

### 9.5. SPECIFIC HEATS OF A GAS MIXTURE

— As per Gibbs-Dalton law, the internal energy of a mixture of gases is given by

$$mu = \Sigma m_i u_i \quad \dots(i) \quad [\text{from eqn. (9.5)}]$$

Also  $u = c_v T$   $\dots(ii)$  [from perfect gas equation]

Now from (i) and (ii), we have

$$mc_v T = \Sigma m_i c_{vi} T$$

$$\therefore mc_v = \Sigma m_i c_{vi}$$

or  $c_v = \Sigma \frac{m_i}{m} c_{vi} \quad \dots(9.19)$

Similarly from equations,  $mh = \Sigma m_i h_i$

and  $h = c_p T$ , we get

$$mc_p T = \Sigma m_i c_{pi} T$$

$$\therefore mc_p = \Sigma m_i c_{pi}$$

or  $c_p = \Sigma \frac{m_i}{m} c_{pi} \quad \dots(9.20)$

From eqns. (9.18) and (9.19),

$$c_p - c_v = \Sigma \frac{m_i}{m} c_{pi} - \Sigma \frac{m_i}{m} c_{vi} = \Sigma \frac{m_i}{m} (c_{pi} - c_{vi})$$

Also  $c_{pi} - c_{vi} = R_i$ , therefore,

$$c_p - c_v = \Sigma \frac{m_i}{m} R_i$$

Also from eqn. (9.12),  $R = \Sigma \frac{m_i}{m} R_i$ , therefore for the mixture

$$c_p - c_v = R$$

The following equations can be applied to a mixture of gases

$$\gamma = \frac{c_p}{c_v}; \quad c_v = \frac{R}{\gamma - 1}; \quad c_p = \frac{\gamma R}{\gamma - 1}$$

It should be borne in mind that  $\gamma$  must be determined from the eqn.  $\gamma = \frac{c_p}{c_v}$ ; there is no weighted mean expression as there is for  $R$ ,  $c_v$  and  $c_p$ .

— In problems on mixtures it is often convenient to work in moles and the specific heats can be expressed in terms of the mole. These are known as *molar heats*, and are denoted by  $C_p$  and  $C_v$ .

Molar heats are defined as follows :

$$C_p = Mc_p \quad \text{and} \quad C_v = Mc_v \quad \dots(9.21)$$

But  $c_p - c_v = R$

$$\therefore C_p - C_v = Mc_p - Mc_v = M(c_p - c_v) = MR$$

But  $MR = R_0$

$$\therefore C_p - C_v = R_0 \quad \dots(9.22)$$

Also  $U = mc_v T = \frac{mMc_v T}{M}$

Again,  $\frac{m}{M} = n$  and  $Mc_v = C_v$

$$\therefore U = nC_v T \quad \dots(9.23)$$

Similarly,  $H = nC_p T \quad \dots(9.24)$

By the Gibbs-Dalton law,

$$U = \sum U_i \quad \text{and} \quad H = \sum H_i$$

$$\therefore nC_v T = \sum n_i C_{vi} T \quad \text{and} \quad nC_p T = \sum n_i C_{pi} T$$

i.e.,  $C_v = \sum \frac{n_i}{n} C_{vi} \quad \dots(9.25)$

and  $C_p = \sum \frac{n_i}{n} C_{pi} \quad \dots(9.26)$

### 9.6. ADIABATIC MIXING OF PERFECT GASES

— Fig. 9.3 shows two gases A and B separated from each other in a closed vessel by a thin diaphragm. If the diaphragm is removed or punctured then the gases mix and each then occupies the total volume, behaving as if the other gas were not present. This process is equivalent to a *free expansion* of each gas, and is *irreversible*. The process can be simplified by the assumption that it is *adiabatic*; this means that the vessel is perfectly thermally insulated and there will therefore be an *increase in entropy of the system*.

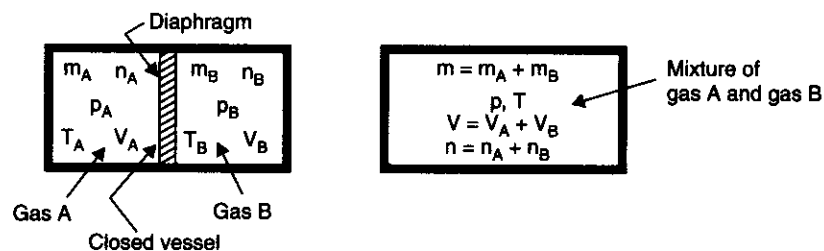


Fig. 9.3

In a *free expansion process*, the internal energy initially is equal to the internal energy finally. In this case, from eqn. (9.23),

$$U_1 = n_A C_{vA} T_A + n_B C_{vB} T_B$$

and

$$U_2 = (n_A C_{vA} + n_B C_{vB}) T$$

If this result is extended to any number of gases, we have

$$U_1 = \sum n_i C_{vi} T_i \quad \text{and} \quad U_2 = T \sum n_i C_{vi}$$

Then

$$U_1 = U_2$$

i.e.,

$$\sum n_i C_{vi} T_i = T \sum n_i C_{vi}$$

i.e.,

$$T = \frac{\sum n_i C_{vi} T_i}{\sum n_i C_{vi}} \quad \dots(9.27)$$

— When two streams of fluid meet to form a *common stream in steady flow*, they give another form of mixing (Fig. 9.4).

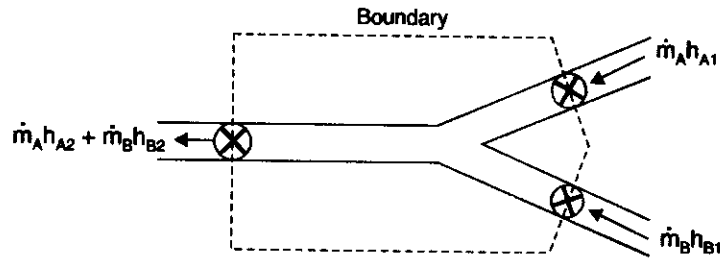


Fig. 9.4

Applying steady-flow energy equation to the *mixing section* (neglecting changes in kinetic and potential energy), we get

$$\dot{m}_A h_{A_1} + \dot{m}_B h_{B_1} + Q = \dot{m}_A h_{A_2} + \dot{m}_B h_{B_2} + W$$

In case of *adiabatic flow* :  $Q = 0$ , and also  $W = 0$  in this case

$$\therefore \dot{m}_A h_{A_1} + \dot{m}_B h_{B_1} = \dot{m}_A h_{A_2} + \dot{m}_B h_{B_2}$$

Also  $h = c_p T$ , hence,

$$\dot{m}_A c_{pA} T_A + \dot{m}_B c_{pB} T_B = \dot{m}_A c_{pA} T + \dot{m}_B c_{pB} T$$

For any number of gases this becomes

$$\sum \dot{m}_i c_{pi} T_i = T \sum \dot{m}_i c_{pi}$$

i.e., 
$$T = \frac{\sum \dot{m}_i c_{pi} T_i}{\sum \dot{m}_i c_{pi}} \quad \dots(9.28)$$

Also,  $C_p = M c_p$  and  $M = m/n$

$\therefore n C_p = m c_p$

Hence, 
$$T = \frac{\sum n_i C_{pi} T_i}{\sum n_i C_{pi}} \quad \dots(9.29)$$

Eqns. (9.28) and (9.29) represent *one condition which must be satisfied in an adiabatic mixing process of perfect gas in steady flow*. In a particular problem some other information must be known (e.g., specific volume or the final pressure) before a complete solution is possible.

### 9.7. GAS AND VAPOUR MIXTURES

Fig. 9.5 (i) shows a vessel of fixed volume which is maintained at a constant temperature. The vessel is *evacuated* and the absolute pressure is therefore *zero*.

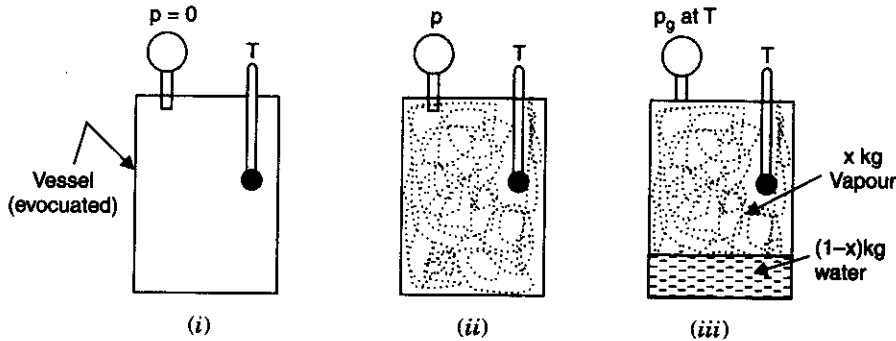


Fig. 9.5

In Fig. 9.5 (ii) a small quantity of water is introduced into the vessel and it evaporated to occupy the whole volume. For a small quantity of water introduced, the pressure in the vessel will be less than the saturation pressure corresponding to the temperature of the vessel. At this condition of pressure and temperature the vessel will be occupied by *superheated vapour*. As more water is introduced the pressure increases and the water continues to evaporate until such a condition is reached that the *volume can hold no water*. Any additional water introduced into the vessel after this will not evaporate but will exist as water, the condition being as in Fig. 9.5 (iii), which shows the vapour in contact with its liquid per kg of water introduced, the vessel can be thought of as containing either  $(1 - x)$  kg of water plus  $x$  kg of dry saturated vapour, or as containing 1 kg of wet steam of dryness fraction  $x$ .

The *temperature remains constant during the whole process of evaporation*. If the temperature is now raised by the addition of heat, then more vapour will evaporate and the pressure in the vessel will increase. Eventually the *vessel will contain a superheated vapour as before, but at a higher pressure and temperature*.

In Fig. 9.5 the vessel is considered to be initially evacuated, but the water would evaporate in exactly the same way, if the vessel contains a gas or a mixture of gases. As stated in the Gibbs-Dalton law, each constituent behaves as if it occupies the whole vessel at the temperature of the vessel. When a little water is sprayed into a vessel containing a gas mixture, then the vapour forced will exert the saturation pressure corresponding to the temperature of the vessel, and this is the partial pressure of the vapour in the mixture.

In case there is a *saturated vapour in a mixture*, then the partial pressure of the vapour can be found from tables at the temperature of the mixture. This means that a saturated vapour obeys the Gibbs-Dalton law ; *this is only a good approximation at low values of the total pressure*.

Mixtures of air and water vapour have been considered in this chapter ; in chapter 9 moist atmospheric air (*i.e.*, a mixture of dry air and water vapour) has been considered as a separate topic-*Psychrometrics*.

**Example 9.1.** A vessel of  $0.35 \text{ m}^3$  capacity contains  $0.4 \text{ kg}$  of carbon monoxide (molecular weight = 28) and  $1 \text{ kg}$  of air at  $20^\circ\text{C}$ . Calculate :

- (i) The partial pressure of each constituent,
- (ii) The total pressure in the vessel, and

The gravimetric analysis of air is to be taken as 23.3% oxygen (molecular weight = 32) and 76.7% nitrogen (molecular weight = 28).

**Solution.** Capacity of the vessel,  $V = 0.35 \text{ m}^3$   
 Mass of carbon monoxide =  $0.4 \text{ kg}$   
 Mass of air =  $1 \text{ kg}$   
 Temperature,  $T = 20^\circ\text{C}$  or  $293 \text{ K}$

Mass of oxygen present in 1 kg of air =  $\frac{23.3}{100} \times 1 = 0.233 \text{ kg}$

Mass of nitrogen present in 1 kg of air =  $\frac{76.7}{100} \times 1 = 0.767 \text{ kg}$

But, characteristic gas constant,

$$R = \frac{R_0}{M} \quad \dots(i)$$

where,  $R_0 =$  Universal gas constant ( $= 8.314 \text{ kJ/kg K}$ ), and  
 $M =$  Molecular weight.

Also, the characteristic gas equation is given by

$$pV = mRT \quad \dots(ii)$$

$$\therefore pV = \frac{mR_0T}{M} \quad \dots(iii)$$

*i.e.*, 
$$p = \frac{mR_0T}{MV} \quad \dots(iv)$$

Hence, for a constituent,

$$p_i = \frac{m_i R_0 T}{M_i V} \quad \dots(v)$$

Substituting the values, we get the partial pressures as follows :

(i) **Partial pressures :**

$$\text{For } O_2, \quad p_{O_2} = \frac{0.233 \times (8.314 \times 10^3) \times 293}{32 \times 0.35 \times 10^5} = 0.5068 \text{ bar. (Ans.)}$$

$$\text{For } N_2, \quad p_{N_2} = \frac{0.767 \times (8.314 \times 10^3) \times 293}{28 \times 0.35 \times 10^5} = 1.9065 \text{ bar. (Ans.)}$$

$$\text{For } CO, \quad p_{CO} = \frac{0.40 \times (8.314 \times 10^3) \times 293}{28 \times 0.35 \times 10^5} = 0.9943 \text{ bar. (Ans.)}$$

(ii) **Total pressure in the vessel, p :**

$$p = \Sigma p_i = p_{O_2} + p_{N_2} + p_{CO} \\ = 0.5068 + 1.9065 + 0.9943 = 3.4076 \text{ bar. (Ans.)}$$

**Example 9.2.** *The gravimetric analysis of air and other data are as follows :*

Constituent	Percentage	Molecular weight
Oxygen	23.14	32
Nitrogen	75.53	28
Argon	1.28	40
Carbon dioxide	0.05	44

Calculate : (i) Gas constant for air ;

(ii) Apparent molecular weight.

**Solution.** Using the relation,  $R = \frac{R_0}{M}$  ... (i)

$$R_{O_2} = \frac{8.314}{32} = 0.2598 \text{ kJ/kg K}$$

$$R_{N_2} = \frac{8.314}{28} = 0.2969 \text{ kJ/kg K}$$

$$R_{Ar} = \frac{8.314}{40} = 0.2078 \text{ kJ/kg K}$$

$$R_{CO_2} = \frac{8.314}{44} = 0.1889 \text{ kJ/kg K}$$

(i) **Gas constant for air :**

Now using the equation,

$$R = \sum \frac{m_i}{m} R_i, \text{ we have} \quad \dots(ii)$$

$$R = 0.2314 \times 0.2598 + 0.7553 \times 0.2969 + 0.0128 \times 0.2078 + 0.0005 \times 0.1889 \\ = 0.0601 + 0.2242 + 0.00266 + 0.00009 = 0.2871 \text{ kJ/kg K}$$

Hence gas constant for air = 0.2871 kJ/kg K. (Ans.)

(ii) **Apparent molecular weight :**

Now from eqn. (i), we have  $M = \frac{8.314}{0.2871} = 28.96$

Hence apparent molecular weight = 28.96. (Ans.)

**Example 9.3.** Following is the gravimetric analysis of air :

Constituent	Percentage
Oxygen	23.14
Nitrogen	75.53
Argon	1.28
Carbon dioxide	0.05

Calculate the analysis by volume and the partial pressure of each constituent when the total pressure is 1 bar.

**Solution.** We know that the analysis by volume  $V_i/V$ , is the same as the mole fraction  $n_i/n$ . Also  $n_i = m_i/M_i$ ; therefore considering 1 kg of mixture and using a tabular method, we have

Constituent	$m_i$	$M_i$	$n_i = \frac{m_i}{M_i}$	$\frac{n_i}{n} \times 100\% = \frac{V_i}{V} \times 100\%$ . (Ans.)
Oxygen	0.2314	32	0.00723	$\frac{0.00723 \times 100}{0.03453} = 20.94\%$ . (Ans.)
Nitrogen	0.7553	28	0.02697	$\frac{0.02697 \times 100}{0.03453} = 78.10\%$ . (Ans.)
Argon	0.0128	40	0.00032	$\frac{0.00032 \times 100}{0.03453} = 0.93\%$ . (Ans.)
Carbon dioxide	0.0005	44	0.00001	$\frac{0.00001 \times 100}{0.03453} = 0.03\%$ . (Ans.)
$n = \sum n_i = 0.03453$				

Also,  $\frac{p_i}{p} = \frac{V_i}{V} = \frac{n_i}{n}$

$\therefore p_i = \frac{n_i}{n} p$  hence

For  $O_2$ ,  $P_{O_2} = 0.2094 \times 1 = 0.2094 \text{ bar. (Ans.)}$

For  $N_2$ ,  $P_{N_2} = 0.7810 \times 1 = 0.7810 \text{ bar. (Ans.)}$

For Ar,  $P_{Ar} = 0.0093 \times 1 = 0.0093 \text{ bar. (Ans.)}$

For  $CO_2$ ,  $P_{CO_2} = 0.0003 \times 1 = 0.0003 \text{ bar. (Ans.)}$

**Example 9.4.** A vessel contains at 1 bar and 20°C a mixture of 1 mole of CO<sub>2</sub> and 4 moles of air. Calculate for the mixture :

- (i) The masses of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> and the total mass ;
- (ii) The percentage carbon content by mass ;
- (iii) The apparent molecular weight and the gas constant for the mixture ;
- (iv) The specific volume of the mixture.

The volumetric analysis of air can be taken as 21% oxygen and 79% nitrogen.

**Solution.** The pressure in the vessel,  $p = 1$  bar  
 Temperature in the vessel,  $T = 20 + 273 = 293$  K  
 No. of moles of CO<sub>2</sub> = 1 mole  
 No. of moles of air = 4 mole

From equation,  $n_i = \left(\frac{V_i}{V}\right)n$ , we have

$$n_{O_2} = 0.21 \times 4 = 0.84$$

$$n_{N_2} = 0.79 \times 4 = 3.16$$

(i) From equation,  $m_i = n_i M_i$ , we have

$$m_{CO_2} = 1 \times 44 = 44 \text{ kg. (Ans.)}$$

$$m_{O_2} = 0.84 \times 32 = 26.88 \text{ kg. (Ans.)}$$

and

$$m_{N_2} = 3.16 \times 28 = 88.48 \text{ kg. (Ans.)}$$

The total mass,  $m = m_{CO_2} + m_{O_2} + m_{N_2}$

$$= 44 + 26.88 + 88.48 = 159.36 \text{ kg. (Ans.)}$$

(ii) Since the molecular weight of carbon is 12, therefore, there are 12 kg of carbon present for every mole of CO<sub>2</sub>,

$$\text{i.e., Percentage carbon in mixture} = \frac{12 \times 100}{159.36} = 7.53\% \text{ by mass. (Ans.)}$$

(iii) From equation  $n = \sum n_i$ , we have

$$\begin{aligned} n &= n_{CO_2} + n_{O_2} + n_{N_2} \\ &= 1 + 0.84 + 3.16 = 5.0 \end{aligned}$$

Now using the equation  $M = \sum \frac{n_i}{n} M_i$ , we have

$$\begin{aligned} M &= \frac{1}{5} \times 44 + \frac{0.84}{5} \times 32 + \frac{3.16}{5} \times 28 \\ &= 8.8 + 5.376 + 17.696 = 31.872 \end{aligned}$$

i.e., Apparent molecular weight = 31.872. (Ans.)

From equation,  $R = \frac{R_0}{M}$ , we have

$$R = \frac{8.314}{31.872} = 0.2608 \text{ kJ/kg K}$$

i.e., **Gas constant for the mixture = 0.2608 kJ/kg K. (Ans.)**

(iv) To find specific volume of the mixture,  $v$  using the relation :

$$pv = RT$$

$$v = \frac{RT}{p} = \frac{0.2608 \times 10^3 \times 293}{1 \times 10^5} = 0.7641 \text{ m}^3/\text{kg}$$

i.e., **Specific volume of the mixture = 0.7641 m<sup>3</sup>/kg. (Ans.)**

**Example 9.5.** A mixture of hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) is to be made so that the ratio of  $H_2$  to  $O_2$  is 2 : 1 by volume. If the pressure and temperature are 1 bar and 25°C respectively, calculate :

(i) The mass of  $O_2$  required ;

(ii) The volume of the container.

**Solution.** Pressure,  $p = 1$  bar

Temperature,  $T = 25 + 273 = 298$  K

Ratio of  $H_2$  to  $O_2$  = 2 : 1 by volume.

(i) **The mass of  $O_2$  required :**

Let the mass of  $O_2$  per kg of  $H_2 = x$  kg

Now, 
$$n_i = \frac{m_i}{M_i}$$

$$\therefore n_{H_2} = \frac{1}{2} = 0.5$$

and

$$n_{O_2} = \frac{x}{32}$$

From equation,  $\frac{V_i}{V} = \frac{n_i}{n}$ , we have

$$\frac{V_{H_2}}{V_{O_2}} = \frac{n_{H_2}}{n_{O_2}} \quad \text{and} \quad \frac{V_{H_2}}{V_{O_2}} = 2 \text{ (given)}$$

$$\therefore \frac{0.5}{x/32} = 2 \quad \therefore x = \frac{32 \times 0.5}{2} = 8$$

i.e., Mass of  $O_2$  per kg of  $H_2 = 8$  kg. **(Ans.)**

(ii) **The volume of the container,  $V$  :**

The total number of moles in the vessel per kg of  $H_2$  is

$$n = n_{H_2} + n_{O_2} = 0.5 + \frac{x}{32} = 0.5 + \frac{8}{32} = 0.75$$

Now using the relation,

$$pV = nR_0T$$

$$\therefore V = \frac{nR_0T}{p} = \frac{0.75 \times (8.314 \times 10^3)}{1 \times 10^5} \times 298 = 18.58 \text{ m}^3$$

i.e., **The volume of the container = 18.58 m<sup>3</sup>. (Ans.)**

**Example 9.6.** A gaseous mixture of composition by volume, 78%  $H_2$  and 22% CO is contained in a vessel. It is desired that the mixture should be made in proportion 52%  $H_2$  and 48% CO by removing some of the mixture and adding some CO. Calculate per mole of mixture the mass of mixture to be removed, and mass of CO to be added.

Assume that the pressure and temperature in the vessel remain constant during the procedure.



**Solution.** Composition of mixture by volume :  $H_2 = 78\%$ ,  $CO = 22\%$

Final composition desired :  $H_2 = 52\%$ ,  $CO = 48\%$

Since the pressure and temperature remain constant, then the number of moles in the vessel remain the same throughout.

$\therefore$  Moles of mixture removed = Moles of CO added.

Let  $x$  kg of mixture be removed and  $y$  kg of CO be added.

For the mixture, 
$$M = \sum \frac{V_i}{V} M_i$$

$$\therefore M = 0.78 \times 2 + 0.22 \times 28 = 7.72$$

Also from equation,  $n = \frac{m}{M}$ , we have

$$\text{Moles of mixture removed} = \frac{x}{7.72} = \text{moles of CO added} = \frac{y}{28}$$

From equation,  $\frac{V_i}{V} = \frac{n_i}{n}$ , we have

Moles of  $H_2$  in the mixture removed

$$= 0.78 \times \frac{x}{7.72} = 0.101 x$$

and Moles of  $H_2$  initially =  $0.78 \times 1 = 0.78$

Hence, Moles of  $H_2$  remaining in vessel =  $0.78 - 0.101 x$

But 1 mole of the new mixture is 52%  $H_2$  and 48% CO, therefore

$$0.78 - 0.101 x = 0.52$$

$$\therefore 0.101 x = 0.26 \quad \text{or} \quad x = 2.57$$

i.e., **Mass of mixture removed = 2.57 kg. (Ans.)**

Also since 
$$\frac{x}{7.72} = \frac{y}{28}$$

$$\therefore y = \frac{28}{7.72} \times x = \frac{28}{7.72} \times 2.57 = 9.32 \text{ kg}$$

i.e., **Mass of CO added = 9.32 kg. (Ans.)**

**Example 9.7.** In an engine cylinder a gas has a volumetric analysis of 13%  $CO_2$ , 12.5%  $O_2$ , and 74.5%  $N_2$ . The temperature at the beginning of expansion is  $950^\circ C$  and the gas mixture expands reversibly through a volume ratio of 8 : 1, according to the law  $pv^{1.2} = \text{constant}$ . Calculate per kg of gas :

(i) The workdone ;

(ii) The heat flow ;

(iii) Change of entropy per kg of mixture.

The values of  $c_p$  for the constituents  $CO_2$ ,  $O_2$  and  $N_2$  are 1.235 kJ/kg K, 1.088 kJ/kg K and 1.172 kJ/kg K respectively.

**Solution.** From equation  $m_i = n_i M_i$ , the conversion from volume fraction to mass fraction is as follows :

Consider 1 mole of the mixture.

Constituent	$n_i$	$M_i$	$m_i = n_i M_i$	$\frac{m_i}{m} = \text{Fraction by mass}$
CO <sub>2</sub>	0.13	44	5.72	$\frac{5.72}{30.58} = 0.187$
O <sub>2</sub>	0.125	32	4.00	$\frac{4.0}{30.58} = 0.131$
N <sub>2</sub>	0.745	28	20.86	$\frac{20.86}{30.58} = 0.682$
			$\Sigma m_i = 30.58$	

Now using the equation  $c_p = \sum \frac{m_i}{m} c_{pi}$

$$\therefore c_p = 0.187 \times 1.235 + 0.131 \times 1.088 + 0.682 \times 1.172$$

$$= 0.231 + 0.1425 + 0.799 = 1.1725 \text{ kJ/kg K}$$

From equations,  $R = \sum \frac{m_i}{m} R_i$  and  $R_i = \frac{R_0}{M_i}$ , we have

$$R = 0.187 \times \frac{8.314}{44} + 0.131 \times \frac{8.314}{32} + 0.682 \times \frac{8.314}{28}$$

$$= 0.0353 + 0.0340 + 0.2025 = 0.2718 \text{ kJ/kg K}$$

From equation,  $c_p - c_v = R$ , we have

$$c_v = 1.1725 - 0.2718 = 0.9 \text{ kJ/kg K}$$

(i) The workdone,  $W$  :

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

$T_2$  can be found by using the equation

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1} = \left(\frac{1}{8}\right)^{1.2-1} = 0.659$$

$$\therefore T_2 = (950 + 273) \times 0.659 = 805.9 \text{ K}$$

$$\therefore W = \frac{0.2718(1223 - 805.9)}{1.2 - 1} = 566.8 \text{ kJ/kg. (Ans.)}$$

(ii) The heat flow,  $Q$  :

Also from equation,

$$u_2 - u_1 = c_v(T_2 - T_1) \dots \text{ for 1 kg}$$

$$= 0.9(805.9 - 1223) = -375.39 \text{ kJ/kg}$$

Now from the non-flow energy equation,

$$Q = (u_2 - u_1) + W = -375.39 + 566.8 = 191.41 \text{ kJ/kg}$$

i.e., Heat supplied = 191.41 kJ/kg. (Ans.)

(iii) Change of entropy per kg of mixture :

Refer Fig. 9.6. The change of entropy between state 1 and state 2 can be found by imagining the process replaced by two other processes 1 to A and A to 2.

For isothermal process 1-A

$$s_A - s_1 = R \log_e \frac{v_2}{v_1}$$

$$= 0.2718 \log_e 8 = 0.565 \text{ kJ/kg K}$$

For constant volume process A-2 :

$$s_A - s_2 = c_v \int_2^A \frac{dT}{T} = c_v \log_e \frac{T_1}{T_2}$$

$$= 0.9 \log_e \frac{1223}{805.9}$$

i.e.,  $s_A - s_2 = 0.375 \text{ kJ/kg K}$

Then by subtraction,

$$s_2 - s_1 = 0.565 - 0.375 = 0.19 \text{ kJ/kg K}$$

i.e., **Change of entropy per kg of mixture**

$$= 0.19 \text{ kJ/kg K. (Ans.)}$$

**Example 9.8.** The following is the volumetric analysis of a producer gas : CO = 28%, H<sub>2</sub> = 13%, CH<sub>4</sub> = 4%, CO<sub>2</sub> = 4%, N<sub>2</sub> = 51%. The values of C<sub>p</sub> for the constituents CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub> are 29.27 kJ/mole K, 28.89 kJ/mole K, 35.8 kJ/mole K, 37.22 kJ/mole K, 29.14 kJ/mole K respectively. Calculate the values of C<sub>p</sub>, C<sub>v</sub>, c<sub>p</sub> and c<sub>v</sub> for the mixture.

**Solution.** Using the relation

$$C_p = \sum \frac{n_i}{n} C_{pi}$$

∴  $C_p = 0.28 \times 29.27 + 0.13 \times 28.89 + 0.04 \times 35.8 + 0.04 \times 37.22 + 0.51 \times 29.14$   
 i.e.,  $C_p = 29.733 \text{ kJ/mole K. (Ans.)}$

Also  $C_p - C_v = R_0$

∴  $C_v = C_p - R_0 = 29.733 - 8.314 = 21.419 \text{ kJ/mole K. (Ans.)}$

To find the molecular weight, using the equation :

$$M = \sum \frac{n_i}{n} M_i$$

$$= 0.28 \times 28 + 0.13 \times 2 + 0.04 \times 16 + 0.04 \times 44 + 0.51 \times 28 = 24.78$$

Now  $c_p = \frac{C_p}{M} = \frac{29.733}{24.78} = 1.199 \text{ kJ/kg K. (Ans.)}$

and  $c_v = \frac{C_v}{M} = \frac{21.419}{24.78} = 0.864 \text{ kJ/kg K. (Ans.)}$

**Example 9.9.** The analysis by weight of a perfect gas mixture at 20°C and 1.3 bar is 10% O<sub>2</sub>, 70% N<sub>2</sub>, 15% CO<sub>2</sub> and 5% CO. For a reference state of 0°C and 1 bar determine :

(i) Partial pressures of the constituents ; (ii) Gas constant of mixture.

**Solution.** Using the relation,  $M = \frac{1}{\sum \frac{m_{fi}}{M_i}}$

where,  $M$  = Molecular weight of the mixture ;  
 $m_{fi}$  = Mass fraction of a constituent, ;  
 $M_i$  = Molecular weight of a constituent.

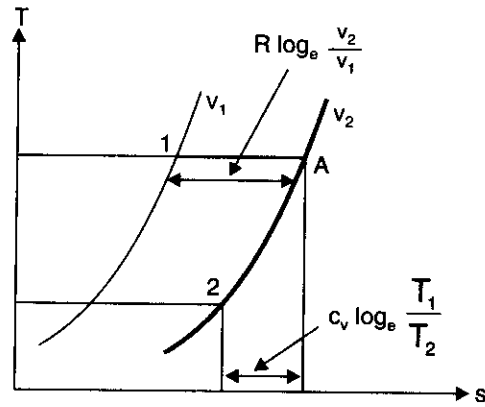


Fig. 9.6

$$M = \frac{1}{\frac{(m_f)_{O_2}}{M_{O_2}} + \frac{(m_f)_{N_2}}{M_{N_2}} + \frac{(m_f)_{CO_2}}{M_{CO_2}} + \frac{(m_f)_{CO}}{M_{CO}}} = \frac{1}{\frac{0.1}{32} + \frac{0.7}{28} + \frac{0.15}{44} + \frac{0.05}{28}}$$

$$= \frac{1}{0.03332} = 30 \text{ kg/kg mole}$$

Considering 1 kg of the mixture

$$n = \frac{m}{M} = \frac{1}{30} = 0.033$$

Now mole fraction  $x_i = \frac{n_i}{\sum n_i} = \frac{n_i}{n} = \frac{m_i/M_i}{n}$

$$\therefore x_{O_2} = \frac{(0.1/32)}{0.033} = 0.094 ; \quad x_{N_2} = \frac{(0.7/28)}{0.033} = 0.757$$

$$x_{CO_2} = \frac{(0.15/44)}{0.033} = 0.103 ; \quad x_{CO} = \frac{(0.05/28)}{0.033} = 0.054$$

(i) **Partial pressures of the constituents :**

$$P_{O_2} = x_{O_2} \times p = 0.094 \times 1.3 = \mathbf{0.132 \text{ bar. (Ans.)}}$$

$$P_{N_2} = x_{N_2} \times p = 0.757 \times 1.3 = \mathbf{0.984 \text{ bar. (Ans.)}}$$

$$P_{CO_2} = x_{CO_2} \times p = 0.103 \times 1.3 = \mathbf{0.1334 \text{ bar. (Ans.)}}$$

$$P_{CO} = x_{CO} \times p = 0.054 \times 1.3 = \mathbf{0.0702 \text{ bar. (Ans.)}}$$

(ii) **Gas constant of mixture,  $R_{\text{mix}}$  :**

$$R_{\text{mix}} = \frac{R_0}{M} = \frac{8.314}{30} = \mathbf{0.277 \text{ kJ/kg K. (Ans.)}}$$

**Example 9.10.** A mixture of ideal gases consists of 4 kg of nitrogen and 6 kg of carbon dioxide at a pressure of 4 bar and a temperature of 20°C. Find :

- (i) The mole fraction of each constituent,
- (ii) The equivalent molecular weight of the mixture,
- (iii) The equivalent gas constant of the mixture,
- (iv) The partial pressures and partial volumes,
- (v) The volume and density of the mixture, and
- (vi) The  $c_p$  and  $c_v$  of the mixture.

If the mixture is heated at constant volume to 50°C, find the changes in internal energy, enthalpy and entropy of the mixture. Find the changes in internal energy, enthalpy and entropy of the mixture if the heating is done at constant pressure.

Take  $\gamma$  : for  $CO_2 = 1.286$  and for  $N_2 = 1.4$ .

**Solution.** (i) **The mole fraction of each constituent :**

Since mole fraction,  $x_i = \frac{n_i}{\sum n_i}$

$$\therefore x_{N_2} = \frac{\frac{4}{28}}{\frac{4}{28} + \frac{6}{44}} = \frac{0.1428}{0.1428 + 0.1364} = \frac{0.1428}{0.2792} = \mathbf{0.511. (Ans.)}$$

$$x_{\text{CO}_2} = \frac{\frac{6}{44}}{\frac{4}{28} + \frac{6}{44}} = \frac{0.1364}{0.1428 + 0.1364} = 0.488. \quad (\text{Ans.})$$

(ii) The equivalent molecular weight of the mixture,  $M$  :

$$M = 0.511 \times 28 + 0.488 \times 44 = 35.78 \text{ kg/kg mole.} \quad (\text{Ans.})$$

(iii) The equivalent gas constant of the mixture,  $R_{\text{mix}}$  :

$$\text{Total mass,} \quad m = m_{\text{N}_2} + m_{\text{CO}_2} = 4 + 6 = 10 \text{ kg}$$

$$\begin{aligned} \therefore R_{\text{mix}} &= \frac{m_{\text{N}_2} R_{\text{N}_2} + m_{\text{CO}_2} R_{\text{CO}_2}}{m} \\ &= \frac{4 \times \left(\frac{8.314}{28}\right) + 6 \times \left(\frac{8.314}{44}\right)}{10} \quad \left[ \because R = \frac{R_0}{M} \right] \\ &= 0.232 \text{ kJ/kg K.} \quad (\text{Ans.}) \end{aligned}$$

(iv) The partial pressures and partial volumes :

$$P_{\text{N}_2} = x_{\text{N}_2} \times p = 0.511 \times 4 = 2.044 \text{ bar.} \quad (\text{Ans.})$$

$$P_{\text{CO}_2} = x_{\text{CO}_2} \times p = 0.488 \times 4 = 1.952 \text{ bar.} \quad (\text{Ans.})$$

$$V_{\text{N}_2} = \frac{m_{\text{N}_2} R_{\text{N}_2} T}{p} = \frac{4 \times \frac{8.314}{28} \times 293 \times 10^3}{4 \times 10^5} = 0.87 \text{ m}^3. \quad (\text{Ans.})$$

$$V_{\text{CO}_2} = \frac{m_{\text{CO}_2} R_{\text{CO}_2} T}{p} = \frac{6 \times \frac{8.314}{44} \times 293 \times 10^3}{4 \times 10^5} = 0.83 \text{ m}^3. \quad (\text{Ans.})$$

(v) The volume and density of the mixture :

Total volume of the mixture,

$$V = \frac{mRT}{p} = \frac{m_{\text{N}_2} R_{\text{N}_2} T}{p_{\text{N}_2}} = \frac{m_{\text{CO}_2} R_{\text{CO}_2} T}{p_{\text{CO}_2}}$$

$$\therefore V = \frac{10 \times 0.232 \times 293 \times 10^3}{4 \times 10^5} = 1.699 \text{ m}^3. \quad (\text{Ans.})$$

Density of the mixture,

$$\rho_{\text{mix}} = \rho_{\text{N}_2} + \rho_{\text{CO}_2} = \frac{m}{V} = \frac{10}{1.699} = 5.88 \text{ kg/m}^3. \quad (\text{Ans.})$$

(vi)  $c_p$  and  $c_v$  of the mixture :

$$c_{p_{\text{N}_2}} - c_{v_{\text{N}_2}} = R_{\text{N}_2}$$

$$\therefore c_{v_{\text{N}_2}} = \frac{R_{\text{N}_2}}{\gamma - 1} = \frac{8.314}{28(1.4 - 1)} = 0.742 \text{ kJ/kg K.}$$

and

$$c_{p_{\text{N}_2}} = 1.4 \times 0.742 = 1.039 \text{ kJ/kg K}$$

$$\text{Now } c_{v\text{CO}_2} = \frac{R_{\text{CO}_2}}{\gamma - 1} = \frac{8.314}{44(1.286 - 1)} \quad [\because \gamma \text{ for CO}_2 = 1.286]$$

$$= 0.661 \text{ kJ/kg K}$$

$$\text{and } c_{p\text{CO}_2} = 1.286 \times 0.661 = 0.85 \text{ kJ/kg K}$$

**For the mixture :**

$$c_p = \frac{m_{\text{N}_2} c_{p\text{N}_2} + m_{\text{CO}_2} c_{p\text{CO}_2}}{m_{\text{N}_2} + m_{\text{CO}_2}}$$

$$= \frac{4 \times 1.039 + 6 \times 0.85}{(4 + 6)} = 0.925 \text{ kJ/kg K. (Ans.)}$$

$$c_v = \frac{m_{\text{N}_2} c_{v\text{N}_2} + m_{\text{CO}_2} c_{v\text{CO}_2}}{m_{\text{N}_2} + m_{\text{CO}_2}}$$

$$= \frac{4 \times 0.742 + 6 \times 0.661}{(4 + 6)} = 0.693 \text{ kJ/kg K. (Ans.)}$$

**When the mixture is heated at constant volume :**

**Change in internal energy,**

$$U_2 - U_1 = mc_v(T_2 - T_1) = 10 \times 0.693(50 - 20) = 207.9 \text{ kJ. (Ans.)}$$

**Change in entropy,**

$$H_2 - H_1 = mc_p(T_2 - T_1) = 10 \times 0.925(50 - 20) = 277.5 \text{ kJ. (Ans.)}$$

**Change in entropy,**

$$S_2 - S_1 = mc_v \log_e \frac{T_2}{T_1} + mR \log_e \frac{V_2}{V_1}$$

$$= mc_v \log_e \frac{T_2}{T_1} \quad (\because V_1 = V_2)$$

$$= 10 \times 0.693 \times \log_e \left( \frac{273 + 50}{273 + 20} \right) = 0.675 \text{ kJ/kg K. (Ans.)}$$

**When the mixture is heated at constant pressure :**

If the mixture is heated at constant pressure  $\Delta U$  and  $\Delta H$  will remain the same.

The change in entropy will be

$$S_2 - S_1 = mc_p \log_e \frac{T_2}{T_1} - mR \log_e \frac{p_2}{p_1}$$

$$= mc_p \log_e \frac{T_2}{T_1} \quad (\because p_1 = p_2)$$

$$= 10 \times 0.925 \log_e \left( \frac{323}{293} \right) = 0.902 \text{ kJ/kg K. (Ans.)}$$

**Example 9.11.** A vessel of  $1.8 \text{ m}^3$  capacity contains oxygen at 8 bar and  $50^\circ\text{C}$ . The vessel is connected to another vessel of  $3.6 \text{ m}^3$  capacity containing carbon monoxide at 1 bar and  $20^\circ\text{C}$ . A connecting valve is opened and the gases mix adiabatically. Calculate :

(i) The final temperature and pressure of the mixture ;

(ii) The change of entropy of the system.

Take : For oxygen  $C_v = 21.07 \text{ kJ/mole K}$ .

For carbon monoxide  $C_v = 20.86 \text{ kJ/mole K}$ .

**Solution.** Using the relation,  $n = \frac{pV}{R_0T}$

$$\therefore n_{O_2} = \frac{8 \times 10^5 \times 1.8}{(8.314 \times 10^3) \times 323} = 0.536 \text{ (where } T_{O_2} = 50 + 273 = 323 \text{ K)}$$

and 
$$n_{CO} = \frac{1 \times 10^5 \times 3.6}{(8.314 \times 10^3) \times 293} = 0.1478 \text{ (where } T_{CO} = 20 + 273 = 293 \text{ K).}$$

(i) **Final temperature (T) and pressure (p) of the mixture :**

**Before mixing :**

$$U_1 = \sum n_i C_{vi} T_i = 0.536 \times 21.07 \times 323 + 0.1478 \times 20.86 \times 293$$

i.e., 
$$U_1 = 4551.15 \text{ kJ}$$

**After mixing :**

$$U_2 = T \sum n_i C_{vi} = T (0.536 \times 21.07 + 0.1478 \times 20.86)$$

i.e., 
$$U_2 = 14.37 T$$

**For adiabatic mixing,**

$$U_1 = U_2$$

$$\therefore 4551.15 = 14.37 T$$

$$\therefore T = \frac{4551.15}{14.37} = 316.7 \text{ K}$$

$\therefore$  Temperature of the mixture = 316.7 - 273 = **43.7°C. (Ans.)**

Now 
$$p = \frac{nR_0T}{V}$$

$$\therefore p = \frac{(0.536 + 0.1478) \times 8.314 \times 10^3 \times 316.7}{(1.8 + 3.6) \times 10^5} = 3.33 \text{ bar}$$

i.e., Pressure after mixing = 3.33 bar. (Ans.)

(ii) **Change of entropy of the system :**

Change of entropy of the system = change of entropy of the O<sub>2</sub> + change of entropy of CO  
..... Gibbs-Dalton law

Referring to Fig. 9.7, the change of entropy of O<sub>2</sub> can be calculated by replacing the process undergone by the oxygen by the two processes 1 to A and A to 2.

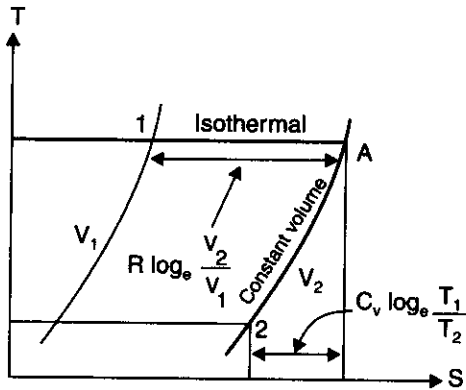


Fig. 9.7

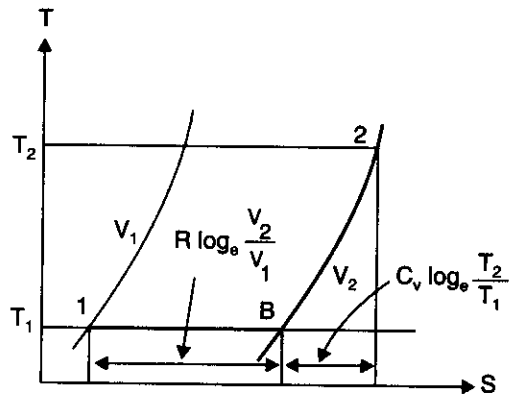


Fig. 9.8

For an *isothermal process 1-A* :

$$S_A - S_1 = mR \log_e \frac{V_A}{V_1}$$

or

$$\begin{aligned} S_A - S_1 &= nR_0 \log_e \frac{V_A}{V_1} \\ &= 0.536 \times 8.314 \times \log_e \frac{5.4}{1.8} = 4.896 \text{ kJ/K} \end{aligned}$$

For *constant volume process A-2* :

$$S_A - S_2 = mc_v \int_2^A \frac{dT}{T} = mc_v \log_e \frac{T_1}{T_2}$$

$$\text{i.e., } S_A - S_2 = nC_v \log_e \frac{T_1}{T_2} = 0.536 \times 21.07 \times \log_e \frac{323}{316.7} = 0.222 \text{ kJ/K}$$

$$\begin{aligned} \therefore S_2 - S_1 &= (S_A - S_1) - (S_A - S_2) \\ &= 4.896 - 0.222 = 4.674 \text{ kJ/K} \end{aligned}$$

Referring to Fig. 9.8, the change of entropy of CO can be found in a similar way to the above,

$$\begin{aligned} \text{i.e., } S_2 - S_1 &= (S_B - S_1) + (S_2 - S_B) \\ \therefore S_2 - S_1 &= nR_0 \log_e \frac{V_B}{V_1} + nC_v \log_e \frac{T_2}{T_1} \\ &= 0.1478 \times 8.314 \times \log_e \frac{5.4}{3.6} + 0.1478 \times 20.86 \log_e \frac{316.7}{293} \\ &= 0.498 + 0.239 = 0.737 \text{ kJ/K} \end{aligned}$$

Hence the change of entropy of the whole system is given by

$$(S_2 - S_1)_{\text{system}} = (S_2 - S_1)_{\text{O}_2} + (S_2 - S_1)_{\text{CO}}$$

$$\text{i.e., } \text{Change of entropy of system} = 4.674 + 0.737 = \mathbf{5.411 \text{ kJ/K. (Ans.)}}$$

**Example 9.12.** Two vessels, A and B, both containing nitrogen, are connected by a valve which is opened to allow the contents to mix and achieve an equilibrium temperature of 30°C. Before mixing the following information is known about the gases in the two vessels.

Vessel	Pressure (p)	Tem. (t)	Contents
A	16 bar	55°C	0.6 kg mole
B	6.4 bar	25°C	3.6 kg

- (a) Calculate : (i) The final equilibrium pressure ;  
(ii) The amount of heat transferred to the surroundings ;
- (b) If the vessel had been perfectly insulated, calculate :  
(i) The final temperature ;  
(ii) The final pressure.

Assume  $\gamma = 1.4$ .

**Solution.** Refer Fig. 9.9.

**Vessel A :**

$$p_A V_A = n_A R_0 T_A$$

(where  $V_A$  = volume of vessel A)



$$16 \times 10^5 \times V_A = 0.6 \times 8.314 \times 10^3 \times (55 + 273)$$

$$\therefore V_A = 1.022 \text{ m}^3$$

The mass of gas in vessel A

$$m_A = n_A M_A = 0.6 \times 28 = 16.8 \text{ kg}$$

Characteristic gas constant  $R$  of nitrogen

$$R = \frac{8.314}{28} = 0.297 \text{ kJ/kg K}$$

**Vessel B :**

$$p_B V_B = m_B R T_B$$

$$6.4 \times 10^5 \times V_B = 3.0 \times 0.297 \times 10^3 \times (25 + 273)$$

$$\therefore V_B = 0.415 \text{ m}^3$$

Total volume of A and B

$$V = V_A + V_B = 1.022 + 0.415 = 1.437 \text{ m}^3$$

Total mass of gas

$$m = m_A + m_B = 16.8 + 3 = 19.8 \text{ kg}$$

Final temperature after mixing

$$T = 30 + 273 = 303 \text{ K}$$

(a) (i) **Final equilibrium pressure,  $p$  :**

$$pV = mRT$$

$$\text{or } p \times 1.437 = 19.8 \times 0.297 \times 303 \times 10^3 = 12.4 \times 10^5 \text{ N/m}^2$$

$$\text{i.e., } p = 12.4 \text{ bar. (Ans.)}$$

$$\text{Also } c_v = \frac{R}{\gamma - 1} = \frac{0.297}{1.4 - 1} = 0.743 \text{ kJ/kg K.}$$

(ii) **Amount of heat transferred,  $Q$  :**

As there is no work transfer, the amount of heat transfer,

$$Q = \text{change of internal energy}$$

$$= U_2 - U_1$$

Measuring the internal energy above the datum of absolute zero (at  $T = 0 \text{ K}$ ,  $u = 0 \text{ kJ/kg}$ ).

Internal energy  $U_1$  (before mixing)

$$= m_A c_v T_A + m_B c_v T_B$$

$$= 16.8 \times 0.743 \times 328 + 3.0 \times 0.743 \times 298 = 4758.5 \text{ kJ}$$

Final internal energy  $U_2$  (after mixing)

$$= m c_v T = 19.8 \times 0.743 \times 303 = 4457.5 \text{ kJ}$$

$$\therefore Q = U_2 - U_1 = 4457.5 - 4758.5 = -301 \text{ kJ. (Ans.)}$$

(b) **If the vessel were insulated :**

(i) **Final temperature,  $t_2$  :**

If the vessel were insulated

$$Q = U_2 - U_1 = 0$$

$$\text{i.e., } U_1 = U_2$$

$$m_A c_v T_A + m_B c_v T_B = m c_v T$$

$$\therefore T = \frac{m_A c_v T_A + m_B c_v T_B}{m c_v} = \frac{m_A T_A + m_B T_B}{m}$$

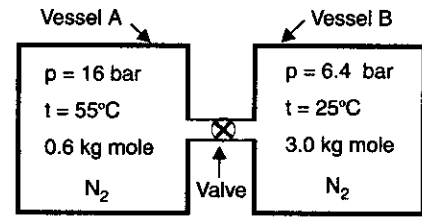


Fig. 9.9

$$= \frac{16.8 \times 328 + 3.0 \times 298}{19.8} = 323.5 \text{ K}$$

i.e.,  $t = 323.5 - 273 = 50.5^\circ\text{C}$ . (Ans.)

(ii) **Final pressure, p :**

$$pV = mRT$$

or 
$$p = \frac{mRT}{V} = \frac{19.8 \times 0.297 \times 10^3 \times 323.5}{1.437} = 13.24 \times 10^5 \text{ N/m}^2$$

i.e.,  $p = 13.24 \text{ bar}$ . (Ans.)

**Example 9.13.** Calculate the increase in entropy when 3 kg of  $O_2$  at  $50^\circ\text{C}$  are mixed with 9 kg of  $N_2$  at the same temperature. The initial pressure of each constituent is 11 bar and is the same as that of the mixture.

**Solution.** 
$$x_{O_2} = \frac{p_{O_2}}{p} = \frac{3/32}{3/32 + 9/28} = 0.225$$

$$x_{N_2} = \frac{p_{N_2}}{p} = \frac{9/28}{3/32 + 9/28} = 0.774$$

Increase of entropy due to diffusion

$$\begin{aligned} \Delta S &= -m_{O_2} R_{O_2} \log_e \frac{p_{O_2}}{p} - m_{N_2} R_{N_2} \log_e \frac{p_{N_2}}{p} \\ &= -3 \times \left( \frac{8.314}{32} \right) \log_e 0.225 - 9 \times \left( \frac{8.314}{28} \right) \times \log_e 0.774 \\ &= 1.1626 + 0.6846 = 1.8472 \text{ kJ/kg K.} \end{aligned}$$

**Example 9.14.** 2.5 kg of  $N_2$  at 15 bar and  $40^\circ\text{C}$  is contained a rigid vessel. Adequate quantity of  $O_2$  is added to increase the pressure to 20 bar while the temperature remains constant at  $40^\circ\text{C}$ .

Calculate the mass of  $O_2$  added.

**Solution.**  $m_{N_2} = 2.5 \text{ kg}$ ,  $M_{N_2} = 28$

Initial pressure,  $p_{N_2} = 15 \text{ bar}$

Final pressure,  $p_{\text{total}} (= p_{N_2} + p_{O_2}) = 20 \text{ bar}$

Temperature =  $40^\circ\text{C}$

In this process, the number of nitrogen moles remains constant at

$$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{2.5}{28} = 0.0893$$

After the oxygen is added,  $p_{N_2} = 15 \text{ bar}$ , since the volume remains unchanged

$$p_{O_2} = p_{\text{total}} - p_{N_2} = 20 - 15 = 5 \text{ bar}$$

$$\text{Now } p_{N_2} = \frac{n_{N_2} R_0 T}{V} \quad \dots(i)$$

$$\text{and } p_{O_2} = \frac{n_{O_2} R_0 T}{V} \quad \dots(ii)$$

Dividing (ii) by (i), we get

$$\frac{p_{O_2}}{p_{N_2}} = \frac{n_{O_2}}{n_{N_2}}$$

$$\therefore n_{O_2} = \frac{p_{O_2} \times n_{N_2}}{p_{N_2}} = \frac{5 \times 10^5 \times 0.0893}{15 \times 10^5} = 0.0297$$

$\therefore$  Mass of  $O_2$  added,

$$\begin{aligned} m_{O_2} &= n_{O_2} \times M_{O_2} \\ &= 0.0297 \times 32 = \mathbf{0.9504 \text{ kg. (Ans.)}} \end{aligned}$$

**Example 9.15.** Given that air consists of 21% oxygen and 79% nitrogen by volume. Determine :

- (i) The moles of nitrogen per mole of oxygen ;
- (ii) The partial pressure of oxygen and nitrogen if the total pressure is atmosphere ;
- (iii) The kg of nitrogen per kg of mixture.

**Solution.** Let  $n_{O_2} = 1.0$  and  $V =$  volume of air

$$\text{so that } V_{O_2} = 0.21V ; V_{N_2} = 0.79V$$

Let  $V$  contain  $n = n_{O_2} + n_{N_2}$  moles of air at  $p$  and  $T$ .

(i) Moles of  $N_2$  per mole of  $O_2$  :

$$\text{Now } pV_{O_2} = n_{O_2} R_0 T \quad \dots(i)$$

$$\text{and } pV_{N_2} = n_{N_2} R_0 T \quad \dots(ii)$$

Dividing (i) by (ii), we get

$$\frac{V_{O_2}}{V_{N_2}} = \frac{n_{O_2}}{n_{N_2}}$$

$$\therefore n_{N_2} = \frac{n_{O_2} \times V_{N_2}}{V_{O_2}} = \frac{1 \times 0.79V}{0.21V} = \mathbf{3.76 \text{ moles. (Ans.)}}$$

(ii)  $p_{O_2}$  and  $p_{N_2}$  :

$$\text{Now } x_{O_2} = \frac{n_{O_2}}{4} = \frac{p_{O_2}}{p} \quad (n = n_{O_2} + n_{N_2})$$

(where  $p =$  total pressure  $= 1 \text{ atm.}$ )

$$\therefore p_{O_2} = \frac{n_{O_2}}{n} \times p = \frac{1}{(1 + 3.76)} \times 1 = \mathbf{0.21 \text{ atm. (Ans.)}}$$

Again, 
$$x_{N_2} = \frac{n_{N_2}}{n} = \frac{p_{N_2}}{p}$$

$$\therefore p_{N_2} = \frac{n_{N_2}}{n} \times p = \frac{3.76}{1 + 3.76} \times 1 = 0.79 \text{ atm. (Ans.)}$$

(iii) The kg of nitrogen per kg of mixture :

$$\begin{aligned} \frac{m_{N_2}}{m_{N_2} + m_{O_2}} &= \frac{n_{N_2} M_{N_2}}{n_{N_2} M_{N_2} + n_{O_2} M_{O_2}} \\ &= \frac{3.76 \times 28}{3.76 \times 28 + 1 \times 32} = 0.77 \text{ kg N}_2/\text{kg mix. (Ans.)} \end{aligned}$$

**Example 9.16.** Air ( $N_2 = 77\%$ ,  $O_2 = 23\%$  by weight) at  $25^\circ\text{C}$  and 12 bar is contained in a vessel of capacity  $0.6 \text{ m}^3$ . Some quantity of  $\text{CO}_2$  is forced into the vessel so that the temperature remains at  $25^\circ\text{C}$  but the pressure rises to 18 bar.

Find the masses of  $O_2$ ,  $N_2$  and  $\text{CO}_2$  in the cylinder.

**Solution.** Volume of the vessel,  $V = 0.6 \text{ m}^3$

Temperature (constant),  $T = 25 + 273 = 298 \text{ K}$

Initial pressure = 12 bar

Final pressure = 18 bar

Now 
$$pV = nR_0T$$

or 
$$n = \frac{pV}{R_0T} = \frac{12 \times 10^5 \times 0.6}{8.314 \times 10^3 \times 298} = 0.29$$

Also 
$$R_{\text{air}} = \left( \frac{m_{O_2}}{M_{O_2}} + \frac{m_{N_2}}{M_{N_2}} \right) \frac{R_0}{m} \quad (m = n \times M)$$

Considering 100 kg of air

$$m_{O_2} = 23 \text{ kg, } m_{N_2} = 77 \text{ kg}$$

$$\therefore R_{\text{air}} = \left( \frac{23}{32} + \frac{77}{28} \right) \times \frac{8.314}{100} = 0.288 \text{ kJ/kg K}$$

$$M_{\text{air}} = \frac{R_0}{R_{\text{air}}} = \frac{8.314}{0.288} = 28.87$$

Now 
$$pV = mRT$$

$$\therefore m = \frac{pV}{RT} = \frac{12 \times 10^5 \times 0.6}{0.288 \times 298 \times 10^3} = 8.39 \text{ kg of air}$$

**Mass of  $O_2$ ,**  $m_{O_2} = 0.23 \times 8.39 = 1.93 \text{ kg. (Ans.)}$

**Mass of  $N_2$ ,**  $m_{N_2} = 0.77 \times 8.39 = 6.46 \text{ kg. (Ans.)}$

**After adding  $\text{CO}_2$  in the vessel :**

$$p_{N_2} + p_{O_2} = 12 \text{ bar} \quad \dots \text{ before adding } \text{CO}_2$$

$$p_{\text{CO}_2} + (p_{N_2} + p_{O_2}) = 18 \text{ bar} \quad \dots \text{ after adding } \text{CO}_2$$

or

$$p_{\text{CO}_2} + 12 = 18$$

$$p_{\text{CO}_2} = 6 \text{ bar}$$

Now

$$p_{\text{CO}_2} = \frac{m_{\text{CO}_2} R_{\text{CO}_2} T_{\text{CO}_2}}{V}$$

∴

$$m_{\text{CO}_2} = \frac{p_{\text{CO}_2} V}{R_{\text{CO}_2} T_{\text{CO}_2}} = \frac{6 \times 10^5 \times 0.6}{\left(\frac{8.314}{44}\right) \times 298 \times 10^3} = 6.39 \text{ kg}$$

i.e.,

**Mass of CO<sub>2</sub> = 6.39 kg. (Ans.)**

**Example 9.17.** A vessel of 6 m<sup>3</sup> capacity contains two gases A and B in proportion of 45 per cent and 55 per cent respectively at 30°C. If the value of R for the gases is 0.288 kJ/kg K and 0.295 kJ/kg K and if the total weight of the mixture is 2 kg, calculate :

- (i) The partial pressure ; (ii) The total pressure ;  
 (iii) The mean value of R for the mixture.

**Solution.** Capacity of the vessel,  $V = 6 \text{ m}^3$

%age content of gas A = 45%

%age content of gas B = 55%

R for gas A,  $R_A = 0.288 \text{ kJ/kg K}$

R for gas B,  $R_B = 0.295 \text{ kJ/kg K}$

Total weight of the mixture = 2 kg

Temperature,  $T = 30 + 273 = 303 \text{ K}$ .

(i) The partial pressures,  $p_A, p_B$  :

$$m_A = 2 \times 0.45 = 0.9 \text{ kg}$$

$$m_B = 2 \times 0.55 = 1.1 \text{ kg}$$

Now,

$$p_A V = m_A R_A T_A$$

∴

$$p_A = \frac{m_A R_A T_A}{V} = \frac{0.9 \times 0.288 \times 303 \times 10^3}{6 \times 10^5} = 0.13 \text{ bar. (Ans.)}$$

and

$$p_B = \frac{m_B R_B T_B}{V} = \frac{1.1 \times 0.295 \times 303 \times 10^3}{6 \times 10^5} = 0.164 \text{ bar. (Ans.)}$$

(ii) The total pressure,  $p$  :

$$p = p_A + p_B = 0.13 + 0.164 = 0.294 \text{ bar. (Ans.)}$$

(iii) The mean value of R for the mixture,  $R_m$  :

$$\begin{aligned} R_m &= \frac{m_A R_A + m_B R_B}{m_A + m_B} \\ &= \frac{0.9 \times 0.288 + 1.1 \times 0.295}{(0.9 + 1.1)} = 0.292 \text{ kJ/kg K} \end{aligned}$$

i.e., **Mean value of R for the mixture = 0.292 kJ/kg K. (Ans.)**

**Example 9.18.** The pressure and temperature of mixture of 4 kg of O<sub>2</sub> and 6 kg of N<sub>2</sub> are 4 bar and 27°C respectively. For the mixture determine the following :

- (i) The mole fraction of each component ; (ii) The average molecular weight ;  
 (iii) The specific gas constant ; (iv) The volume and density ;  
 (v) The partial pressures and partial volumes.

**Solution.** Mass of oxygen,  $m_{O_2} = 4$  kg

Mass of nitrogen,  $m_{N_2} = 6$  kg

Pressure,  $p = 4$  bar

Temperature,  $T = 27 + 273 = 300$  K.

(i) **The mole fraction of each component :**

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

$$\therefore n_{O_2} = \frac{4}{32} = 0.125 \quad \text{and} \quad n_{N_2} = \frac{6}{28} = 0.214$$

Now 
$$x_{O_2} = \frac{0.125}{0.125 + 0.214} = 0.3687. \quad (\text{Ans.})$$

and

$$x_{N_2} = \frac{0.214}{0.125 + 0.214} = 0.6313. \quad (\text{Ans.})$$

(ii) **The average molecular weight,  $M$  :**

$$M = \frac{n_{O_2} M_{O_2} + n_{N_2} \times M_{N_2}}{n_{O_2} + n_{N_2}} = \frac{0.125 \times 32 + 0.214 \times 28}{0.125 + 0.214} = 29.475$$

*i.e.*, **Average molecular weight = 29.475. (Ans.)**

(iii) **The specific gas constant,  $R$  :**

$$R = \frac{R_0}{M} = \frac{8.314}{29.475} = 0.282 \text{ kJ/kg K.} \quad (\text{Ans.})$$

(iv) **The volume and density :**

$$pV = mRT \text{ for mixture}$$

$$V = \frac{mRT}{p} = \frac{(4 + 6) \times 0.282 \times 10^3 \times 300}{4 \times 10^5} = 2.115 \text{ m}^3. \quad (\text{Ans.})$$

$$\text{Density, } \rho = \rho_{O_2} + \rho_{N_2}$$

$$\rho_{O_2} = \frac{m_{O_2}}{V} = \frac{4}{2.115} = 1.891 \text{ kg/m}^3$$

$$\rho_{N_2} = \frac{m_{N_2}}{V} = \frac{6}{2.115} = 2.837 \text{ kg/m}^3$$

$$\therefore \rho = 1.891 + 2.837 = 4.728 \text{ kg/m}^3. \quad (\text{Ans.})$$

(v) **The partial pressures and partial volumes :**

$$p_{O_2} V = n_{O_2} R_0 T$$

$$\therefore p_{O_2} = \frac{n_{O_2} R_0 T}{V} = \frac{0.125 \times 8.314 \times 10^3 \times 300}{2.115 \times 10^5} = 1.474 \text{ bar.} \quad (\text{Ans.})$$

and

$$p_{N_2} = 4 - 1.474 = 2.526 \text{ bar.} \quad (\text{Ans.})$$

$$V_{O_2} = x_{O_2} V = 0.3687 \times 2.115 = 0.779 \text{ m}^3. \quad (\text{Ans.})$$

$$V_{N_2} = x_{N_2} V = 0.6313 \times 2.115 = 1.335 \text{ m}^3. \quad (\text{Ans.})$$

**Example 9.19.** 4 kg of carbon dioxide at 40°C and 1.4 bar are mixed with 8 kg of nitrogen at 160°C and 1.0 bar to form a mixture at a final pressure of 0.7 bar. The process occurs adiabatically in a steady flow apparatus. Calculate :

- (i) The final temperature of the mixture ;
  - (ii) The change in entropy.
- Take value of  $c_p$  : for  $CO_2 = 0.85 \text{ kJ/kg K}$  and  $N_2 = 1.04 \text{ kJ/kg K}$ .

**Solution.** Refer Fig. 9.10.

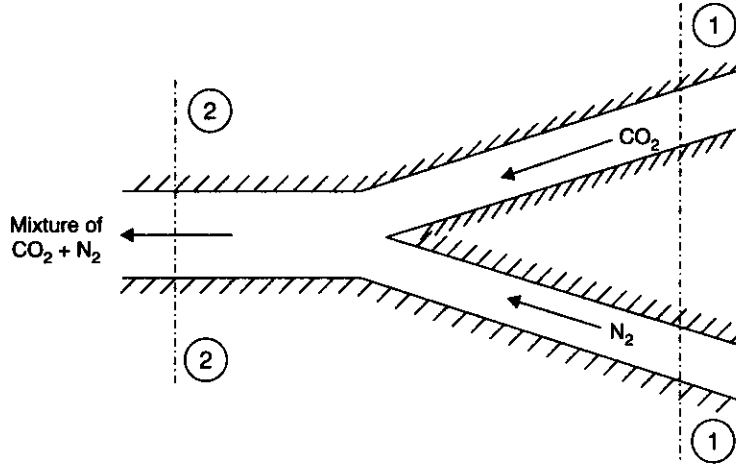


Fig. 9.10

(i) **Final temperature,  $T_2$  :**

In this process,  $W = 0, Q = 0$

∴ The steady flow equation may be written as

$$H_1 = H_2$$

i.e.,  $(mh_1)_{CO_2} + (mh_1)_{N_2} = (mh_2)_{\text{mixture}} = (mh_2)_{CO_2} + (mh_2)_{N_2}$

or  $[m(h_1 - h_2)]_{CO_2} + [m(h_1 - h_2)]_{N_2} = 0$

or  $[mc_p(T_1 - T_2)]_{CO_2} + [mc_p(T_1 - T_2)]_{N_2} = 0$

or  $4 \times 0.85(40 - T_2) + 8 \times 1.04(160 - T_2) = 0$

or  $136 - 3.4T_2 + 1331.2 - 8.32T_2 = 0$

or  $1467.2 - 11.72T_2 = 0$

∴  $T_2 = 125.2^\circ\text{C} = 398.2 \text{ K. (Ans.)}$

(ii) **Change in entropy :**

Now  $n_{CO_2} = \frac{4}{44} = 0.0909$

$$n_{N_2} = \frac{8}{28} = 0.2857$$

∴  $n = n_{CO_2} + n_{N_2} = 0.0909 + 0.2857 = 0.3766$

Again,  $\frac{P(CO_2)_2}{p_2} = x_{CO_2}$  [ $p_2$  = pressure of the mixture]

$$\therefore p_{(\text{CO}_2)_2} = 0.7 \times \frac{0.0909}{0.3766} = 0.17 \text{ bar}$$

$$\text{Similarly, } p_{(\text{N}_2)_2} = 0.7 \times \frac{0.2857}{0.3766} = 0.53 \text{ bar}$$

$\therefore$  Change in entropy,  $\Delta S$

$$\begin{aligned} &= \left[ mc_p \log_e \frac{T_2}{T_1} - mR \log_e \frac{p_2}{p_1} \right]_{\text{CO}_2} + \left[ mc_p \log_e \frac{T_2}{T_1} - mR \log_e \frac{p_2}{p_1} \right]_{\text{N}_2} \\ &= 4 \left[ 0.85 \log_e \frac{398.2}{313} - \frac{8.314}{44} \log_e \frac{0.17}{1.4} \right] + 8 \left[ 1.04 \log_e \frac{398.2}{433} - \frac{8.314}{28} \log_e \frac{0.53}{1.0} \right] \\ &= 4(0.2046 + 0.3984) + 8(-0.0871 + 0.1885) = 3.2232 \text{ kJ/K} \end{aligned}$$

i.e., **Change in entropy = 3.2232 kJ/K. (Ans.)**

**Example 9.20.** An insulated vessel containing 1 mole of oxygen at a pressure of 2.5 bar and a temperature of 293 K is connected through a valve to a second insulated rigid vessel containing 2 mole nitrogen at a pressure of 1.5 bar and a temperature of 301 K. The valve is opened and adiabatic mixing takes place. Assuming that oxygen and nitrogen are perfect gases calculate the entropy change in the mixing process.

Assume the following specific heats at constant volume :

$$c_{v(\text{O}_2)} = 0.39 \text{ kJ/kg K}$$

$$c_{v(\text{N}_2)} = 0.446 \text{ kJ/kg K.}$$

**Solution.** Consider the system within the boundary of Fig. 9.11.

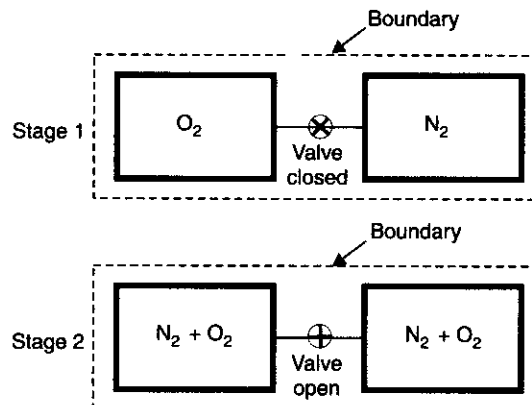


Fig. 9.11

In the process :  $Q = 0$ ,  $W = 0$ , hence by the first law for a non-flow process  $\Delta U = 0$ . Let  $T_2$  be the final temperature of the mixture.

$$\therefore \left[ m_{\text{O}_2} c_{v(\text{O}_2)} T_{\text{O}_2} + m_{\text{N}_2} c_{v(\text{N}_2)} T_{\text{N}_2} \right] = \left[ m_{\text{O}_2} c_{v(\text{O}_2)} + m_{\text{N}_2} c_{v(\text{N}_2)} \right] T_2$$

$$\text{or } [(1 \times 32) \times 0.39 \times 293 + (2 \times 28) \times 0.446 \times 301] = (1 \times 32 \times 0.39 + (2 \times 28) \times 0.446) T_2$$

$$\text{or } T_2 = \frac{32 \times 0.39 \times 293 + 56 \times 0.446 \times 301}{32 \times 0.39 + 56 \times 0.446} = \frac{11174.4}{37.45} = 298.4 \text{ K}$$



Now entropy change in the mixing process is given by

$$\Delta S = m_{O_2} \Delta_{s(O_2)} + m_{N_2} \Delta_{s(N_2)}$$

where  $\Delta_s = c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{V_2}{V_1}$

Now to find initial and final volumes of  $O_2$  and  $N_2$  using the relation,

$$V = \frac{nR_0T}{p}$$

$$\therefore \text{The initial volume of } O_2 = \frac{1 \times 8.314 \times 293 \times 10^3}{2.5 \times 10^5} = 9.74 \text{ m}^3$$

and Initial volume of  $N_2 = \frac{2 \times 8.314 \times 301 \times 10^3}{1.5 \times 10^5} = 33.4 \text{ m}^3$

$$\text{Final volume of the mixture} = 9.74 + 33.4 = 43.14 \text{ m}^3$$

$$\begin{aligned} \text{Thus } \Delta S &= \left[ (1 \times 32) \left\{ 0.39 \times \log_e \frac{298.4}{293} + \frac{8.314}{32} \log_e \frac{43.14}{9.74} \right\} \right] \\ &\quad + \left[ (2 \times 28) \left\{ 0.446 \times \log_e \frac{298.4}{301} + \frac{8.314}{28} \log_e \frac{43.14}{33.4} \right\} \right] \\ &= 12.60 + 4.04 = 16.64 \text{ kJ} \end{aligned}$$

*i.e.*, Entropy change in the mixing process = 16.64 kJ. (Ans.)

**Example 9.21.** A tank of capacity  $0.45 \text{ m}^3$  is insulated and is divided into two sections through a partition. One section initially contains  $H_2$  at 3 bar and  $130^\circ\text{C}$  and has a volume of  $0.3 \text{ m}^3$  and the other section initially holds  $N_2$  at 6 bar and  $30^\circ\text{C}$ . The gases are then allowed to mix after removing the adiabatic partition. Determine :

- (i) The temperature of the equilibrium mixture ;
- (ii) The pressure of the mixture ;
- (iii) The change in entropy for each component and total value.

$$\text{Assume : } c_{v(N_2)} = 0.744 \text{ kJ/kg K, } c_{v(H_2)} = 10.352 \text{ kJ/kg K}$$

$$c_{p(N_2)} = 1.041 \text{ kJ/kg K, } c_{p(H_2)} = 14.476 \text{ kJ/kg K.}$$

**Solution.** Total capacity of the tank,  $V = 0.45 \text{ m}^3$

$$V_{H_2} = 0.3 \text{ m}^3 ; \quad T_{H_2} = 130 + 273 = 403 \text{ K}$$

$$p_{H_2} = 3 \text{ bar ; } \quad V_{N_2} = 0.15 \text{ m}^3 \quad (\text{i.e., } 0.45 - 0.3 = 0.15 \text{ m}^3)$$

$$p_{N_2} = 6 \text{ bar ; } \quad T_{N_2} = 30 + 273 = 303 \text{ K.}$$

(i) **Temperature of equilibrium mixture,  $T_2$  :**

$$\text{Now } p_{H_2} V_{H_2} = m_{H_2} R_{H_2} T_{H_2}$$

$$\therefore m_{H_2} = \frac{3 \times 10^5 \times 0.3}{\left(\frac{8.314}{2}\right) \times 403 \times 10^3} = 0.0537 \text{ kg} \quad \left[ \because R = \frac{R_0}{M} \right]$$

and

$$p_{N_2} V_{N_2} = m_{N_2} R_{N_2} T_{N_2}$$

$$\therefore m_{N_2} = \frac{6 \times 10^5 \times 0.15}{\left(\frac{8.314}{28}\right) \times 303 \times 10^3} = 1.0 \text{ kg}$$

According to the first law for a closed system

$$\Delta U = 0$$

i.e.,  $U_{\text{initial}} = U_{\text{final}}$

or  $m_{H_2} c_{v(H_2)} T_{(H_2)_1} + m_{N_2} c_{v(N_2)} T_{(N_2)_1} = m_{H_2} c_{v(H_2)} T_{(H_2)_2} + m_{N_2} c_{v(N_2)} T_{(N_2)_2}$

or  $m_{H_2} c_{v(H_2)} [T_{(H_2)_2} - T_{(H_2)_1}] + m_{N_2} c_{v(N_2)} [T_{(N_2)_2} - T_{(N_2)_1}] = 0$

or  $0.0537 \times 10.352 [T_{(H_2)_2} - 403] + 1.0 \times 0.744 [T_{(N_2)_2} - 303] = 0$

$$T_{(H_2)_2} = T_{(N_2)_2} = T_2$$

or  $0.556(T_2 - 403) + 0.744(T_2 - 303) = 0$

or  $0.556T_2 - 224 + 0.744T_2 - 225.4 = 0$

$$\therefore T_2 = 345.7 \text{ K}$$

i.e., Temperature of the mixture = **345.7 K. (Ans.)**

(ii) Pressure of the mixture,  $p_2$  :

Now  $p_{(H_2)_2} V = m_{H_2} R_{H_2} T_2$

$$\therefore p_{(H_2)_2} = \frac{0.0537 \times \left(\frac{8.314}{2}\right) \times 345.7 \times 10^3}{0.45 \times 10^5} = 1.71 \text{ bar}$$

Similarly  $p_{(N_2)_2} = \frac{1.0 \times \left(\frac{8.314}{28}\right) \times 345.7 \times 10^3}{0.45 \times 10^5} = 2.28 \text{ bar}$

$$\therefore p_2 = p_{(H_2)_2} + p_{(N_2)_2} = 1.71 + 2.28 = \mathbf{3.99 \text{ bar. (Ans.)}}$$

(iii) Change in entropy :

Now  $(\Delta S)_{H_2} = m \left( c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1} \right)_{H_2}$

$$= 0.0537 \left[ 14.476 \log_e \frac{345.7}{403} - \frac{8.314}{2} \log_e \frac{1.71}{3} \right]$$

$$= \mathbf{0.00626 \text{ kJ/K. (Ans.)}}$$

$$(\Delta S)_{H_2} = m \left( c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1} \right)$$

$$= 1.0 \left[ 1.041 \log_e \frac{345.7}{303} - \frac{8.314}{28} \log_e \frac{2.28}{6} \right]$$

$$= \mathbf{0.424 \text{ kJ/K. (Ans.)}}$$

$$\therefore \Delta S = (\Delta S)_{\text{H}_2} + (\Delta S)_{\text{N}_2} = 0.00626 + 0.424 = 0.43026 \text{ kJ/K}$$

i.e., **Total change in entropy = 0.43026 kJ/K. (Ans.)**

**Example 9.22.** A perfect gas mixture consists of 4 kg of  $\text{N}_2$  and 6 kg of  $\text{CO}_2$  at a pressure of 4 bar and a temperature of  $25^\circ\text{C}$ . Calculate  $c_v$  and  $c_p$  of the mixture.

If the mixture is heated at constant volume to  $50^\circ\text{C}$ , find the change in internal energy, enthalpy and entropy of the mixture.

$$\begin{aligned} \text{Take : } c_{v(\text{N}_2)} &= 0.745 \text{ kJ/kg K}, & c_{v(\text{CO}_2)} &= 0.653 \text{ kJ/kg K} \\ c_{p(\text{N}_2)} &= 1.041 \text{ kJ/kg K}, & c_{p(\text{CO}_2)} &= 0.842 \text{ kJ/kg K}. \end{aligned}$$

**Solution.**  $m_{\text{N}_2} = 4 \text{ kg}$ ,  $m_{\text{CO}_2} = 6 \text{ kg}$ ,  $p_{\text{mix}} = 4 \text{ bar}$

$$T_1 = 25 + 273 = 298 \text{ K}, \quad T_2 = 50 + 273 = 323 \text{ K}$$

$$c_{v(\text{mix})} = ?, \quad c_{p(\text{mix})} = ?$$

Using the relation,

$$(m_{\text{N}_2} + m_{\text{CO}_2})c_{v(\text{mix})} = m_{\text{N}_2}c_{v(\text{N}_2)} + m_{\text{CO}_2}c_{v(\text{CO}_2)}$$

$$(4 + 6)c_{v(\text{mix})} = 4 \times 0.745 + 6 \times 0.653$$

$$\therefore c_{v(\text{mix})} = \frac{4 \times 0.745 + 6 \times 0.653}{4 + 6} = \mathbf{0.6898 \text{ kJ/kg K. (Ans.)}$$

$$\text{Similarly, } c_{p(\text{mix})} = \frac{4 \times 1.041 + 6 \times 0.842}{4 + 6} = \mathbf{0.9216 \text{ kJ/kg K. (Ans.)}$$

**Change in internal energy,  $\Delta U$  :**

$$\begin{aligned} \Delta U &= [mc_v(T_2 - T_1)]_{\text{mix}} \\ &= (4 + 6) \times 0.6898(323 - 298) = \mathbf{172.45 \text{ kJ. (Ans.)} \end{aligned}$$

**Change in enthalpy,  $\Delta H$  :**

$$\begin{aligned} \Delta H &= [mc_p(T_2 - T_1)]_{\text{mix}} \\ &= (4 + 6) \times 0.9216(323 - 298) = \mathbf{230.4 \text{ kJ. (Ans.)} \end{aligned}$$

**Change in entropy,  $\Delta S$  :**

$$\begin{aligned} (\Delta s) &= \left( c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1} \right) \\ &= \left( c_v \log_e \frac{T_2}{T_1} \right) \quad (\because v_2 = v_1) \end{aligned}$$

$$\therefore (\Delta s)_{\text{N}_2} = \left( c_v \log_e \frac{T_2}{T_1} \right)_{\text{N}_2}$$

$$\text{and } (\Delta s)_{\text{CO}_2} = \left( c_v \log_e \frac{T_2}{T_1} \right)_{\text{CO}_2}$$

$$\text{Hence, } \Delta S = \left( mc_v \log_e \frac{T_2}{T_1} \right)_{\text{N}_2} + \left( mc_v \log_e \frac{T_2}{T_1} \right)_{\text{CO}_2}$$

$$= 4 \times 0.745 \log_e \frac{323}{298} + 6 \times 0.653 \log_e \frac{323}{298}$$

$$= \mathbf{0.5557 \text{ kJ/K. (Ans.)}}$$

**Note.**  $\Delta S$  may also be found out as follows :

$$\Delta S = (m_{N_2} + m_{CO}) c_{v(\text{mix})} \log_e \frac{T_2}{T_1}$$

$$= (4 + 6) \times 0.6898 \log_e \frac{323}{298} = 0.5557 \text{ kJ/K.}$$

## HIGHLIGHTS

1. According to Dalton's law :
  - (i) The pressure of a mixture of gases is equal to the sum of the partial pressures of the constituents.
  - (ii) The partial pressure of each constituent is that pressure which the gas would exert if it occupied alone that volume occupied by the mixture at the same temperature.
2. According to Gibbs-Dalton law :
  - (i) The internal energy, enthalpy and entropy of a gaseous mixture are respectively equal to the sum of the internal energies, enthalpies and entropies of the constituents.
  - (ii) Each constituent has that internal energy, enthalpy and entropy, which it would have if it occupied alone that volume occupied by the mixture at the temperature of the mixture.
3. The characteristic equation for mixture is given as :

$$pV = nR_0T$$

where  $n$  = Number of moles of mixture, and

$R_0$  = Universal gas constant.

4. Molecular weight ( $M$ ) may be found out by using the following relations :

$$M = \sum \frac{n_i}{n} M_i \quad \text{and} \quad M = \frac{1}{\sum \frac{m_i}{M_i}}$$

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

5. The following condition must be satisfied in an adiabatic mixing process of perfect gas in steady flow :

$$T = \frac{\sum m_i c_{pe} T_i}{\sum m_i c_{pi}} = \frac{\sum n_i C_{pi} T_i}{\sum n_i C_{pi}}$$

## OBJECTIVE TYPE QUESTIONS

**Choose the Correct Answer :**

1. In an ideal gas the partial pressure of a component is
  - (a) inversely proportional to the square of the mole fraction
  - (b) directly proportional to the mole fraction
  - (c) inversely proportional to the mole fraction
  - (d) equal to the mole fraction.
2. The value of the universal gas constant is
 

(a) 8.314 J/kg K	(b) 83.14 kJ/kg K
(c) 848 kJ/kg K	(d) 8.314 kJ/kg K.

3. In a mixture of gases, the partial pressure  $p_i$  of any constituent gas can be found by

$$(a) p_i = n_i RT/V$$

$$(b) p_i = m_i RT/V_i$$

$$(c) p_i = n_i R_0 T/V_i$$

$$(d) p_i = n_i R_0 T/V$$

where,  $R$  = Characteristic gas constant,

$R_0$  = Universal gas constant,

$V$  = Volume of the mixture,

$V_i$  = Volume of the  $i$ th constituent, and

$T$  = Temperature of the mixture.

4. Mole fraction of a component of gas mixture is equal to

$$(a) 1/f$$

$$(b) f^2$$

$$(c) f$$

$$(d) f/p$$

where,  $f$  = Volume fraction, and

$p$  = Pressure of the mixture.

5. In a gaseous mixture the specific volume of each component is given by

$$(a) V/m$$

$$(b) V_i/m_i$$

$$(c) V/m_i$$

$$(d) \text{none of the above.}$$

where,  $V$  = Volume of the mixture,

$V_i$  = Volume of the  $i$ th component,

$m$  = Mass of mixture, and

$m_i$  = Mass of the  $i$ th component.

### Answers

1. (b)

2. (d)

3. (d)

4. (c)

5. (c).

### THEORETICAL QUESTIONS

- Define the following terms :
  - Partial pressure
  - Mole fraction
  - Volume fraction of a gas constituent in a mixture.
- Explain briefly Dalton's law and Gibbs-Dalton law.
- State and explain Amagat's law or Leduc's law.
- Prove 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.
- Prove the following relation

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

where,  $M$  = Molecular weight of the mixture,

$n_i$  = Number of moles of an any constituent,

$m_{fi}$  = Mass fraction of the constituent, and

$M_i$  = Molecular weight of the constituent.

### UNSOLVED EXAMPLES

- 0.45 kg of carbon monoxide (28) and 1 kg of air at 15°C are contained in a vessel of volume 0.4 m<sup>3</sup>. Calculate the partial pressure of each constituent and the total pressure in the vessel. The gravimetric analysis of air is to be taken as 23.3% oxygen (32) and 76.7% nitrogen (28).

$$[\text{Ans. } p_{\text{O}_2} = 0.4359 \text{ bar ; } p_{\text{N}_2} = 1.64 \text{ bar, } p_{\text{CO}} = 0.962 \text{ bar}]$$

2. A mixture of CO and O<sub>2</sub> is to be prepared in the proportion of 7 kg to 4 kg in a vessel of 0.3 m<sup>3</sup> capacity. If the temperature of the mixture is 15°C, determine the pressure to which the vessel is subjected. If the temperature is raised to 40°C, what will then be the pressure in the vessel? [Ans. 29.9 bar, 32.5 bar]
3. Assuming that air may be treated as a mixture of ideal gases which has a mass composition 23.2% oxygen and 76.8% nitrogen, find the gas constant and apparent molecular weight of air. [Ans. 0.288 kJ/kg K, 28.86]
4. A mixture of 1 mole CO<sub>2</sub> and 3.5 moles of air is contained in a vessel at 1 bar and 15°C. The volumetric analysis of air can be taken as 21% oxygen and 79% nitrogen. Calculate for the mixture: (i) The masses of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>, and the total mass. (ii) The percentage carbon content by mass. (iii) The apparent molecular weight and the gas constant for the mixture. (iv) The specific volume of the mixture. [Ans. (i) 44 kg, 23.55 kg, 77.5 kg; (ii) 8.27%; (iii) 32.2, 0.2581 kJ/kg K; (iv) 0.7435 m<sup>3</sup>/kg]
5. A mixture of H<sub>2</sub> and O<sub>2</sub> is to be made so that the ratio of H<sub>2</sub> to O<sub>2</sub> is 2 to 1 by volume. Calculate the mass of O<sub>2</sub> required and the volume of the container, per kg of H<sub>2</sub>, if the pressure and temperature are 1 bar and 15°C respectively. [Ans. 8 kg, 17.96 m<sup>3</sup>]
6. A vessel contains a gaseous mixture of composition by volume, 80% H<sub>2</sub> and 20% CO. It is desired that the mixture should be made in proportion 50% H<sub>2</sub> and 50% CO by removing some of the mixture and adding some CO. Calculate per mole of mixture the mass of mixture to be removed, and the mass of CO to be added. The pressure and temperature in the vessel remain constant during the procedure. [Ans. 2.7 kg, 10.5 kg]
7. The gas in an engine cylinder has a volumetric analysis of 12% of CO<sub>2</sub>, 11.5% O<sub>2</sub> and 76.5% N<sub>2</sub>. The temperature at the beginning of expansion is 1000°C and the gas mixture expands reversibly through a volume ratio of 7 : 1, according to a law  $pv^{1.25} = \text{constant}$ . Calculate the work done and the heat flow per kg of gas. The values of  $c_p$  for the constituents are as follows:  $c_p$  for CO<sub>2</sub> = 1.235 kJ/kg K;  $c_p$  for O<sub>2</sub> = 1.088 kJ/kg K;  $c_p$  for N<sub>2</sub> = 1.172 kJ/kg K. [Ans. 536.3 kJ/kg; 96 kJ/kg (heat supplied)]
8. A producer gas has the following volumetric analysis: 29% CO, 12% H<sub>2</sub>, 3% CH<sub>4</sub>, 4% CO<sub>2</sub>, 52% N<sub>2</sub>. Calculate the values of  $C_p$ ,  $C_v$ ,  $c_p$  and  $c_v$  for the mixture. The values of  $C_p$  for the constituents are as follows: for CO  $C_p = 29.27$  kJ/mole K; for H<sub>2</sub>  $C_p = 28.89$  kJ/mole K; for CH<sub>4</sub>  $C_p = 35.8$  kJ/mole K; for CO<sub>2</sub>  $C_p = 37.22$  kJ/mole K; for N<sub>2</sub>  $C_p = 29.14$  kJ/mole K. [Ans. 29.676 kJ/mole K, 21.362 kJ/mole K; 1.178 kJ/kg K; 0.8476 kJ/kg K]
9. An exhaust gas is analysed and is found to contain, by volume, 78% N<sub>2</sub>, 12% CO<sub>2</sub> and 10% O<sub>2</sub>. What is the corresponding gravimetric analysis? Calculate the mass of mixture per mole, and the density if the temperature is 550°C and the total pressure is 1 bar. [Ans. 72% N<sub>2</sub>, 17.3% CO<sub>2</sub>, 10.6% O<sub>2</sub>; 30.28 kg/mole; 0.442 kg/m<sup>3</sup>]
10. A vessel of 3 m<sup>3</sup> capacity contains a mixture of nitrogen and carbon dioxide, the analysis by volume showing equal quantities of each. The temperature is 15°C and the total pressure is 3.5 bar. Determine the mass of each constituent. [Ans. 6.14 kg N<sub>2</sub>; 9.65 kg CO<sub>2</sub>]
11. A mixture is made up of 25% N<sub>2</sub>, 35% O<sub>2</sub>, 20% CO<sub>2</sub> and 20% CO by volume. Calculate: (i) The molecular weight of the mixture. (ii)  $C_p$  and  $C_v$  for the mixture. (iii)  $\gamma$  for the mixture. (iv) The partial pressure of each constituent when the total pressure is 1.5 bar. (v) The density of the mixture at 1.5 bar and 15°C. [Ans. (i) 32.6; (ii) 30.9, 22.53 kJ/mole K; (iii) 1.37; (iv) 0.375, 0.525, 0.3, 0.3 bar; (v) 2.04 kg/m<sup>3</sup>]
12. A mixture of ideal gases consists of 3 kg of nitrogen and 5 kg of carbon dioxide at a pressure of 3 bar and a temperature of 20°C. Find (i) the mole fraction of each constituent, (ii) the equivalent molecular weight of the mixture, (iii) the equivalent gas constant of the mixture, (iv) the partial pressures and partial volumes, (v) the volume and density of the mixture, and (vi) the  $c_p$  and  $c_v$  of the mixture. If the mixture is heated at constant volume to 40°C, find the changes in internal energy, enthalpy and entropy of the mixture. Find the changes in internal energy, enthalpy and entropy of the mixture if the heating is done at constant pressure. Take  $\gamma$ : for CO<sub>2</sub> = 1.286 and N<sub>2</sub> = 1.4. [Ans. (i) 0.485, 0.515; (ii) 36.25 kg/kg mole; (iii) 0.229 kJ/kg K; (iv) 1.455 bar, 1.545 bar; 0.87 m<sup>3</sup>, 0.923 m<sup>3</sup>; (v) 1.79 m<sup>3</sup>, 4.46 kg/m<sup>3</sup>; (vi) 0.92 kJ/kg K, 0.69 kJ/kg K; 110.4 kJ, 147.2 kJ, 0.368 kJ/kg K; 0.49 kJ/kg K]
13. A vessel of 1.5 m<sup>3</sup> capacity contains oxygen at 7 bar and 40°C. The vessel is connected to another vessel of 3 m<sup>3</sup> capacity containing carbon monoxide at 1 bar and 15°C. A connecting valve is opened and the

gases mix adiabatically. Calculate : (i) The final temperature and pressure of the mixture. (ii) The change in entropy of the system.

Assume : For oxygen  $C_v = 21.07$  kJ/mole K

For carbon monoxide  $C_v = 20.86$  kJ/mole K.

[Ans. (i) 34°C, 3 bar ; (ii) 4.108 kJ/K]

14. Two vessels both containing nitrogen, are connected by a valve which is opened to allow the contents to mix and achieve an equilibrium temperature of 27°C. Before mixing the following information is known about the gases in the two vessels.

Vessel A

$p = 15$  bar

$t = 50^\circ\text{C}$

Contents = 0.5 kg mole

Vessel B

$p = 6$  bar

$t = 20^\circ\text{C}$

Contents = 2.5 kg

Calculate the final equilibrium pressure and amount of heat transferred to the surroundings. If the vessel had been perfectly insulated, calculate the final temperature and pressure which would have been reached.

Take  $\gamma = 1.4$ .

[Ans. 11.68 bar, -226.2 kJ, 45.5°C, 12.4 bar]

15. Find the increase in entropy when 2 kg of oxygen at 60°C are mixed with 6 kg of nitrogen at the same temperature. The initial pressure of each constituent is 10.3 bar and is the same as that of the mixture.

[Ans. 1.2314 kJ/kg K]

16. A gas mixture contains hydrogen, nitrogen and carbon monoxide in equal molar proportions. Treating the components of the mixture as perfect gases, determine the gas constant and the ratio of specific heats for the mixture. Calculate the work required to compress 1 kg of the mixture in reversible adiabatic flow through a pressure ratio of 2 from an initial temperature of 15°C when kinetic and potential energy changes are negligible.

[Ans. 0.43 kJ/kg K, 1.4, -82.76 kJ]

17. 2 kg of nitrogen at 20 bar and 38°C is contained in a rigid vessel. A sufficient quantity of oxygen is added to increase the pressure to 26.66 bar while the temperature remains constant at 38°C.

Calculate the mass of oxygen added.

[Ans. 0.761 kg]

18. Air ( $\text{N}_2 = 77\%$ ,  $\text{O}_2 = 23\%$  by weight) at 20°C and 10 bar is contained in a vessel of capacity of 0.5 m<sup>3</sup>. Some quantity of carbon dioxide is forced into the vessel so that the temperature remains at 20°C but the pressure rises to 15 bar. Find the masses of oxygen, nitrogen and carbon dioxide in the cylinder. The universal gas constant is 8.3143 kJ/kg K.

[Ans. 1.35 kg, 4.54 kg, 4.51 kg]

19. A vessel of 5 m<sup>3</sup> capacity contains a mixture of two gases in proportion of 40 per cent and 60 per cent at 20°C. If the value of  $R$  for the gases is 0.287 kJ/kg K and 0.294 kJ/kg K and if the total weight of the mixture is 1.5 kg, calculate :

(i) The partial pressure ;

(ii) Total pressure ;

(iii) Mean value of  $R$  for the mixture.

[Ans. 0.1 bar ; 0.155 bar ; 0.291 kJ/kg K]

20. A mixture consisting of 6 kg of  $\text{O}_2$  and 9 kg of  $\text{N}_2$  has a pressure of 3 bar and temperature of 20°C. For the mixture determine the following :

(i) The mole fraction of each component ;

(ii) The average molecular weight ;

(iii) The specific gas constant ;

(iv) The volume and density ;

(v) The partial pressures and partial volumes.

[Ans. (i) 0.3684, 0.6315 ; (ii) 29.475 ; (iii) 0.282 kJ/kg K ;

(iv) 4.13 m<sup>3</sup>, 3.629 kg/m<sup>3</sup> ; (v) 1.1 bar, 1.894 bar ; 1.52 m<sup>3</sup>, 2.61 m<sup>3</sup>]

21. A closed vessel of 0.1 m<sup>3</sup> capacity contained air at 1 bar pressure and 27°C. Hydrogen was added and the total pressure in the vessel was raised to 1.2 bar at the same temperature. Find the weight of oxygen, nitrogen and hydrogen finally in the vessel and their respective partial pressures.

Air contains 77%  $\text{N}_2$  by weight. Take the value of universal gas constant as 8.3143 kJ/kg K and molecular weight of air as 29.

[Ans.  $m_{\text{O}_2} = 0.0267$  kg,  $m_{\text{N}_2} = 0.0893$  kg,  $m_{\text{H}_2} = 0.001603$  kg]

22. A vessel of capacity 0.3 m<sup>3</sup> is insulated and divided into two sections by a partition. One section is 0.2 m<sup>3</sup> in volume and initially contains  $\text{H}_2$  at 2 bar and 127°C. The remaining section initially holds  $\text{N}_2$  at 4 bar and 27°C. The adiabatic partition is then removed, and the gases are allowed to mix. Determine :

- (i) The temperature of the equilibrium mixture,  
(ii) The pressure of the mixture, and  
(iii) The change in entropy for each component and total value.

$$c_{v(N_2)} = 0.744 \text{ kJ/kg K}, \quad c_{v(H_2)} = 10.352 \text{ kJ/kg K}$$

$$c_{p(N_2)} = 1.041 \text{ kJ/kg K}, \quad c_{p(H_2)} = 14.476 \text{ kJ/kg K}.$$

[Ans. (i) 342.6 K ; (ii) 2.661 bar ; (iii)  $(\Delta S)_{H_2} = 0.00235 \text{ kJ/K}$  ;  
 $(\Delta S)_{N_2} = 0.1908 \text{ kJ/K}$  ;  $\Delta S = 0.19315 \text{ kJ/K}$ ]

23. 3 kg of  $N_2$  and 5 kg of  $CO_2$  at a pressure of 3 bar and a temperature of  $20^\circ\text{C}$  comprise a perfect gas mixture. Calculate  $c_p$  and  $c_v$  of the mixture.  
If the mixture is heated at constant volume to  $40^\circ\text{C}$ , find the change in internal energy, enthalpy and entropy of the mixture.

Take :  $c_{v(N_2)} = 0.7448$  and  $c_{p(N_2)} = 1.0416 \text{ kJ/kg K}$

$c_{v(CO_2)} = 0.6529$  and  $c_{p(CO_2)} = 0.8418 \text{ kJ/kg K}$ .

[Ans. 0.6873 kJ/kg K, 0.9167 kJ/kg K ; 109.96 kJ, 146.67 kJ, 0.363 kJ/K]