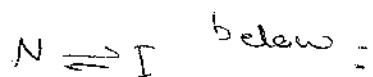


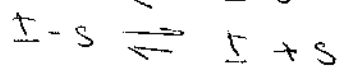
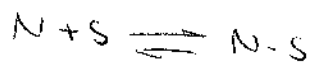
Q.1 The rate law for isomerization of n-pentene (N) to i-pentene (I) over alumina



$$-r_N = \frac{k (C_N - C_I/k_c)}{(1 + K_N C_N + K_I C_I)^2}$$

Suggest the mechanism which agree the rate law.

① The first mechanism :-



let be the limiting step its surface reaction

$$r_a = k_a [C_N C_{S_e} - \frac{1}{K_a} C_N^-]$$

$$r_s = k_s [C_N - \frac{1}{K_s} C_I^-]$$

$$r_d = -k_d [C_I C_{S_e} - \frac{1}{K_d} C_I^-]$$

$$K_c = \frac{C_I}{C_N} = \frac{C_I^- / K_d C_{S_e}}{C_N / K_a C_{S_e}} = \frac{C_I^-}{C_N} \times \frac{K_a}{K_d} \Rightarrow K_s = \frac{K_a}{K_d}$$

$$C_N = K_a C_N C_{S_e} \Rightarrow C_N = \frac{C_N^-}{K_a C_{S_e}}$$

$$K_s = C_I^- / C_N$$

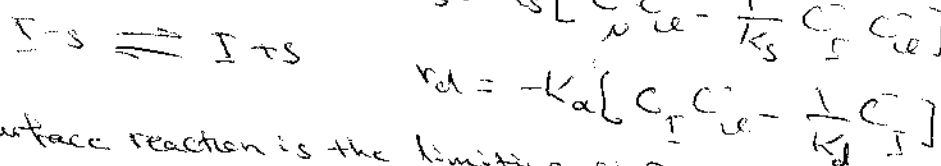
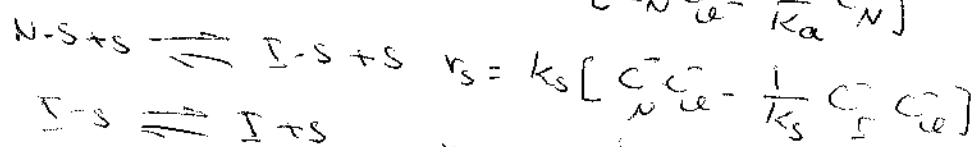
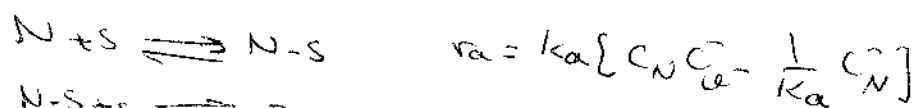
$$C_I^- = K_d C_I C_{S_e} \Rightarrow C_I^- = \frac{C_I^-}{K_d C_{S_e}}$$

$$C_m = C_{S_e} + C_N^- + C_I^- = C_{S_e} + K_a C_N C_{S_e} + K_d C_I C_{S_e} = C_{S_e} [1 + K_a C_N + K_d C_I]$$

$$\begin{aligned} \therefore r_s &= \frac{1}{K_s} \left[K_a C_N C_{S_e} - \frac{K_d C_{S_e} C_I}{K_s} \right] = \frac{1}{K_s} C_{S_e} \left[K_a C_N - \frac{K_d}{K_s} C_I \right] \\ &= \frac{k_s \times C_m \times K_a \left[C_N - \frac{K_d}{K_s K_a} C_I \right]}{[1 + K_a C_N + K_d C_I]} = \frac{k_s C_m \times K_a \left[C_N - \frac{1}{K_{eq}} C_I \right]}{[1 + K_a C_N + K_d C_I]} \end{aligned}$$

The last equation don't agree with the suggest equation so must be change the rate limiting for the same mechanism - but the adsorption and desorption when take it the limiting step don't agree with the suggest mechanism. So must change the mechanism.

② The second mechanism :-



Let be the surface reaction is the limiting step.

$$C_N = K_a C_N C_{Ue} \Rightarrow C_N = C_N / K_a C_{Ue}$$

$$K_s = \frac{C_I^- C_{Ue}}{C_N C_{Ue}} = \frac{C_I^-}{C_N}$$

$$C_I^- = K_d C_I C_{Ue} \Rightarrow C_I = C_I / K_d C_{Ue}$$

$$K_{eq} = \frac{C_I}{C_N} = \frac{C_I / K_d C_{Ue}}{C_N / K_a C_{Ue}} = \frac{C_I}{C_N} \times \frac{K_a}{K_d} = K_s \frac{K_a}{K_d}$$

$$\therefore C_m = (C_{Ue} + K_a C_N C_{Ue} + K_d C_I C_{Ue}) \Rightarrow C_{Ue} [1 + K_a C_N + K_d C_I]$$

$$\therefore r_s = k_s [K_a C_N C_{Ue} - \frac{1}{K_s} K_d C_I C_{Ue}]$$

$$r_s = k_s C_{Ue}^2 [K_a C_N - \frac{K_d}{K_s} C_I]$$

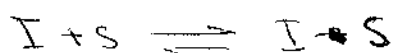
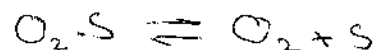
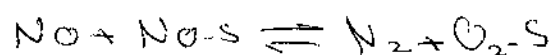
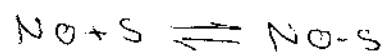
$$r_s = \frac{k_s K_a C_{Ue}^2 [C_N - \frac{1}{K_s K_a} C_I]}{[1 + K_a C_N + K_d C_I]^2}$$

$$= \frac{k_s K_a C_m^2 [C_N - \frac{1}{K_e} C_I]}{[1 + K_a C_N + K_d C_I]^2} = \frac{k [C_N - \frac{1}{K_e} C_I]}{[1 + K_a C_N + K_d C_I]^2}$$

The equation agree with the original equation so the ~~rate~~ limiting step is the surface reaction and its according to 2nd mechanism.

Q.2

The Following heterogeneous reaction is taking place in a system in which there is an inert adsorbing gas (inhibitor) present:



Develop the rate assuming that surface reaction is limiting.

Solution :-

$$r_a = k_a [C_{\text{NO}} C_{\text{S}} - \frac{1}{K_a} C_{\text{NO-S}}] \text{ ---- (1)}$$

$$r_s = k_s [C_{\text{NO}} C_{\text{NO-S}} - \frac{1}{K_s} C_{\text{N}_2} C_{\text{O}_2\text{-S}}] \text{ ---- (2)}$$

$$r_d = -k_d [C_{\text{O}_2\text{-S}} C_{\text{S}} - \frac{1}{K_d} C_{\text{O}_2}] \text{ ---- (3)}$$

$$r_i = k_i [C_{\text{I}} C_{\text{S}} - \frac{1}{K_i} C_{\text{I-S}}] \text{ ---- (4)}$$

$$C_{\text{NO-S}} = K_a C_{\text{NO}} C_{\text{S}}$$

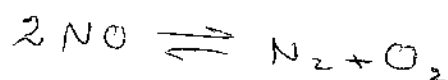
$$C_{\text{NO}} = \frac{C_{\text{NO-S}}}{K_a C_{\text{S}}}$$

$$C_{\text{O}_2\text{-S}} = K_d C_{\text{O}_2} C_{\text{S}}$$

$$C_{\text{O}_2} = \frac{C_{\text{O}_2\text{-S}}}{K_d C_{\text{S}}}$$

$$C_{\text{I-S}} = K_i C_{\text{I}} C_{\text{S}}$$

From the mechanism, the overall equation is:



$$\text{So the } K_{eq} = \frac{C_{\text{N}_2} \times C_{\text{O}_2}}{C_{\text{NO}}^2} \Rightarrow \frac{C_{\text{N}_2} \times C_{\text{O}_2} / K_d C_{\text{S}}}{C_{\text{NO}}^2 / K_a^2 C_{\text{S}}^2}$$

$$K_{eq} = \frac{C_{\text{N}_2} \times C_{\text{O}_2}}{C_{\text{NO}} \times C_{\text{NO}}} \times \frac{K_a \times K_a \times C_{\text{S}}}{K_d}$$

$$\text{where } C_{\text{NO}} = \frac{C_{\text{NO-S}}}{K_a C_{\text{S}}}$$

$$\therefore K_{eq} = \frac{C_{\text{N}_2} \times C_{\text{O}_2}}{C_{\text{NO}} \times C_{\text{NO}}} \times \frac{K_a}{K_d}$$

From the surface reaction

$$K_s = \frac{C_{\text{N}_2} \times C_{\text{O}_2}}{C_{\text{NO}} \times C_{\text{NO}}}$$

$$\therefore K_{eq} = K_s \times \frac{K_a}{K_d}$$

(1)

(3)

$$C_m = C_u + C_{NO} + C_{O_2} + C_I$$

$$= [C_u + K_a C_{NO} C_u + K_d C_{O_2} C_u + K_I C_I C_u]$$

$$C_m = C_u [1 + K_a C_{NO} + K_d C_{O_2} + K_I C_I]$$

$$\therefore r_s = k_s \left[C_{NO} * K_a C_{NO} C_u - \frac{1}{K_s} C_{N_2} * K_d C_{O_2} C_u \right]$$

$$r_s = k_s C_u \left[K_a C_{NO}^2 - \frac{K_d}{K_s} C_{N_2} C_{O_2} \right]$$

$$r_s = \frac{k_s C_m K_a \left[C_{NO}^2 - \frac{K_d}{K_a - K_s} C_{N_2} C_{O_2} \right]}{[1 + K_a C_{NO} + K_d C_{O_2} + K_I C_I]}$$

$$r_s = \frac{k_s C_m K_a \left[C_{NO}^2 - \frac{1}{K_{eq}} C_{N_2} C_{O_2} \right]}{[1 + K_a C_{NO} + K_d C_{O_2} + K_I C_I]}$$

Q. 3

Evaluate the concentration difference for SO_2 between bulk gas and Pellet surface and comment on the significance of external diffusion. Neglect possible temperature differences. The reactor consists of a fixed bed of $\frac{1}{8} \times \frac{1}{8}$ in cylindrical pellets through which the gases passed at a superficial mass velocity of 147 lb/hr-ft² and at a pressure of 790 mm Hg. The temperature of the catalyst pellets was 480°C and the bulk mixture contained 6.42 mole % SO_2 and 93.58 mole % air. The external area of the catalyst pellets is 5.12 ft²/lb material.

Mean Conversion of SO_2	r, g moles SO_2 /hr.g catalyst	P_b atm		
		SO_2	SO_3	O_2
0-1	0.0956			
0-6	0.0189	0.0603	0.0067	0.201
		0.0273	0.0409	0.187

Solution

At 480°C the viscosity of air is about 0.09 lb/hr-ft. The Partical diameter to employ is the diameter of the sphere with the same area as that of the cylindrical pellets. Hence πd_p^2 will equal the sum of the areas of the lateral and end surfaces of the cylinder:

$$\pi d_p^2 = \pi dL + 2 \frac{\pi d^2}{4} = \pi \frac{1}{96} \left(\frac{1}{96} \right) + 2 \frac{\pi}{4} \left(\frac{1}{96} \right)^2$$

$$d_p^2 = \frac{3}{2} \left(\frac{1}{96} \right)^2 \pi$$

$$d_p = 0.0128 \text{ ft}$$

$$Re = \frac{d_p G}{\mu} = \frac{0.0128(147)}{0.09} = 21$$

$$\text{From Fig } j_D = 0.37$$

$$C_b - C_s = \frac{r_p}{a_m} \frac{(M/P_D)^{2/3}}{j_D G / \mu}$$

To estimate the diffusivity for SO_2 -air mixture is

From table 1 for air

$$\frac{C}{K_B} = 97 \text{ K} \quad G = 3.617 \text{ A}^\circ$$

and for SO_2

$$\frac{C}{K_B} = 252 \text{ K} \quad G = 4.29 \text{ A}^\circ$$

$$G_{AB} = \frac{1}{2} (3.617 + 4.29) = 3.953$$

$$C_{AB} = K_B [97(252)]^{\frac{1}{2}}$$

At the temperature of 480°C

$$\frac{K_B T}{C_{AB}} = \frac{K_B (753)}{K_B [97(252)]^{\frac{1}{2}}} = 4.8$$

and so from table

$$D_{\text{SO}_2\text{-air}} = 0.001853 \frac{753^{3/2} \left[\frac{1}{64} + \frac{1}{28} \right]^{1/2}}{\frac{790}{760} \times (3.953)^2 \times 0.85} = 0.285 \text{ cm}^2/\text{sec} \quad \text{or } 1.1 \text{ ft}^2/\text{hr}$$

The density of air will be

$$\frac{28.9}{359} \left[\frac{273}{480+273} \right] \left(\frac{790}{760} \right) = 0.0304 \text{ lb/ft}^3$$

then the Schmidt group is

$$\frac{\mu}{\rho D} = \frac{0.09}{0.0304 \times 1.1} = 2.69$$

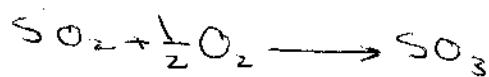
$$C_b - C_s = \frac{0.0956}{5-12} \left(\frac{2.69 \times \frac{2}{3}}{0.37 \times \frac{147}{0.0304}} \right) = 2.02 \times 10^{-5} \frac{\text{lb mole}}{\text{ft}^3}$$

The numerical results are meaningful if they are converted to Partial pressures -

$$(P_b - P_s)_{\text{SO}_2} = R_g T [C_b - C_s] = 0.73 [1.8(480+273)] 2.02 \times 10^{-5} = 0.02 \text{ atm}$$

Q. 4

Suppose that only the fluid temperature had been measured in the previous example - what error would have been introduced by assuming this to be equal to the catalyst temperature?



The heat of reaction is approximately $-23,000 \text{ Cal/g mole}$ at 480°C , and the activation energy may be taken as $20,000 \frac{\text{Cal}}{\text{g mole}}$

Solution

$$T_s - T_b = \frac{r_p (-\Delta H)}{h a_m}$$

Expressing h in terms of j_H and using Eq

$$j_H = \frac{h}{c_p G} \left(\frac{c_p M}{k} \right)^{2/3} = f \left(\frac{Pr}{Re} \right)$$

$$\text{So } T_s - T_b = \frac{r_p}{a_m} \frac{(-\Delta H) Pr^{2/3}}{j_H c_p G}$$

For air at 480°C $Pr = c_p M / k = 0.7$ and $c_p = 0.26 \frac{\text{Btu}}{\text{lb} \cdot ^\circ\text{F}}$

$Re = 21$ then from fig $j_H = 0.6$

$$\therefore T_s - T_b = \frac{0.0956}{5.12} \times \frac{23000 \times 1.8 \times (0.7)^{2/3}}{0.6 \times 0.26 \times 147} = 27^\circ\text{F or } 15^\circ\text{C}$$

Hence

$$\Theta = \frac{T_s - T_b}{T_b} = \frac{15}{738} = 0.02$$

$$\alpha = \frac{E}{R_g T_b} = \frac{20000}{1.98 \times 738} = 13.5$$

$$\gamma = e^{\alpha \Theta / (1 + \Theta)}$$

$$= e^{13.5 \times 0.02 / 1.02} = 1.3$$

Q. 5

Hydrazine has been studied extensively for use in monopropellant thrusters for space flights of long duration. For example, the thrusters are used for attitude control of communication satellites. Here the decomposition of hydrazine over a packed bed of alumina-supported iridium catalyst is of interest. In proposed study, a 20% hydrazine in 98% helium mixture is to be passed over a packed bed of cylindrical particles 0.25 cm in diameter and 0.5 cm in length at a gas-phase velocity of 15 m/s and a temperature of 750 K. The kinematic viscosity of helium at this temperature is $4.5 \times 10^{-4} \text{ m}^2/\text{s}$. The hydrazine decomposition reaction is believed to be external mass-transfer limited under these conditions. If the packed bed is 0.05 m in length, what conversion can be expected. Assume isothermal operation.

Additional data

$$D_{AB} = 0.69 \times 10^{-4} \text{ m}^2/\text{s} \text{ at } 298 \text{ K}$$

Bed porosity = 30%.

Bed fluidity 95-7%.

Solution

$$X = 1 - e^{-(K_c a / u) L}$$

A. Thoenes - Kramers Solution

$$\begin{aligned} dp &= \left(\frac{6u}{\pi} \right)^{1/3} = \left(6 \frac{\pi D^2}{4} \frac{L}{\pi} \right)^{1/3} \\ &= \left[1.5 (0.0025 \text{ m})^2 \times 0.005 \right]^{1/3} \\ &= 3.61 \times 10^{-3} \text{ m} \end{aligned}$$

Surface area per volume of bed

$$a = 6 \left(\frac{1 - \epsilon_b}{d_p} \right) = 6 \left(\frac{1 - 0.3}{3.6 \times 10^{-3}} \right) = 1166 \text{ m}^2/\text{m}^3$$

Mass transfer coefficient

$$Re = \frac{d_p u}{\nu} = \frac{3.61 \times 10^{-3} \times 15}{4.5 \times 10^{-4}} = 120.3$$

$$\gamma = \frac{2\pi r L_p + 2\pi r^2}{\pi d_p^2} = \frac{2 \times (0.0025/2) (0.005 + 2(0.0025/2)^2)}{(3.61 \times 10^{-3})^2}$$

$$= 1.2$$

$$Re^- = \frac{Re}{(1 - \epsilon_b) \gamma} = \frac{120.3}{0.7 \times 1.2} = 143.2$$

Correcting the diffusivity to 750 K

$$D_{AB}(750 \text{ K}) = D_{AB}(298) \left(\frac{750}{298} \right)^{1.75} = 0.69 \times 10^{-4} \frac{\text{m}^2}{\text{sec}} \times 5.03$$
$$= 3.47 \times 10^{-4} \text{ m}^2/\text{s}$$

$$Sc = \frac{\nu}{D_{AB}} = \frac{4.5 \times 10^{-4}}{3.47 \times 10^{-4}} = 1.3$$

$$Sh^* = (143.2)^{1/2} \times (1.3)^{1/3} = 11.97 \times 1.09 = 13.05$$

$$K_c = \frac{D_{AB}(1 - \epsilon_b)}{d_p \epsilon_b} \times Sh^* = \left(\frac{3.47 \times 10^{-4}}{3.61 \times 10^{-3}} \right) \left(\frac{1 - 0.3}{0.3} \right) \times 1.2 \times 13.05$$
$$= 3.52$$

$$x = 1 - e \left[-3.52 \times \frac{1166}{15} \times 0.05 \right] = 1 - 1.14 \times 10^{-6} \approx 1$$

B. Colburn J_D Factor: Calculate the surface-area-average Particle diameter
 For cylindrical Pellets the external surface area is.

$$A = \pi d L_p + 2\pi \left(\frac{d^2}{4}\right)$$

$$d_p = \sqrt{\frac{A}{\pi}} = \sqrt{\frac{\pi d L_p + 2\pi (d^2/4)}{\pi}}$$

$$= \sqrt{0.0025 \times 0.005 + \frac{(0.0025)^2}{2}}$$

$$= 3.95 \times 10^{-3} \text{ m}$$

$$Re = \frac{d_p u}{\nu} = \frac{3.95 \times 10^{-3} \times 15}{4.5 \times 10^{-4}} = 131.6$$

$$G_b J_D = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}$$

$$= \frac{0.765}{(131.6)^{0.82}} + \frac{0.365}{(131.6)^{0.386}} = 0.014 + 0.055$$

$$= 0.069$$

$$J_D = \frac{0.069}{0.3} = 0.23$$

$$Sh = Sc^{1/3} \cdot Re(J_D)$$

$$= (1.3)^{1/3} \times (131.6) \times 0.23 = 33.0$$

$$k_c = \frac{D_{AB}}{d_p} Sh = \frac{3.47 \times 10^{-4}}{3.95 \times 10^{-3}} (33) = 2.9 \text{ m/s}$$

then

$$X = 1 - \exp \left[(-2.9) \left(\frac{1063}{15} \right) \times 0.05 \right]$$

$$= 1 - 0.000127 \approx 1.0$$

Q. 6

The Catalytic reaction $A \rightarrow 4R$ is run at 3-2 atm and 117°C in a plug flow reactor which contains 0.01 kg of catalyst and uses a feed consisting of the partially converted product of 20 liters/hr of pure unreacted A. Suppose the following rate concentration data are available :

C_A mol/liter	0.039	0.0575	0.075	0.092
$-r_A$ mol A/hr.Kg Cat	3.4	5.4	7.6	9.1

Directly from this data, and without using a rate equation, find the size of packed bed needed to treat 2000 mol/hr of pure A at 117°C (or $C_{A0} = 0.1$ mole/liter) to 35% conversion.

Solution

$$\frac{W}{F_{A0}} = \int_0^{0.35} \frac{dx_A}{-r_A}$$

$-r_A$	$\frac{1}{-r_A}$	C_A	$X_A = \frac{1 - C_A/0.1}{1 + 3C_A/0.1}$
3.4	0.294	0.039	0.2812
5.4	0.186	0.0575	0.1563
7.6	0.1316	0.075	0.0778
9.1	0.11	0.092	0.02275

The needed $1/(-r_A)$ versus X_A data are determined in table and are plotted. Integrating graphically then gives

$$\int_0^{0.35} \frac{dx}{-r_A} = 0.0735$$

$$W = (2000 \frac{\text{mole A}}{\text{hr}}) (0.0735 \frac{\text{hr.Kg Cat}}{\text{mole A}}) = 147 \text{ Kg Cat.}$$