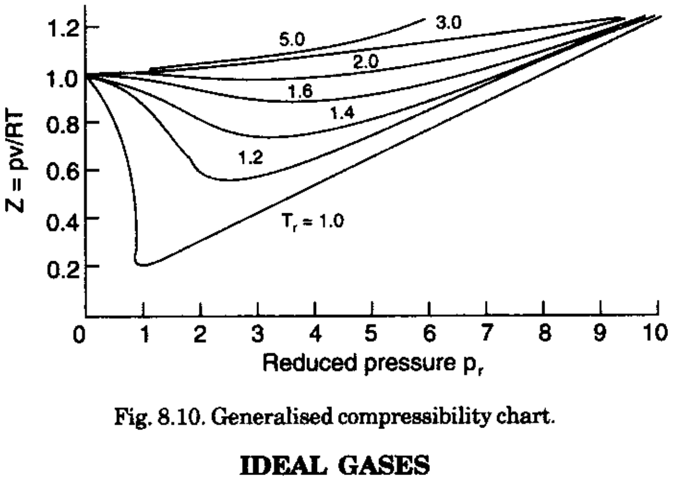


Fig. 8.10. Generalised compressibility chart.

IDEAL GASES

Example 8.1. *The volume of a high altitude chamber is 40 m³. It is put into operation by reducing pressure from 1 bar to 0.4 bar and temperature from 25°C to 5°C.*

How many kg of air must be removed from the chamber during the process ? Express this mass as a volume measured at 1 bar and 25°C.

Take R = 287 J/kg K for air.

Solution. $V_1 = 40\ \text{m}^3$ $V_2 = 40\ \text{m}^3$

$p_1 = 1$ bar $p_2 = 0.4$ bar

$T_1 = 25 + 273 = 298$ K $T_2 = 5 + 273 = 278$ K

kg of air to be removed :

Assuming nitrogen to be a perfect gas,

$$p_1V_1 = m_1RT_1 \qquad \left(\text{or } m_1 = \frac{p_1V_1}{RT_1}\right)$$

$$p_2V_2 = m_2RT_2 \qquad \left(\text{or } m_2 = \frac{p_2V_2}{RT_2}\right)$$

Mass of air removed during the process = (m_1-m_2) kg

$$(m_1-m_2) = \frac{p_1V_1}{RT_1} - \frac{p_2V_2}{RT_2}$$

$$= \frac{1}{R}\left(\frac{p_1V_1}{T_1} - \frac{p_2V_2}{T_2}\right) = \frac{1}{287}\left[\frac{(1\times10^5)\times40}{298} - \frac{(0.4\times10^5)\times40}{278}\right]$$

$$= \mathbf{26.71\ kg.} \quad \textbf{(Ans.)}$$

Volume of this mass of gas at 1 bar and 25°C is given by

$$V = \frac{mRT}{p} = \frac{26.71\times287\times298}{1\times10^5} = \mathbf{22.84\ m^3.} \quad \textbf{(Ans.)}$$

Example 8.2. *A steel flask of 0.04 m³ capacity is to be used to store nitrogen at 120 bar, 20°C. The flask is to be protected against excessive pressure by a fusible plug which will melt and allow the gas to escape if the temperature rises too high.*

(i) How many kg of nitrogen will the flask hold at the designed conditions ?

(ii) At what temperature must the fusible plug melt in order to limit the pressure of a full flask to a maximum of 150 bar ?

Solution. Capacity of the steel flask, $V = 0.04$ m³

Pressure, $p = 120$ bar

Temperature, $T = 20 + 273 = 293$ K

(*i*) **kg of nitrogen the flask can hold :**

Now, R for nitrogen (molecular weight, $M = 28$)

$$= \frac{R_0}{M} = \frac{8314}{28} = 296.9 \text{ J/kg K}$$

Assuming nitrogen to be a perfect gas, we get

Mass of nitrogen in the flask at designed condition

$$= m = \frac{pV}{RT} = \frac{120\times10^5\times0.04}{296.9\times293} = \mathbf{5.51\ kg.} \ \textbf{(Ans.)}$$

(*ii*) **Temperature at which fusible plug should melt, t :**

When the fusible plug is about to melt

$$p = 150 \text{ bar} ;\ V = 0.04 \text{ m}^3 ;\ m = 5.51 \text{ kg}$$

Therefore, temperature t at which fusible plug must melt is given by

$$T = \frac{pV}{mR} = \frac{150\times10^5\times0.04}{5.51\times296.9} = 366.7 \text{ K}$$

$$\therefore \qquad \mathbf{t} = 366.7 - 273 = \mathbf{93.7°C.} \quad \textbf{(Ans.)}$$

Example 8.3. *A balloon of spherical shape 6 m in diameter is filled with hydrogen gas at a pressure of 1 bar abs. and 20°C. At a later time, the pressure of gas is 94 per cent of its original pressure at the same temperature :*

(*i*) *What mass of original gas must have escaped if the dimensions of the balloon is not changed ?*

(*ii*) *Find the amount of heat to be removed to cause the same drop in pressure at constant volume.*

Solution. Diameter of the spherical balloon = 6 m

Pressure of hydrogen gas, $p_1 = 1$ bar abs.

Temperature of hydrogen gas, $T_1 = 20°\text{C}$ or 293 K

At a later time pressure of the gas, $p_2 = 0.94 p_1$ at 293 K.

(*i*) **Mass of original gas escaped :**

$$\Delta m = m_1 - m_2$$

[where m_1 and m_2 are the initial and final masses of the gas]

$$= \frac{p_1V_1}{RT_1} - \frac{p_2V_2}{RT_2} = \frac{V_1}{RT_1}(p_1 - p_2) \quad [\because \; V_1 = V_2,\ T_1 = T_2 \text{ and } p_2 = 0.94p_1]$$

$$= \frac{V_1}{RT_1}(p_1 - 0.94p_1) = \frac{p_1V_1}{RT_1}(1 - 0.94)$$

$\therefore$ **%age mass escaped** $= \dfrac{\Delta m}{m_1} \times 100$

$$= \frac{\dfrac{p_1V_1}{RT_1}(1-0.94)}{\dfrac{p_1V_1}{RT_1}} = \mathbf{6\%}. \quad \textbf{(Ans.)}$$

(*ii*) **Amount of heat to be removed :**

Using the gas equation,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

or

$$\frac{p_1}{T_1} = \frac{0.94p_1}{T_2} \qquad (\because \; V_1 = V_2 \text{ and } p_2 = 0.94p_1)$$

$$\therefore \quad T_2 = 0.94T_1 = 0.94 \times 293 = 275.4 \text{ K or } 2.42°\text{C}$$

The heat to be removed is given by

$$Q = mc_v(T_1 - T_2)$$

where

$$m = \frac{p_1V_1}{RT_1} = \frac{1 \times 10^5 \times \frac{4}{3}\pi \times 3^3}{\frac{8314}{2} \times 293} = 9.28 \text{ kg} \qquad \left[\begin{array}{lr} \because & MR = 8314 \\ \therefore & R = \dfrac{8314}{2} \\ \text{as } M \text{ for } H_2 = 2 & \end{array}\right]$$

$c_v = 10400$ J/kg K for H_2

$\therefore$ Q (heat to be removed) = 9.28 × 10400 (293 – 275.4) = **1.69 MJ. (Ans.)**

Example 8.4. *A vessel of capacity 3 m^3 contains 1 kg mole of N_2 at 90°C.*

(*i*) *Calculate pressure and the specific volume of the gas.*

(*ii*) *If the ratio of specific heats is 1.4, evaluate the values of c_p and c_v.*

(*iii*) *Subsequently, the gas cools to the atmospheric temperature of 20°C ; evaluate the final pressure of gas.*

(iv) Evaluate the increase in specific internal energy, the increase in specific enthalpy, increase in specific entropy and magnitude and sign of heat transfer.

Solution. Mass of N_2, m = 1 kg mole *i.e.,* 28 kg

Capacity of the vessel, $V_1 = 3\ m^3$

Temperature, $T_1 = 90 + 273 = 363$ K

(*i*) **Pressure (p_1) and specific volume (v_1) of the gas :**

Using the relation

$$p_1V_1 = mRT_1$$

$$p_1 \times 3 = 28 \times \left(\frac{8314}{28}\right) \times 363 \qquad \left[\because\ R = \frac{R_0}{M} = \frac{8314}{28}\right]$$

$$\therefore \quad \mathbf{p_1 = 1005994\ J/m^2\ or\ 10.06\ bar.}\quad \textbf{(Ans.)}$$

Specific volume, $\mathbf{v_1} = \frac{V_1}{m} = \frac{3}{28} = \mathbf{0.107\ m^3/kg.}$ **(Ans.)**

(*ii*) $\mathbf{c_p = ?,\ c_v = ?}$

$$\frac{c_p}{c_v} = 1.4 \text{ (given)} \qquad ...(i)$$

But $$c_p - c_v = R = \frac{8314}{28} \qquad ...(ii)$$

Solving for c_p and c_v between (*i*) and (*ii*)

$$\mathbf{c_p = 1.039\ kJ/kg\ K\ ;\ \ c_v = 0.742\ kJ/kg\ K.}\quad \textbf{(Ans.)}$$

(*iii*) **Final pressure of the gas after cooling to 20°C :**

Initially	*After cooling*
$p_1 = 10.06$ bar	$p_2 = ?$
$V_1 = 3\ m^3$	$V_2 = 3\ m^3$
$T_1 = 363$ K	$T_2 = 20 + 273 = 293$ K

Now, $$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

or $$\frac{p_1}{T_1} = \frac{p_2}{T_2} \qquad (\text{as } V_1 = V_2)$$

$$\therefore \quad \mathbf{p_2} = \frac{p_1T_2}{T_1} = \frac{10.06 \times 293}{363} = \mathbf{8.12\ bar.}\quad \textbf{(Ans.)}$$

(*iv*) $\mathbf{\Delta u,\ \Delta h,\ \Delta s,\ Q}$ **:**

For a perfect gas,

Increase in specific internal energy

$$\mathbf{\Delta u} = c_v(T_2 - T_1) = 0.742(293 - 363) = \mathbf{-\ 51.94\ kJ/kg.}\quad \textbf{(Ans.)}$$

Increase in specific enthalpy,

$$\mathbf{\Delta h} = c_p(T_2 - T_1) = 1.039(293 - 363) = \mathbf{-\ 72.73\ kJ/kg.}\quad \textbf{(Ans.)}$$

Increase in specific entropy,

$$\mathbf{\Delta s} = c_v \log_e \left(\frac{T_2}{T_1}\right) + R \log_e \left(\frac{v_2}{v_1}\right)$$

But $v_1 = v_2$

$$\therefore \quad \Delta s = c_v \log_e \left(\frac{T_2}{T_1}\right) = 0.742 \log_e \left(\frac{293}{363}\right) = \mathbf{-\ 0.1589\ kJ/kg\ K.} \quad \textbf{(Ans.)}$$

Now, $Q = \Delta u + W$

Here $W = 0$ as change in volume is zero

$\therefore \quad Q = \Delta u$

$\therefore$ **Heat transfer,** $\mathbf{Q} = -\ 51.94$ kJ/kg $= -\ 51.94 \times 28 =$ **– 1454.32 kJ. (Ans.)**

Example 8.5. (*a*) *1 kg of air at a pressure of 8 bar and a temperature of 100°C undergoes a reversible polytropic process following the law* $pv^{1.2}$ *= constant. If the final pressure is 1.8 bar determine :*

(*i*) *The final specific volume, temperature and increase in entropy ;*

(*ii*) *The work done and the heat transfer.*

Assume $R = 0.287$ *kJ/kg K and* $\gamma = 1.4$.

(*b*) *Repeat (a) assuming the process to be irreversible and adiabatic between end states.*

Solution. (*a*) Mass of air, $m = 1$ kg

Pressure, $p_1 = 8$ bar

Temperature, $T_1 = 100 + 273 = 373$ K

The law followed : $pv^{1.2} =$ constant

Final pressure, $p_2 = 1.8$ bar

Characteristic gas constant, $R = 0.287$ kJ/kg K

Ratio of specific heats, $\gamma = 1.4$

(*i*) **$\mathbf{v_2}$, $\mathbf{T_2}$ and $\mathbf{\Delta s}$:**

Assuming air to be a perfect gas,

$$p_1 v_1 = RT_1$$

$$\therefore \quad v_1 = \frac{RT_1}{p_1} = \frac{(0.287 \times 1000) \times 373}{8 \times 10^5} = 0.1338 \text{ m}^3/\text{kg}$$

Also, $p_1 v_1^{1.2} = p_2 v_2^{1.2}$

$$\text{or} \quad \frac{v_2}{v_1} = \left(\frac{p_1}{p_2}\right)^{1/1.2}$$

$$\text{or} \quad v_2 = v_1 \left(\frac{p_1}{p_2}\right)^{1/1.2} = 0.1338 \left(\frac{8}{1.8}\right)^{1/1.2} = 0.4637 \text{ m}^3/\text{kg}$$

i.e., Final specific volume, $\mathbf{v_2} =$ **0.4637 m³/kg. (Ans.)**

Again, $p_2 v_2 = RT_2$

$$T_2 = \frac{p_2 v_2}{R} = \frac{1.8 \times 10^5 \times 0.4637}{(0.287 \times 1000)} = 290.8 \text{ K}$$

i.e., Final temperature, $\mathbf{t_2} = 290.8 - 273 =$ **17.8°C. (Ans.)**

Increase in entropy Δs is given by,

$$\Delta s = c_v \log_e \left(\frac{T_2}{T_1}\right) + R \log_e \left(\frac{v_2}{v_1}\right)$$

But $$\gamma = \frac{c_p}{c_v} = 1.4 \text{ (given)} \qquad ...(i)$$

and $$c_p - c_v = R \ (= 0.287 \text{ kJ/kg K for air}) \qquad ...(ii)$$

Solving for c_v between (i) and (ii),

$$c_v = 0.717 \text{ kJ/kg K}$$

$$\therefore \quad \Delta s = 0.717 \log_e \left(\frac{290.8}{373}\right) + 0.287 \log_e \left(\frac{0.4637}{0.1338}\right)$$

$$= -0.1785 + 0.3567 = 0.1782 \text{ kJ/kg K}$$

i.e., Increase in entropy, Δs = **0.1782 kJ/kg K. (Ans.)**

(*ii*) **Work done and heat transfer :**

The work done in a polytropic process is given by,

$$W = \frac{p_1v_1 - p_2v_2}{n-1} = \frac{R(T_1 - T_2)}{n-1}$$

$$= \frac{0.287\,(373 - 290.8)}{(1.2-1)} = 117.96 \text{ kJ/kg}$$

i.e., **Work done = 117.96 kJ/kg. (Ans.)**

Heat transfer, $Q = \Delta u + W$

where $$\Delta u = c_v(T_2 - T_1)$$

$$= 0.717\,(290.8 - 373) = -58.94 \text{ kJ/kg}$$

$$\therefore \quad Q = -58.94 + 117.96 = 59.02 \text{ kJ/kg}$$

Hence **heat transfer = 59.02 kJ/kg. (Ans.)**

(*b*) (*i*) Though the process is assumed now to be irreversible and adiabatic, the end states are given to be the same as in (*a*). Therefore, **all the properties at the end of the process are the same as in (a). (Ans.)**

(*ii*) As the process is adiabatic, Q (heat transfer) = **0. (Ans.)**

$$\Delta u = \Delta u \text{ in } (a)$$

Applying first law for this process

$$Q = \Delta u + W$$

$$0 = \Delta u + W$$

or $$W = -\Delta u$$

$$= -(-58.94) = 58.94$$

$\therefore$ **Work done = 58.94 kJ/kg. (Ans.)**

Example 8.6. *Two spheres each 2.5 m in diameter are connected to each other by a pipe with a valve as shown in Fig. 8.11. One sphere contains 16 kg of air and other 8 kg of air when the valve is closed. The temperature of air in both sphere is 25°C. The valve is opened and the whole system is allowed to come to equilibrium conditions. Assuming there is no loss or gain of energy, determine the pressure in the spheres when the system attains equilibrium.*

Neglect the volume of the pipe.

Solution. Volume of each sphere $= \frac{4}{3}\pi R^3 = \frac{4}{3}\pi \times \left(\frac{2.5}{2}\right)^3 = 8.18 \text{ m}^3$

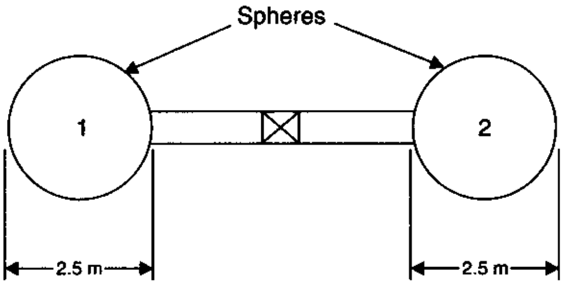


Fig. 8.11

The temperature in both spheres is same (25°C)

i.e., $$T_1 = T_2 = 25 + 273 = 298 \text{ K}$$

As no energy exchange occurs, the temperature reached after equilibrium is 298 K.

Mass of air in sphere 1, $m_1 = 16$ kg

Mass of air in sphere 2, $m_2 = 8$ kg

After opening the valve

Total volume, $V = 8.18 + 8.18 = 16.36 \text{ m}^3$

Total mass, $m = m_1 + m_2 = 16 + 8 = 24$ kg

Now using characteristic gas equation

$$pV = mRT$$

$$\therefore \quad p = \frac{mRT}{V} = \frac{24 \times 287 \times 298}{16.36} = 1.255 \times 10^5 \text{ N/m}^2 \text{ or } 1.255 \text{ bar}$$

Hence **pressure in the spheres when the system attains equilibrium = 1.255 bar. (Ans.)**

Example 8.7. *CO_2 flows at a pressure of 10 bar and 180°C into a turbine, located in a chemical plant, and there it expands reversibly and adibatically to a final pressure of 1.05 bar. Calculate the final specific volume, temperature and increase in entropy. Neglect changes in velocity and elevation.*

If the mass flow rate is 6.5 kg/min. evaluate the heat transfer rate from the gas and the power delivered by the turbine.

Assume CO_2 to be a perfect gas and c_v = 0.837 kJ/kg K.

Solution. *At entry to turbine* *At exit of turbine*

Pressure, $p_1 = 10$ bar Pressure, $p_2 = 1.05$ bar

Temperature, $T_1 = 180 + 273 = 453$ K

Since the expansion is reversible and adiabatic, therefore, the equation pv^γ = constant is applicable.

$$\therefore \quad p_1 v_1^\gamma = p_2 v_2^\gamma \quad \text{...}(i)$$

Eliminating v_1 and v_2 using the perfect gas equation

$$v = \frac{RT}{p}$$

We can write equation (*i*) as

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma - 1)/\gamma}$$

$$\therefore \qquad \frac{453}{T_2} = \left(\frac{10}{1.05}\right)^{(\gamma-1)/\gamma}$$

$$c_v = 0.837 \text{ kJ/kg K (given)}$$

$$R = \frac{R_0}{M} = \frac{8.314}{44} \quad \text{(Molecular weight of } CO_2 = 44)$$

$$= 0.1889 \text{ kJ/kg K}$$

Also $\quad c_p - c_v = R$

$$\therefore \qquad c_p - 0.837 = 0.1889$$

$$c_p = 1.0259 \text{ kJ/kg K}$$

$$\therefore \qquad \gamma = \frac{c_p}{c_v} = \frac{1.0259}{0.837} = 1.23$$

Substituting for γ in equation (*ii*)

$$\frac{453}{T_2} = \left(\frac{10}{1.05}\right)^{(1.23-1)/1.23}$$

$$\therefore \qquad T_2 = 297 \text{ K}$$

Final temperature $= 297 - 273 =$ **24°C. (Ans.)**

$$p_2 v_2 = RT_2$$

$$\therefore \qquad 1.05 \times 10^5 \times v_2 = (0.1889 \times 1000) \times 297$$

$$\therefore \qquad v_2 = \frac{(0.1889 \times 1000) \times 297}{1.05 \times 10^5} = 0.5343 \text{ m}^3\text{/kg}$$

i.e., **Final specific volume = 0.5343 m³/kg. (Ans.)**

As the process is reversible and adiabatic

$$\Delta s = 0$$

i.e., **Increase in entropy = 0. (Ans.)**

Since the process is adiabatic, therefore, **heat transfer rate from turbine = 0. (Ans.)**

Applying steady flow energy equation (S.F.E.E.) on unit time basis,

$$\dot{m}\left[h_1 + \frac{C_1^2}{2} + Z_1\right] + \dot{Q} = \dot{m}\left[h_2 + \frac{C_2^2}{2} + Z_2\right] + W$$

By data changes in velocity and elevation are negligible, and $Q = 0$.

$\therefore$ S.F.E.E. reduces to

i.e.,

$$W = \dot{m}(h_1 - h_2)$$

$$= \dot{m}\, c_p (T_1 - T_2) \qquad \left[as\ \frac{dh}{dT} = c_p,\ h_1 - h_2 = c_p\,(T_1 - T_2)\right]$$

$$= \frac{6.5}{60} \times 1.0259\,(453 - 297) = 17.34 \text{ kW}$$

Hence power delivered by the turbine = 17.34 kW. (Ans.)

Example 8.8. *A certain quantity of air initially at a pressure of 8 bar and 280°C has a volume of 0.035 m³. It undergoes the following processes in the following sequence in a cycle :*

(*a*) *Expands at constant pressure to 0.1 m³,* (*b*) *Follows polytropic process with n = 1.4, and*

(*c*) *A constant temperature process (which completes the cycle).*

Evaluate the following :

(*i*) *The heat received in the cycle ;*

(*ii*) *The heat rejected in the cycle ;*

(*iii*) *Efficiency of the cycle.*

Solution. Fig. 8.12 shows the cycle on *p-V* and *T-s* planes.

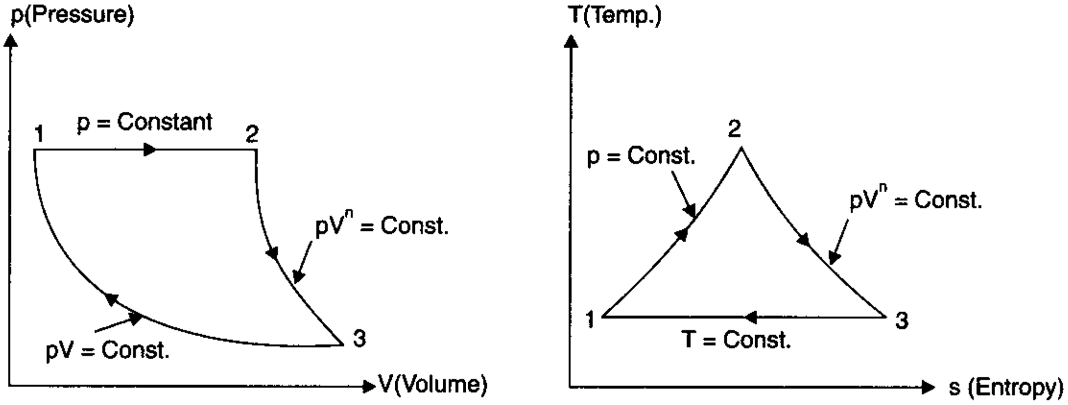


Fig. 8.12

Pressure, $p_1 = 8$ bar

Volume, $V_1 = 0.035 \text{ m}^3$

Temperature, $T_1 = 280 + 273 = 553$ K

Pressure, $p_2 = 8$ bar $(= p_1)$

Volume, $V_2 = 0.1 \text{ m}^3$

Index, $n = 1.4$

To find mass of air, use the relation

$$p_1V_1 = mRT_1$$

$$\therefore \quad m = \frac{p_1V_1}{RT_1} = \frac{8 \times 10^5 \times 0.035}{287 \times 553} = 0.1764 \text{ kg}$$

From $$p_2V_2 = mRT_2$$

$$T_2 = \frac{p_2V_2}{mR} = \frac{8 \times 10^5 \times 0.1}{0.1764 \times 287} = 1580 \text{ K}$$

Also, $$p_2V_2^{1.4} = p_3V_3^{1.4}$$

and $$\frac{T_2}{T_3} = \left(\frac{p_2}{p_3}\right)^{(1.4-1)/1.4}$$

But $T_3 = T_1$ as 1 and 3 are on an isothermal line.

$$\therefore \quad \frac{1580}{553} = \left(\frac{8}{p_3}\right)^{0.4/1.4}$$

$$2.857 = \left(\frac{8}{p_3}\right)^{0.2857}$$

$$p_3 = \frac{8}{(2.857)^{1/0.2857}} = \frac{8}{(2.857)^{3.5}} = 0.2 \text{ bar}$$

Now, $p_3V_3 = mRT_3$

$\therefore$ $0.2 \times 10^5 \times V_3 = 0.1764 \times 287 \times 553$

$\therefore$ $$V_3 = \frac{0.1764 \times 287 \times 553}{0.2 \times 10^5} = 1.399 \text{ m}^3$$

(*i*) **The heat received in the cycle :**

Applying first law to the constant pressure *process 1-2,*

$$Q = \Delta U + W$$

$$W = \int_1^2 pdV \qquad \text{(as the process is reversible)}$$

$$= p(V_2 - V_1)$$

$$= 8 \times 10^5 (0.1 - 0.035)$$

$= 52000$ J or 52 kJ (work done by air)

$\therefore$ $Q = m \times c_v(T_2 - T_1) + 52$

$= 0.1764 \times 0.71(1580 - 553) + 52 = 180.6$ kJ

i.e., Heat received = 180.6 kJ

Applying first law to reversible polytropic *process 2-3*

$$Q = \Delta U + W$$

But $$W = \frac{p_2V_2 - p_3V_3}{n-1} = \frac{mR(T_2 - T_3)}{n-1}$$

$= \dfrac{0.1764 \times 0.287 (1580 - 553)}{1.4 - 1} = 129.98$ kJ (work done **by air**)

$\therefore$ $Q = mc_v(T_3 - T_2) + 129.98$

$= 0.1764 \times 0.71 (553 - 1580) + 129.98$

$= -128.6 + 129.98 = 1.354$ kJ (heat received)

$\therefore$ **Total heat received in the cycle** = 180.6 + 1.354 = **181.954 kJ. (Ans.)**

(*ii*) **The heat rejected in the cycle :**

Applying first law to reversible isothermal *process 3-1,*

$$Q = \Delta U + W$$

$$W = p_3V_3 \log_e \left(\frac{V_1}{V_3}\right)$$

$$= 0.2 \times 10^5 \times 1.399 \times \log_e \left(\frac{0.035}{1.399}\right) \times 10^{-3}$$

$= -103.19$ kJ (work done **on** the air)

$\therefore$ $Q = mc_v(T_1 - T_3) + W$

$= 0 - 103.19 = -103.19$ kJ $\qquad (\because\ T_1 = T_3)$

Hence heat rejected in the cycle = 103.19 kJ. (Ans.)

(*ii*) **Efficiency of the cycle, η_{cycle} :**

$$\eta_{cycle} = \frac{\text{Heat received} - \text{Heat rejected}}{\text{Heat received}}$$

$$= \frac{181.954 - 103.19}{181.954} = 0.433 \text{ or } 43.3\%$$

i.e., **Efficiency of the cycle = 43.3%. (Ans.)**

REAL GASES

Example 8.9. *One kg of CO_2 has a volume of 1 m^3 at 100°C. Compute the pressure by*

(*i*) *Van der Waals' equation*

(*ii*) *Perfect gas equation.*

Solution. (*i*) **Using Van der Waals' equation** :

Molar specific volume, $\bar{v} = 1 \times 44 = 44 \text{ m}^3/\text{kg-mol}$ $(\because M \text{ for } CO_2 = 44)$

Temperature, $T = 100 + 273 = 373$ K

The values of a and b for CO_2 (from Table 8.1)

$a = 362850 \text{ Nm}^4/(\text{kg-mol})^2$

and $b = 0.0423 \text{ m}^3/\text{kg-mol}$

$R_0 = 8314$ Nm/kg-mol K

Van der Waals' equation is written as

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_0T$$

or

$$p = \left(\frac{R_0T}{\bar{v} - b} - \frac{a}{\bar{v}^2}\right)$$

Substituting the values in the above equation, we get

$$\therefore \quad p = \frac{8314 \times 373}{44 - 0.0423} - \frac{362850}{44^2}$$

$= 70548 - 187 =$ **70361 N/m² or 0.7036 bar. (Ans.)**

(*ii*) **Using perfect gas equation :**

$$p\bar{v} = R_0T$$

$$\therefore \quad p = \frac{R_0T}{\bar{v}} = \frac{8314 \times 373}{44} = \textbf{70480 N/m}^2 \textbf{ or 0.7048 bar. (Ans.)}$$

Example 8.10. *A container of 3 m^3 capacity contains 10 kg of CO_2 at 27°C. Estimate the pressure exerted by CO_2 by using :*

(*i*) *Perfect gas equation*

(*ii*) *Van der Waals' equation*

(*iii*) *Beattie Bridgeman equation.*

Solution. Capacity of the container, $V = 3 \text{ m}^3$

Mass of CO_2, $m = 10$ kg

Temperature of CO_2, $T = 27 + 273 = 300$ K

Pressure exerted by CO_2, p :

(*i*) **Using perfect gas equation :**

Characteristic gas constant, $R = \frac{R_0}{M} = \frac{8314}{44} = 188.95$ Nm/kg K (for CO_2)

Using perfect gas equation

$$pV = mRT$$

$$\therefore \quad p = \frac{mRT}{V} = \frac{10 \times 188.95 \times 300}{3}$$

$$= \mathbf{188950\ N/m^2\ or\ 1.889\ bar.\ (Ans.)}$$

(*ii*) **Using Van der Waals' equation :**

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_0 T$$

$$p = \frac{R_0 T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

From Table 8.1

For CO_2 : $a = 362850$ Nm^4/(kg-mol)^2

$b = 0.0423$ m^3/(kg-mol)

$$\bar{v} = \text{Molar specific volume} = \frac{3 \times 44}{10} = 13.2 \text{ m}^3/\text{kg-mol}$$

Now substituting the values in the above equation, we get

$$p = \frac{8314 \times 300}{13.2 - 0.0423} - \frac{362850}{(13.2)^2}$$

$$= 189562 - 2082.5 = \mathbf{187479.5\ N/m^2\ or\ 1.875\ bar.\quad (Ans.)}$$

(*iii*) **Using Beattie Bridgeman equation :**

$$p = \frac{R_0 T(1-e)}{(\bar{v})^2}(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

where p = pressure, $A = A_0\left(1 - \frac{a}{\bar{v}}\right)$, $B = B_0\left(1 - \frac{b}{\bar{v}}\right)$ and $e = \frac{c}{\bar{v}T^3}$

From Table 8.2 $A_0 = 507.2836$, $a = 0.07132$

$B_0 = 0.10476$, $b = 0.07235$

$C = 66 \times 10^4$

$$\therefore \quad A = 507.2836\left(1 - \frac{0.07132}{13.2}\right) = 504.5$$

$$B = 0.10476\left(1 - \frac{0.07235}{13.2}\right) = 0.1042$$

$$C = \frac{66 \times 10^4}{13.2 \times (300)^3} = 0.001852$$

Now substituting the various values in the above equation, we get

$$p = \frac{8314 \times 300(1 - 0.001852)}{(13.2)^2}(13.2 + 0.1042) - \frac{504.5}{(13.2)^2}$$

$$= 190093 - 2.89 \simeq 1.9 \times 10^5 \text{ N/m}^2 = \mathbf{1.9\ bar.\quad (Ans.)}$$

Example 8.11. *One kg-mol of oxygen undergoes a reversible non-flow isothermal compression and the volume decreases from 0.2 m³/kg to 0.08 m³/kg and the initial temperature is 60°C. If the gas obeys Van der Waals' equation find :*

(i) The work done during the process (ii) The final pressure.

Solution. The Van der Waals' equation is written as

$$\left(p + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = R_0 T$$

where p = pressure of the gas ; a, b = constants ; $\bar{v}$ = molar volume ; R_0 = universal gas constant

From Table 8.1

For O_2 : $a = 139250 \text{ Nm}^4/(\text{kg-mol})^2$

$b = 0.0314 \text{ m}^3/\text{kg-mol}$

and $R_0 = 8314 \text{ Nm/kg-mol K}$

$\bar{v}_1 = 0.2 \times 32 = 6.4 \text{ m}^3/\text{kg-mol}$

$\bar{v}_2 = 0.08 \times 32 = 2.56 \text{ m}^3/\text{kg-mol}$.

(*i*) **Work done during the process :**

The work done per kg mole of O_2 is given by

$$W = \int_1^2 p \, . d\bar{v} = \int_1^2 \left[\left(\frac{R_0 T}{\bar{v} - b}\right) - \frac{a}{\bar{v}^2}\right] d\bar{v}$$

$$= R_0 T \left[\log_e(\bar{v} - b)\right]_{\bar{v}_1}^{\bar{v}_2} + \left[\frac{a}{\bar{v}}\right]_{\bar{v}_1}^{\bar{v}_2}$$

$$= R_0 T \left[\log_e\left(\frac{\bar{v}_2 - b}{\bar{v}_1 - b}\right)\right] + \left[a\left(\frac{1}{\bar{v}_2} - \frac{1}{\bar{v}_1}\right)\right]$$

$$= 8314 \times (60 + 273)\left[\log_e\left(\frac{2.56 - 0.0314}{6.4 - 0.0314}\right)\right] + \left[139250\left(\frac{1}{2.56} - \frac{1}{6.4}\right)\right]$$

$= -\ 2557359 + 32636 = -$ **2524723 Nm/kg-mol. (Ans.)**

(*ii*) **The final pressure, p_2 :**

$$p_2 = \frac{R_0 T}{\bar{v}_2 - b} - \frac{a}{\bar{v}_2^{\,2}}$$

$$= \frac{8314 \times 333}{2.56 - 0.0314} - \frac{139250}{(2.56)^2}$$ = **1073651 N/m² or 10.73 bar. (Ans.)**

Example 8.12. *If the values for reduced pressure and compressibility factor for ethylene are 20 and 1.25 respectively, compute the temperature.*

Solution. Reduced pressure, $p_r = 20$

Compressibility factor, $Z = 1.25$

Temperature, T = ?

From the generalised compressibility chart on $Z - p_r$ co-ordinates corresponding to $p_r = 20$ and $Z = 1.25$, $T_r = 8.0$.

Now, since $T = T_c \, T_r$

∴ $\mathbf{T} = 282.4 \times 8.0$ [From Table 8.3, $T_c = 282.4$ K]

= **2259.2 K. (Ans.)**

Example 8.13. *Calculate the density of N_2 at 260 bar and 15°C by using the compressibility chart.*

Solution. Pressure, $p = 260$ bar

Temperature, $T = 15 + 273 = 288$ K

Density, $\rho = ?$

For N_2 (from Table 8.3) : $p_c = 33.94$ bar

$T_c = 126.2$ K

Now
$$p_r = \frac{p}{p_c} = \frac{260}{33.94} = 7.6$$

and
$$T_r = \frac{T}{T_c} = \frac{288}{126.2} = 2.28$$

From the compressibility chart for $p_r = 7.6$ and $T_r = 2.28$, $Z \simeq 1.08$

Also
$$Z = \frac{pv}{RT} = \frac{p}{\rho RT}$$, where ρ stands for density

or
$$\rho = \frac{p}{ZRT} = \frac{260 \times 10^5}{1.08 \times \frac{8314}{28} \times 288} = \mathbf{281.5\ kg/m^3}.$$ **(Ans.)**

Example 8.14. *What should be the temperature of 1.3 kg of CO_2 gas in a container at a pressure of 200 bar to behave as an ideal ?*

Solution. Pressure, $p = 200$ bar

Temperature, $\mathbf{T} = ?$

For CO_2 (from Table 8.3) $p_c = 73.86$ bar

$T_c = 304.2$ K

As the gas behaves like an ideal gas, $Z = 1$

$$p_r = \frac{p}{p_c} = \frac{200}{73.86} = 2.7$$

From compressibility chart for $Z = 1$, $p_r = 2.7$

$T_r = 2.48$

$\therefore$ $\mathbf{T} = T_r \times T_c = 2.48 \times 304.2 = \mathbf{754.4\ K.}$ **(Ans.)**

Example 8.15. *A spherical shaped balloon of 12 m diameter contains H_2 at 30°C and 1.21 bar. Find the mass of H_2 in the balloon using real gas equation.*

Solution. Diameter of spherical balloon = 12 m

$\therefore$ Volume, $V = 4/3\ \pi \times (6)^3 = 904.78\ m^3$

Temperature, $T = 30 + 273 = 303$ K

Pressure, $p = 1.21$ bar

Mass of H_2 in the balloon, m :

For H_2 (from Table 8.3) $p_c = 12.97$ bar

$T_c = 33.3$ K

Now,
$$p_r = \frac{p}{p_c} = \frac{1.21}{12.97} = 0.093$$

$$T_r = \frac{T}{T_c} = \frac{303}{33.3} = 9.1$$

From compressibility charge, corresponding to $p_r = 0.093$ and $T_r = 9.1$

$$Z \simeq 1$$

(This indicates that the gas having higher critical pressure and lower critical temperature behaves like an ideal gas at normal pressure and temperature conditions.)

Also, $$pV = ZmRT$$

or $$\mathbf{m} = \frac{pV}{ZRT} = \frac{1.21 \times 10^5 \times 904.78}{1 \times \left(\frac{8314}{2}\right) \times 303} = \mathbf{86.9\ kg.} \quad \textbf{(Ans.)}$$

Example 8.16. *Determine the value of compressibility factor at critical point (Z_{cp}) for the Van der Waals' gas.*

Solution. Refer Fig. 8.13.

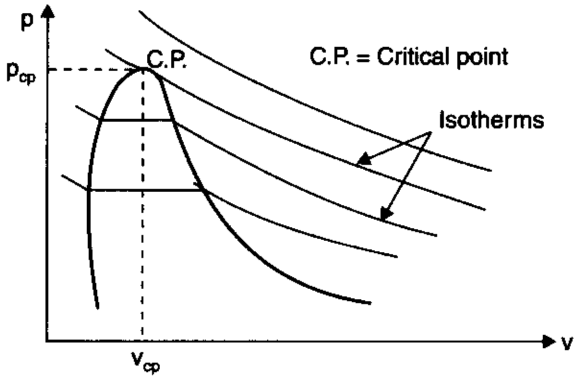


Fig. 8.13

From the isotherms plotted on *p-v* diagram in Fig. 8.13 it can be seen that the critical isotherms has an inflection point, whose *tangent is horizontal* at the *critical point.*

$$\left(\frac{\partial p_c}{\partial v}\right)_{cp} = 0 \text{ and } \left|\frac{\partial^2 p}{\partial v^2}\right|_{cp} = 0$$

The Van der Waal's equation at the critical point is

$$p_{cp} = \frac{R_0 T_{cp}}{\bar{v}_{cp} - b} - \frac{a}{\bar{v}_{cp}^{\,2}} \qquad ...(i)$$

As T_{cp} is constant $$\left(\frac{\partial p_{cp}}{\partial v_{cp}}\right) = -\frac{R_0 T_{cp}}{(\bar{v}_{cp} - b)^2} + \frac{2a}{\bar{v}_{cp}^{\,3}} = 0 \qquad ...(ii)$$

$$\left(\frac{\partial^2 p_{cp}}{\partial v_{cp}^{\,2}}\right) = \frac{2R_0 T_{cp}}{(\bar{v}_{cp} - b)^3} - \frac{6a}{(\bar{v}_{cp})^4} = 0 \qquad ...(iii)$$

$\left(\frac{3}{\bar{v}_{cp}}\right) \times (ii) + (iii)$ gives

$$-\frac{3R_0 T}{\bar{v}_{cp}(\bar{v}_{cp} - b)^2} + \frac{2R_0 T}{(\bar{v}_{cp} - b)^3} = 0$$

or
$$\frac{3}{\bar{v}_{cp}} = \frac{2}{(\bar{v}_{cp} - b)}$$

or
$$\bar{v}_{cp} = 3b$$

Substituting for b in (ii), we get

$$-\frac{R_0 T_{cp}}{[\bar{v}_{cp} - (1/3)\bar{v}_{cp}]^2} + \frac{2a}{(\bar{v}_{cp})^3} = 0$$

$$\therefore \quad a = \frac{9}{8} R_0 T_{cp} \bar{v}_{cp}$$

Substituting for a and b in (i), we get

$$p_{cp} = \frac{R_0 T_{cp}}{\bar{v}_{cp} - (1/3)\bar{v}_{cp}} - \frac{(9/8) R_0 T_{cp} \bar{v}_{cp}}{\bar{v}_{cp}^2}$$

$$\therefore \quad \frac{p_{cp} \bar{v}_{cp}}{R_0 T_{cp}} = \frac{1}{(2/3)} - \frac{(9/8)}{1}$$

But
$$\frac{p_{cp} \bar{v}_{cp}}{R_0 T_{cp}} = Z_{cp}$$

$$\therefore \quad Z_{cp} = \frac{3}{2} - \frac{9}{8} = \frac{3}{8}. \quad \textbf{(Ans.)}$$

HIGHLIGHTS

1. An *'ideal gas'* is defined as a gas having no forces of intermolecular attraction. It obeys the law $pv = RT$. The specific heat capacities are *not constant* but are functions of temperature.
   A *'perfect gas'* obeys the law $pv = RT$ and has *constant* specific heat capacities.
2. The relation between the independent properties, such as pressure, specific volume and temperature for a pure substance is known as *'equation of state'*.
3. Each point on a p-v-T surface represents an equilibrium state and a line on the surface represents a process.
4. *Joule's law* states that the specific internal energy of a gas depends only on the temperature of the gas and is independent of both pressure and volume.
5. Van der Waals' equation may be written as

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

where a and b are constants for the particular fluid and R is the gas constant.

OBJECTIVE TYPE QUESTIONS

Choose the Correct Answer :

1. (*a*) A perfect gas does not obey the law $pv = RT$
   (*b*) A perfect gas obeys the law $pv = RT$ and has constant specific heat
   (*c*) A perfect gas obeys the law $pv = RT$ but have variable specific heat capacities.
2. Boyle's law states that, when temperature is constant, the volume of a given mass of a perfect gas
   (*a*) varies directly as the absolute pressure
   (*b*) varies inversely as the absolute pressure
   (*c*) varies as square of the absolute pressure
   (*d*) does not vary with the absolute pressure.
3. Charle's law states that if any gas is heated at constant pressure, its volume
   (*a*) changes directly as it absolute temperature
   (*b*) changes inversely as its absolute temperature
   (*c*) changes as square of the absolute temperature
   (*d*) does not change with absolute temperature.
4. The equation of the state per kg of a perfect gas is given by
   (*a*) $p^2v = RT$
   (*b*) $pv = RT$
   (*c*) $pv^2 = RT$
   (*d*) $p^2v^2 = RT$.
   where p, v, R and T are the pressure, volume, characteristic gas constant and temperature of the gas respectively.
5. The equation of state of an ideal gas is a relationship between the variables :
   (*a*) pressure and volume
   (*b*) pressure and temperature
   (*c*) pressure, volume and temperature
   (*d*) none of the above.
6. Joule's law states that the specific internal energy of a gas depends only on
   (*a*) the pressure of the gas
   (*b*) the volume of the gas
   (*c*) the temperature of the gas
   (*d*) none of the above.
7. Equation for specific heat at constant pressure of an ideal gas is given by
   (*a*) $c_p = a + KT + K_1T^2 + K_2T^3$
   (*b*) $c_p = a + KT^2 + K_1T^3 + K_2T^4$
   (*c*) $c_p = a + KT^2 + K_1T^4 + K_2T$
   (*d*) $c_p = a + KT^2 + K_1T^3 + K_2T^2$.
   where a, K, K_1 and K_2 are constants.
8. Van der Waals' equation may be written as
   (*a*) $\left(p + \frac{a}{v}\right)(v - b) = RT$
   (*b*) $\left(p + \frac{a}{v^2}\right)(v - b) = RT$
   (*c*) $\left(p + \frac{a}{v^2}\right)(v^2 - b) = RT$
   (*d*) $\left(p + \frac{a}{v^2}\right)(v^2 - b) = RT^2$.

Answers

1\. (*b*) 2. (*b*) 3. (*a*) 4. (*b*) 5. (*c*) 6. (*c*) 7. (*a*)
8\. (*b*).

THEORETICAL QUESTIONS

1. What is an ideal gas ?
2. What is the difference between an ideal and a perfect gas ?
3. What are semi-perfect or permanent gases ?
4. Define 'Equation of state'.
5. State Boyle's and Charle's laws and derive an equation of the state for a perfect gas.
6. What is a p-v-T surface ? Draw a portion of a such a surface.
7. Derive the relationship between the two principal specific heats and characteristic gas constant for a perfect gas.
8. Write a short note on Van der Waals' equation.

UNSOLVED PROBLEMS

IDEAL GASES

1. A vessel of 0.03 m^3 capacity contains gas at 3.5 bar pressure and 35°C temperature. Determine the mass of the gas in the vessel. If the pressure of this gas is increased to 10.5 bar while the volume remains constant, what will be the temperature of the gas ?

   For the gas take $R = 290$ J/kg K. **[Ans.** 0.118 kg, 650°C]

2. The tyre of an automobile contains a certain volume of air at a gauge pressure of 2 bar and 20°C. The barometer reads 75 cm of Hg. The temperature of air in the tyre rises to 80°C due to running of automobile for two hours. Find the new pressure in the tyre.

   Assume that the air is an ideal gas and tyre does not stretch due to heating. **[Ans.** 2.62 bar]

3. A tank made of metal is designed to bear an internal gauge pressure of 7 bar. The tank is filled with a gas at a pressure of 5.5 bar abs., and 15°C. The temperature in the tank may reach to 50°C when the tank stands in the sun.
   - (*i*) If the tank does not expand with temperature, will the design pressure be exceeded on a day when atmospheric pressure is 1 bar and air in the tank reaches 50°C when exposed to hot sun ?
   - (*ii*) What temperature would have to be reached to raise the air pressure to the design limit ?

   [Ans. (*i*) 6.16 bar, (*ii*) 147°C]

4. A vessel of spherical shape is 1.5 m in diameter and contains air at 40°C. It is evacuated till the vacuum inside the vessel is 735 mm of mercury. Determine :
   - (*i*) The mass of air pumped out ;
   - (*ii*) If the tank is then cooled to 10°C what is the pressure in the tank ?

   The barometer reads 760 mm of mercury. Assume that during evacuation, there is no change in temperature of air. **[Ans.** (*i*) 1.91 kg, (*ii*) 3 kPa]

5. A balloon of spherical shape is 8 m in diameter and is filled with hydrogen at a pressure of 1 bar abs. and 15°C. At a later time, the pressure of gas is 95 per cent of its original pressure at the same temperature.
   - (*i*) What mass of original gas must have escaped if the dimensions of the balloon are not changed ?
   - (*ii*) Find the amount of heat to be removed to cause the same drop in pressure at constant volume.

   [Ans. (*i*) 5 per cent, (*ii*) 3.26 MJ]

6. Find the molecular weight and gas constant for the gas whose specific heats are as follows :

   $c_p = 1.967$ kJ/kg K, $c_v = 1.507$ kJ/kg K. **[Ans.** 180.461 kJ/kg K]

7. A constant volume chamber of 0.3 m^3 capacity contains 1 kg of air at 20°C. Heat is transferred to the air until its temperature is 200°C. Find :
   - (*i*) Heat transferred ;
   - (*ii*) Change in entropy and enthalpy. **[Ans.** (*i*) 128.09 kJ, (*ii*) 0.339 kJ/kg K, 180.8 kJ]

8. 1 kg of air at 20°C occupying a volume of 0.3 m^3 undergoes a reversible constant pressure process. Heat is transferred to the air until its temperature is 200°C. Determine :
   - (*i*) The work and heat transferred.
   - (*ii*) The change in internal energy, enthalpy and entropy.

   [Ans. (*i*) 51.5 kJ, 180.8 kJ ; (*ii*) 128.09 kJ, 180.8 kJ, 0.479 kJ/kg K]

9. A balloon of spherical shape, 10 m in diameter is filled with hydrogen at 20°C and atmospheric pressure. The surrounding air is at 15°C and barometer reads 75 mm of Hg. Determine the load lifting capacity of the balloon. **[Ans.** 587.2 kg]

10. Air expands in a cylinder in a reversible adiabatic process from 13.73 bar to 1.96 bar. If the final temperature is to be 27°C, what would be the initial temperature ?

    Also calculate the change in specific enthalpy, heat and work transfers per kg of air.

    [Ans. 524 K, 224.79 kJ/kg, zero, 160.88 kJ/kg]

11. 1 kg mole of N_2 is contained in a vessel of volume 2.5 m^3 at 100°C.
    - (*i*) Find the mass, the pressure and the specific volume of the gas.
    - (*ii*) If the ratio of the specific heats is 1.4, evaluate the values of c_p and c_v.

(*iii*) Subsequently, the gas cools to the atmospheric temperature of 30°C, evaluate the final pressure of the gas.

(*iv*) Evaluate the increase in specific internal energy, the increase in specific enthalpy, increase in specific entropy and magnitude and sign of heat transfer.

[**Ans.** (*i*) 28 kg, 12.37 bar, 0.089 m^3/kg ; (*ii*) c_p = 1.038 kJ/kg K, c_v = 0.745 kJ/kg K ; (*iii*) 10.22 bar ; (*iv*) – 52.16 kJ/kg, – 72.67 kJ/kg, – 0.1536 kJ/kg K, 1465.1 kJ]

12. The pressure and volume of a gas, during a process, change from 1 bar absolute and 2 m^3 respectively to 6 bar absolute and 0.4 m^3 respectively. During the process the increase in the enthalpy of the gas is 200 kJ. Taking c_v = 10.4 kJ/kg K, determine c_p, R and ΔU. [**Ans.** 13 kJ/kg K, 2.6 kJ/kg K, 160 kJ]

13. 1 kg of air at 27°C is heated reversibly at constant pressure until the volume is doubled and then heated reversibly at constant volume until the pressure is doubled. For the total path find :

(*i*) The work ; (*ii*) Heat transfer ;

(*iii*) Change of entropy. [**Ans.** (*i*) 86.14 kJ, (*ii*) 728.36 kJ, (*iii*) 1.186 kJ/kg K]

14. A mass of air initially at 260°C and a pressure of 6.86 bar has a volume of 0.03 m^3. The air is expanded at constant pressure to 0.09 m^3, a polytropic process with $n = 1.5$ is then carried out, followed by a constant temperature process which completes the cycle. All processes are reversible. Find (*i*) The heat received and rejected in the cycle, (*ii*) The efficiency of the cycle.
Show the cycle on p-v and T-s planes. [**Ans.** (*i*) 143.58 kJ, – 20.3 kJ ; (*ii*) 38.4%]

REAL GASES

15. One kg-mol of oxygen undergoes a reversible non-flow isothermal compression and the volume decreases from 0.15 m^3/kg to 0.06 m^3/kg and the initial temperature is 50°C. The gas obeys Van der Waals' equation during the compression. Find :

(*i*) The work done during the process ;

(*ii*) The final pressure. [**Ans.** (*i*) – 6706500 Nm/kg-mol, (*ii*) 13.825 bar]

16. Determine the compressibility factor for O_2 at (*i*) 100 bar – 70°C and (*ii*) at 5 bar and 30°C. [**Ans.** (*i*) 0.71, (*ii*) 0.98]

17. Determine the pressure of air at 205°C having a specific volume of 0.00315 m^3/kg by means of :

(*i*) Ideal gas equation.

(*ii*) Van der Waals' equation ;

(*iii*) Beattie-Bridgeman equation. [**Ans.** (*i*) 435.7 bar, (*ii*) 557.3 bar, (*iii*) 525.8 bar]

9

Gases and Vapour Mixtures

9.1. INTRODUCTION

- A *pure substance* is defined as *a substance having a constant and uniform chemical composition.* A homogeneous mixture of gases which do not react with one another may, therefore, be considered a pure substance. For example, air is a homogeneous mixture of nitrogen, oxygen and traces of other substances like argon, helium, carbon dioxide, etc., and as they do not react with one another, air is regarded a pure substance. The properties of such a mixture can be determined and tabulated just like those of any other pure substance. The properties of air and some combustion products have been determined and tabulated in gas tables. But it is not possible to determine the properties of the unlimited number of mixtures possible, the properties of the mixtures are determined from the properties of the constituent gases.
- In this chapter the mixtures to be considered are those composed of perfect gases, and perfect gases and vapours. The properties of such mixtures are important in combustion calculations. Air and water vapour mixtures are considered later in the chapter with reference to surface condensers, but for moist atmospheric air there is a special nomenclature and this is considered in a separate chapter on *Psychrometrics*.

9.2. DALTON'S LAW AND GIBBS-DALTON LAW

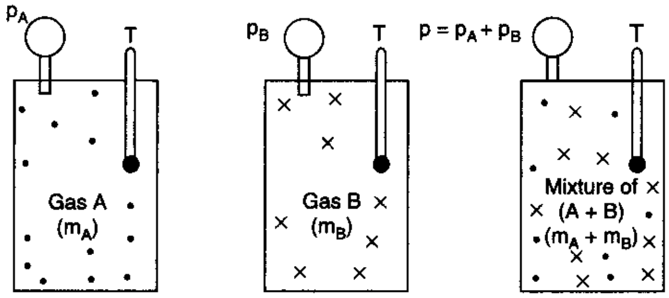
Dalton's law

Let us consider a closed vessel of volume V at temperature T, which contains a mixture of perfect gases at a known pressure. If some of the mixture were removed, then the pressure would be *less* than the initial value. If the gas removed were the full amount of one of the constituents then the reduction in pressure would be equal to the contribution of that constituent to the initial total pressure. Each constituent contributes to the total pressure by an amount which is known as the *partial pressure* of the constituent.

The *relationship between the partial pressures of the constituents* is expressed by Dalton's law, as follows :

- *The pressure of a mixture of gases is equal to the sum of the partial pressures of the constituents.*
- *The partial pressure of each constituent is that pressure which the gas would exert if it occupied alone that volume occupied by the mixtures at the same temperature.*

This is expressed diagrammatically in Fig. 9.1. The gases A and B, originally occupying volume V at temperature T are mixed in the third vessel which is of the *same volume* and is *at the same temperature*.



(*i*) (*ii*) (*iii*)

Fig. 9.1

By the *consideration of mass*,

$$m = m_A + m_B \qquad ...(9.1)$$

By *Dalton's law*,

$$p = p_A + p_B \qquad ...(9.2)$$

Dalton's law is based on experiment and is found to be obeyed more accurately by gas mixtures at low pressures. As shown in Fig. 9.1 each occupant occupies the whole vessel. The example given in Fig. 9.1 and relationship in eqns. (9.1) and (9.2) refer to a mixture of two gases, but the law can be extended to any number of gases,

i.e.,

$$m = m_A + m_B + m_C + ... \text{ or } m = \Sigma\, m_i \qquad ...(9.3)$$

where m_i = Mass of a constituent.

Similarly

$$p = p_A + p_B + p_C + ... \text{ or } p = \Sigma p_i \qquad ...(9.4)$$

where p_i = The partial pressure of a constituent.

Gibbs-Dalton law

Dalton's law was re-formulated by Gibbs to include a second statement on the properties of mixtures. The combined statement is known as the Gibbs-Dalton law, and is as follows :

— *The internal energy, enthalpy, and entropy of a gaseous mixture are respectively equal to the sums of the internal energies, enthalpies, and entropies, of the constituents.*

— *Each constituent has that internal energy, enthalpy and entropy, which it could have if it occupied alone that volume occupied by the mixture at the temperature of the mixture.*

This statement leads to the following equations :

$$mu = m_A u_A + m_A u_B + ... \text{ or } mu = \Sigma\, m_i u_i \qquad ...(9.5)$$

and

$$mh = m_A h_A + m_B h_B + ... \text{ or } mh = \Sigma\, m_i h_i \qquad ...(9.6)$$

and

$$ms = m_A s_A + m_B s_B + ... \text{ or } ms = \Sigma\, m_i s_i \qquad ...(9.7)$$

— ***Properties of air.*** The properties of air which is the most common mixture are given below :

Constituent	*Molecular weight*	*Chemical symbol*	*Volumetric analysis %*	*Gravimetric analysis %*
Oxygen	31.999	O_2	20.95	23.14
Nitrogen	28.013	N_2	78.09	75.53
Argon	39.948	Ar	0.93	1.28
Carbon dioxide	44.01	CO_2	0.03	0.05

Mean molecular weight of air = 28.96

Gas constant $R = 0.287$ kJ/kg K

For *approximate* calculations the air is said to be composed of oxygen and 'atmospheric nitrogen'.

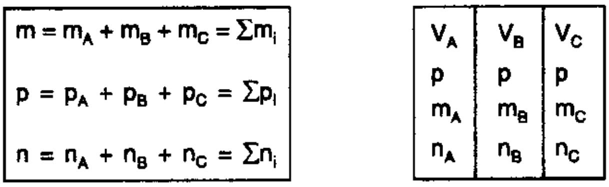
Constituent	*Molecular weight*	*Volumetric analysis %*	*Gravimetric analysis %*
Oxygen	32	21	23.3
Atmospheric nitrogen	28	79	76.7
Nitrogen/Oxygen	—	3.76 : 1	3.29 : 1

Note. Volumetric analysis is the analysis by **volume** ; gravimetric analysis is the analysis by **weight or mass.**

9.3. VOLUMETRIC ANALYSIS OF A GAS MIXTURE

It is usual practice to quote the analysis of a mixture by volume as this is the most convenient for practical determinations. In article 11.15, the analysis of exhaust or flue gases by means of the Orsat apparatus is described. The volume of the gas sample is measured at atmospheric pressure, and the temperature is held constant by means of a water jacket round the gas sample. The constituents are absorbed chemically one by one, and the remainder of the sample is measured after each absorption ; the difference in volume gives the partial volume occupied by the constituent in the mixture.

Let us consider a volume V of a gaseous mixture at a temperature T, consisting of three constituents A, B and C [Fig. 9.2 (*a*)]. Let us further assume that each of the constituents is compressed to a pressure p equal to the total pressure of the mixture, and let the *temperature remain constant*. The partial volumes then occupied by the constituents will be V_A, V_B and V_C.



(*a*) (*b*)

Fig. 9.2

Now using the eqn. $pV = mRT$, we get

$$m_A = \frac{p_A V}{R_A T} \quad \text{... referring to Fig. 9.2 (a)}$$

and

$$m_A = \frac{p V_A}{R_A T} \quad \text{... referring to Fig. 9.2 (b)}$$

Now equating the two values for m_A, we have

$$\frac{p_A V}{R_A T} = \frac{p V_A}{R_A T} \quad i.e., \quad p_A V = p V_A$$

or

$$V_A = \frac{p_A}{p} V$$

In general therefore,

$$V_i = \frac{p_i}{p} V \qquad ...(9.8)$$

i.e.,
$$\Sigma V_i = \sum \frac{p_i V}{p} = \frac{V}{p} \Sigma p_i$$

Now from eqn. (9.4), $p = \Sigma p_i$, therefore,

$$\Sigma V_i = V \qquad ...(9.9)$$

Thus, the *volume of a mixture of gases is equal to the sum of the volumes of the individual constituents when each exists alone at the pressure and temperature of the mixture.*

This is the statement of another empirical law, *the law of partial volumes*, sometimes called *Amagat's law* or *Leduc's law*.

— The analysis of mixtures, oftenly, is simplified if it is carried out in moles. The mole is given by the equation

$$n = \frac{m}{M}$$

where, n = Number of moles,

m = Mass of gas, and

M = Molecular weight.

According to *Avogadro's law*, the *number of moles of any gas is proportional to the volume of the gas at a given pressure and temperature.* Referring to Fig. 9.2 (a), the volume V contains n moles of the mixture at p and T. In Fig. 9.2 (b), the gas A occupies a volume V_A at p and T, and this volume contains n_A moles. Similarly there are n_B moles of gas B in volume V_B and n_C moles of gas C in volume V_C.

From eqn. (9.9), $\Sigma V_i = V$

or $V_A + V_B + V_C = V$

∴ The *total number of moles in the vessel must equal the sum of the moles of the individual constituents,*

$$n = n_A + n_B + n_C = \Sigma n_i \qquad ...(9.10)$$

9.4. THE APPARENT MOLECULAR WEIGHT AND GAS CONSTANT

The Apparent Molecular Weight

In a gas mixture if a gas occupies a total volume of V at a temperature T, then from the definition of partial pressure and equation $pV = nR_0T$, we have

$$p_iV = n_iR_0T \qquad ...(9.11)$$

(where R_0 is the *universal gas constant*)

∴ $\Sigma p_iV = \Sigma n_iR_0T$

i.e., $V \Sigma p_i = R_0T \Sigma n_i$

Also $p = \Sigma p_i$ [from eqn. (9.4)]

∴ $pV = R_0T \Sigma n_i$

Also $n = \Sigma n_i$ [from eqn. (9.10)]

∴ $pV = nR_0T$

The *mixture therefore acts as a perfect gas,* and *this is the characteristic equation for mixture.*

An apparent molecular weight is defined by the equation

$$M = \frac{m}{n}$$

where, m = Mass of the mixture, and

n = Number of moles of mixture.

The Gas Constant

The ***apparent gas constant*** (similarly as above) is defined by the equation

$$R = \frac{R_0}{M}$$

It can be assumed that a mixture of perfect gases obeys all the perfect gas laws.

In order to determine the gas constant for the mixture in terms of the gas constants of the constituents let us consider the equation $pV = mRT$ both for the mixture and for a constituent as follows

$$pV = mRT$$

and $$p_iV = m_iR_iT$$

Then $$\Sigma\, p_iV = \Sigma\, m_iR_iT$$

$\therefore$ $$V\,\Sigma\, p_i = T\,\Sigma\, m_iR_i$$

Also $$p = \Sigma\, p_i$$

$\therefore$ $$pV = T\,\Sigma\, m_iR_i$$

or $$pV = mRT = T\,\Sigma\, m_iR_i$$

i.e., $$mR = \Sigma\, m_iR_i$$

or $$R = \Sigma\, \frac{m_i}{m}\, R_i \qquad \text{...(9.12)}$$

where $\frac{m_i}{m}$ = mass fraction of a constituent.

— From equation (9.11), $p_iV = n_iR_0T$, and combining this with eqn. (9.8) $\left(V_i = \frac{p_i}{p}V\right)$ applied to the mixture (*i.e.,* $pV = nR_0T$), we have

$$\frac{p_iV}{pV} = \frac{n_iR_0T}{nR_0T}$$

or $$\frac{p_i}{p} = \frac{n_i}{n} \qquad \text{...(9.13)}$$

On combining this with eqn. (9.8), we get

$$\frac{p_i}{p} = \frac{n_i}{n} = \frac{V_i}{V} \qquad \text{...(9.14)}$$

This means that the *molar analysis is identical with the volumetric analysis,* and *both are equal to the ratio of the partial pressure to the total pressure.*

— The *apparent molecular weight* can be also be determined by the following method.

Let us apply characteristic equation to each constituent and to mixture, we have

$$m_i = \frac{p_iV}{R_iT}$$

$$m = \frac{pV}{RT}$$

Also $m = \Sigma m_i$ [from eqn. (9.3)]

$$\therefore \quad \frac{pV}{RT} = \sum \frac{p_i V}{R_i T}$$

$$\therefore \quad \frac{p}{R} = \sum \frac{p_i}{R_i}$$

Using the relation $R = \dfrac{R_0}{M}$, and substituting, we have

$$\frac{pM}{R_0} = \sum \frac{p_i M_i}{R_0}$$

or

$$pM = \sum p_i M_i$$

i.e.,

$$M = \sum \frac{p_i}{p} M_i \qquad \text{...(9.15)}$$

Now using eqn. (9.14), we have

$$M = \sum \frac{V_i}{V} M_i \qquad \text{...(9.16)}$$

and

$$M = \sum \frac{n_i}{n} M_i \qquad \text{...(9.17)}$$

Alternately

$$p = \Sigma p_i = p_A + p_B + \text{......} \, p_i$$

Also $pV = mRT$

Similarly $p_A V = m_A R_A T$

$p_B V = m_B R_B T$

$$\therefore \quad pV = p_A V + p_B V + \text{......}$$

or

$$mRT = m_A R_A T + m_B R_B T + \text{......}$$

$$\therefore \quad mR = m_A R_A + m_B R_B + \text{......}$$

But $R = \dfrac{R_0}{M}$, $R_A = \dfrac{R_0}{M_A}$, $R_2 = \dfrac{R_0}{M_B}$

Substituting this in the above equation, we get

$$m \frac{R_0}{M} = m_A \frac{R_0}{M_A} + m_B \frac{R_0}{M_B} + \text{......}$$

$$\therefore \quad \frac{1}{M} = \frac{m_A}{m} \cdot \frac{1}{M_A} + \frac{m_B}{m} \cdot \frac{1}{M_B} + \text{......}$$

$$= \frac{m_{fA}}{M_A} + \frac{m_{fB}}{M_B} + \text{......}$$

where m_{fA}, m_{fB} etc. are the *mass fractions* of the constituents.

$$\therefore \quad \frac{1}{M} = \sum \frac{m_{fi}}{M_i}$$

$$\therefore \quad M = \frac{1}{\sum \dfrac{m_{fi}}{M_i}} \qquad \text{...(9.18)}$$