Kingdom of Saudi Arabia

MINISTRY OF EDUCATION

UNIVERSITY OF BISHA

Engineering College

Thermodynamics -2

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Course Objectives: -

At the end of this course, the students should be able to:

1. Understand the performance and operation principles of the heat engine and their applications on thermodynamics problems.

2. Analyse of the most power plant system

3. Design of the most power plant system.

Gases Mixture:-

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.

Example -1 :-

A vessel of volume 0.2 m^3 contains nitrogen at 1.013 bar and I5 ^{o}C. If 0.2 kg of nitrogen is removed from the vessel and the temperature of gas is returned to initial temperature. If 0.2 kg of nitrogen is pumped into the vessel, calculate the new pressure when the vessel has returned to its initial temperature. The molar mass of nitrogen is 28 kg/kmol, and it may be assumed to be a perfect gas.

Solution

(1) $R_o = MR \qquad R = \frac{R_o}{M} = \frac{8.314}{28} = \underline{\underline{0.2969\,{}^{KJ}/_{kg.k}}}$

$$PV = mRT \qquad m1 = \frac{P_1V_1}{RT_1} = \frac{1.0325\times10^5\times0.2}{0.2\times288\times10^3} = \underline{\underline{0.237kg}}$$

$$m_2 = m_1 - m = 0.237 - 0.2 = 0.037kg$$

$$p_2 = \frac{m_2RT_2}{V} = \frac{0.037\times0.2969\times288\times10^3}{0.2\times10^5} = \underline{\underline{0.158\ bar}}$$

$$(2)\quad m_3 = m_1 + 0.2 = 0.237 + 0.2 = 0.437\ kg$$

$$p3 = \frac{m3RT}{V} = \frac{0.437\times0.2969\times288\times10^3}{0.2\times10^5} = \underline{\underline{1.87\ bar}}$$

Example:-

A certain perfect gas of mass 0.01kg occupies a volume of 0.003 m^3 at pressure of 7bar and temperature of 131^oC. The gas is allowed to expand until the pressure is 1bar and the final volume is 0.02m^3. Calculate:

a)The molar mass of the gas.

b)The final temperature.

Solution

$$R=\frac{PV}{mT} \qquad R=\frac{7\times10^{5}\times0.003}{0.01\times404\times10^{3}}=0.521\ kJ/kg.k$$

$$but\ R_o=MR \qquad M=\frac{R_o}{R}=\frac{8.314}{0.521}=\underline{\underline{15.95\approx16\ kg/kmol}}$$

$$PV=mRT \qquad T=\frac{PV}{mR}=\frac{1\times10^{5}\times0.02}{0.521\times0.01\times10^{3}}$$

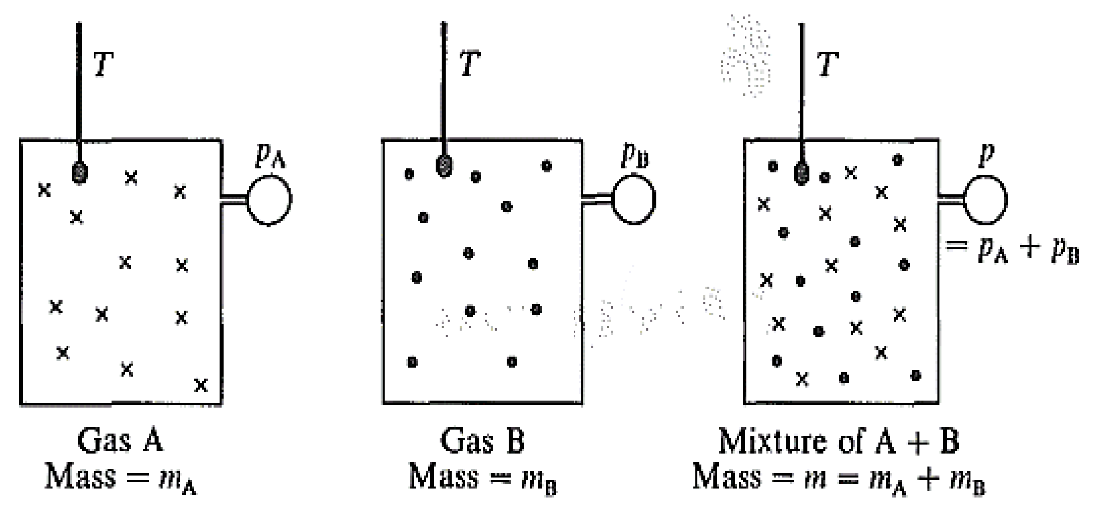
$$=\underline{\underline{385k=112\,^{o}C}}$$

Dalton's law and the Gibbs-Dalton law:-

Consider a closed vessel of volume Vat 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.



$$m_T = m_A + m_B = \sum_{i=1}^{n} m_i$$

$$P_T = P_A + P_B = \sum_{i=1}^{n} P_i$$

❖ Example:-

Convert the volumetric analysis to gravimetric analysis if.

$N_2 = 81.2\%$, $CO = 2.2\%$, $O_2 = 1.6\%$, $CO_2 = 15\%$.

Solution

Constituent	Chemical symbol	Molar mass (kg/kmol)	Analysis By volume	Constituent mass	Analysis By mass
CO_2	CO_2	44	0.15	6.6	0.217
O_2	O_2	32	0.016	0.512	0.0168
CO	CO	28	0.022	0.616	0.0202
N_2	N_2	28	0.812	22.736	0.746
Σ				30.464	

- **In General the air analysis become as**

O_2	N_2	Analysis type
21%	79%	Volumetric analysis
23.3%	76.7%	Gravimetric analysis

- **Example:-**

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

$$mass\ of\ O_2 = \frac{23.3}{100} \times 1 = 0.233kg$$

$$mass\ of\ N_2 = \frac{76.7}{100} \times 1 = 0.767kg$$

$$from\quad R = \frac{R_o}{M}\quad and\quad PV = mRT = nMRT$$

$$Pi = \frac{miRoT}{miV} \qquad \therefore P_{O2} = \frac{0.233 \times 8.314 \times 288}{32 \times 0.4 \times 10^2} = \underline{\underline{43.59kPa}} = \underline{\underline{0.4359\ bar}}$$

$$P_{N2} = \frac{0.767 \times 8.314 \times 288}{28 \times 0.4 \times 10^2} = \underline{\underline{1.6399\ bar}}$$

$$PCO = \frac{0.45 \times 8.314 \times 288}{28 \times 0.4 \times 10^2} = \underline{\underline{0.9621\ bar}}$$

$$P_T = \sum P_i = 0.4359 + 1.6399 + 0.9621 = 3.038\ bar$$

Gibbs-Dalton's law:-

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, ofa 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

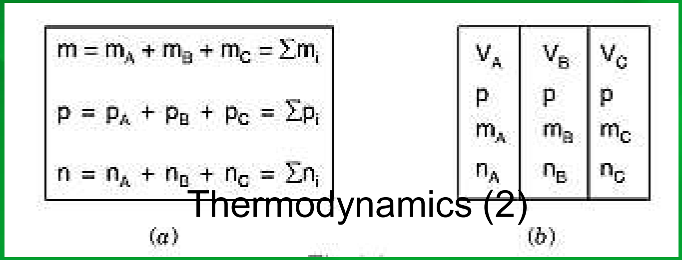
$$MU = m_a u_a + m_b u_b + m_c u_c + \dots\dots\dots\dots + etc = \sum_{i=1}^{n} m_i u_i$$

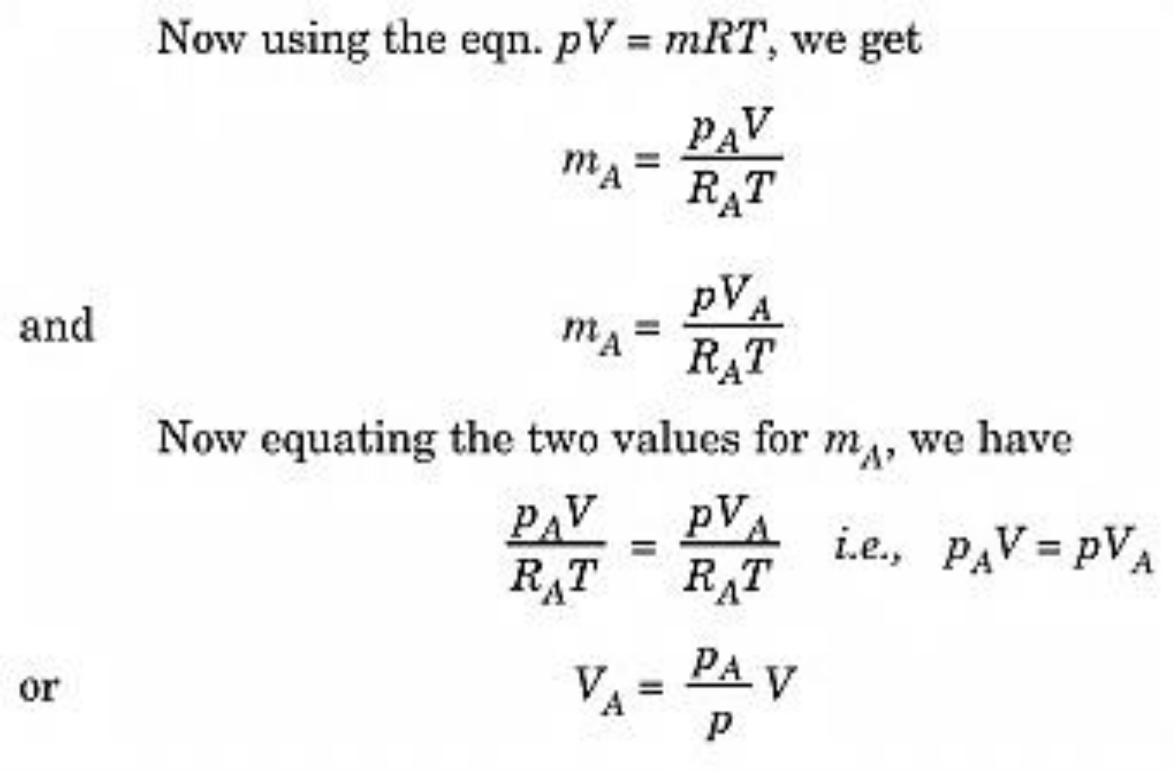
$$Mh = m_a h_a + m_b h_b + m_c h_c + \dots\dots\dots\dots + etc = \sum_{i=1}^{n} m_i h_i$$

$$MS = m_a s_a + m_b s_b + m_c s_c + \dots\dots\dots\dots + etc = \sum_{i=1}^{n} m_i s_i$$

Volumetric analysis of a 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 VA' VB' and Ve. From equation (2.6) pV = mRT, therefore, referring to Fig. (a)





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

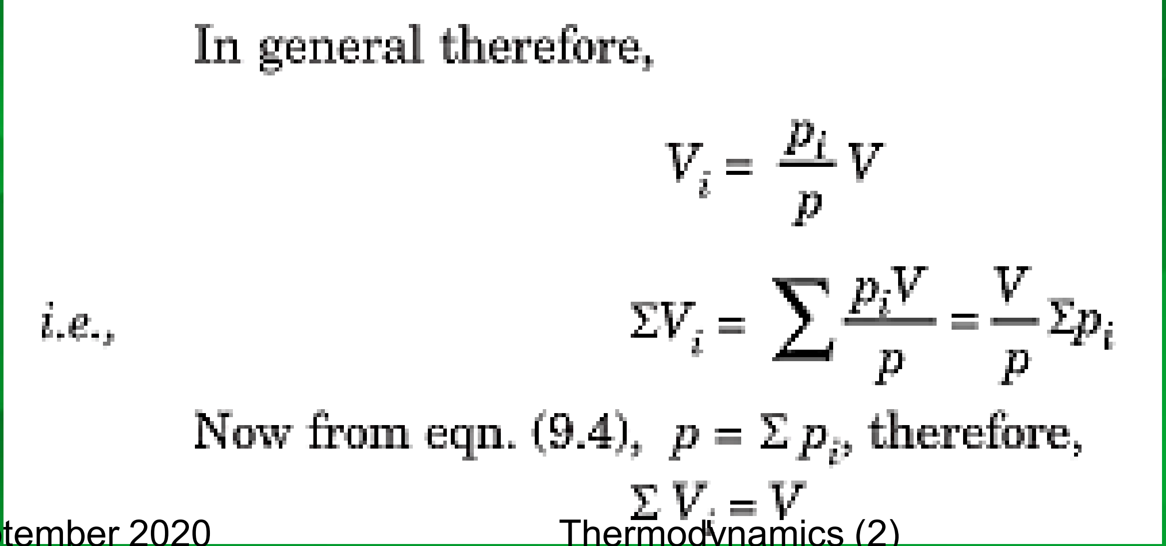
$$m_A = \frac{p_A V}{R_A T}$$

and
$$m_A = \frac{p V_A}{R_A T}$$

Now equating the two values for m_A, we have

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

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



In general therefore,

$$V_i = \frac{p_i}{p} V$$

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

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

$$\Sigma V_i = V$$

The molar mass and specific gas constant:-

For each mixture has certain volume and temperature

$PV = nR_oT$ for partial pressure $P_iV = n_iR_oT$

$\sum(P_iV) = \sum(n_iR_oT) = R_oT\sum n_i$

$V\sum P_i = R_oT\sum n_i$ but $\sum P_i = P$, $\sum n$

$PV = nR_oT$

For each mixture the molar mass is defined by the equation.

$M = \frac{m}{n} \quad [kg/kmol]$ **, and also the specific gas constant is defined by the equation** $R = \frac{Ro}{M}$

from $PV = mRT$ and $P_iV = m_iR_iT$

$$\sum(P_iV) = T\sum m_iR_i \quad \therefore \quad PV = mR\cancel{T} = \cancel{T}\sum m_iR_i \quad \therefore \underline{\underline{R = \sum \frac{m_i}{m} R_i}}$$

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

For molar mass:-

$$\textit{from}\quad PV=nRoT \qquad \text{for partial} \qquad PiV=miRiT$$

$$\frac{Pi}{P}=\frac{ni\,\cancel{RoT}}{n\,\cancel{RoT}} \qquad \therefore\ \frac{Pi}{P}=\frac{ni}{n}=\frac{Vi}{V}$$

$$\textit{also}\ \text{from}\quad PV=mRT \qquad \text{or}\quad PiV=miRiT$$

$$m=\frac{PV}{RT}\quad,\qquad mi=\frac{PiV}{RiT}\quad,\ \sum mi=m=\frac{V}{T}\sum\frac{Pi}{Ri}=\frac{PV}{RT}$$

$$\textit{but}\quad R=\frac{Ro}{M}\quad,\qquad Ri=\frac{Ro}{Mi}\ ,\qquad \therefore\frac{PM}{\cancel{Ro}}=\sum\frac{PiMi}{\cancel{Ro}}$$

$$\therefore M=\underline{\underline{\sum\frac{ni}{n}Mi}}=\sum\frac{Pi}{P}Mi=\sum\frac{Vi}{V}Mi$$

- **Example:-**

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 6.1 on p. 148.

Molar mass:- N2 = 28.013 , Ar = 39.948 , O2 = 31.999,CO2 = 44.01

Solution

$$from \quad \mathrm{R}=\frac{Ro}{M} \qquad \mathrm{R}_{\mathrm{O}_2}=\frac{8.314}{31.999}=0.2598\,kJ/kg.k$$

$$\mathrm{R}_{\mathrm{N}_2}=\frac{8.314}{28.013}=0.2968\,kJ/kg.k \quad , \qquad \mathrm{R}_{\mathrm{Ar}}=\frac{8.314}{39.948}=0.2081\,kJ/kg.k$$

$$\mathrm{R}_{\mathrm{CO}_2}=\frac{8.314}{44.01}=0.1889\,kJ/kg.k \qquad , \text{from} \qquad \mathrm{R}=\sum\frac{mi}{m}Ri$$

$$R=(0.2314\times o.2598)+(0.7553\times 0.2968)+(0.0128\times 0.2081)+(0.0005$$
$$\times 0.1889)= \ 0.2871 \ kJ/kg.k$$

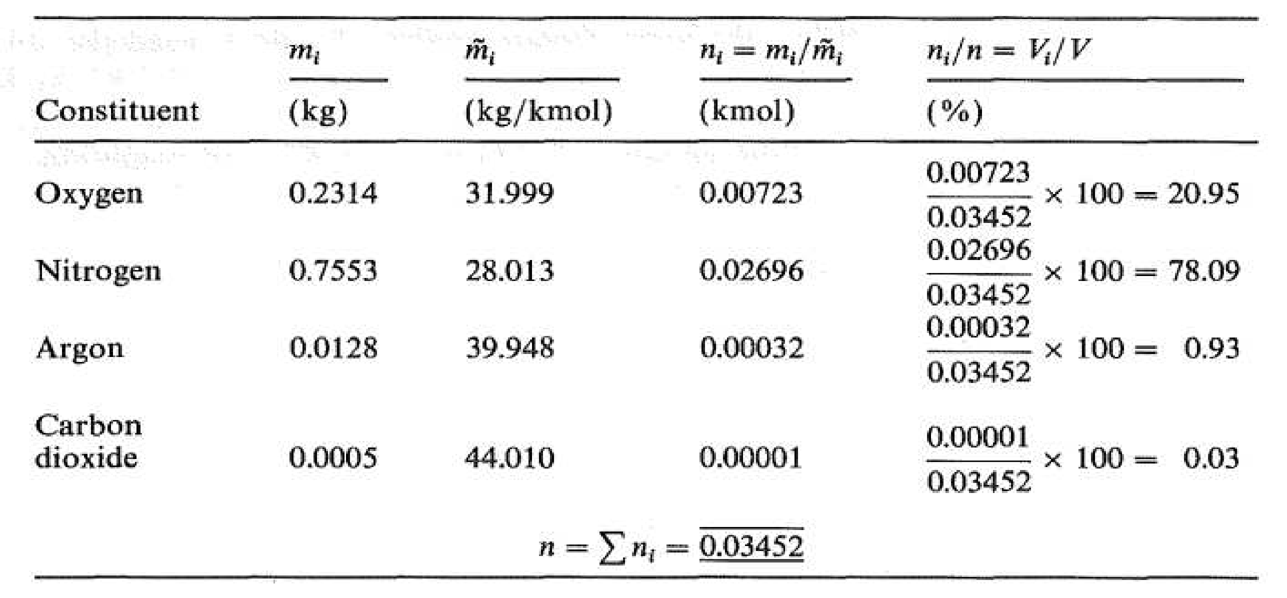
$$from \quad \mathrm{M}=\frac{Ro}{R}=\frac{8.314}{0.2871}=28.960\,kg/kmol$$

- ❖ **Example:-**

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 $\frac{Pi}{P} = \frac{ni}{n} = \frac{Vi}{V}$ **and** $ni = \frac{mi}{m}$



Constituent	m_i (kg)	$\tilde{m}_i$ (kg/kmol)	$n_i = m_i/\tilde{m}_i$ (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	$\frac{0.00001}{0.03452} \times 100 = 0.03$
			$n = \sum n_i = \underline{0.03452}$	

$$from \quad \frac{Pi}{P} = \frac{ni}{n} \qquad \therefore \ \mathrm{Pi} = \frac{ni}{n} P$$

$$for \ _{O_2} \quad \mathrm{P}_{\mathrm{O_2}} = 0.2095 \times 1 = 0.2095 \text{ bar}$$

$$for \ _{N_2} \quad \mathrm{P}_{\mathrm{N_2}} = 0.7809 \times 1 = 0.7809 \text{ bar}$$

$$for \ _{Ar} \quad \mathrm{P}_{\mathrm{Ar}} = 0.0093 \times 1 = 0.0093 \text{ bar}$$

$$for \ _{CO_2} \quad \mathrm{P}_{\mathrm{CO_2}} = 0.0003 \times 1 = 0.0003 \text{ bar}$$

❖ Example:-

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 12kg/kmol , 32 kg/ kmol and 28 kg/ kmol respectively.

Solution

$$(1) \quad \textit{from} \quad \text{equation} \quad \text{ni}=\frac{Vi}{V}n \quad \text{we have}$$

$$\text{n}_{\text{O2}} = 0.21 \times 3.5 = \quad 0.735 \text{ kmol}$$

$$\text{n}_{\text{N2}} = 0.79 \times 3.5 = \quad 2.765 \text{ kmol}$$

$$\text{from equation} \quad \text{mi=ni} \cdot \text{Mi}$$

$$\text{m}_{\text{O2}} = 0.735 \times 32 = \quad 23.55 \text{ kg}$$

$$\text{m}_{\text{CO2}} = 1 \times 44 = \quad 44 \text{ kg}$$

$$\text{m}_{\text{N2}} = 2.765 \times 28 = \quad 77.5 \text{ kg}$$

$$\text{Total mass} \quad \text{m=m}_{\text{O2}} + \text{m}_{\text{CO2}} + \text{m}_{\text{N2}} = \underline{\underline{145.05\,kg}}$$

(2) The molar mass of carbon is $12\,kg/kmol$, there for there are 12kg of carbon percent in 1kmol of carbon dioxide .

Percentage carbon in mixture = $\dfrac{12\times100}{145.05}=8.27\%$ mass

(3) From equation $n=\sum ni \quad \therefore n_T=n_{O2}+n_{N2}+n_{CO2}=4.5kmol$

From $M_T=\sum \dfrac{ni}{n}Mi \qquad M_T=\left(\dfrac{1}{4.5}\times44\right)+\left(\dfrac{0.735}{4.5}\times32\right)+\left(\dfrac{2.765}{4.5}\times28\right)=32.2\,kg/kmol$

From equation $R=\dfrac{Ro}{M}=\dfrac{8.3145}{32.2}=0.258\,kJ/kg.k$

(4)From equation Pv=RT $\therefore\ v=\dfrac{RT}{P}=\dfrac{0.258\times288\times103}{1\times105}=\underline{\underline{0.7435\ \ m3/kg}}$

- **Example:-**

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 I bar and ١٥° 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))

$$ni=\frac{mi}{mi} \quad \therefore\ \mathrm{n}_{\mathrm{H2}}=\frac{1}{2}=0.5\ \ \mathrm{kmoL} \qquad n_{o2}=\frac{x}{32}=\frac{x}{32}kmoL$$

From equation $\dfrac{vi}{v}=\dfrac{ni}{n}$

$$\frac{v_{H2}}{v_{O2}} = \frac{n_{H2}}{n_{O2}} \quad \therefore \frac{v_{H2}}{v_{O2}} = 2 \ \text{(given)} \qquad \therefore \ \frac{0.5}{x/32} = 2 \text{ e } \therefore \ \text{x} = \frac{32 \times 0.5}{2} = 8 \text{ kg}$$

$\therefore$ mass of oxygen per kilogram of hydrogen=8 kg , the total amount of substonce in the vessel per kilogram of H_2 is .

$$n_T = n_{H_2} + n_{o_2} = 0.5 + \frac{x}{32} = 0.5 + \frac{8}{32} = \underline{\underline{0.75 \text{ kmoL}}}$$

$$Form \text{ equation} \quad Pv = nR_oT \quad \therefore \text{V} = \frac{nR_oT}{P}$$

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

❖ **Example:-**

A vessel contains a gaseous mixture. of composition by volume, 80% Hz and 20% CO. It is desired that the mixture should be made in the proportion 50% Hz 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/kmole and 28 kg/kmole,

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

$let \ \ x \ kg$ of mixture be removed and y kg of CO be a dded

from equation $M=\sum \frac{Vi}{V} Mi \quad \therefore \ M=(0.8\times 2)+(0.2\times 28)=7.2 \ kg/kmol$

then using equation $n=\frac{m}{M}$ amount of substance of mixture removed $=\frac{x}{7.2} kg$

$$amount \ \ of \ \ subst\,an\,ce \ of \ \ CO \ \ added = \frac{y}{28} kmol$$

$$\therefore \frac{x}{7.2}=\frac{y}{28} \rightarrow (1)$$

from $\frac{ni}{n}=\frac{Vi}{V}$ we have

amount of substance of H2 intitially $=0.8\times 1=0.8$ kmol

amount of substance of H2 in the mixture removed $=0.8\times\left(\frac{x}{7.2}\right)=\frac{x}{9}$ kmol

Hence amount of substance of H2 remaining in the vesel $=\left(0.8-\frac{x}{9}\right)$ kmol

But 1 kmol of the new mixture is 50% H2 and 50% CO there for

$0.8-\frac{x}{9}=0.5 \quad \therefore x=2.7$ kg $\therefore$ the mass of mixture removed $=2.7$ kg

also since $\frac{x}{7.2}=\frac{y}{28} \qquad \therefore y=\frac{28}{7.2}x=10.5$ kg (mass of CO a dded)

❖ Specific heat capacities of a gas mixture:-

It was shown in previous section that as a consequence of the Gibbs-Dalton law the internal energy of a mixture of gases is given by equation.

$$mU = \sum m_i u_i \ , \qquad \text{but u=Cv}\cdot\text{T} \quad \text{so} \quad \text{m}\cdot\text{Cv}\cdot\cancel{T} = \cancel{T}\sum m_i Cv_i$$

$$\text{m}\cdot\text{Cv} = \sum m_i Cv_i \qquad \therefore\ \underline{\underline{\text{Cv} = \sum \frac{m_i}{m} Cv_i}}$$

Similarly for Enthalpy

$$mh = \sum m_i h_i \qquad \text{but h=Cp}\cdot\text{T} \quad \text{so} \quad \text{mCp}\cancel{T} = \cancel{T}\sum m_i Cp_i$$

So

$$\text{so}\ \ \underline{\underline{\text{Cp}=\sum \frac{m_i}{\text{m}} Cp_i}}$$

$$Cp - Cv = \sum \frac{m_i}{m} Cp_i - \sum \frac{m_i}{m} Cv_i = \sum \frac{m_i}{m}(Cp_i - Cv_i) = \sum \frac{m_i}{m} R_i$$

❖ Example:-

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 CP for the constituents averaged over the temperature are as follows: CP for CO_2 =1.271 kJ /kg K; CP for O_2=1.110 kJ/kg K; CP for N_2 =1.196 kJ/kg K.

Solution

From equation $m_i = n_i . M_i$ there for a conversion from volumetric fraction to mass fraction is as given in the table below.

constituent	n_i (kmol)	M_i (kg/kmol)	$m = n_i . m_i$	Mass fraction m_i/m
Carbon dioxide	**0.120**	**44**	**5.28**	$\frac{5.28}{3.36} = 0.174$
Oxygen	**0.115**	**32**	**3.68**	$\frac{3.68}{3.36} = 0.121$
Nitrogen	**0.765**	**28**	**21.40**	$\frac{21.40}{3.36} = 0.705$
Σ			**3.36**	

$$from \quad equation \quad R_T = \sum \frac{m_i}{m} R_i \quad and \quad R_i = \frac{R_o}{M_i}$$

$$R_T = \left(0.174 \times \frac{8.314}{44}\right) + \left(0.121 \times \frac{8.314}{32}\right) + \left(0.705 \times \frac{8.314}{28}\right) = 0.274\, kJ/kg.k$$

$$Cp_T = \sum \frac{m_i}{m} Cp_i$$

$$Cp_T = (0.174 \times 1.271) + (0.121 \times 1.11) + (0.705 \times 1.196) = \underline{\underline{1.199\, kJ/kg.k}}$$

$$from\, Cp - Cv = R \qquad \therefore\ Cv = Cp - R = 1.199 - 1.274 = \underline{\underline{0.925\, kJ/kg.k}}$$

$$work\ done\ per\ kg\ of\ gas\quad w = \frac{R(T_2 - T_1)}{n-1}. \qquad \therefore from\quad PV^n = C$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1} = \left(\frac{1}{7}\right)^{1.25-1} . \qquad \therefore\ T_2 = \frac{T_1}{7^{0.25}} = \frac{1273}{1.627} = 782.6k$$

$$then \qquad w = \frac{0.274 \times (782.6 - 1273)}{1.25 - 1} = \underline{\underline{+537.5\, kJ/kg}} \qquad Also\ \ from\ \ Q = \Delta u + w$$

$$but\ \ \Delta u = u_2 - u_1 = Cv(T_2 - T_1) = 0.925(782.6 - 1273) = -453.6\, kJ/kg$$

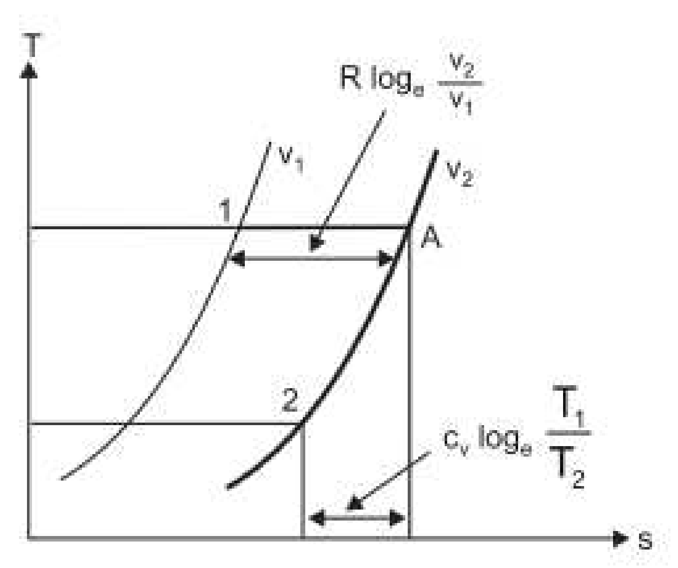
$$Q = \Delta u + w = -453.6 + 537.5 = \underline{\underline{83.9\, kJ/kg}}$$

- **Example:-**

Calculate for the data of example above, the change of entropy per kilogram of mixture.

Solution

Referring to figure 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.



$$\textit{for isothermal process } 1 \rightarrow A$$

$$\therefore \quad S_A - S_1 = RLn\left(\frac{V_2}{V_1}\right) = 0.274\left(\frac{7}{1}\right) = 0.533\,kJ/kg.k$$

$$\textit{for cons}\tan t\textit{ volume process } A \rightarrow 2$$

$$\therefore \quad S_A - S_2 = CvLn\left(\frac{T_1}{T_2}\right) = 0.925\left(\frac{1273}{782.6}\right) = 0.45\,kJ/kg.k$$

$$\textit{then by substraction } S_A - S_2 = 0.533 - 0.450 = 0.083\,kJ/kg.k$$

- ## Molar heat capacities:-

It is often convenient to use amount of substance. in problems on mixtures, and to define heat capacities expressed in terms of the amount of substance. These are known as molar heat capacities, and are denoted by $C\tilde{P}$ and $C\tilde{V}$ Molar heat capacities are defined as follows:

$$C\tilde{p} = M \cdot Cp \;, \qquad C\tilde{v} = M \cdot Cv \quad , \; but Cp - Cv = R$$

$$so \quad C\tilde{p} - C\tilde{v} = M(Cp - Cv) = MR = R_o$$

$$from\ equation \quad U = mCvT \quad and \quad m = nM$$

$$U = m \cdot Cv \cdot T = n \cdot M \cdot Cv \cdot T = n \cdot C\tilde{v} \cdot T$$

$$H = m \cdot Cp \cdot T = n \cdot M \cdot Cp \cdot T = n \cdot C\tilde{p} \cdot T$$

By Gibbs – Dalton law:

$$U = m_a u_a + m_b u_b + \dots\dots = \sum U_i$$

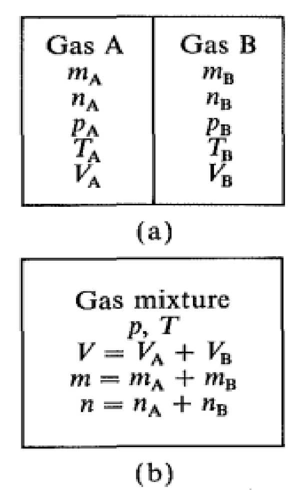
$$H = m_a h_a + m_b h_b + \dots\dots = \sum H_i$$

$$U = n \cdot C\tilde{v} \cdot T = \sum n \cdot C\tilde{v} \cdot T \qquad \therefore \underline{\underline{C\tilde{v} = \sum \frac{ni}{n} \cdot C\tilde{v}}}$$

$$H = n \cdot C\tilde{p} \cdot T = \sum n \cdot C\tilde{p} \cdot T \qquad \therefore \underline{\underline{C\tilde{p} = \sum \frac{ni}{n} \cdot C\tilde{p}}}$$

❖ Adiabatic mixture 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. In section 4.5 it is shown that there is always an increase in entropy of a thermally isolated system which. undergoes an irreversible process.



$$U_1 = n_A \cdot C\tilde{v}_A \cdot T_A + n_B \cdot C\tilde{v}_B \cdot T_B \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$U_2 = n_A \cdot C\tilde{v}_A \cdot T + n_B \cdot C\tilde{v}_B \cdot T \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

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$$U_1 = \sum n_i \cdot C\tilde{v}_i \cdot T_i \qquad\qquad U_2 = \sum n_i \cdot C\tilde{v}_i \cdot T$$

$$but \qquad U_1 = U_2 \qquad\qquad \therefore \ \sum n_i \cdot C\tilde{v}_i \cdot T_i = \sum n_i \cdot C\tilde{v}_i \cdot T$$

$$\underline{\underline{T = \frac{\sum n_i C\tilde{v}_i T_i}{\sum n_i C\tilde{v}_i}}}$$

❖ EXAMPLE:-

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 $C\tilde{P}$, $C\tilde{V}$, CP, and CV, for the mixture. The values of $C\tilde{P}$ for the constituents are as. follows:

for .CO,$C\tilde{P}$ =29.27 kJ/kmol K; for H_2, $C\tilde{P}$ = 28.89 kl /kmol K; for CH_4, $C\tilde{P}$ = 35.80 kJ/kmol K; . for CO_2, $C\tilde{P}$ = 37.22 k.l/kmol K; for N2, $C\tilde{P}$ = 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

$$from \quad C\tilde{p} = \sum \frac{ni}{n} C\tilde{p}i$$

$$C\tilde{p} = (0.29 \times 29.27) + (0.12 \times 23.89) + (0.03 \times 35.80) +$$
$$(0.04 \times 37.22) + (0.52 \times 29.14) = \underline{\underline{29.6707\, kJ/kmol.k}}$$

$$from \quad C\tilde{p} - C\tilde{v} = R_o \quad C\tilde{v} = 29.6707 - 8.3145 = \underline{\underline{21.3562\, kJ/kmol.k}}$$

$$The\ molar\ mass\ can\ be\ found\ from\ equation \quad M = \sum \frac{ni}{n} Mi$$

$$M = (0.29 \times 28) + (0.12 \times 2) + (0.03 \times 16) +$$
$$(0.04 \times 44) + (0.52 \times 28) = \underline{\underline{25.16\, kg/kmol}}$$

$$From \quad C\tilde{p} = M \cdot Cp \quad \therefore\ Cp = \frac{C\tilde{p}}{M} \quad \therefore Cp = \frac{29.6707}{25.16} = \underline{\underline{1.1793\, kJ/kg.k}}$$

$$C\tilde{v} = M \cdot Cv \quad \therefore\ Cv = \frac{C\tilde{v}}{M} \quad \therefore Cv = \frac{21.3562}{25.16} = \underline{\underline{0.8488\, kJ/kg.k}}$$

❖ **EXAMPLE:-**

A vessel of 1.5m^3 capacity contains oxygen at 7 bar and 40 ^{o}C, The vessel is connected to another vessel of 3 m^3 capacity containing carbon monoxide at 1 bar and 15^{o}C, A connecting valve is opened and the gases mix adiabatically. Calculate:

1. **the final temperature and pressure of the mixture.**
2. **the change in entropy of the system.**

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

$$From \quad n = \frac{PV}{RoT} \qquad n_{O2} = \frac{7\times10^5\times1.5}{8.314\times313\times10^3} = 0.4035$$

$$n_{co} = \frac{1\times10^5\times3}{8.314\times288\times10^3} = 0.1253$$

$$U_1 = \sum niC\tilde{v}Ti = (0.4035\times21.07\times313) + (0.1253\times21.86\times288) = 3413.8kJ$$

$$U_2 = \sum niC\tilde{v}T = (0.4035\times21.07\times T) + (0.1253\times21.86\times T) = 11.118T$$

$$for\ addiabatic\ mixing \quad U_1 = U_2 \qquad \therefore 3413.8 = 11.118T \qquad \therefore \underline{\underline{T = 307k}}$$

$$fromP = \frac{nRoT}{V} = \frac{(0.4035+0.1253)\times8.314\times307\times10^3}{(1.5+3)\times10^5} = 3\ bar$$

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

$$\text{From } 1 \rightarrow A \quad S_A - S_1 = R\ln\frac{v_A}{v_1} \quad or$$

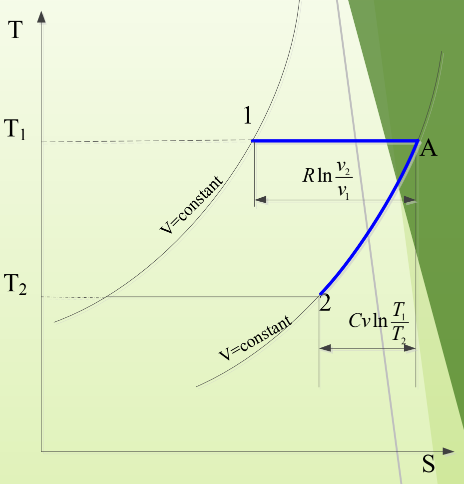
$$S_A - S_1 = mR\ln\frac{v_A}{v_1} = nRo\ln\frac{v_A}{v_1}$$

$$S_A - S_1 = 0.4035\times 8.314\ln\left(\frac{4.5}{1.5}\right) = 3.686\,kJ/k$$

$$from S_A - S_2 = nC\tilde{v}\ln\frac{T_1}{T_2}$$

$$S_A - S_2 = 0.4035\times 21.07\ln\left(\frac{313}{307}\right) = 0.1683\,kJ/k$$

$$S_2 - S_1 = 3.686 - 0.168 = \underline{\underline{3.518\,kJ/k}}$$



The change of entropy of the carbon well calculated by replacing the process undergone by the carbon by the two processes 1 to B and B to 2 referring to Figure.

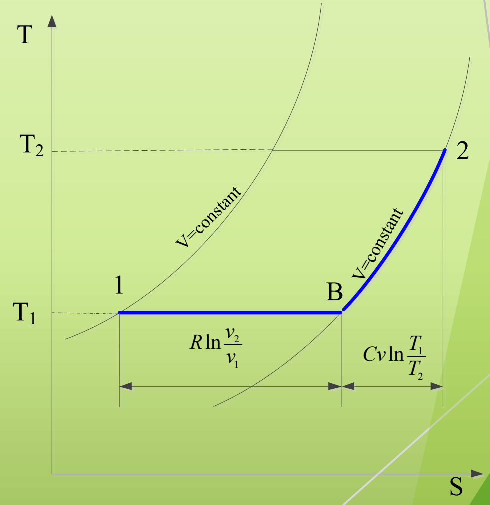
$$\text{From } 1 \rightarrow B \quad S_B - S_1 = nRo\ln\frac{v_A}{v_1}$$

$$S_B - S_1 = 0.1235\times 8.314\ln\left(\frac{4.5}{3}\right) = 0.4163 \quad kJ/k$$

$$from \quad S_A - S_2 = nC\tilde{v}\ln\frac{T_2}{T_1}$$

$$S_A - S_2 = 0.1235\times 20.86\ln\left(\frac{307}{288}\right) = 0.1646\,kJ/k$$

$$S_2 - S_1 = (S_B - S_1) - (S_A - S_2) = 0.59\,kJ/k$$

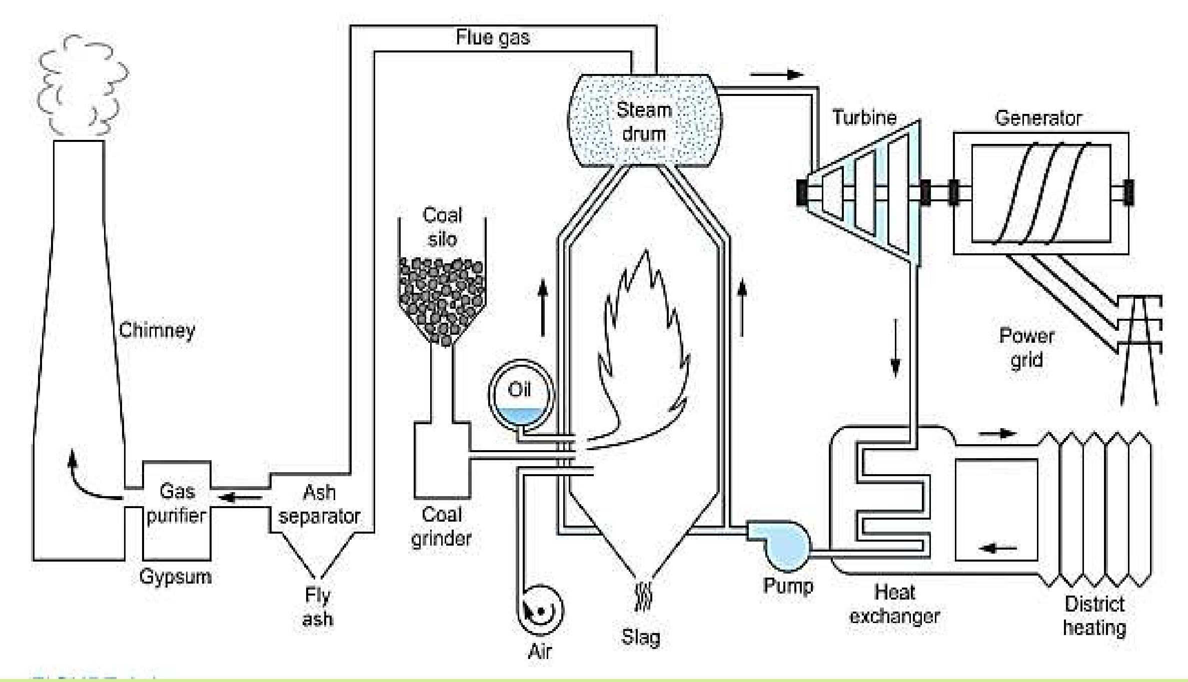


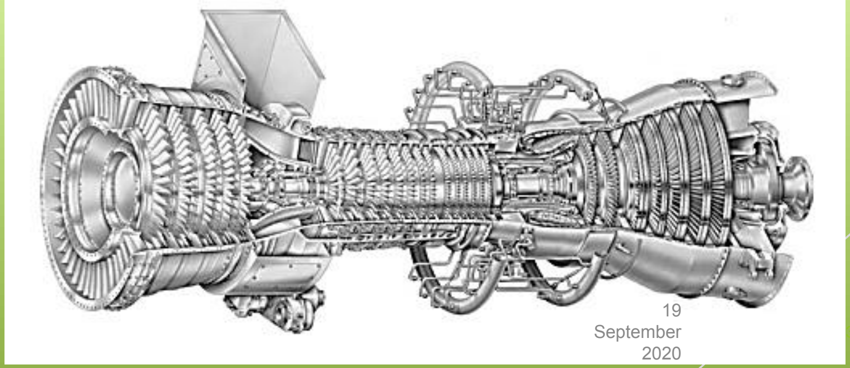
Hence, the change of entropy of the whole system given by

$$(S_2 - S_1)_{system} = (S_2 - S_1)_{O2} + (S_2 - S_1)_{CO} = \underline{\underline{4.108\,kJ/k}}$$

SECOND PART

THERMAL POWER CYCLES





- **Thermodynamic Cycles:-**
- **Thermal Power Cycles:-**
- **Introduction:-**

Thermodynamic cycles can be primarily classified based on their utility such as for power generation, refrigeration etc. Based on this thermodynamic cycles categorized as:

I. Power cycles.

II. Refrigeration and heat pump cycles.

III. Power cycles: Thermodynamic cycles which are used in devices producing power are called power cycles. Power production using working fluid either in vapour form or in gaseous form. When vapour is the working fluid then they are called vapour power cycles, whereas in case of working fluid being gas these are called gas power cycles. Thus, power cycles shall be of two types,

  a. Vapour power cycle.
  b. Gas power cycle.

Vapour power cycles can be classified further as,

1. **Carnot vapour power cycle.**
2. **Rankine cycle.**
3. **Reheat cycle.**
4. **Regenerative cycle.**

Gas power cycles classified as,

1. **Carnot gas power cycle.**
2. **Otto cycle.**
3. **Diesel cycle.**
4. **Dual cycle.**
5. **Stirling cycle.**
6. **Ericsson cycle.**
7. **Brayton cycle**

Here in the present text Carnot, Rankine, reheat and regenerative cycles are discussed.

I. Refrigeration and heat pump cycles: Thermodynamic cycles used for refrigeration and heat pump are under this category. Similar to power cycles, here also these cycles can be classified as “air cycles” and “vapour cycles” based on type of working fluid used.