Differentiating both sides, we get

$$\frac{1}{2.302p} \cdot \frac{dp}{dT} = \frac{3276.6}{T^2} - \frac{0.652}{2.302\,T}$$

or
$$\frac{dp}{dT} = 2.302 \times 3276.6 \times \frac{p}{T^2} - 0.652\,\frac{p}{T} \quad \text{...(ii)}$$

From (*i*) and (*ii*), we have

or
$$\frac{h_{fg}}{v_g T} = 2.302 \times 3276.6 \times \frac{p}{T^2} - 0.652\,\frac{p}{T} \quad \text{...(iii)}$$

We know that $\log_{10} p = 7.0323 - \frac{3276.6}{T} - 0.652 \log_{10} T$ ... (given)

At $p = 0.1$ bar,

$$\log_{10} (0.1) = 7.0332 - \frac{3276.6}{T} - 0.652 \log_{10} T$$

$$-1 = 7.0323 - \frac{3276.6}{T} - 0.652 \log_{10} T$$

or
$$0.652 \log_{10} T = 8.0323 - \frac{3276.6}{T}$$

or
$$\log_{10} T = 12.319 - \frac{5025.4}{T}$$

Solving by hit and trial method, we get

$$T = 523 \text{ K}$$

Substituting this value in eqn. (*iii*), we get

$$\frac{294.54 \times 10^3}{v_g \times 523} = 2.302 \times 3276.6 \times \frac{0.1 \times 10^5}{(523)^2} - 0.652 \times \frac{0.1 \times 10^5}{523}$$

$$\frac{563.17}{v_g} = 275.75 - 12.46$$

i.e.,
$$\mathbf{v_g = 2.139\ m^3/kg.} \quad \textbf{(Ans.)}$$

HIGHLIGHTS

1. Maxwell relations are given by

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \;;\; \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \;;\; \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T.$$

2. The specific heat relations are

$$c_p - c_v = \frac{vT\beta^2}{K} \;;\; c_v = T\left(\frac{\partial s}{\partial T}\right)_v \;;\; c_p = T\left(\frac{\partial s}{\partial T}\right)_p.$$

3. Joule-Thomson co-efficient is expressed as

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h.$$

4. Entropy equations (*Tds* equations) :

$$Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \qquad ...(1)$$

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \qquad ...(2)$$

5. Equations for *internal energy* and *enthalpy* :

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \qquad ...(1)$$

$$du = c_v dT + \left\{T\left(\frac{\partial p}{\partial T}\right)_v - p\right\} dv \qquad ...[1\ (a)]$$

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p \qquad ...(2)$$

$$dh = c_p dT + \left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\} dp \qquad ...[2\ (a)]$$

OBJECTIVE TYPE QUESTIONS

Choose the Correct Answer :

1. The specific heat at constant pressure (c_p) is given by

(*a*) $c_p = T\left(\frac{\partial s}{\partial T}\right)_p$ (*b*) $c_p = T\left(\frac{\partial T}{\partial s}\right)_p$

(*c*) $c_p = T\left(\frac{\partial v}{\partial T}\right)_p$ (*d*) $c_p = T\left(\frac{\partial v}{\partial T}\right)_p$.

2. The specific heat relation is

(*a*) $(c_p - c_v) = \frac{vT\beta^2}{K}$ (*b*) $(c_p - c_v) = \frac{vTK}{\beta^2}$

(*c*) $(c_p - c_v) = \frac{pTK}{\beta^2}$ (*d*) $(c_p - c_v) = \frac{v^2T\beta}{K}$.

3. The relation of internal energy is

(*a*) $du = \left(\frac{K}{\beta}c_v\right)dp + \left(\frac{c_p}{v\beta} - p\right)dv$ (*b*) $du = \left(\frac{K}{\beta}c_v\right)dp + \left(\frac{c_p}{v\beta} + p\right)dv$

(*c*) $du = \left(\frac{K}{\beta}c_p\right)dp + \left(\frac{c_p}{v\beta} - v\right)dv$ (*d*) $du = \left(\frac{K}{\beta}c_p\right)dp + \left(\frac{c_v}{v\beta} - p\right)dv$.

4. *Tds* equation is

(*a*) $Tds = c_v dT + \frac{T\beta}{K} dv$ (*b*) $Tds = c_p dT - \frac{T\beta}{K} dv$

(*c*) $Tds = c_v dT + \frac{TK}{\beta} dv$ (*d*) $Tds = c_v dT + \frac{T\beta}{K} dp$.

Answers

1. (*a*) 2. (*a*) 3. (*a*) 4. (*a*).

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

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

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 $(\beta) = 5 \times 10^{-5}$/K
   Isothermal compressibility $(K) = 8.6 \times 10^{-12}$ m²/N
   Specific volume $(v) = 0.114 \times 10^{-3}$ m³/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.*