Thermodynamics

2nd Semester, 4th Chapter

Mixtures
Dalton’s Law and Gibbs – Dalton Law
Volumetric Analysis of a Gas Mixture
Molecular Weight
Gas Constant and Specific Heat of Gas Mixture
Adiabatic Mixing of Gas Mixture

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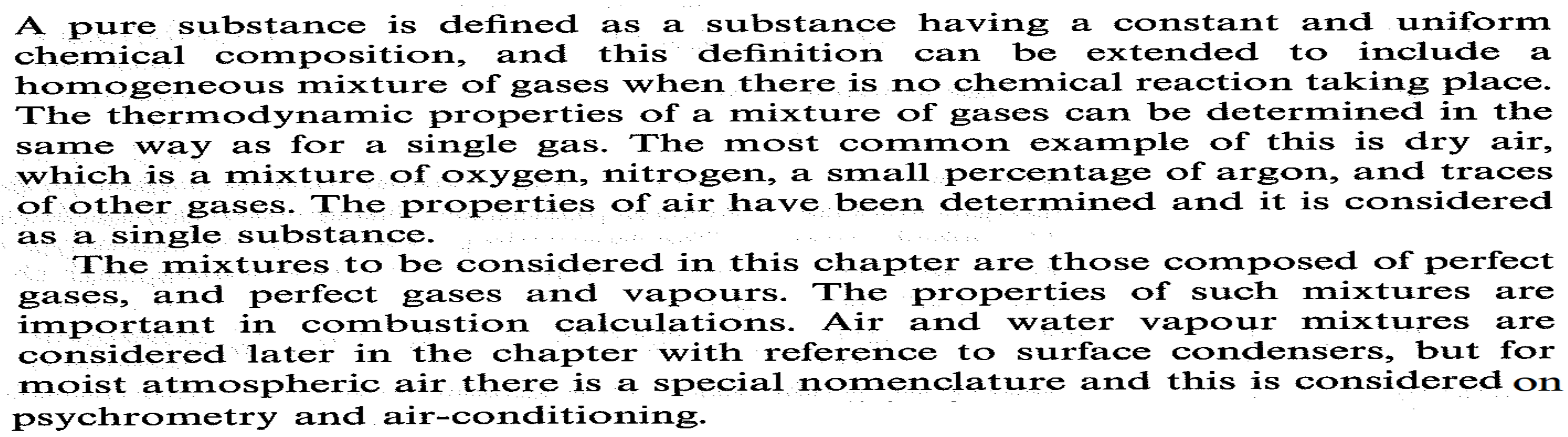
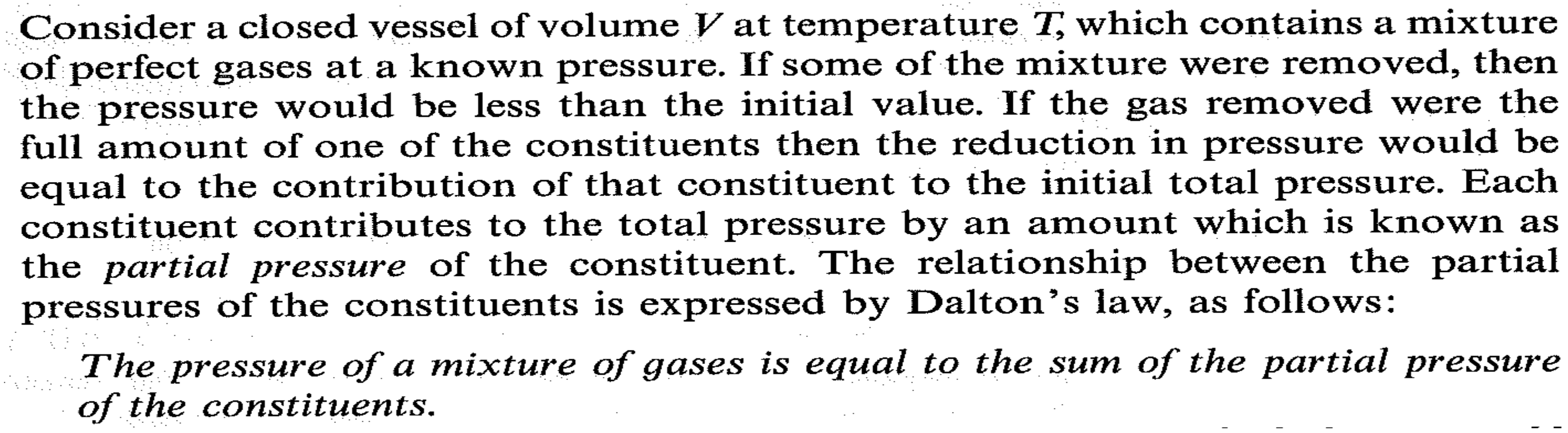
Introduction



A pure substance is defined as a substance having a constant and uniform chemical composition, and this definition can be extended to include a homogeneous mixture of gases when there is no chemical reaction taking place. The thermodynamic properties of a mixture of gases can be determined in the same way as for a single gas. The most common example of this is dry air, which is a mixture of oxygen, nitrogen, a small percentage of argon, and traces of other gases. The properties of air have been determined and it is considered as a single substance.

The mixtures to be considered in this chapter 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 on psychrometry and air-conditioning.

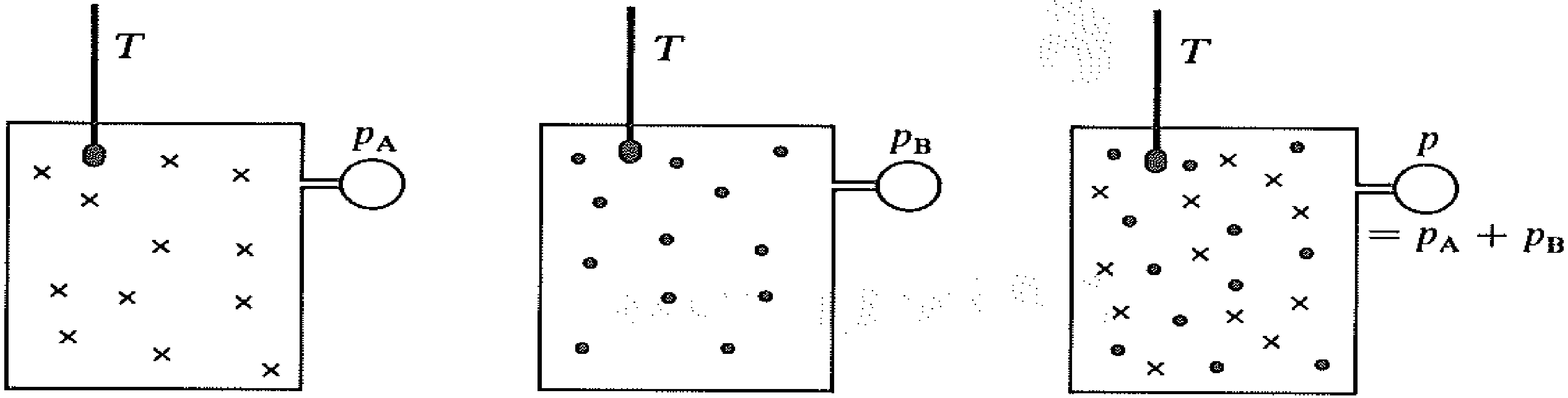
Dalton’s Law and Gibbs – Dalton Law



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 pressure 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 mixture at the same temperature.



Gas A
Mass $= m_A$

Gas B
Mass $= m_B$

Mixture of A + B
Mass $= m = m_A + m_B$

This is expressed diagrammatically in Fig. 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.

By the conservation of mass

$$m = m_A + m_B$$

By Dalton's law

$$p = p_A + p_B$$

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. each constituent occupies the whole vessel. The example given in Fig. and the relationships in equations and refer to a mixture of two gases, but the law can be extended to any number of gases,

$$m = m_A + m_B + m_C + \text{etc.} \quad \text{or} \quad m = \sum m_i$$

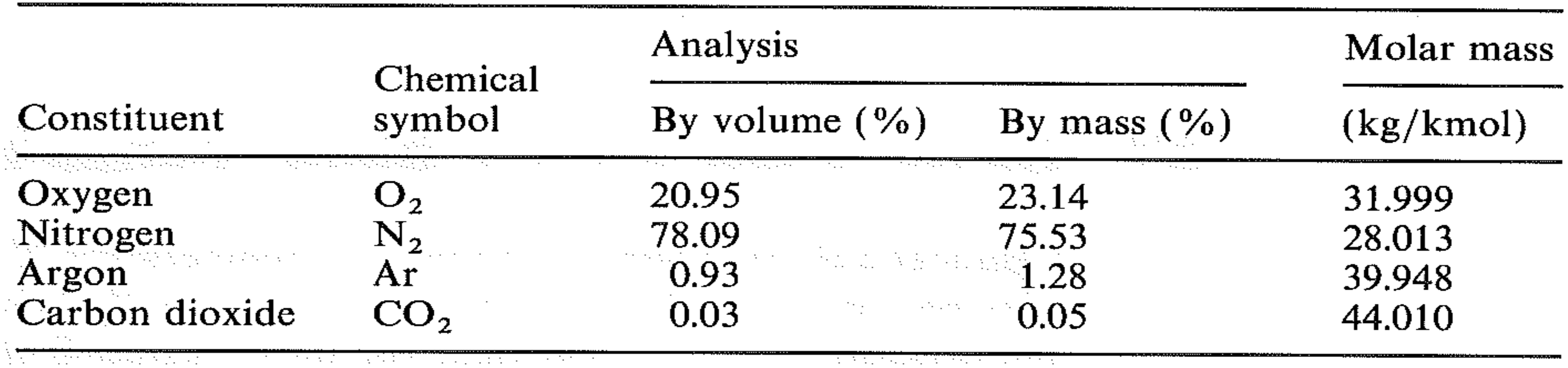
where m_i is the mass of a constituent. Similarly

$$p = p_A + p_B + p_C + \text{etc.} \quad \text{or} \quad p = \sum p_i$$

where p_i is the partial pressure of a constituent.

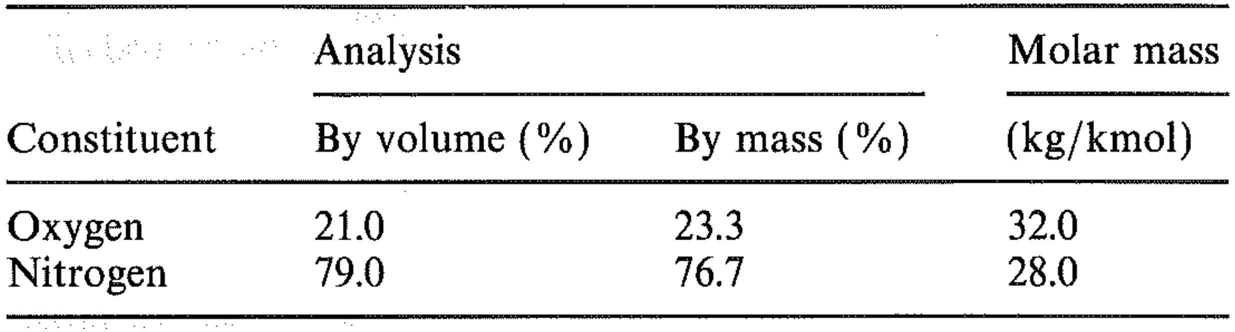
Air is the most common mixture and since it will be referred to frequently, its composition is as given in Table . The mean molar mass of air is 28.96 kg/kmol, and the specific gas constant R is 0.2871 kJ/kg K. For approximate calculations the air is said to be composed of oxygen and 'atmospheric nitrogen' (see Table). Note: volumetric analysis is the analysis by volume; gravimetric analysis is the analysis by mass.

Analysis of Air



Constituent	Chemical symbol	Analysis		Molar mass
		By volume (%)	By mass (%)	(kg/kmol)
Oxygen	O_2	20.95	23.14	31.999
Nitrogen	N_2	78.09	75.53	28.013
Argon	Ar	0.93	1.28	39.948
Carbon dioxide	CO_2	0.03	0.05	44.010

Approximate Analysis for Air



Constituent	Analysis		Molar mass
	By volume (%)	By mass (%)	(kg/kmol)
Oxygen	21.0	23.3	32.0
Nitrogen	79.0	76.7	28.0

Example 1

A vessel of volume 0.4 m^3 contains 0.45 kg of carbon monoxide and 1 kg of air, at 15 °C. 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 and 76.7% nitrogen. Take the molar masses of carbon monoxide, oxygen and nitrogen as 28, 32 and 28 kg/kmol.

Solution

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

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

$$\text{Gas Constsnt} \quad \mathbf{R_{gas}} = \frac{\text{universial gas constant}}{\text{M}\mathit{oulecolar\ mass}} = \frac{\mathbf{R^o}}{\mathbf{M}}$$

$$\mathbf{PV = m\, R_{gas}\, T = m\, \frac{R^o}{M}\, T}$$

$$\mathbf{P = \frac{m\, R^o\, T}{M\, V}}$$

For a constituent

$$\mathbf{P_i = \frac{m_i\, R^o\, T}{M_i\, V}}$$

The volume V is 0.4 m^3 and the temperature T is $(15 + 273) = 288$ K. Therefore we have for O_2

$$p_{O_2} = \frac{0.233 \times 8.3145 \times 288}{32 \times 0.4} = 43.59\ \mathrm{kN/m^2}$$

$$= \frac{43.59 \times 10^3}{10^5} = 0.4359\ \mathrm{bar}$$

$$p_{N_2} = \frac{0.767 \times 8.3145 \times 288}{28 \times 0.4} = 163.99\ \mathrm{kN/m^2}$$

$$= \frac{163.99 \times 10^3}{10^5} = 1.6399\ \mathrm{bar}$$

$$p_{CO} = \frac{0.45 \times 8.3145 \times 288}{28 \times 0.4} = 96.21\ \mathrm{kN/m^2}$$

$$= \frac{96.21 \times 10^3}{10^5} = 0.9621\ \mathrm{bar}$$

The total pressure in the vessel is given by equation

$$p = \sum p_i = 0.436 + 1.640 + 0.962 = 3.038\ \mathrm{bar}$$

Pressure in vessel = 3.038 bar

Dalton's law was reformulated 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 would have if it occupied alone that volume occupied by the mixture at the temperature of the mixture.*

This statement leads to the equations

$$mu = m_A u_A + m_B u_B + \text{etc.} \quad \text{or} \quad mu = \sum m_i u_i$$

$$mh = m_A h_A + m_B h_B + \text{etc.} \quad \text{or} \quad mh = \sum m_i h_i$$

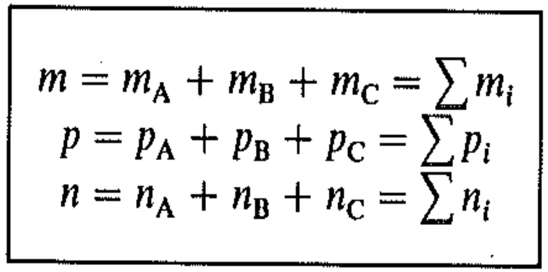
$$ms = m_A s_A + m_B s_B + \text{etc.} \quad \text{or} \quad ms = \sum m_i s_i$$

Volumetric Analysis of Gas Mixture

The analysis of a mixture of gases is often quoted by volume as this is the most convenient for practical determinations.

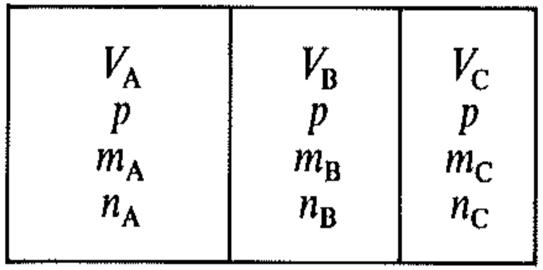
Consider a volume V of a gaseous mixture at a temperature T, consisting of three constituents A, B, and C as in Fig. (a). Let each of the constituents be compressed to a pressure p equal to the total pressure of the mixture, and let the temperature remain constant. The partial volumes then occupied by the constituents will be V_A, V_B, and V_C. From equation $pV = mRT$, therefore, referring to Fig. (a)

$$m_A = \frac{p_A V}{R_A T}$$



$$m = m_A + m_B + m_C = \sum m_i$$
$$p = p_A + p_B + p_C = \sum p_i$$
$$n = n_A + n_B + n_C = \sum n_i$$

(a)



(b)

Referring to the fig. b

$$\mathbf{m_A = \frac{P\,V_A}{R_A\,T}}$$

$$\mathbf{\frac{P\,V_A}{R_A\,T} = \frac{P_A V}{R_A\,T}}$$

$$\mathbf{P\,V_A = P_A V} \quad \text{or} \quad \mathbf{V_A = \frac{P_A}{p}\,V}$$

In general

$$\mathbf{V_i = \frac{P_i}{p}\,V}$$

$$\mathbf{\Sigma V_i = \frac{\Sigma P_i}{p}\,V}$$

But $\mathbf{\Sigma P_i} = P$, thus

$$\mathbf{\Sigma V_i = V}$$

Therefore 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 amount of substance is defined and is given by equation as $n = m/\tilde{m}$. By Avogadro's law, the amount of substance of any gas is proportional to the volume of the gas at a given pressure and temperature. Referring to Fig. (a), the volume V contains an amount of substance n of the mixture at p and T. In Fig. (b), the gas A occupies a volume V_A at p and T, and this volume contains an amount of substance n_A. Similarly there are amounts of substance n_B of gas B in volume V_B, and n_C of gas C in volume V_C. Now from equation ,

$$\Sigma V_i = V \quad \text{or} \quad V_A + V_B + V_C + \ldots = V$$

Therefore the total amount of substance in the vessel must equal the sum of the amounts of substance of the individual constituents,

$$n_A + n_B + n_C + \ldots = n \quad \text{or} \quad \Sigma n_i = n$$

The Molar Mass and Specific Heat Gas Constant

For any gas in a gas mixture occupying a total volume of V at a temperature T, from equation $pV = n\tilde{R}T$, and the definition of partial pressure, we have

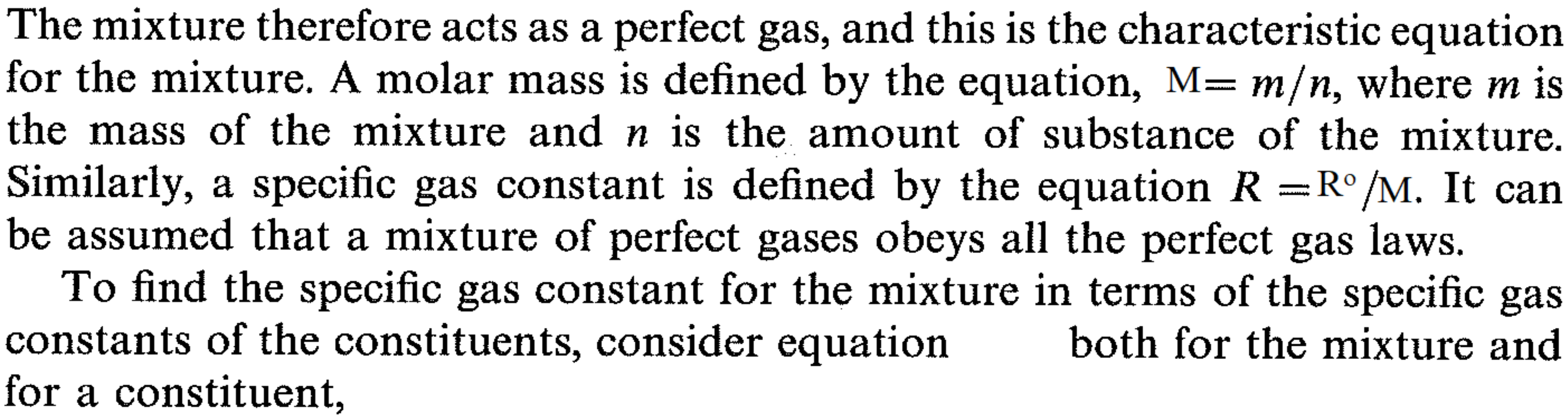
$$P_i V = n_i R^o T$$

$$\Sigma (P_i V) = \Sigma (n_i R^o T)$$

$$V \Sigma P_i = R^o T \Sigma n_i$$

But $\Sigma P_i = P$, and $\Sigma n_i = n$ thus

$$PV = n R^o T$$



The mixture therefore acts as a perfect gas, and this is the characteristic equation for the mixture. A molar mass is defined by the equation, $M = m/n$, where m is the mass of the mixture and n is the amount of substance of the mixture. Similarly, a specific gas constant is defined by the equation $R = R^o/M$. It can be assumed that a mixture of perfect gases obeys all the perfect gas laws.

To find the specific gas constant for the mixture in terms of the specific gas constants of the constituents, consider equation both for the mixture and for a constituent,

$$PV = m R T \qquad \text{and} \qquad P_i V = m_i R_i T$$

$$\Sigma P_i V = \Sigma m_i R_i T \qquad \text{then} \qquad V \Sigma P_i = T \Sigma m_i R_i$$

But $\Sigma P_i = P$, therefore $P V = T \Sigma m_i R_i$

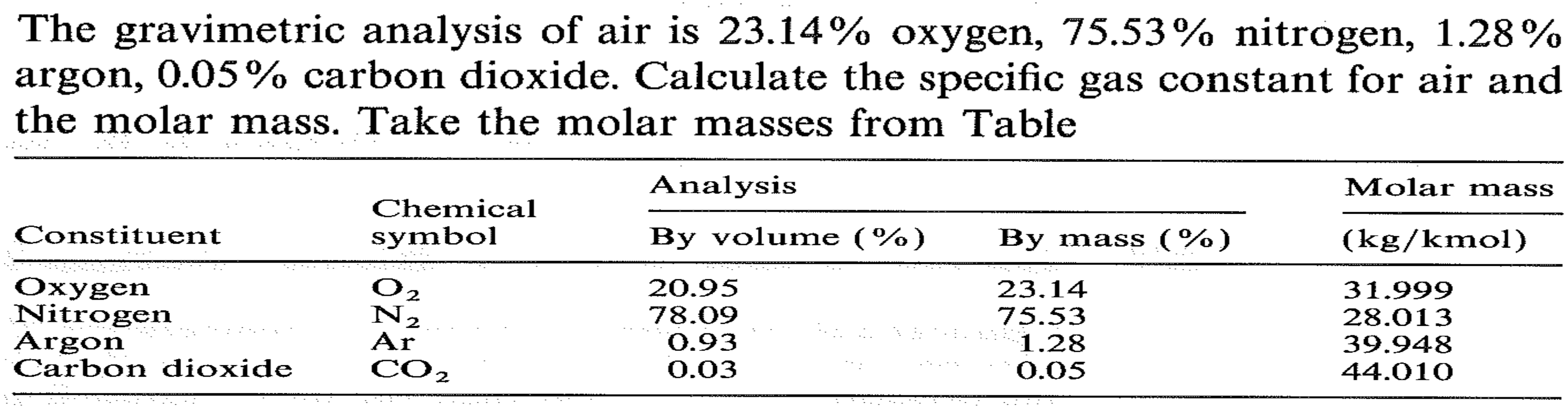
Then $P V = m R T = T \Sigma m_i R_i$

$$m R T = T \Sigma m_i R_i \,, \qquad m R = \Sigma m_i R_i$$

$$R = \Sigma \frac{m_i}{m} R_i$$

Where $\frac{m_i}{m}$ is the mass fraction of constituent

Example 2

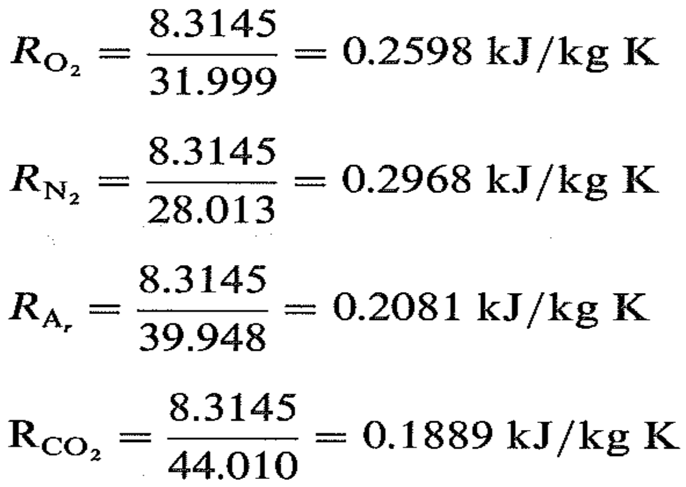


The gravimetric analysis of air is 23.14% oxygen, 75.53% nitrogen, 1.28% argon, 0.05% carbon dioxide. Calculate the specific gas constant for air and the molar mass. Take the molar masses from Table

Constituent	Chemical symbol	Analysis: By volume (%)	Analysis: By mass (%)	Molar mass (kg/kmol)
Oxygen	O_2	20.95	23.14	31.999
Nitrogen	N_2	78.09	75.53	28.013
Argon	Ar	0.93	1.28	39.948
Carbon dioxide	CO_2	0.03	0.05	44.010

Solution

From Equation $R = \frac{R^o}{M}$, therfore



$$R_{O_2} = \frac{8.3145}{31.999} = 0.2598 \text{ kJ/kg K}$$

$$R_{N_2} = \frac{8.3145}{28.013} = 0.2968 \text{ kJ/kg K}$$

$$R_{A_r} = \frac{8.3145}{39.948} = 0.2081 \text{ kJ/kg K}$$

$$R_{CO_2} = \frac{8.3145}{44.010} = 0.1889 \text{ kJ/kg K}$$

$$R = \Sigma \frac{m_i}{m} R_i$$

$$R = (0.2314 \times 0.2598) + (0.7553 \times 0.2968) + (0.0128 \times 0.2081)$$

$$+ (0.0005 \times 0.1889) = 0.2871 \text{ kJ/kg K}$$

i.e. Specific gas constant for air = 0.2871 kJ/kg K

From Equation $M_{air} = \dfrac{R^o}{R_{air}}$, therefore

$$M_{air} = \frac{8.3145}{0.2871} = 28.960 \text{ kg/kmol}$$

i.e. Molar mass of air = 28.96 kg/kmol

When the approximate analysis for air is used (i.e. 23.3% O_2 and 76.7% N_2 by mass), it is usual practice to take R as 0.287 kJ/kg K and $\tilde{m}$ as 29 kg/kmol.

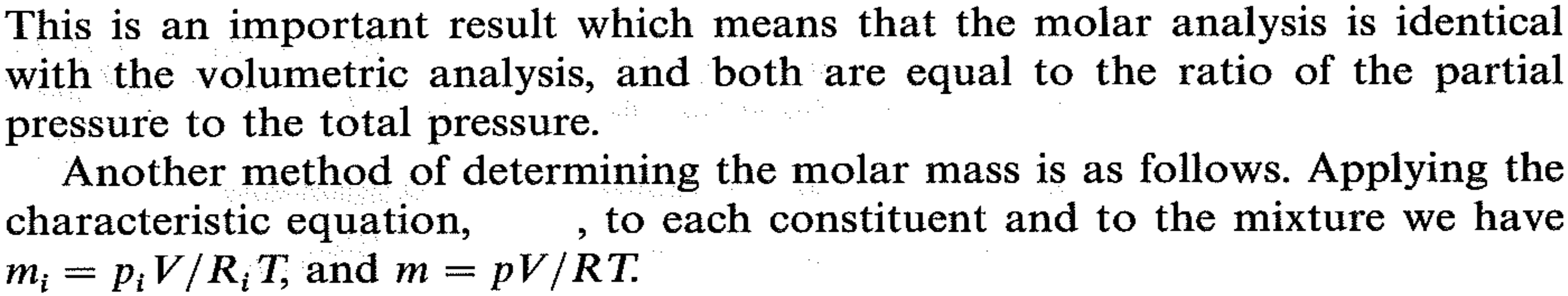
From Equations $\mathbf{P_i V = n_i R^o T}$, and $\mathbf{P V = n R^o T}$

$$\frac{P_i V}{P V} = \frac{n_i R^o T}{n R^o T}$$

$$\frac{P_i}{P} = \frac{n_i}{n}$$

Combined with equation $V_i = \dfrac{P_i}{p} V$

$$\frac{P_i}{P} = \frac{n_i}{n} = \frac{V_i}{V}$$



This is an important result which 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.

Another method of determining the molar mass is as follows. Applying the characteristic equation, , to each constituent and to the mixture we have $m_i = p_i V/R_i T$, and $m = pV/RT$.

From Equation m = Σmi , therefore

$$\frac{P\ V}{R\ T} = \Sigma \frac{P_i\ V}{R_i\ T}$$

$$\frac{P}{R} = \Sigma \frac{P_i}{R_i}$$

From Equation $R = \frac{R^o}{M}$

$$\frac{M\ P}{R^o} = \Sigma \frac{M_i\ P_i}{R^o}$$

$$P\ M = \Sigma\ P_i\ M_i$$

$$M = \Sigma \frac{P_i}{P} M_i$$

From Equation $\frac{P_i}{P} = \frac{n_i}{n} = \frac{V_i}{V}$, obtained

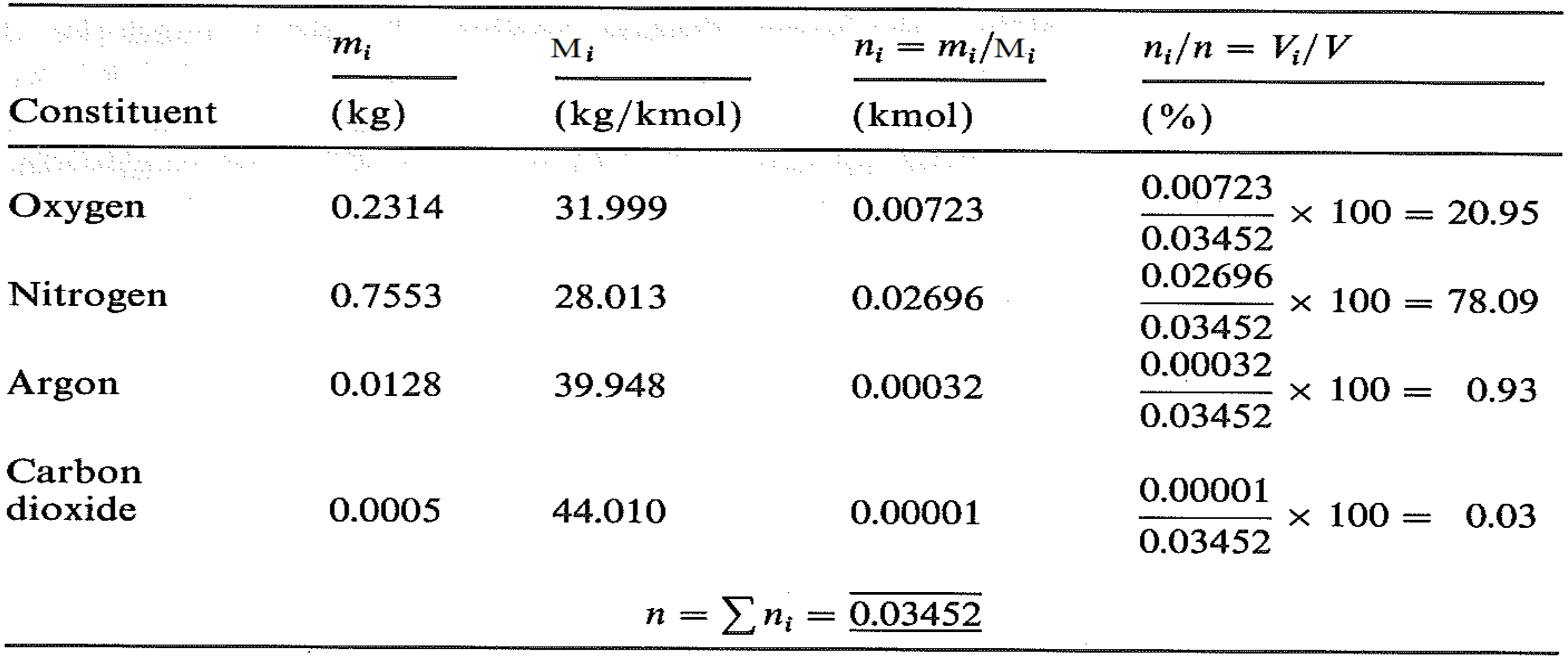
$$M = \Sigma \frac{P_i}{P} M_i = \Sigma \frac{n_i}{n} M_i = \Sigma \frac{V_i}{V} M_i$$

Example 3

The gravimetric analysis of air is 23.14% oxygen, 75.53% nitrogen, 1.28% argon, and 0.05% carbon dioxide. Calculate the analysis by volume and the partial pressure of each constituent when the total pressure is 1 bar.

Solution

From equation the analysis by volume, V_i/V, is the same as the fraction n_i/n. Also from equation , $n_i = m_i/\mathrm{M}$, therefore considering 1 kg of mixture we have the tabular solution shown in Table



Constituent	m_i (kg)	M_i (kg/kmol)	$n_i = m_i/\mathrm{M}_i$ (kmol)	$n_i/n = V_i/V$ (%)
Oxygen	0.2314	31.999	0.00723	$\frac{0.00723}{0.03452} \times 100 = 20.95$
Nitrogen	0.7553	28.013	0.02696	$\frac{0.02696}{0.03452} \times 100 = 78.09$
Argon	0.0128	39.948	0.00032	$\frac{0.00032}{0.03452} \times 100 = 0.93$
Carbon dioxide	0.0005	44.010	0.00001	$\frac{0.00001}{0.03452} \times 100 = 0.03$
			$n = \sum n_i = \underline{0.03452}$	

From equation , $p_i/p = V_i/V = n_i/n$, therefore, $p_i = (n_i/n)p$, hence using the volume fractions from Table

for O_2 $p_{O_2} = 0.2095 \times 1 = 0.2095$ bar

for N_2 $p_{N_2} = 0.7809 \times 1 = 0.7809$ bar

for Ar $p_{A_r} = 0.0093 \times 1 = 0.0093$ bar

for CO_2 $p_{CO_2} = 0.0003 \times 1 = 0.0003$ bar

Example 4

A mixture of 1 kmol CO_2 and 3.5 kmol 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_2, O_2, and N_2, and the total mass;
(ii) the percentage carbon content by mass;
(iii) the molar mass and the specific gas constant for the mixture;
(iv) the specific volume of the mixture.

Take the molar masses of carbon, oxygen and nitrogen as 12 kg/kmol, 32 kg/kmol and 28 kg/kmol respectively.

Solution

(i) From equation , $n_i = (V_i/V)n$, we have

$$n_{O_2} = 0.21 \times 3.5 = 0.735 \text{ kmol}$$

and $$n_{N_2} = 0.79 \times 3.5 = 2.765 \text{ kmol}$$

From equation , $m_i = n_i \mathrm{M}_i$, therefore

$$m_{CO_2} = 1 \times 44 = 44 \text{ kg}$$

$$m_{O_2} = 0.735 \times 32 = 23.55 \text{ kg}$$

and $$m_{N_2} = 2.765 \times 28 = 77.5 \text{ kg}$$

$$\text{Total mass, } m = m_{O_2} + m_{N_2} + m_{CO_2}$$

$$= 23.55 + 77.5 + 44 = 145.05 \text{ kg}$$

i.e. $$\text{Percentage carbon in mixture} = \frac{12 \times 100}{145.05} = 8.27\% \text{ by mass}$$

(iii) From equation (6.10), $n = \sum n_i$, then

$$n = n_{CO_2} + n_{O_2} + n_{N_2} = 1 + 0.735 + 2.765 = 4.5 \text{ kmol}$$

Then using equation (6.17),

$$\mathrm{M} = \sum\left(\frac{n_i}{n}\mathrm{M}_i\right)$$

we have

$$M = \left(\frac{1}{4.5} \times 44\right) + \left(\frac{0.735}{4.5} \times 32\right) + \left(\frac{2.765}{4.5} \times 28\right) = 32.2 \text{ kg/kmol}$$

i.e. Molar mass of mixture = 32.2 kg/kmol

From equation (2.9), $R = R^{\circ}/M$, we have

$$R = \frac{8.3145}{32.2} = 0.2581 \text{ kJ/kg K}$$

i.e. Specific gas constant for the mixture = 0.2581 kJ/kg K

(iv) From equation , $pv = RT$, therefore

$$v = \frac{RT}{p} = \frac{0.2581 \times 288 \times 10^3}{1 \times 10^5} = 0.7435 \text{ m}^3/\text{kg}$$

where $T = 15 + 273 = 288$ K.
i.e. specific volume of the mixture at 1 bar and 15 °C is 0.7435 m^3/kg.

Example 5

A mixture of H_2 and O_2 is to be made so that the ratio of H_2 to O_2 is 2 to 1 by volume. Calculate the mass of O_2 required and the volume of the container, per kilogram of H_2, if the pressure and temperature are 1 bar and 15 °C respectively. Take the molar masses of hydrogen and oxygen as 2 kg/kmol and 32 kg/kmol.

Solution

Let the mass of O_2 per kilogram of H_2 be x.

From equation , $n_i = m_i/M_i$, therefore

$$n_{H_2} = \frac{1}{2} = 0.5 \text{ kmol} \quad \text{and} \quad n_{O_2} = \frac{x}{32} \text{ kmol}$$

From equation , $V_i/V = n_i/n$, therefore

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

i.e. $$\frac{0.5}{x/32} = 2 \quad \text{therefore } x = \frac{32 \times 0.5}{2} = 8 \text{ kg}$$

i.e. Mass of oxygen per kilogram of hydrogen = 8 kg

The total amount of substance in the vessel per kilogram of H_2 is

$$n = n_{H_2} + n_{O_2} = 0.5 + \frac{x}{32} = 0.5 + \frac{8}{32} = 0.5 + 0.25 = 0.75 \text{ kmol}$$

Then from equation ,

$$pV = nR^{o}T$$

therefore

$$V = \frac{0.75 \times 8.3145 \times 288 \times 10^3}{1 \times 10^5} = 17.96 \text{ m}^3$$

Example 6

A vessel contains a gaseous mixture of composition by volume, 80% H_2 and 20% CO. It is desired that the mixture should be made in the proportion 50% H_2 and 50% CO by removing some of the mixture and adding some CO. Calculate per kilomole 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.

Take the molar mass of hydrogen and carbon monoxide as 2 kg/kmol and 28 kg/kmol.

Solution

Since the pressure and temperature remain constant, then the amount of substance in the vessel remains the same throughout. Therefore the amount of substance of mixture removed is equal to the amount of substance of CO added.

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

For the mixture, from equation

$$M = \sum \frac{V_i}{V} M_i$$

therefore,

$$M = (0.8 \times 2) + (0.2 \times 28) = 7.2 \text{ kg/kmol}$$

Then using equation , $n = m/M$, we have

$$\text{amount of substance of mixture removed} = \frac{x}{7.2} \text{ kmol}$$

$$\text{amount of substance of CO added} = \frac{y}{28} \text{ kmol}$$

and $x/7.2 = y/28$

From equation , $V_i/V = n_i/n$, therefore

$$\text{amount of substance of } H_2 \text{ in the mixture removed} = 0.8 \times \frac{x}{7.2} = \frac{x}{9}\ \text{kmol}$$

and $\quad$ amount of substance of H_2 initially $= 0.8 \times 1 = 0.8$ kmol

Hence $\quad$ amount of substance of H_2 remaining in vessel $= \left(0.8 - \frac{x}{9}\right)$ kmol

But 1 kmol of the new mixture is 50% H_2 and 50% CO, therefore

$$0.8 - \frac{x}{9} = 0.5$$

i.e. $\quad x = (0.8 - 0.5) \times 9 = 2.7$ kg

i.e. $\quad$ Mass of mixture removed $= 2.7$ kg

Also since $x/7.2 = y/28$, therefore

$$y = \frac{28}{7.2} \times x = \frac{28 \times 2.7}{7.2} = 10.5\ \text{kg}$$

i.e. $\quad$ Mass of CO added $= 10.5$ kg

Specific Heat Capacities of Gas Mixture

It was shown in section that as a consequence of the Gibbs–Dalton law the internal energy of a mixture of gases is given by equation , $mu = \sum m_i u_i$. Also for a perfect gas from equation , $u = c_v T$. Hence substituting we have

$$mc_v T = \sum m_i c_{v_i} T$$

therefore

$$mc_v = \sum m_i c_{v_i}$$

or $$c_v = \sum \frac{m_i}{m} c_{v_i}$$

Similarly from equation , $mh = \sum m_i h_i$, and from equation (2.18), $h = c_p T$, therefore

$$mc_p T = \sum m_i c_{p_i} T$$

therefore

$$mc_p = \sum m_i c_{p_i}$$

or $$c_p = \sum \frac{m_i}{m} c_{p_i}$$

From equations

$$c_p - c_v = \sum \frac{m_i}{m} c_{p_i} - \sum \frac{m_i}{m} c_{v_i} = \sum \frac{m_i}{m} (c_{p_i} - c_{v_i})$$

Using equation , $c_{p_i} - c_{v_i} = R_i$, therefore

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

Also from equation , $R = \sum \frac{m_i}{m} R_i$, therefore for the mixture

$$c_p - c_v = R$$

The equations , can be applied to a mixture of gases,

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

It should be noted that γ must be determined from equation ; there is no weighted mean expression as there is for R, c_v, and c_p.

Example 7

The gas in an engine cylinder has a volumetric analysis of 12% CO_2, 11.5% O_2, and 76.5% N_2. The temperature at the beginning of expansion is 1000 °C and the gas mixture expands reversibly through a volume ratio of 7 to 1, according to a law $pv^{1.25}$ = constant. Calculate the work done and the heat flow per unit mass of gas. The values of c_p for the constituents averaged over the temperature are as follows: c_p for $CO_2 = 1.271$ kJ/kg K; c_p for $O_2 = 1.110$ kJ/kg K; c_p for $N_2 = 1.196$ kJ/kg K.

Solution

From equation $m_i = n_i M_i$, therefore a conversion from volume fraction to mass fraction is as given in Table . Then using equation and the mass fractions from Table

$$c_p = \sum \frac{m_i}{m} c_{p_i}$$

therefore

$$c_p = (0.174 \times 1.271) + (0.121 \times 1.110) + (0.705 \times 1.196)$$

$$= 1.199 \text{ kJ/kg K}$$

	n_i	M_i	$m_i = n_i M_i$	
Constituent	(kmol)	(kg/kmol)	(kg)	m_i/m
Carbon dioxide	0.120	44	5.28	5.28/30.36 = 0.174
Oxygen	0.115	32	3.68	3.68/30.36 = 0.121
Nitrogen	0.765	28	21.40	21.40/30.36 = 0.705
		$m = \sum m_i =$	30.36	

From equation , $R = \sum(m_i/m)R_i$, and from equation , $R_i = R^o/M_i$, therefore

$$R = \left(0.174 \times \frac{8.3145}{44}\right) + \left(0.121 \times \frac{8.3145}{32}\right) + \left(0.705 \times \frac{8.3145}{28}\right)$$

$$= 0.274 \text{ kJ/kg K}$$

Then from equation , $c_p - c_v = R$, we have

$$c_v = 1.199 - 0.274 = 0.925 \text{ kJ/kg K}$$

The work done per kg of gas can be obtained from equation

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

T_2 can be found using equation

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1} = \left(\frac{1}{7}\right)^{0.25}$$

$$T_2 = \frac{T_1}{7^{0.25}} = \frac{1273}{1.627} = 782.6 \text{ K}$$

where $T_1 = 1000 + 273 = 1273$ K. Therefore

$$W = \frac{0.274(782.6 - 1273)}{1.25 - 1} = -537.5 \text{ kJ/kg}$$

i.e. Work done *by* the gas mixture $= +537.5$ kJ/kg

Also from equation , for unit mass, $u_2 - u_1 = c_v(T_2 - T_1)$, therefore

$$u_2 - u_1 = 0.925(782.6 - 1273) = -453.6 \text{ kJ/kg}$$

Finally, from the non-flow energy equation , $Q + W = (u_2 - u_1)$,

i.e. $Q - 537.5 = -453.6$ therefore $Q = 83.9$ kJ/kg

i.e. Heat supplied $= 83.9$ kJ/kg

Example 9

A producer gas has the following volumetric analysis: 29% CO, 12% H_2, 3% CH_4, 4% CO_2, 52% N_2. Calculate the values of $\tilde{c}_p$, $\tilde{c}_v$, c_p, and c_v for the mixture. The values of $\tilde{c}_p$ for the constituents are as follows: for CO, $\tilde{c}_p = 29.27$ kJ/kmol K; for H_2, $\tilde{c}_p = 28.89$ kJ/kmol K; for CH_4, $\tilde{c}_p = 35.80$ kJ/kmol K; for CO_2, $\tilde{c}_p = 37.22$ kJ/kmol K; for N_2, $\tilde{c}_p = 29.14$ kJ/kmol K.

The molar masses may be taken as follows: for H_2, 2 kg/kmol; for CH_4, 16 kg/kmol; for CO_2, 44 kg/kmol; for N_2, 28 kg/kmol.

Solution

From equation

$$\tilde{c}_p = \sum \frac{n_i}{n} \tilde{c}_{p_i}$$

Therefore,

$$\tilde{c}_p = (0.29 \times 29.27) + (0.12 \times 23.89) + (0.03 \times 35.80) + (0.04 \times 37.22) + (0.52 \times 29.14)$$

i.e. $\tilde{c}_p = 29.6707$ kJ/kmol K

From equation

$$\tilde{c}_p - \tilde{c}_v = R^o$$

therefore

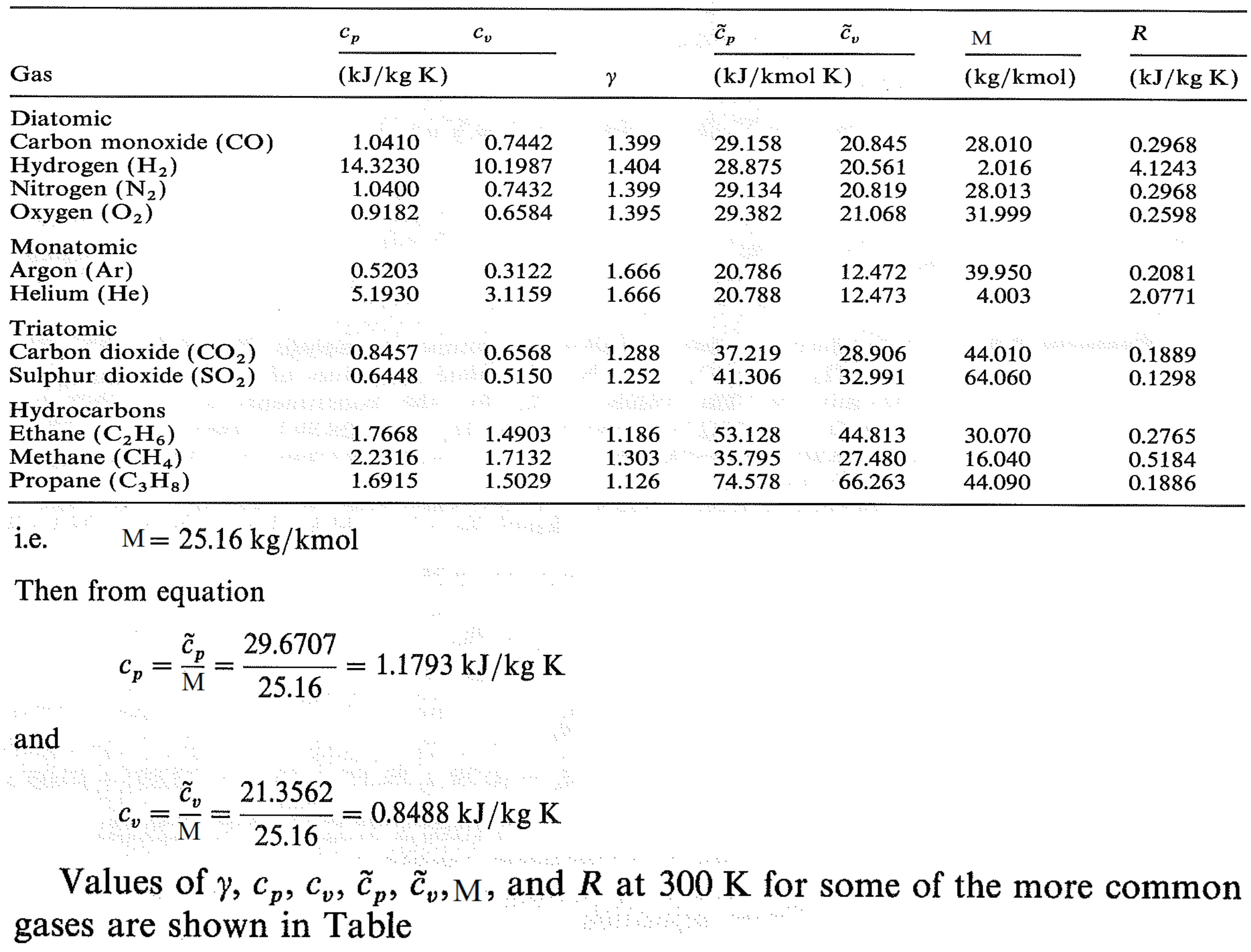
$$\tilde{c}_v = \tilde{c}_p - R^o = 29.6707 - 8.3145 = 21.3562 \text{ kJ/kmol K}$$

i.e. $\tilde{c}_v = 21.3562$ kJ/kmol K

The molar mass can be found from equation , i.e.

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

$$= (0.29 \times 28) + (0.12 \times 2) + (0.03 \times 16) + (0.04 \times 44) + (0.52 \times 28)$$



Gas	c_p	c_v	γ	$\tilde{c}_p$	$\tilde{c}_v$	M	R
	(kJ/kg K)			(kJ/kmol K)		(kg/kmol)	(kJ/kg K)
Diatomic							
Carbon monoxide (CO)	1.0410	0.7442	1.399	29.158	20.845	28.010	0.2968
Hydrogen (H_2)	14.3230	10.1987	1.404	28.875	20.561	2.016	4.1243
Nitrogen (N_2)	1.0400	0.7432	1.399	29.134	20.819	28.013	0.2968
Oxygen (O_2)	0.9182	0.6584	1.395	29.382	21.068	31.999	0.2598
Monatomic							
Argon (Ar)	0.5203	0.3122	1.666	20.786	12.472	39.950	0.2081
Helium (He)	5.1930	3.1159	1.666	20.788	12.473	4.003	2.0771
Triatomic							
Carbon dioxide (CO_2)	0.8457	0.6568	1.288	37.219	28.906	44.010	0.1889
Sulphur dioxide (SO_2)	0.6448	0.5150	1.252	41.306	32.991	64.060	0.1298
Hydrocarbons							
Ethane (C_2H_6)	1.7668	1.4903	1.186	53.128	44.813	30.070	0.2765
Methane (CH_4)	2.2316	1.7132	1.303	35.795	27.480	16.040	0.5184
Propane (C_3H_8)	1.6915	1.5029	1.126	74.578	66.263	44.090	0.1886

i.e. $\quad \mathrm{M} = 25.16$ kg/kmol

Then from equation

$$c_p = \frac{\tilde{c}_p}{\mathrm{M}} = \frac{29.6707}{25.16} = 1.1793 \text{ kJ/kg K}$$

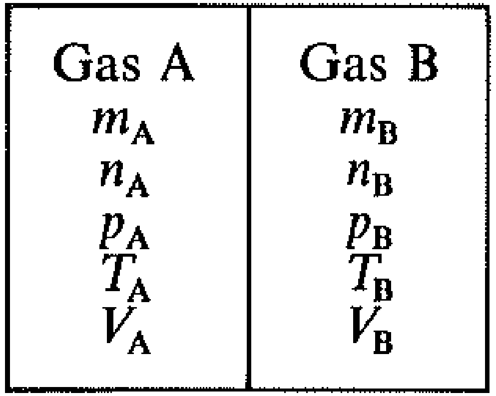
and

$$c_v = \frac{\tilde{c}_v}{\mathrm{M}} = \frac{21.3562}{25.16} = 0.8488 \text{ kJ/kg K}$$

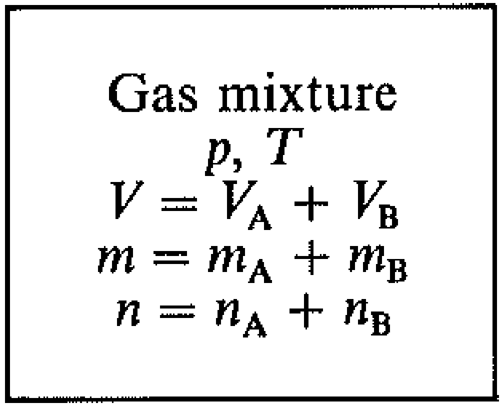
Values of γ, c_p, c_v, $\tilde{c}_p$, $\tilde{c}_v$, M, and R at 300 K for some of the more common gases are shown in Table

Adiabatic Mixing of Perfect Gases

Consider two gases A and B separated from each other in a closed vessel by a thin diaphragm, as shown in Fig. (a). If the diaphragm is punctured or removed, then the gases mix as in Fig. (b), 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 therefore there will be an increase in entropy of the system. t is shown that there is always an increase in entropy of a thermally isolated system which undergoes an irreversible process.



(a)



(b)

It is shown that in a free expansion process the internal energy initially is equal to the internal energy finally. In this case, from equation

$$U_1 = n_A \tilde{c}_{v_A} T_A + n_B \tilde{c}_{v_B} T_B$$

and

$$U_2 = (n_A \tilde{c}_{v_A} + n_B \tilde{c}_{v_B}) T$$

Extending this result to any number of gases,

$$U_1 = \sum n_i \tilde{c}_{v_i} T_i \quad \text{and} \quad U_2 = T \sum n_i \tilde{c}_v$$

Then $\quad U_1 = U_2$

i.e. $\quad \sum n_i \tilde{c}_{v_i} T_i = T \sum n_i \tilde{c}_{v_i}$

i.e. $\quad T = \dfrac{\sum n_i \tilde{c}_{v_i} T_i}{\sum n_i \tilde{c}_{v_i}}$

Example 10

A vessel of 1.5 m³ capacity contains oxygen at 7 bar and 40 °C. The vessel is connected to another vessel of 3 m³ 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.

For oxygen, $\tilde{c}_v = 21.07$ kJ/kmol K; for carbon monoxide, $\tilde{c}_v = 20.86$ kJ/kmol K.

Solution

From equation $\quad n = \dfrac{pV}{\tilde{R}T}$

Therefore

$$n_{O_2} = \frac{7 \times 10^5 \times 1.5}{8.3145 \times 313 \times 10^3} = 0.4035 \quad \text{where } T_{O_4} = 40 + 273 = 313\ \text{K}$$

and

$$n_{CO} = \frac{1 \times 10^5 \times 3}{8.3145 \times 288 \times 10^3} = 0.1253 \quad \text{where } T_{CO} = 15 + 273 = 288 \text{ K}$$

Before mixing

$$U_1 = \sum(n_i \tilde{c}_{v_i} T_i) = (0.4035 \times 21.07 \times 313) + (0.1253 \times 20.86 \times 288)$$

i.e. $U_1 = 3413.8$ kJ

After mixing

$$U_2 = T\sum(n_i \tilde{c}_{v_i}) = T\{(0.4035 \times 21.07) + (0.1253 \times 20.86)\}$$

i.e. $U_2 = 11.118 \times T$

For adiabatic mixing, $U_1 = U_2$, therefore

$$3413.8 = 11.118 \times T \quad \text{therefore } T = \frac{3413.8}{11.118} = 307 \text{ K}$$

i.e. Temperature of mixture = 307 − 273 = 34 °C

From equation

$$p = \frac{nR^{o}T}{V}$$

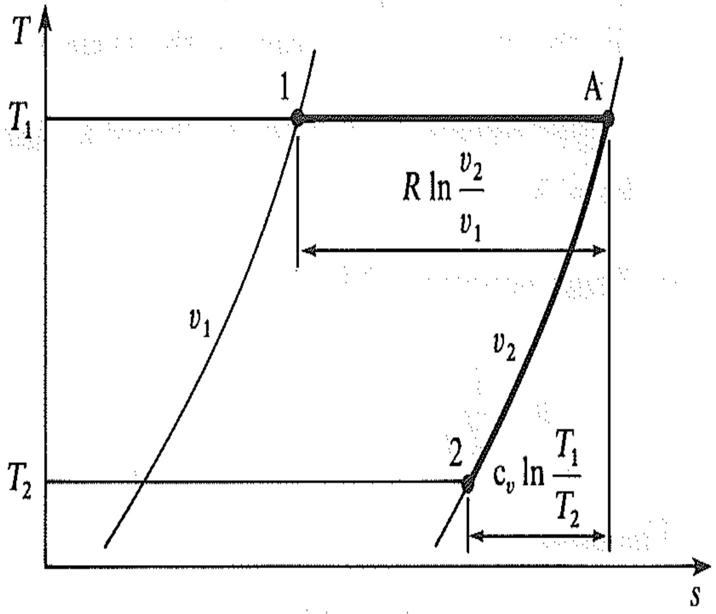
Therefore

$$p = \frac{(0.4035 + 0.1253) \times 8.3145 \times 307 \times 10^3}{(1.5 + 3.0) \times 10^5} = 3 \text{ bar}$$

i.e. Pressure after mixing = 3 bar

(ii) The change of entropy of the system is equal to the change of entropy of the oxygen plus the change of entropy of the carbon monoxide; this follows from the Gibbs–Dalton law.

Referring to Fig. , the change of entropy of the oxygen can be calculated by replacing the process undergone by the oxygen by the two processes 1 to A and A to 2.



For an isothermal process from 1 to A, from equation , we have

$$s_A - s_1 = R\ln\left(\frac{V_A}{V_1}\right) \quad \text{or} \quad S_A - S_1 = mR\ln\left(\frac{V_A}{V_1}\right)$$

i.e. $$S_A - S_1 = nR^{o}\ln\left(\frac{V_A}{V_1}\right) = 0.4035 \times 8.3145 \times \ln\left(\frac{4.5}{1.5}\right) = 3.686\ \text{kJ/K}$$

At constant volume from A to 2,

$$s_A - s_2 = c_v\int_2^A \frac{dT}{T} = c_v\ln\left(\frac{T_1}{T_2}\right) \quad \text{or} \quad S_A - S_2 = mc_v\ln\left(\frac{T_1}{T_2}\right)$$

$$S_A - S_2 = n\tilde{c}_v\ln\left(\frac{T_1}{T_2}\right) = 0.4035 \times 21.07 \times \ln\left(\frac{313}{307}\right) = 0.1683\ \text{kJ/K}$$

therefore

$$S_2 - S_1 = 3.686 - 0.168 = 3.518\ \text{kJ/K}$$

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

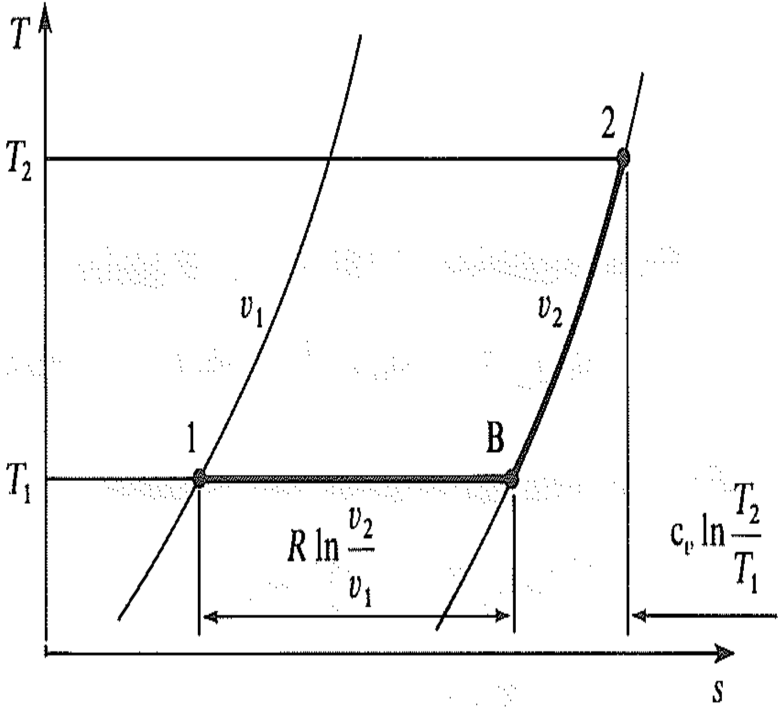
i.e. $$S_2 - S_1 = (S_B - S_1) + (S_2 - S_B)$$

therefore

$$S_2 - S_1 = nR^o \ln\left(\frac{V_B}{V_1}\right) + n\tilde{c}_v \ln\left(\frac{T_2}{T_1}\right)$$

$$= \left\{0.1253 \times 8.314 \times \ln\left(\frac{4.5}{3}\right)\right\}$$

$$+ \left\{0.1253 \times 20.86 \times \ln\left(\frac{307}{288}\right)\right\}$$



therefore

$$S_2 - S_1 = 0.590 \text{ kJ/K}$$

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

$$(S_2 - S_1)_{\text{system}} = (S_2 - S_1)_{O_2} + (S_2 - S_1)_{CO}$$

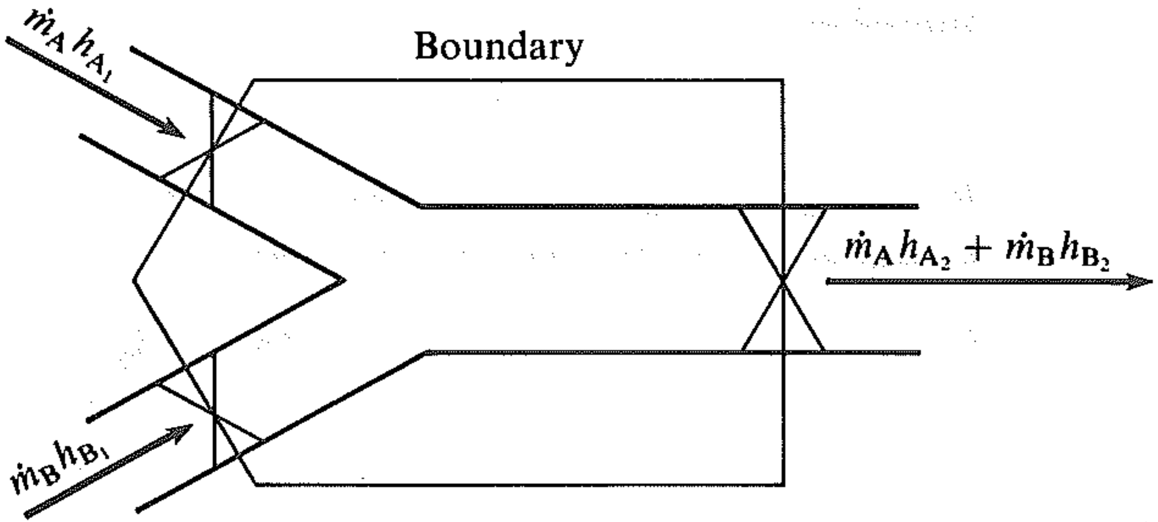
i.e. Change of entropy of system = 3.518 + 0.590 = 4.108 kJ/K

Another form of mixing is that which occurs when streams of fluid meet to form a common stream in steady flow. This is shown diagrammatically in Fig. 6.7. The steady-flow energy equation can be applied to the mixing section, and changes in kinetic and potential energy are usually negligible,

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

For adiabatic flow $Q = 0$, and also $W = 0$ in this case, therefore

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



Mixing of two fluid streams

From equation , $h = c_p T$, hence

$$\dot{m}_A c_{p_A} T_A + \dot{m}_B c_{p_B} T_B = \dot{m}_A c_{p_A} T + \dot{m}_B c_{p_B} T$$

For any number of gases this becomes

$$\sum(\dot{m}_i c_{p_i} T_i) = T\sum(\dot{m}_i c_{p_i})$$

i.e. $$T = \frac{\sum(\dot{m}_i c_{p_i} T_i)}{\sum(\dot{m}_i c_{p_i})}$$

Also, since from equation , $\tilde{c}_p = \dot{m}c_p$, and $\text{M} = m/n$ from equation then

$$n\tilde{c}_p = mc_p$$

Hence, $$T = \frac{\sum(n_i \tilde{c}_{p_i} T_i)}{\sum(n_i \tilde{c}_{p_i})}$$

Equations represents one condition which must be satisfied in an adiabatic mixing process of perfect gases in steady flow. In a particular problem some other information must be known (e.g. the final pressure or specific volume) before a complete solution is possible. To find the change of entropy in such a process the procedure is as described above for adiabatic mixing by a free expansion. The entropy change of each gas is found and the results added together.