



Solution of Full Syllabus Examination

SET- 2

1.

$$(a) \lambda = \frac{1}{\sqrt{2\pi\sigma^2 N^*}} = \frac{V}{\sqrt{2\pi\sigma^2} \cdot N}$$

When $V = \text{constant}$; λ becomes constant; λ independent on temperature.

$$(b) (Z_{AA})_1 = \frac{1}{\sqrt{2}} \pi \sigma \langle C \rangle N^* = 1 \times 10^{28} \text{ cm}^3 \text{ s}^{-1} \\ = \frac{1}{\sqrt{2}} \pi \sigma^2 \cdot \sqrt{\frac{8RT}{\pi m}} \left(\frac{N_A P}{RT} \right)^2 \therefore (Z_{AA})_1 \propto P^2$$

$$\frac{(Z_{AA})_2}{(Z_{AA})_1} = \left(\frac{P_2}{P_1} \right)^2 = (2)^2 = 4$$

$$\therefore (Z_{AA})_2 = 2 \times (Z_{AA})_1 = 4 \times 10^{28} \text{ cm}^3 \text{ s}^{-1}$$

2.

(b) Average momentum = $m \cdot \langle c \rangle$

$$\text{according to condition: } 32 \times \sqrt{\frac{8RT_{O_2}}{\pi \times 32}} = 28 \times \sqrt{\frac{8R \times 269K}{\pi \times 28}}$$

$$(32)^{\cancel{2}} \frac{\cancel{8}RT_{O_2}}{\cancel{\pi} \times \cancel{32}} = (28)^{\cancel{2}} \times \frac{\cancel{8}R \times 269}{\cancel{\pi} \times \cancel{28}} \text{ (squaring both sides).}$$



$$T_{O_2} = \frac{28 \times 269}{32} = 235.37K = -37.62^\circ C.$$

7.

(b) Hints: For isothermal process $dT = 0$ and for free expansion $w = 0$.

From 1st law of thermodynamics $dE = dq + dw$

or, $q = \Delta E - w$ (for finite change)

$q = 0$ (This is adiabatic condition)

9.

(b) For step 1:- $\Delta V = (+)$ ve (as expansion); $\Delta P = 0$ (isobaric)

$\Delta T = +$ ve (as increase in volume at constant P will be attended by increase in temperature)

$$\Delta S = (+) \text{ ve } (\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) \quad V_2 > V_1).$$

For step 2:- $\Delta V = (+)$ ve; $\Delta S = 0$ (adia. rev process)

$\Delta E = (-)$ ve; $\Delta T = (-)$ ve; $\Delta P = (-)$ ve

For step 3:- Sign of various quantities will just be opposite in step 1.

For step 4:- Sing of various quantities will be just opposite in step II.

10.

(a) See note: TQ. 2.74

(b) See note: TQ. 2.75

12.

(a) See note: (Thermodynamics)

13.



$$(b) w = -P_{\text{ext}} (V_g - V_l) \approx -P_{\text{ext}} V_g = -nRT$$

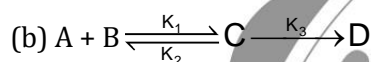
assuming ideal behaviour of vapour and $V_{\text{vap}} \gg V_{\text{liq}}$

$$W = -\left(\frac{100\text{g}}{18\text{g.mol}^{-1}}\right) (1.987 \text{ cal. k}^{-1} \text{ mol}^{-1}) 373 = -4117.5 \text{ cal.}$$

$$Q = (100\text{g}) (540 \text{ cal. gm}^{-1}) = 54000 \text{ cal.}$$

$$\begin{aligned} \Delta E &= Q + w = 54000 - 41174.5 \text{ cal} \\ &= 4982.5 \text{ cal.} \end{aligned}$$

14.



$$\text{Rate} = k_3 [C],$$

$$\text{Now, } \frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C]$$

$$\text{applying steady state approximation } \frac{d[C]}{dt} = 0$$

$$\therefore [C] = \frac{k_1}{k_2 + k_3} [A][B]$$

$$\therefore \text{Rate} = \frac{k_3 k_1}{k_2 + k_3} [A][B]$$

15. (a) Let the order be (n).

For nth order rxn, we get

$$K = \frac{1}{t(n-1)} \left\{ [A]^{1-n} - [A]_0^{1-n} \right\}$$

$$\text{K.t. } (n-1) = [A]^{1-n} - [A]_0^{1-n}$$



$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{1-n}} = K.t (n - 1)$$

For $n = 2$, we get $\frac{1}{[A]} = \frac{1}{[A]_0} + Kt$ which gives above potential.

\therefore This is 2nd order reaction.

From this equation we get, slope = $K = 3 \times 10^{-2} \text{ lit mol}^{-1}\text{s}^{-1}$ and intercept = $\frac{1}{[A]_0} = \frac{1}{100} =$

0.01 mol. lit⁻¹

Half life period of 2nd order reaction is given by

$$t_{1/2} = \frac{1}{K[A]_0} = \frac{1}{3 \times 10^{-2} \times 0.01} \text{ sec} = 3333.33 \text{ sec}$$

16.

(b) For 2nd order rxn: $t = \frac{1}{K} \cdot \frac{x}{a(a-x)}$ and $t_{1/4} = \frac{1}{k} \cdot \frac{a/4}{a(a-a/4)} = \frac{1}{3ka}$

again, $t_{1/2} = \frac{1}{ka}$ (for 2nd order)

$$\therefore \frac{t_{1/2}}{t_{1/4}} = 3 \quad \therefore t_{1/2} = 3 \times t_{1/4} = 3 \times 30 \text{ min} = 90 \text{ min.}$$

$$\text{again, } K = \frac{1}{t_{1/2}} \times \frac{1}{a} = \frac{1}{90} \times \frac{1}{200/760} = 0.0422 \text{ atm. min}^{-1}.$$