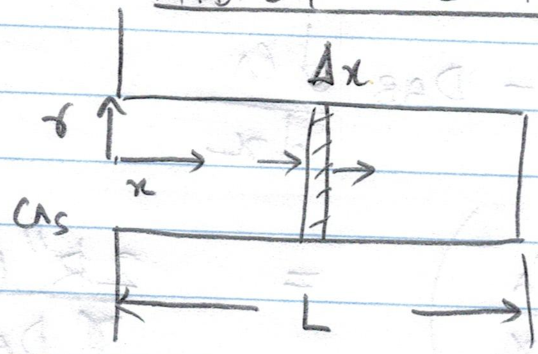
MIDSEM SOLUTIONS

1)



- Because of poisoning the surface decreases which is determined by a factor α.

Total surface area available for reaction $A = (1-\alpha) A_0$

$$A / A_0 = (1-\alpha)$$

$$-r_A'' = \frac{\text{moles}}{\text{Area } s} = \frac{\text{moles}}{A \cdot s}$$

+2

$$-r_A'' \text{(defined based on total area)} = \frac{\text{moles}}{A \cdot s} \cdot \frac{A_0}{A_0} = \frac{\text{moles}}{A \cdot s}(1-\alpha)$$

Applying mole balance on a small element Δx (pseudo-steady state)

+2

$$\pi r^2 W_{Ax}\Big|_x - \pi r^2 W_{Ax}\Big|_{x+\Delta x} - 2\pi r \Delta x \, k''(1-\alpha) C_A(x) = 0$$

$$W_{Ax} = -D_{AB}\frac{dC_A}{dx}$$

$\Delta x \rightarrow 0$

$$-\frac{d}{dx}\left(-D_{AB}\frac{dC_A}{dx}\right) = \frac{2k''(1-\alpha)}{\gamma D_{AB}} C_A$$

$$\frac{d^2\psi}{dX^2} = \frac{2k''(1-\alpha)L^2\psi}{\gamma D_{AB}}$$

$X = \frac{x}{L}$

$\psi = \frac{C_A}{C_{A_S}}$

+6

$$\phi_{1P}^{P} = L\sqrt{\frac{2k''(1-\alpha)}{\gamma D_{AB}}}$$

Thiele modulus

$$\frac{d^2\psi}{dX^2} = \phi_{1P}^2\psi$$

B.C.

$$\left.\frac{d\psi}{dX}\right|_{X=1} = 0$$

+2

$\psi = 1$ at $X = 0$

$$\rightarrow \psi = \frac{\cosh\left[\phi_{1P}^{P}(1-X)\right]}{\cosh\phi_{1P}^{P}}$$

+2

(2)

$$\eta = \frac{-D_{AB}\left.\frac{dC_A}{dx}\right|_{x=0} \cdot \cancel{\pi} r^{\cancel{2}}}{k''(1-\alpha)C_{As}\; 2\cancel{\pi}\cancel{r} L}$$

$$= \frac{-D_{AB}\frac{C_{As}}{L}\left.\frac{d\psi}{dx}\right|_{x=0}}{k''(1-\alpha)C_{As}}\frac{r}{2L}$$

$$= \frac{-D_{AB}\frac{C_{As}}{L}\left(-\phi_{1p}\tanh\phi_{1p}\right)}{k''(1-\alpha)C_{As}}\frac{r}{2L}$$

$$= \frac{D_{AB}\frac{\cancel{C_{As}}}{L}\phi_{1p}\tanh\phi_{1p}}{\frac{2k''L^2(1-\alpha)\cancel{C_{As}}}{r D_{AB}}}$$

+2

$$= D_{AB}\left[\frac{\tanh\phi_{1p}}{\phi_{1p}}\right]$$

$$\Upsilon = \frac{D_{AB}\frac{C_{As}}{L}\cdot\phi_{1p}\tanh\phi_{1p}}{D_{AB}\frac{C_{As}}{L}\phi_1\tanh\phi_1}$$

+2

$$\frac{\phi_{1p}}{\phi_1} = \sqrt{(1-\alpha)}$$

+2

$$Y = \frac{\tanh\left(\phi_1 \sqrt{1-\alpha}\right)}{\tanh \phi_1} \left(\sqrt{1-\alpha}\right)$$

$\phi_1 \longrightarrow$ small

$$\tanh \phi_1 \approx \phi_1$$

$$Y = (1-\alpha)$$

+2

$\phi_1 \longrightarrow$ large $\qquad \tanh \phi_1 \approx 1$

$$Y = \sqrt{1-\alpha}$$

③

2 a) $$(T-T_s)_{max} = \frac{-\Delta H_{rxn} D_e C_{As}}{k_e}$$

$$= \frac{80 \times 1000 \frac{J}{\cancel{mol}} \; 10^{-1} \cancel{\times 10^{-4}} \frac{\cancel{m^2}}{s} \times 4 \times 10^{-5} \, 10^{-1} \cancel{\times 10^{6}} \frac{\cancel{mole}}{\cancel{m^3}}}{\cancel{10}^{2} \times 16 \times \cancel{10^{-4}} \; J / \cancel{m} \cdot s \cdot {}^\circ C}$$

$$= \frac{\cancel{4} \times \cancel{80}^{20} \times 10 \; \frac{J}{S}}{\cancel{4}\, \cancel{16} \; J/s\,{}^\circ C}$$

+5

$= 200^\circ C$

↳ too high to neglect temperat difference in the pellet.

b) $$(T-T_s)_{max} = \frac{50 \times 1000 \times \cancel{10^{-2}} \times \cancel{4} \times 10^{-4}}{4\,\cancel{16} \times \cancel{10^{-3}}}$$

+5

$= 12.5 \; {}^\circ C$

↳ can be neglected.

3) $-r_A'(obs) = 11.7\times10^{-6}\ \frac{mol}{gm\text{-}s}$

$$C_{Ab} = \frac{-r_A'(obs)}{\Omega k_1'}$$

$\sigma_c = 1$ (uniform pore size)

$\phi_p = 0.5$

$T = 463\,k$

$P = 25\ bar$

$\tau = 5$

+3

$$C_{Ab} = \frac{11.7\times10^{-6}}{1.06\times10^{-6}}\ \frac{\frac{mol}{gm\text{-}s}}{\frac{m^3}{gm\text{-}s}}$$

$$= 11.038\ mol/m^3$$

$$D_e = \frac{D_{AB}\,\phi_p}{\tau}$$

+2

$$= 1.9\times10^{-4}\ \frac{cm^2}{s}\times\frac{0.5}{5}$$

$$= 1.9\times10^{-5}\ cm^2/s$$

$$C_W = \frac{-r_A'(obs)\,\rho_c R^2}{D_e\,C_{As}}$$

$$S_p k_c\,(C_{Ab} - C_{As}) = 11.7\times10^{-6}$$

+3

$$C_{As} = 11.038 - \frac{11.7}{17.3\times1.07}$$

$$C_{As} = 10.406\ \frac{mol}{m^3}$$

$$C_W = \frac{11.7\times10^{-6}\times(0.17)^2\times\cancel{10^{-6}}\times\cancel{10^{6}}}{1.9\times10^{-5}\times10^{-4}\times10.406}$$

+3

$$= 17.1 \quad 771$$

significant diffusion effects.

b) $$\phi = R\sqrt{\frac{k_1'' S_a \rho_c}{D_e}} = R\sqrt{\frac{k_1'\rho_c}{D_e}}$$

+3 $$\eta k_1' C_{As} = -r_A'(obs)$$

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh\phi} - \frac{1}{\phi}\right]$$

+3

+5

$$\frac{-r_A'(obs)}{k_1' C_{As}} = \frac{3}{R\sqrt{\frac{k_1'\rho_c}{D_e}}}\left[\frac{1}{\tanh R\sqrt{\frac{k_1'\rho_c}{D_e}}} - \frac{1}{R\sqrt{\frac{k_1'\rho_c}{D_e}}}\right]$$

$$\frac{-r_A'(obs)}{C_{As}} + \frac{3}{R^2}\frac{D_e}{\cancel{k_1'}\rho_c}\times\cancel{k_1'} = \frac{3}{R}\sqrt{\frac{D_e k_1'}{\rho_c}} \Big/ \tanh\left(R\sqrt{\frac{k_1'\rho_c}{D_e}}\right)$$

$$\frac{11.7\times10^{-6}}{10.406}\frac{\frac{mol}{gm\text{-}s}}{\frac{mol}{m^3}} + \frac{3}{(0.17\times10^{-3})^2}\frac{1.9\times10^{-9}}{10^6} = \ldots$$

$$1.124\times10^{-6} + 0.1972\times10^{-6} = 1.321\times10^{-6}$$

$$\frac{1.321\times10^{-6}}{3}\times 0.17\times10^{-3}\sqrt{\frac{10^{6}}{1.9\times10^{-9}}} = \frac{\sqrt{k_1'}}{\tanh\left(R\sqrt{\frac{k_1'\rho_c}{De}}\right)}$$

$$1.717\times10^{-3} = \frac{\sqrt{k_1'}}{\tanh\left(R\sqrt{\frac{k_1'\rho_c}{De}}\right)}$$

+5

$$k_1' = 2.95\times10^{-6}\ \frac{m^3}{gm\cdot s}$$

$$\phi = 0.17\times10^{-3}\sqrt{\frac{2.95\times10^{-6}\times10^{6}}{1.9\times10^{-9}}}$$

+4

$$\phi = 6.698$$

$$\eta = \frac{3}{6.698}\left(\frac{1}{\tanh(6.698)} - \frac{1}{6.698}\right)$$

$$= 0.381$$

c)

$$\Omega k_1' C_{Ab} = -r_A' \text{ (obs)}$$

$$\Omega k_1' = k' \text{ (obs)}$$

$$1.06 \times 10^{-6} = \Omega \times 2.95 \times 10^{-6}$$

$$\rightarrow \Omega = 0.359$$

+4

(5)

4) $CH_3COCH_3 + CH_3COCH_3 \xrightarrow{k_1} CH_3COCH_3 + CH_3\cdot + CH_3CO\cdot$ $E_a = 84$ kcal/mol

$CH_3CO\cdot \xrightarrow{k_2} CH_3\cdot + CO$ $E_a = 10$ kcal/mol

$CH_3\cdot + CH_3COCH_3 \xrightarrow{k_3} CH_4 + CH_3COCH_2\cdot$ $E_a = 15$ kcal/mol

$CH_3COCH_2\cdot \xrightarrow{k_4} CH_3\cdot + CH_2CO$ $E_a = 48$ kcal/mol

$CH_3\cdot + CH_3COCH_2\cdot \xrightarrow{k_5} C_2H_5COCH_3$ $E_a = 5$ kcal/mol

$$+\frac{d[CH_3COCH_3]}{dt} = -k_1[CH_3COCH_3]^2 - k_3[CH_3\cdot][CH_3COCH_3]$$

$$0 \cong \frac{d[CH_3\cdot]}{dt} = -k_3[CH_3\cdot][CH_3COCH_3] + k_1[CH_3COCH_3]^2 + k_2[CH_3CO\cdot] + k_4[CH_3COCH_2\cdot] - k_5[CH_3\cdot][CH_3COCH_2\cdot] \quad (i)$$

+5

$$0 \cong \frac{d[CH_3COCH_2\cdot]}{dt} = +k_3[CH_3\cdot][CH_3COCH_3] - k_4[CH_3COCH_2\cdot] - k_5[CH_3COCH_2\cdot][CH_3\cdot] \quad (ii)$$

$$0 \cong \frac{d[CH_3CO\cdot]}{dt} = -k_2[CH_3CO\cdot] + k_1[CH_3COCH_3]^2 \quad (iii)$$

$$[CH_3CO^\bullet] = \frac{k_1[CH_3COCH_3]^2}{k_2}$$

$$k_1[CH_3COCH_3]^2 = k_5[CH_3^\bullet][CH_3COCH_2^\bullet]$$ adding all of 3 eqn

$$[CH_3COCH_2^\bullet] = \frac{k_1[CH_3COCH_3]^2}{k_5[CH_3^\bullet]} \quad \text{(iv)}$$

adding (i) & (iii) and using (iv) we get

$$k_1[CH_3COCH_3]^2 - k_3[CH_3^\bullet][CH_3COCH_3] + \frac{k_4k_1[CH_3COCH_3]^2}{k_5[CH_3^*]} = 0$$

$$k_3k_5[CH_3^\bullet]^2 - k_1k_5[CH_3COCH_3][CH_3^*] - k_1k_4[CH_3COCH_3] = 0$$

+5

$$[CH_3^*] = \frac{k_1k_5[CH_3COCH_3] \pm \sqrt{k_1^2k_5^2[CH_3COCH_3]^2 + 4k_1k_3k_4k_5[CH_3COCH_3]}}{2k_3k_5}$$

Now,

$$k_3 [CH_3^*][CH_3COCH_3] \gg k_1 [CH_3COCH_3]^2$$

$$k_4 [CH_3COCH_2^*] \gg k_5 [CH_3^*][CH_3COCH_2^*]$$

$$k_3 k_4 \gg k_1 k_5 [CH_3COCH_3]$$

$$[CH_3^*] \approx \frac{k_1 k_5 [CH_3COCH_3] \pm 2\sqrt{\dfrac{k_1 k_3 k_4 k_5}{[CH_3COCH_3]}}}{2 k_3 k_5}$$

+5

$$[CH_3^*] \simeq \frac{\sqrt{k_1 k_3 k_4 k_5 [CH_3COCH_3]}}{k_3 k_5}$$

$$\simeq \sqrt{\frac{k_1 k_4}{k_3 k_5}} [CH_3COCH_3]^{1/2}$$

$$-\frac{d[CH_3COCH_3]}{dt} = k_1 [CH_3COCH_3]^2 + \sqrt{\frac{k_3 k_1 k_4}{k_5}} [CH_3COCH_3]^{3/2}$$

$$= k_1 [CH_3COCH_3] \left[k_1 [CH_3COCH_3] + \sqrt{\frac{k_3 k_4 [CH_3COCH_3]}{k_1 k_5}} \right.$$

$$= k_1^{3/2}[CH_3COCH_3]^{3/2}\left\{\sqrt{k_1[CH_3COCH_3]} + \sqrt{\frac{k_3k_4}{k_5k_1^2}}\right\}$$

$$\cong \left(\frac{k_1k_3k_4}{k_5}\right)^{1/2}[CH_3COCH_3]^{3/2}$$

$$\therefore \alpha = 3/2$$

$$E_{a\,apparent} = \frac{1}{2}\left[E_1 + E_3 + E_4 - E_5\right]$$

$$= 71\ \text{Kcal/mol}$$

+5

5) True or False

a) False
b) False
c) True
d) False
e) False
f) False
g) True
h) False
i) False
j) True