

Q.1 a) At 1100 K n-nonane thermally cracks 20 times as rapidly as at 1000 K. Estimate the activation energy for this decomposition.

$$T_2 = 1100 \text{ K.}$$

$$T_1 = 1000 \text{ K.}$$

$$r_2 = 20 r_1$$

$$\ln \left(\frac{r_2}{r_1} \right) = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \left(\frac{20 r_1}{r_1} \right) = \frac{E}{8.314} \left[\frac{1}{1000} - \frac{1}{1100} \right]$$

$$E = 273973 \text{ J/mol.}$$

$$E = 274 \text{ KJ/mol.}$$

Q.1 b) In case of a first order reaction show that the time required for 75% conversion is double the time required for 50% conversion.

For first order reaction.

$$- \frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} = k C_A = k C_{A0} (1 - X_A)$$

$$- \ln (1 - X_A) = kt.$$

For 50% conversion time required is t_1

$$- \ln (1 - 0.5) = kt_1 \quad \text{--- (1)}$$

For 75% conversion time required is t_2

$$\therefore - \ln (1 - 0.75) = kt_2 \quad \text{--- (2)}$$

Dividing eqⁿ (2) by (1).

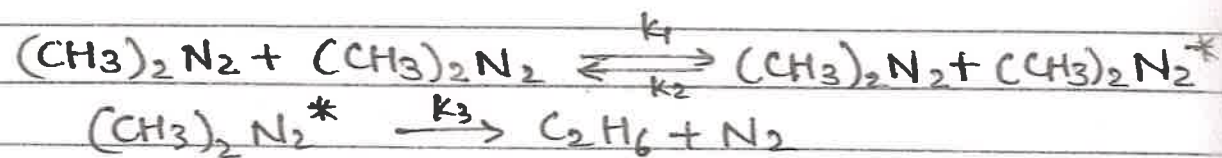
$$\frac{t_2}{t_1} =$$

$$\therefore t_2 = 2 t_1$$

Thus the time required for 75% conversion is double the time required for 50% conversion.

2

Q.2a)



$$r_{\text{N}_2} = k_3 C_{(\text{CH}_3)_2\text{N}_2^*}$$

By PSSH $r_{(\text{CH}_3)_2\text{N}_2^*} = 0$.

$$r_{\text{Azomethane}^*} = 0$$

$$r_{\text{Azomethane}^*} = k_1 C_{\text{Azo}}^2 - k_2 C_{\text{Azo}} \cdot C_{\text{Azo}}^* - k_3 C_{\text{Azo}}^*$$

$$k_1 C_{\text{Azo}}^2 = C_{\text{Azo}}^* [k_2 C_{\text{Azo}} + k_3]$$

$$C_{\text{Azo}}^* = \frac{k_1 C_{\text{Azo}}^2}{[k_3 + k_2 C_{\text{Azo}}]}$$

$$\therefore r_{\text{N}_2} = \frac{k_3 \cdot k_1 C_{\text{Azo}}^2}{[k_3 + k_2 C_{\text{Azo}}]}$$

$$r_{\text{N}_2} = \frac{k_1 C_{\text{Azo}}^2}{1 + (k_2/k_3) C_{\text{Azo}}}$$

$$\therefore r_{\text{N}_2} = \frac{k_1 C_{\text{Azo}}^2}{1 + k_1' C_{\text{Azo}}} \quad \because \frac{k_2}{k_3} = k_1'$$

So the suggested mechanism agrees with the observed rate / experimental rate.

$$r_{\text{N}_2} = \frac{k_1 k_3 C_{\text{Azo}}^2}{k_3 + k_2 C_{\text{Azo}}}$$

At low concentrations.

$$k_2 C_{\text{Azo}} \ll k_3$$

$$r_{\text{N}_2} = k_1 C_{\text{Azo}}^2$$

Q.2b)

Temp (K)	298	308	318	328	338
k sec ⁻¹	1.74 × 10 ⁻⁵	6.61 × 10 ⁻⁵	2.51 × 10 ⁻⁴	7.59 × 10 ⁻⁴	2.40 × 10 ⁻³

$$k \propto e^{-E/RT}$$

$$k = k_0 e^{-E/RT}$$

$$\ln k = \ln k_0 - \frac{E}{RT}$$

Plot a graph of $\ln k$ vs $\frac{1}{T}$

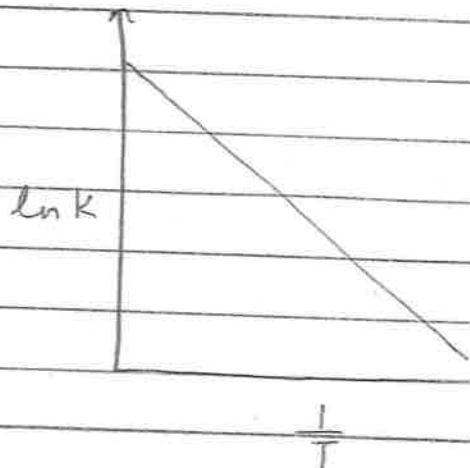
$$\text{Slope} = -E/R$$

$$E = ?$$

$$\text{Intercept} = \ln k_0$$

$$k_0 = ?$$

T (K)	$\frac{1}{T}$	k	$\ln k$
298	0.003356	1.74 × 10 ⁻⁵	-10.45
308	0.00324	6.61 × 10 ⁻⁵	-9.62
318	0.003145	2.51 × 10 ⁻⁴	-8.29
328	0.003049	7.59 × 10 ⁻⁴	-7.18
338	0.002959	2.40 × 10 ⁻³	-6.03



$$y = -8 \times 10^{-5} x + 0.0025$$

$$\text{Slope} = -\frac{E}{R} = -8 \times 10^{-5}$$

$$E = 8 \times 10^{-5} \times 8.314$$

$$= 66.512 \times 10^{-5} \text{ J/mol}$$

$$\text{Intercept} = \ln k_0 = 0.0025$$

$$k_0 =$$

Q.3 a)



Constant Volume batch Reactor

$$P_{A0} = 1 \text{ atm} \quad P_0 = 1 \text{ atm} = \pi_0$$

$$t = 3 \text{ min}$$

$$\pi = P = 1.40 P_0 = 1.4 \times 1 = 1.4 \text{ atm}$$

$$P_A = P_{A0} - \frac{a}{\Delta n} (\pi - \pi_0)$$

$$= 1 - \frac{2}{1} (1.40 - 1)$$

$$= 0.2 \text{ atm}$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

$$\frac{RT}{P_A} - \frac{RT}{P_{A0}} = kt$$

$$k = \frac{RT \left[\frac{1}{P_A} - \frac{1}{P_{A0}} \right]}{t}$$

$$k = \frac{RT \left[\frac{1}{0.2} - \frac{1}{1} \right]}{3}$$

$$k = 1.333 RT$$

$$P_A = P_{A0} (1 - X_A)$$

$$0.2 = 1 (1 - X_A)$$

$$X_A = 0.8$$

For varying volume batch reactor.

For second order.

$$\frac{(1 + \epsilon_A) X_A}{1 - X_A} + \epsilon_A \ln(1 - X_A) = k C_{A0} t$$



$$\epsilon_A = \frac{3 - 2}{2} = 0.5$$

5

$$\therefore \frac{(1+0.5)}{(1-0.8)} \times 0.8 + 0.5 \ln(1-0.8) = 1.333 RT \times \frac{1}{RT} \times t$$

$$\therefore t = 3.906 \text{ min.}$$

$$V = V_0 (1 + \epsilon_A X_A)$$

$$V = V_0 [1 + (0.5) \times 0.8]$$

$$V = 1.4 V_0.$$

$$\text{Fractional increase in volume} = \frac{V - V_0}{V_0}$$

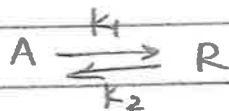
$$= \frac{1.4 V_0 - V_0}{V_0}$$

$$= 0.4$$

$$\therefore \% \text{ increase in volume } 40\%$$

6

Q-3b)



$$C_{A0} = 0.50 \text{ mol/lit.}$$

$$C_{R0} = 0$$

$$x_A = 0.33$$

$$x_{Ae} = 0.667$$

$$M = \frac{C_{R0}}{C_{A0}} = 0$$

The integrated rate equation for 1st order.

$$-\ln \left[1 - \frac{x_A}{x_{Ae}} \right] = \frac{M+1}{M+x_{Ae}} k_1 t$$

$$-\ln \left[1 - \frac{0.333}{0.667} \right] = \frac{1}{0.667} k_1 (8)$$

$$k_1 = 0.0577 \text{ (min}^{-1}\text{)}$$

$$k_c = \frac{C_{Re}}{C_{Ae}} = \frac{M+x_{Ae}}{1-x_{Ae}} = \frac{k_1}{k_2}$$

$$\frac{k_1}{k_2} = \frac{0+0.667}{1-0.667}$$

$$k_2 = k_1 (1-0.667)/(0.667)$$

$$k_2 = 0.0288 \text{ (min}^{-1}\text{)}$$

Therefore, the rate equation is.

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A - k_2 C_R$$

$$-r_A = (0.0577 \text{ min}^{-1}) C_A - (0.0288 \text{ min}^{-1}) C_R \quad \frac{\text{mol}}{\text{lit} \cdot \text{min}}$$

Q.4a)



$$-r_A = (10/hz) C_A$$

The volume of PFR is given by.

$$V = \frac{F_{A0}}{k C_{A0}} \left[(1 + \epsilon_A) \ln \frac{1}{1 - x_A} - \epsilon_A x_A \right]$$

Evaluating the individual terms in this expression gives

$$F_{A0} = 40 \text{ mol/hz}$$

$$k = 10 / \text{hz}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{460000 \text{ Pa}}{(8.314 \text{ Pa} \cdot \text{m}^3 / \text{mol} \cdot \text{K}) (922 \text{ K})} = 60 \text{ mol/m}^3$$

$$\epsilon_A = \frac{7-4}{4} = 0.75$$

$$x_A = 0.8$$

hence the volume of reactor is.

$$\begin{aligned} V &= \frac{40}{(10)(60)} \left[(1 + 0.75) \ln \frac{1}{0.2} - (0.75)(0.8) \right] \\ &= 0.148 \text{ m}^3 \\ &= 148 \text{ liters} \end{aligned}$$

Q. 4b)



$$k_1 = k_2 = k$$

$$-\frac{dC_A}{dt} = k C_A$$

$$\ln \frac{C_{A0}}{C_A} = kt$$

$$C_A = C_{A0} e^{-kt}$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

$$\frac{dC_R}{dt} + k_2 C_R = k C_A = k C_{A0} e^{-kt}$$

$$\frac{dy}{dx} + Py = Q$$

$$IF = e^{\int P dx} = e^{\int k dt} = e^{kt}$$

∴ complete solution:

$$y e^{\int P dx} = \int Q e^{\int P dx} dx + C$$

$$C_R e^{\int k dt} = \int k C_{A0} e^{-kt} e^{\int k dt} dt + C$$

$$C_R e^{kt} = k C_{A0} t + C$$

$$\text{at } t=0 \quad C_R = C_{R0} = 0$$

$$C_R e^{kt} = k C_{A0} t$$

$$\therefore C_R = \frac{k C_{A0} t}{e^{kt}}$$

$$\frac{dC_R}{dt} = 0$$

$$\therefore e^{kt} - kt e^{kt} = 0$$

$$\therefore \boxed{t_{\max} = \frac{1}{k}}$$

$$\therefore C_{R \max} = \frac{k \cdot C_{A0} (1/k)}{e^{k(1/k)}} = \frac{C_{A0}}{e}$$

9

$$0.85 = \frac{30 \Delta T}{-(-6000)}$$

$$X_A = \frac{C_p \Delta T}{-\Delta H_R}$$

$$\Delta H_R = -6000 \text{ cal/mol}$$

$$= -6 \text{ kcal/mol} = -6000 \text{ cal/mol}$$

$$= -41 - [(-20) + (-15)]$$

$$\Delta H_R = 1 \times \Delta H_{fc} - (1 \times \Delta H_A^\circ + 1 \times \Delta H_B^\circ)$$

$$\Delta H_{RT} = \Delta H_R \quad \text{as } \Delta C_p = 0$$

$$\Delta H_{RT} = \Delta H_R + \Delta C_p (T - T_0)$$

$$\Delta C_p = 30 - (15 + 15) = 0$$

$$X_A = \frac{C_p \Delta T}{-\Delta H_R}$$

$$\eta = \frac{1.93 \times 10^5 e^{-5033/T} (C_{A0} (1 - X_A))^2}{X_A}$$

$$k = 1.93 \times 10^5 e^{-5033/T}$$

$$\ln k = 12.17 - \frac{5033}{T}$$

$$\ln k(T) = \frac{-10,000}{T} = \frac{1.987}{T} \left[\frac{1}{1} \right]_{300}$$

$$\ln \left[\frac{k(T)}{k(300)} \right] = -\frac{R}{E} \left[\frac{1}{T} \right]_{300}$$

$$\ln \left(\frac{k_2}{k_1} \right) = -\frac{R}{E} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\eta = \frac{C_{A0} X_A}{X_A} = \frac{k C_{A0} (1 - X_A)^2}{X_A}$$

Material balance for MFR

$$= k C_A^2 = k C_{A0}^2 (1 - X_A)^2$$

$$-r_A = k C_A^2$$



(9.5a)

$$\Delta T = 170 \text{ K}$$

$$\Delta T = T_2 - T_1$$

$$\therefore T_2 = \Delta T + T_1 = 170 + 300 = 470 \text{ K}$$

$$\tau = \frac{X_A}{1.93 \times 10^5 e^{-5033/T} \cdot C_{A0}(1-X_A)^2}$$

$$\tau = \frac{0.85}{1.93 \times 10^5 e^{-5033/470} \cdot 0.1(1-0.85)^2} = 87.56 \text{ sec}$$

$$\tau = \frac{V}{V_0} = \frac{V}{2}$$

$$\therefore V = \tau V_0 = 87.56 \times 2$$

$$V = 175.12 \text{ lit}$$

Q.56) compute K_y at 10 atm if K_p at this pressure is 0.0038 atm^{-1} for the ammonia synthesis reaction from hydrogen and nitrogen at 500°C .



$$K_p = 0.00381 \text{ atm}^{-1}$$

The relationship between K_p and K_y is

$$K_p = K_y P^{\Delta n}$$

$$K_y = \frac{K_p}{P^{\Delta n}}$$

$$\Delta n = 2 - (1+3) = -2$$

$$\therefore K_y = \frac{0.00381}{(10)^{-2}} = 0.381$$