DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC05

1. **(d)** $R=\frac{PV}{T}$

At critical point $V = V_c$

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

Expanding this equation, we have

$$V^3-3V_c.V^2+3V_c^2.V-V_c^3=0 \qquad ..(i)$$

The vander waals equation in critical point is

$$V^3-\left(b+\frac{RT_c}{P_c}\right)V^2+\left(\frac{a}{P_c}\right)V-\frac{ab}{P_c}=0 \qquad ...(ii)$$

Comparing (i) and (ii), we get

$$V_c=3b, P_c=\frac{a}{27b^2}, T_c=\frac{8a}{27Rb}$$

Eliminating constants *a* and *b* from the values of critical constants, we obtain

$$R=\frac{8P_c V_c}{3T_c}$$

2. **(b)** At the same conditions of T and P, $V \alpha n$

$$n_{N_2}=\frac{14}{28}=\frac{1}{2};\ V_{N_2}\alpha\frac{1}{2} \qquad n_{O_3}=\frac{36}{48}=\frac{3}{4};\ V_{O_3}\alpha\frac{3}{4}$$

Hence, $V_{N_2}/V_{O_3}=\frac{2}{3},\ 3V_{N_2}=2V_{O_3}$

3. **(c)** $PV^{\frac{3}{2}}$ = constant.

Again $P=\frac{nRT}{V}$

$\therefore \frac{nRT}{V}\times V^{\frac{3}{2}}$ = constant (K)

or, $TV^{\frac{1}{2}}=\frac{K}{nR}$ = K' (constant)

For two states, $T_1V_1^{\frac{1}{2}}=T_2V_2^{\frac{1}{2}}$

$$T_2=T_1\left(\frac{V_1}{V_2}\right)^{\frac{1}{2}}$$

But $V_2=\frac{V_1}{2}$ (given)

$$\therefore \quad T_2=T_1\left(\frac{V_1}{\frac{V_1}{2}}\right)^{\frac{1}{2}}=T_1\sqrt{2}$$

4. **(a)** $CO_2+C \longrightarrow 2CO$

Stoichiometry ratio is 1 : 2

AT STP, P = 1 atm, T = 273 K, R = 0.0821

Initial moles of CO_2; $n(CO_2\text{initial})=\frac{PV}{RT}$

$=\frac{1\times 0.5}{0.0821\times 273}$ = 0.022 mole

In final mixture no. of moles; $n(CO_2/CO \text{ mixture})$

$=\frac{1\times 0.7}{0.0821\times 273}$ = 0.031

Increase in volume is by = 0.031 – 0.022

= 0.009 mole of gas

Final no. of moles of CO i.e. $n_{(CO\ final)}$

$n_{(CO\ final)}=2n_{(CO2\ initial)}-n_{(CO2\ final)}$

$=2(0.022-n_{(CO2\ final)}) \qquad ...(i)$

$n_{(CO\ final)}=0.044-2n_{(CO2\ final)} \qquad ...(ii)$

$\therefore$ Now, $n_{(CO\ final)}+n_{(CO2\ final)}=0.031$

$n_{(CO2\ final)}=0.031-n_{(CO\ final)} \qquad ...(ii)$

Substituting (ii) in eq. (i)

$n_{(CO\ final)}=0.044-2[0.031-n_{(CO\ final)}]$

$n_{(CO\ final)}=0.044-0.062+2n_{(CO\ final)}$

$n_{(CO\ final)}=0.018$ mol.

Volume of $CO=V=\frac{nRT}{P}=\frac{0.018\times 0.0821\times 273}{1}$

= 0.40 Litre

and volume of CO_2 = 0.7 litre – 0.4 litre

= 0.3 litre

$\therefore$ CO_2 = 300 mL, CO = 400 mL

5. **(a)** Most probable velocity $=\sqrt{\frac{2RT}{M}}$

Average velocity $=\sqrt{\frac{8RT}{\pi M}}$

Root mean square velocity $=\sqrt{\frac{3RT}{M}}$

$\therefore$ Most probable velocity : Average velocity : Root mean square velocity

$$=\sqrt{\frac{2RT}{M}}:\sqrt{\frac{8RT}{\pi M}}:\sqrt{\frac{3RT}{M}}=\sqrt{2}:\sqrt{\frac{8}{\pi}}:\sqrt{3}$$

6. **(b)** The van der Waals equation is

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

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

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

Multiplying throughout by molar volume (V) and dividing by RT, we have

$$\frac{PV}{RT}=\frac{V}{V-b}-\frac{a}{RTV} \text{ or } \frac{PV}{RT}=\left(\frac{V-b}{V}\right)^{-1}-\frac{a}{RTV}$$

$$\text{or } \frac{PV}{RT}=\left(1-\frac{b}{V}\right)^{-1}-\frac{a}{RTV}$$

$$\text{or } \frac{PV}{RT}=1+\frac{b}{V}+\frac{b^2}{V^2}+\frac{b^2}{V^3}-\frac{a}{RTV}$$

$$\text{or } \frac{PV}{RT}=1+\left(b-\frac{a}{RT}\right)\times\frac{1}{V}+\frac{b^2}{V^2}+\frac{b^3}{V^3}$$

Comparing this with virial equation we get

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

7. **(b, c)** Given $V = 10$ litre, $P = 3$ atm, $T = 290$ K

After driving $V = 10$ litre $\quad P = ?$

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2} \qquad \therefore V_1=V_2=10 \text{ lit},$$

$$\therefore \frac{P_1}{T_1}=\frac{P_2}{T_2} \text{ or } P_2=\frac{P_1}{T_1}\times T_2$$

$$\text{or } P_2=3\times\frac{320}{290}=3.3103 \text{ atm.}$$

$\therefore$ Pressure of the gas in the tyre at 47°C = 3.3103 atm.

At pressure 3.103 atm, the volume of tyre is 10 lit.

$\therefore$ Volume of tyre at 3 atm pressure

$$=\frac{3.3103\times 10}{3}=11.03433 \text{ lit.}$$

$\therefore$ The volume which is to be reduced at 3 atm pressure

$$=11.03433-10=1.03433 \text{ lit.}$$

$\therefore$ The volume which is to be reduced at 1 atm pressure

$$=\frac{1.03433\times 3}{1}=3.1029 \text{ lit.}$$

$\therefore$ 3.1029 lit of air should be let out at 1 atm to restore the tyre to 3 atm at 47°C.

8. **(a,c,d)** The critical pressure,

$$P_C=\frac{a}{27b^2}=\frac{371.843\times 10^3}{27\times(40.8)^2\times 10^{-6}}$$

$$=\frac{371.843\times 10^9}{27\times(40.8)^2}=8.273\times 10^6 \text{ Pa}=8.273 \text{ MPa}$$

The critical temperature, $T_C=\frac{8a}{27Rb}$

$R = 8.314$ KPa dm^3 K^{-1} mol^{-1}

$$T_C=\frac{8a}{27Rb}=\frac{8.371.843}{8.314\times 27\times 40.8\times 10^{-3}}$$

$$=324.79=324.8 \text{ K.}$$

The critical volume, $V_C = 3b = 3 \times 40.8 = 122.4$ cm^3

9. **(a, c)** van der Waal's equation is

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT \quad \text{[For n moles of a gas)}$$

a, b are van der Waal's constants

The ideal gas equation is $PV = nRT$ [For n moles of a gas] where P is pressure excerted by ideal gas and V is volume occupied by ideal gas.

In van der Waal's equation the term $\left(P+\frac{n^2a}{V^2}\right)$ represents the pressure exerted by the gas and ($V - nb$) the volume occupied by the gas. At low pressure, when the gas occoupies large volume the intermolecular distance between gaseous moleculas is quite large and in such case there is no significant role played by intermolecular forces and thus the gas behaves like an ideal gas thus (a) is correct

NOTE : Under high pressure the intermolecular distance decreases and the intermolecular forces play a significant role and the gas shows a devation from ideal behaviour. Thus (b) is *not* correct.

a, b i.e. the van der Waal's coefficients defined on the nature of gas and are independent of temperature so (c) is correct.

The pressure $\left(P+\frac{n^2a}{V}\right)$ is not lower than P so (d) is not correct.

Hence the correct answer is (a, c).

10. **(b,c,d)** (a) An ideal gas cannot be liquefied at any temperature for any pressure. It is due to the absence of intermolecular forces.

(b) Helium, a real gas, can be liquefied by cooling it to critical temperature or below and applying high pressure.

(c) The inversion temperature of helium is much below the room temperature. Hence, it shows heating effect during Joule-Thompson porous plug streaming of the gas at ordinary temperatures.

(d) Compressibility factor $\left(Z=\frac{PV}{RT}\right)$ of hydrogen is greater than unity

11. **(5)** Given, $P = 1.56$ atm; $V = 10$ L

$T = 317$ K; $R = 0.082$

$$\text{Total moles } (n)=\frac{PV}{RT}=\frac{1.56\times 10}{0.082\times 317}=0.6 \text{ mol}$$

Let C_xH_8 be a mol, therefore moles of $C_xH_{12} = (0.6 - a)$ mol; mass of C in a mol of $C_xH_{12} = 12ax$ g; mass of C in $(0.6 - a)$ mol of $C_xH_{12} = 12 \times (0.6 - a)$ g

$\therefore$ Total mass of C in mixture $= 12ax + 12x\,(0.6 - a)$ g

$= 41.4$ g

$$\%\text{ of } C \text{ in mixture} = \frac{7.2x}{41.4} \times 100$$

Given % of C = 87%

$$\text{or } \frac{720x}{41.4} = 87 \text{ or } x = 5$$

12. (5) $r_g = \frac{1}{5}.r_{H_2}$

$$\frac{M_g}{M_{H_2}} = \left[\frac{r_{H_2}}{r_g}\right]^2 = (5)^2 = 25; M_g = 2 \times 25 = 50$$

$10\,y = 50 \Rightarrow y = 5$

13. (8) $\frac{r_{CH_4}}{r_x} = 2 = \sqrt{\frac{M_x}{M_{CH_4}}} = \sqrt{\frac{M_x}{16}}$, or $M_x = 64$

$8\,y = 64 \Rightarrow y = 8$

14. (4) v_{rms} of $X = \sqrt{\frac{3RT_x}{M_x}}$; v_{mp} of $Y = \sqrt{\frac{2RT_y}{M_y}}$

Given $v_{rms} = v_{mp}$

$$\Rightarrow \sqrt{\frac{3RT_x}{M_x}} = \sqrt{\frac{2RT_y}{M_y}}$$

$$\Rightarrow M_y = \frac{2RT_yM_x}{3RT_x} = \frac{2 \times 60 \times 40}{3 \times 400} = 4$$

15. (c) The curve representing the gas-liquid equilibrium ends at the *dark* point, the critical point. Above the temperature corresponding to this point, CO_2 can not be liquefied for any value of pressure. Temperature and pressure corresponding to the *dark* point are T_c and P_c.

16. (b) At point B, liquefaction of CO_2 commences and is complete at the point C. Along the line BC the proportion of gas phase of CO_2 decreases and that of liquid phase increases, and hence the volume of the system decreases along the line BC.

17. (b) For one mole of real gas, we have

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

Under conditions of high pressure

$$P + \frac{a}{V^2} \approx P$$

$\therefore$ The above equation becomes

$P(V - b) = RT$

or $PV - Pb = RT$

or $PV = RT + Pb$

18. (d) Since the value of $b = 0$ in case of molecules to be point masses

$\therefore$ The van der Waals' equation will become

$$\left(P + \frac{an^2}{V^2}\right)(V - 0) = nRT \quad (\because b = 0, \text{so } nb = 0)$$

$$\text{or} \quad \left(P + \frac{an^2}{V^2}\right)V = nRT$$

$$\text{or} \quad PV + \frac{an^2}{V} = nRT \quad \text{or} \quad PV = nRT - \frac{an^2}{V}$$

19. A-q; B-p, C-s; D-r

(A) At temperature $< T_i$, $\mu_{JT} = \left[\left(\frac{dT}{dP}\right)_H\right]$ becomes positive, i.e. cooling effect takes place in streaming process. It suggests that the forces between the gas molecules are attractive in nature.

(B) At temperature $> T_i$, μ_{JT} is negative which suggests the existance of repulsive forces between the gas molecules.

(C) At Boyle's temperature and above, a real gas obeys gas laws over a wide range of pressure.

(D) In ideal gas the intermolecular forces do not exist. Hence Joule-Thompson effect is zero.

20. A-r; B-s; C-q; D-p

(A) Pressure correction $= \frac{an^2}{V^2}$

$$= \frac{3.6(L^2 atm\, mol^{-2})}{10^2(L^2)} \times \left(\frac{200}{40}\right)^2 (mol^2) = 0.9\text{L atm}$$

(B) Free space $= V - nb = 10 - 5 \times 0.05 = 9.75L$

(C) Actual volume of gas molecules

$$= \frac{nb}{4} = \frac{5 \times 0.05}{4} = 0.06L$$

(D) Effective volume of gas molecules

$= nb = 5 \times 0.05 = 0.25L$