Solution of Full Syllabus Examination

SET- 4

1. (a) From definition– $\lambda = \sqrt{\dfrac{RT}{\sqrt{2}\pi\sigma^2.N_A.P}}$

$$\therefore \sigma^2 = \left(\frac{0.082\times 276}{\sqrt{2}\times 3.14\times 10^{-5}\times 6.023\times 10^{23}\times 1.01}\right)\frac{\text{lit atm mol}^{-1}.\text{K}^{-1}.\text{K}^{-1}}{\text{cm}\times\text{mol}^{-1}\times\text{atm}}$$

$$\sigma^2 = 0.8379\times 10^{-18}\left(\frac{\text{lit}}{\text{cm}}\right)$$

$$= 0.8379\times 10^{-18}\left(\frac{\text{dm}^3}{\text{cm}}\right)$$

$$\sigma^2 = 0.8379\times 10^{-15}\ \text{cm}^2$$

$$\sigma^2 = 8.379\times 10^{-16}\ \text{cm}^2$$

$$\sigma = 2.89\times 10^{-8}\ \text{cm} = 2.89\ \text{Å}$$

1. (b) As $P \to 0$, $Z = a_1$

again when $P \to 0$, $Z = 1$ (for ideal behaviour)

$\therefore a_1 = 1$

Thus, $Z = 1 + a_2P + a_3P^3$

Pressure P_0 can not be (–) ve, So a_2 and a_3 should have opposite sign. Now, at P_0, $Z < 1$ (shows minima)

and $Z = 1 + a_2P_0 + a_3P_0^2$

$$= 1 - a_2 . \frac{a_2}{3a_3} - a_3 . \frac{a_2^2}{4a_3^2} = 1 - \frac{a_2^2}{2a_3} - \frac{a_3 . a_2^2}{4a_3^2}$$

$$= 1 - \frac{a_2^2}{4a_3}$$

a_2^2 is always is always (+) ve. Thus a_3 should (–) ve so that Z < 1 at temperature T_1 and P_0. So a_3 is (–) ve.

3. (a) Lennard-Jones Potential:-

It is a mathematical approximation that illustrates the energy of interactions between two non-bounding atoms or molecules based on their distance of separation.

The equation takes into account the difference between attractive forces (dipole-dipole, dipole – induced dipole, and London interactions) and repulsive forces. The Lennard – Jones potential is given the following equation.

$$V = 4 \in \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

Where,

V = intermolecular potential between two atoms or molecules

σ = van der Waal's radius

r = Distance separating between two molecules.

3. (b) If degrees of freedom for a free molecular system be 'f' excepting the vibrational degree of freedom, at ordinary temperature then

Energy per mole (E) = $\frac{1}{2} f RT$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{1}{2} f R$$

$$C_P = C_V + R = \frac{1}{2} f R + R$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{\frac{f+2}{2}}{\frac{f}{2}} = \frac{f+2}{f} = 1 + \frac{2}{f}$$

8. (b) Thermodynamic criteria of a gas to be ideal–

(i) $\left(\frac{\partial E}{\partial V}\right)_T = 0$ (ii) $\left(\frac{\partial H}{\partial P}\right)_T = 0$ (iii) $\mu_{JT} = 0$ iv) $\Delta H_{mix} = 0$ (v) $\Delta V_{mix} = 0$

10. (b) Efficiency of engine $\eta = \frac{600-300}{600} = 0.5$

$\therefore \frac{w}{Q} = 0.5$ $\therefore$ w = 0.5 × 10^5 KJ = 0.5 × 108J

work done by the engine per sec = 1 × 10^3 J

10^3 J → 1 sec

1 J → $\frac{1}{10^3}$

$0.5\times10^8 \rightarrow \frac{0.5\times10^8}{10^3} = 0.5\times10^5$ sec time required.

12. (b) From the definition dG = VdP – SdT

at constant pressure $\int_{G_1}^{G_2} dG = -\int_{T_1}^{T_2} S.dT$

$$\Delta G = -\int_{T_1}^{T_2} (A + B\ln T)dT$$

$$= -A\int_{T_1}^{T_2} dT - B\int_{T_1}^{T_2} \ln T.dT$$

$$= -A(T_2 - T_1) - B\left[(T_2 \ln T_2 - T_2) - (T_1 \ln T_1 - T_1)\right]$$

$$= -A(T_2 - T_1) - BT_2 \ln T_2 + BT_2 + BT_1 lbnT_1 - BT_1$$

$$= -A(T_2 - T_1) + B(T_2 - T_1) - B[T_2 \ln T_2 - T_1 \ln T_1]$$

$$= (T_2 - T_1)(B - A) - B[T_2 \ln T_2 - T_1 \ln T_1]$$

$$= (400 - 300)(30 - 25) - 30[400 \ln 400 - 300 \ln 300]$$

$\Delta G = 500 - 30 \times 685.45$

$\Delta G = -20063.5J$

13. Let the temperature of hot reservoir be T.

$$\therefore \frac{T - 298}{T} = 0.4 \quad \therefore T = \frac{298}{0.6} = 496.67K$$

To have 50% efficiency let the temperature of the reservoir be T'.

$$\therefore \frac{T' - 298}{T'} = 0.5 \text{ or } T' = 596K$$

So, the temperature of the hot reservoir is to be increased by (596 – 496.67)K

= 99.33K.

15. (a) Let us consider a reversible reaction, $A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$. Where K_1 and K_{-1} are the specific rates for forward and backward reaction respectively.

Equilibrium constant $K = \frac{K_1}{K_{-1}} \quad \therefore K = \frac{A_1.e^{-E_1/RT}}{A_2.e^{-E_2/RT}}$

$$\therefore K = \frac{A_1}{A_2}.e^{-(E_1 - E_2)/RT}$$

A constant catalyst reduces the activation energy by x, so that the activation energy now is (E_1 – x). Similarly, activation energy for backward rxn is (E_2 – x). There is no reason for the change in frequency factor (A).

$\therefore$ Equilibrium constant of the catalyzed reaction

$$K_c = \frac{A_1^c}{A_2^c}.e^{-\left[\frac{(E_1-x)-(E_2-x)}{RT}\right]} = \frac{A_1}{A_2}.e^{-\frac{(E_1-E_2)}{RT}} = K$$

$\therefore$ $K_c = K$; the equilibrium position is not changed.