Assignment 1 : Solution.

Ans. 1 :- Vander waals eq^n:-

$$\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$$

for a

$$P = \frac{an^2}{V^2}$$

$$a = \frac{PV^2}{n^2} = \frac{atm\,L^2}{mol^2} = Pa\,m^6\,mol^{-2}.$$

for b

$$V = nb.$$

$$b = \frac{V}{n} = m^3\,mol^{-1}.$$

Ans 2 :- As, $PV = nRT$

So $P \propto T$

$$\Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$P_1 = 125\,kPa$ $\quad T_1 = 23°C = 296K$

$P_2 = ?$ $\quad T_2 = 11°C = 284K$

$$\Rightarrow P_2 = \frac{P_1 T_2}{T_1}$$

$$= \frac{125 \times 284}{296} = 120\,kPa.$$

Ans 4 $T_c = \frac{8a}{27bR}$ —(1) and $P_c = \frac{a}{27b^2}$ —(2)

$\therefore b = \frac{8a}{27 \cdot T_c \cdot R}$ — *

from (2) $a = P_c \cdot 27b^2$ — (3)

Put (3) in (*)

$\cancel{b} = \frac{8}{\cancel{27} \cdot T_c \cdot R} (P_c \cdot \cancel{27} b^{\cancel{2}})$

$1 = \frac{8bP_c}{T_c R}$

$\boxed{b = \frac{T_c}{P_c} \cdot \frac{R}{8}}$ — (4)

$b = \frac{(304.2\,\cancel{K})}{(72.8\,\cancel{atm})} \cdot \frac{0.082\,l\,\cancel{atm}\,\cancel{K^{-1}}\,mol^{-1}}{8}$

$b = 0.0428\,l\,mol^{-1}$

(4) in (3)

$a = P_c \cdot 27 \cdot \left(\frac{T_c}{P_c} \cdot \frac{R}{8}\right)^2$

or

$a = \frac{27bRT_c}{8}$ from (*)

$= \frac{27}{8} \cdot RT_c \cdot \frac{T_c}{P_c} \cdot \frac{R}{8}$

$a = \frac{27}{8} \cdot 304.2\,\cancel{K} \times 0.082\,l\,atm\,\cancel{K^{-1}} \times 0.0428\,l\,mol^{-1}$

$a = 3.603\,atm\,l^2\,mol^{-2}$

Ans 5 no. of moles of $H_2 = 2.5$

(a) no. of moles of $N_2 = 1.5$

mole fraction for H_2, $X_{H_2} = \frac{2.5}{2.5+1.5} = \frac{2.5}{4}$

$= 0.625$

mole fraction for N_2, $X_{N_2} = \frac{1.5}{2.5+1.5} = \frac{1.5}{4}$

$= 0.375$

(5) Calculation of Partial pressure & Total Pressure

Acc to Ideal gas eqn

$$P_{Total} \cdot V = n_{total} \cdot R \cdot T$$

$$P_{Total} = \frac{n_{Total} \cdot R \cdot T}{V}$$

$$= \frac{4\ mol \times 0.082\ L\,atm\ mol^{-1}\ K^{-1} \times 273.15\ K}{22.4\ L}$$

$$= 3.99\ atm \simeq 4\ atm$$

(b) Partial pressure

$$P_{H_2} = (\text{mole fraction of } H_2)(\text{Total pressure})$$

$$= 0.375 \times 4$$

$$= 1.5\ atm$$

$$P_{N_2} = (\text{mole fraction of } N_2)(\text{Total pressure})$$

$$= (0.625)(4)$$

$$= 2.5\ atm$$

Ans 6: A) Berthelot equation:

$$P = \frac{RT}{V-b} - \frac{a}{TV^2} = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2} + \cdots\right)$$

$$\frac{RT}{V-b} - \frac{a}{TV^2} = \frac{RT}{V} + \frac{BRT}{V^2} + \frac{CRT}{V^3}$$

Dividing whole equation by RT

B - second Virial Coeff

C - 3rd Virial Coeff

$$\frac{1}{V-b} - \frac{a}{RT^2V^2} = \frac{1}{V} + \frac{B}{V^2} + \frac{C}{V^3}$$

multiply both sides by V^3

$$\frac{V^3}{V-b} - \frac{aV}{RT^2} = V^2 + BV + C$$

multiply both sides by $(V-b)$

$$V^3 - \frac{aV(V-b)}{RT^2} = V^2(V-b) + BV(V-b) + C(V-b)$$

$$V^3 - \frac{aV^2}{RT^2} + \frac{baV}{RT^2} = V^3 - V^2b + BV^2 - bBV + CV - bC$$

$$V^3 - \frac{aV^2}{RT^2} + \frac{baV}{RT^2} = V^3 + (B-b)V^2 + (C - bB)V - bC$$

comparing coefficient of V^2 on both sides

$$\frac{-a}{RT^2} = B - b$$

$$\Rightarrow \boxed{B = b - \frac{a}{RT^2}}$$

(b) Dieterici Equation

$$P = \frac{RT}{V_m - b} \exp\left(\frac{-a}{RTV_m}\right)$$

$$= \frac{RT/V_m}{\left(1 - \frac{b}{V_m}\right)} \exp\left(\frac{-a}{RTV_m}\right)$$

using $\frac{1}{1-x} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$ & $e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!}$ we get

$$= RT/V_m \left(1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots\right)\left(1 - \frac{a}{RTV_m} + \frac{a^2}{2R^2T^2V_m^2} - \frac{a^3}{6R^3T^3V_m^3} + \dots\right)$$

$$= \frac{RT}{V_m}\left[1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} - \frac{a}{RTV_m} - \frac{ab}{RTV_m^2} - \frac{ab^2}{RTV_m^3} + \frac{a^2}{2R^2T^2V_m^2} + \dots\right]$$

$$P = \frac{RT}{V_m} + \frac{bRT}{V_m^2} + \frac{b^2RT}{V_m^3} - \frac{aRT}{RTV_m^2}$$

$$\frac{P}{RT} = \frac{1}{V_m} + \frac{b}{V_m^2} + \frac{b^2}{V_m^3} - \frac{a}{RTV_m^2} + \dots$$

$$\frac{P}{RT} = \frac{1}{V_m} + \left(b - \frac{a}{RT}\right) \cdot \frac{1}{V_m^2} + \frac{b^2}{V_m^3}$$

$\downarrow$

Second Virial coefficient.

$$\boxed{B = b - \frac{a}{RT}}$$

Ans 3:- Vander Waals eqn. $\rightarrow$ $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ 6

Berthelot eqn :- $\left[P + \frac{a}{TV^2}\right]\left[V - b\right] = RT$

$$P = \frac{RT}{V-b} - \frac{a}{TV^2} \longrightarrow (1)$$

For Critical constant,

$$\frac{dP}{dV} = 0.$$

$$\Rightarrow \frac{dP}{dV} = \frac{-RT}{(V-b)^2} + \frac{2a}{TV^3} = 0$$

$$\Rightarrow \frac{2a}{TV^3} = \frac{RT}{(V-b)^2} \longrightarrow (1a)$$

$$RT^2 = \frac{2a(V-b)^2}{V^3} \longrightarrow (2)$$

Also, $\frac{d^2P}{dV^2} = 0$

$$\Rightarrow \frac{d^2P}{dV^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{TV^4} = 0$$

$$\Rightarrow \frac{2RT}{(V-b)^3} = \frac{6a}{TV^4}$$

$$RT^2 = \frac{3a(V-b)^3}{V^4} \longrightarrow (3)$$

Equating (2) & (3) :-

$$\frac{2a(V-b)^2}{V^3} = \frac{3a(V-b)^3}{V^4}$$

$$\frac{V-b}{V} = \frac{2}{3}$$

$$\boxed{V_c = 3b}$$

from (1a):-

$$\frac{-RT}{(V-b)^2} + \frac{2a}{TV^3} = 0$$

Put $V_c = 3b$

$$\Rightarrow \frac{-RT}{4b^2} + \frac{2a}{27Tb^3}$$

$$\Rightarrow RT^2 = \frac{8ab^2}{27b^3}$$

$$\boxed{T_c = \left(\frac{8a}{27Rb}\right)^{1/2}}$$

From Berthelot's eq^n:-

$$P = \frac{RT}{V-b} - \frac{a}{TV^2}$$

for Critical constant :-

$$P_c = \frac{RT_c}{V_c-b} - \frac{a}{T_cV_c^2}$$

Put value of T_c & V_c from Above,

$$P_c = \frac{R\left(\frac{8a}{27Rb}\right)^{1/2}}{3b-b} - \frac{a}{\left(\frac{8}{27Rb}\right)^{1/2} \cdot 9b^2}$$

$$P_c\left(\frac{8a}{27Rb}\right)^{1/2} = \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

$$\therefore P_c = \frac{a}{27b^2}\left[\frac{27Rb}{8a}\right]^{1/2}$$

$$\Rightarrow \boxed{P_c = \frac{1}{2b}\left[\frac{Ra}{54b}\right]^{1/2} \text{ or } \frac{1}{12}\left[\frac{2aR}{3b^3}\right]^{1/2}}$$

Dietesici Equation :-

$$P = \frac{RT}{V_m - b}\exp\left[-\frac{a}{RTV_m}\right] \rightarrow (4)$$

$$\frac{dP}{dV} = 0$$

$$\ln P = \ln RT - \ln(V_m - b) - \frac{a}{RTV_m}$$

$$\frac{1}{P}\frac{dP}{dV_m} = 0 - \frac{1}{V_m - b} + \frac{a}{RTV_m^2}$$

$$\frac{1}{P}\cdot\frac{dP}{dV_m}\bigg|_{V_m = V_c} = \frac{-1}{V_c - b} + \frac{a}{RTV_c^2} = 0$$

$$\Rightarrow a(V_c - b) = RTV_c^2 \longrightarrow (5)$$

Second Derivative, :

$$-\frac{1}{P^2}\frac{dP}{dV_m} + \frac{1}{P}\frac{d^2P}{dV_m^2} = \frac{1}{(V_m - b)^2} - \frac{2a}{RTV_m^3}$$

$$-\frac{1}{P^2}\frac{dP}{dV_m}\bigg|_{V_m = V_c} + \frac{1}{P}\frac{d^2P}{dV_m^2}\bigg|_{V_m = V_c} = \frac{1}{(V_c - b)^2} - \frac{2a}{RTV_c^3} = 0$$

$$\Rightarrow 2a(V_c - b)^2 = RTV_3^3 \longrightarrow (6).$$

Divide (6) By (5):

$$\frac{(6)}{(5)} ; \quad 2(V_c - b) = V_c.$$

$$\Rightarrow \boxed{V_c = 2b}$$

Put V_c into (5)

$$a(2b-b) = RT_c\,(2b)^2$$

$$ab = RT_c^2 \cdot 4b^2$$

$$\boxed{T_c = \frac{a}{4Rb}}$$

from (4),

$$P_c = \frac{RT_c}{V_c - b} \exp\left(\frac{-a}{RT_cV_c}\right)$$

$$= \frac{RT_c}{2b-b} \cdot \exp\left[\frac{-a}{R\left[a/4Rb\right] \cdot 2b}\right]$$

$$= \frac{RT_c}{b} \exp(-2) \qquad = \frac{R \cdot a}{4Rb \cdot be^2}$$

$$\boxed{P_c = \frac{a}{4e^2b^2}}$$