Derivation of critical constants from Van der waals constant.

The vander waals equation for n moles is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad -①$$

n = 1 mole.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad -②$$

on expanding the above equation ②

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0 \quad -③$$

multiply eqn by V^2/P

$$\frac{V^2}{P}\left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT\right) = 0$$

$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0 \quad -④$$

Rearrange the equation in power of V

$$V^3 - \left(\frac{RT}{P} + b\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad - \text{⑤}$$

The eqn ⑤ is a cubic equation in V.

$$V = V_c$$

$$V - V_c = 0$$

$$(V - V_c)^3 = 0$$

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad —— \text{⑥}$$

Equate the coefficients of V^2, V and constant terms in eqn ⑤ and ⑥

$$+3V_c V^2 = +\left(\frac{RT_c}{P_c} + b\right)V^2$$

$$3V_c = \frac{RT}{P_c} + b \quad —— \text{⑦}$$

$$\left.\begin{array}{l} T \to T_c \\ P \to P_c \end{array}\right\} - \text{in the eqn ⑤}$$

$$V^3 - \left(\frac{RT_c}{P_c} + b\right)V^2 + \frac{aV}{P_c}$$

$$- \frac{ab}{P_c} = 0.$$

$$3V_c^2 \lambda = \frac{a\lambda}{P_c}$$

$$3V_c^2 = \frac{a}{P_c} \quad \text{---(8)}$$

$$\lambda V_c^3 = \lambda \frac{ab}{P_c}$$

$$V_c^3 = \frac{ab}{P_c} \quad \text{---(9)}$$

Divide eqn (9) by (8)

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \times \frac{P_c}{a}$$

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

$$\boxed{V_c = 3b} \quad \text{---10}$$

Equation ⑩ is substituted in eqn ⑧

$V_c = 3b$

$$3V_c^2 = \frac{a}{Pc}$$

$$3(3b)^2 = \frac{a}{Pc}$$

$$27b^2 = \frac{a}{Pc}$$

$$\boxed{Pc = \frac{a}{27b^2}}$$ ⑪

Sub the values of V_c & Pc in the eqn ⑦

$$3V_c = \frac{RTc}{Pc} + b$$

$$3(3b) = RT_c \times \frac{27b^2}{a} + b$$

$$9b = \frac{27RT_cb^2}{a} + b$$

$$9b - b = \frac{27 RT_c b^2}{a}$$

$$8b = 27 RT_c b^2$$

$$T_c = \frac{8ab}{27 R b^2}$$

$$\boxed{T_c = \frac{8a}{27 Rb}} \quad -\!\!-\!\!(12)$$

The critical constants can be calculated using the values of Van der waals constant of a gas & vice versa.

$$V_c = 3b$$

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

$$P_c = \frac{a}{27 b^2}$$

$$\Leftrightarrow \quad 3V_c^2 = \frac{a}{P_c}$$

$$\boxed{3V_c^2 P_c = a}$$

$$\frac{a}{P_c}$$

$$\frac{a}{3V_c^2} = \frac{a}{3(3b^2)} = \frac{a}{3 \times 9b^2} = \frac{a}{27 b^2}$$

$$P_c = \frac{a}{27b^2} \quad \text{------ (6.32)}$$

Substituting the values of V_c and P_c in equation (6.28),

$$V_c = b + \frac{R T_c}{P}$$

$$(3b) = b + \frac{R T_c}{\left(a \big/ 27 b^2\right)}$$

$$3b - b = \left(\frac{R T_c}{a}\right) 27 b^2$$

$$8 b = \frac{T_c R 27b^2}{a}$$

$$\therefore T_c = \frac{8 a b}{27 R b^2} = \frac{8 a}{27 R b}$$

$$T_c = \frac{8 a}{27 R b} \quad \text{------ (6.33)}$$

The critical constants can be calculated using the values of van der waals constant of a gas and vice versa.

$$a = 3 V_c^2 P_c \quad \text{and} \quad b = \frac{V_c}{3}$$

6.7 Liquefaction of gases

For important commercial operations such as LPG and rocket fuels, we require gases in their liquid state. The liquefication methods are based on the Joule-Thomson effect. He observed appreciable cooling when the compressed gas is forced through an orifice plug into a low-pressure region. This phenomenon of lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect. This effect is observed only below a certain temperature, which is a characteristic one for each gas. This temperature below which a gas obeys Joule-Thomson effect is called inversion temperature (T_i). This value is given using van der waals constants a and b.

$$T_i = \frac{2a}{Rb} \quad \text{--------- (6.34)}$$

Gases like O_2, He, N_2 and H_2 have very low T_c, hence Joule-Thomson effect can be applied for cooling effectively. At the inversion temperature, no rise or fall in temperature of a gas occurs while expanding. But above the inversion temperature, the gas gets heated up when allowed to expand through a hole.

There are different methods used for liquefaction of gases:

1) In **Linde's method,** Joule-Thomson effect is used to get liquid air or any other gas.

2) In **Claude's process,** the gas is allowed to perform mechanical work in addition to Joule-Thomson effect so that more cooling is produced.

3) In **Adiabatic process,** cooling is produced by removing the magnetic property of magnetic material such as gadolinium sulphate. By this method, a temperature of 10^{-4} K i.e. as low as 0 K can be achieved.

① Soln

Volume of freon (V_1) = $1.5 dm^3$

Pressure (P_1) = $0.3 atm$

(T) is constant

1   P_2 = $1.2 atm$

V_2 = ?

$P_1 V_1 = P_2 V_2$

$V_2 = \dfrac{P_1 V_1}{P_2}$

= $\dfrac{0.3 \, atm \times 1.5 dm^3}{1.2 \, atm}$

= $0.375 \, dm^3$

(2)

$V_1 = 0.375 \, dm^3$ $V_2 = 0.125 \, dm^3$

$P_1 = 1.05 \, atm$ $P_2 = ?$

$T = const$

$P_1 V_1 = P_2 V_2$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{10.5 \times 0.375}{0.125}$$

$$= 3.15 \, atm$$

$V_1 = 3.8 \, dm^3$ $T_2 = 0°c = 273 \, k$

$T_1 = ?$ $V_2 = 2.27 \, dm^3$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_1 = \frac{T_2}{V_2} \times V_1 = \frac{273k}{2.27 \, dm^3} \times 3.8 \, dm^3$$

$$T_1 = 457 \, k$$

⑤

$T_1 = 8°C$

$T_1 = 8 + 273 = 281 k$ $V_1 = 2.1 \, mol$

$P_1 = 6.4 \, atm$ $V_2 = ?$

$T_2 = 25°C$

$T_2 = 25 + 273 = 298 k$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \left(\frac{P_1 V_1}{T_1} \right) \times \frac{T_2}{P_2}$$

$$= \frac{6.4 \, atm \times 2.1 \, mol}{281 \, k} \times \frac{298 \, k}{1 \, atm}$$

$$V_2 = 14.25 \, ml .$$

w)

$V_{O_2} = 12 dm^3$ $T = 298$ } Const
$V_{He} = 460 dm^3$ $P = 1 atm$ }
$V_{total} = 5 dm^3$

$P_{O_2} = X_{O_2} \times P_{total}$ no of mole $= \dfrac{V \ in \ litre}{22.4 L}$

$X_{O_2} = \dfrac{n_{O_2}}{n_{O_2} + n_{He}}$

$= \dfrac{0.54}{0.54 + 2.05}$ $n_{O_2} = \dfrac{12 V}{22.4 V} = 0.54 \ knol$

$= \dfrac{0.54}{2.59}$ $n_{He} = \dfrac{46 V}{22.4 V} = 2.05 \ mo$

$= 0.21$

$$P_{total} \times V_{total} = 1 \, atm \times 22.4L$$

$$P_{total} = \frac{1 \, atm \times 22.4L}{5K}$$

$$P_{total} = 4.48 \, atm$$

$$P_{O_2} = X_{O_2} \cdot P_{total}$$

$$= 0.21 \times 4.48 \, atm$$

$$= 0.94 \, atm$$

$$P_{He} = X_{He} \cdot P_{total}$$

$$X_{He} = \frac{n_{He}}{n_{O_2} + n_{He}} = \frac{2.05}{0.54 + 2.05} = \frac{2.05}{2.59} = 0.79$$

$$P_{He} = 0.79 \times 4.48 \, atm = 3.54 \, atm.$$

6. (b)

$$2 KClO_{3(S)} \xrightarrow{\Delta} 2 KCl_{(S)} + 3O_{2(g)}$$
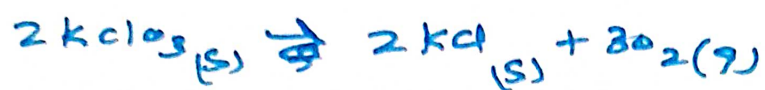
$P_{total} = 772 \ mm \ Hg$

$P_{H_2O} = 26.7 \ mm \ Hg$

$P_{total} = P_{O_2} + P_{H_2O}$

$P_{O_2} = P_{total} - P_{H_2O}$

$P_1 = 26.7 \ mm \ Hg \qquad T_2 = 295 \ k$

$T_1 = 300 \ k \qquad\qquad P_2 = ?$

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

$$P_2 = \left(\frac{P_1}{T_1}\right) T_2 = \frac{26.7 \ mm \ Hg}{300 \ k} \times 295 \ k$$

$$\boxed{P_2 = 26.26 \ mm \ Hg}$$

$$P_{O_2} = 772 - 26.26 = 745.74 \ mm \ Hg$$

(7)

$t_1 = 1.5$ min

$t_2 = 4.73$ min

$$\frac{\text{y hydrocarbon}}{\text{y Bromine}} = \frac{t \text{ Bromine}}{t \text{ hydrocarbon}}$$

($\because$ Volume Const)

$$= \frac{4.73 \text{ min}}{1.5 \text{ min}}$$

$$= 3.15$$

$$\frac{\text{y hydrocarbon}}{\text{y Bromine}} = \sqrt{\frac{m \text{ bromine}}{m \text{ hydrocarbon}}}$$

$$3.15 = \sqrt{\frac{159.8 \text{ gmol}^{-1}}{m \text{ hydrocarbon}}}$$

Squaring on both side

$$(3.15)^2 = \sqrt{\frac{159.8}{m_{Hydro\,Carbon}}}$$

$$3.15 = \frac{159.8}{m_{hydrocarbon}}$$

$$m_{Hydro\,Carbon} = \frac{159.8}{(3.15)^2}$$

$$= 16.1\,g\,mol^{-1}$$

$$n(12) + (2n+2)1 = 16$$
$$12n + 2n + 2 = 16$$
$$14n = 16 - 2$$
$$14n = 14$$
$$n = \frac{14}{14}$$
$$\boxed{n = 1}.$$

∴ General formula
for hydro carbon
$$C_nH_{2n+2}.$$

(8) critical temperature of a gas is defined as the temperature above which it cannot be liquefied even at high pressures.

∴ when cooling starts from 700k H_2O will liquefied first, then followed by a NH_3 & finally CO_2 will liquefied