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Lec. 35 05/12/2012

Advanced Reaction Engineering.

Further Considerations on Energy Balance

Wednesday 5 Dec 1530-1720

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Reaction

$$A \underset{2}{\overset{1}{\rightleftarrows}} B$$

1) k_1 and k_2 are very large.

2) Reaction is essentially at equilibrium

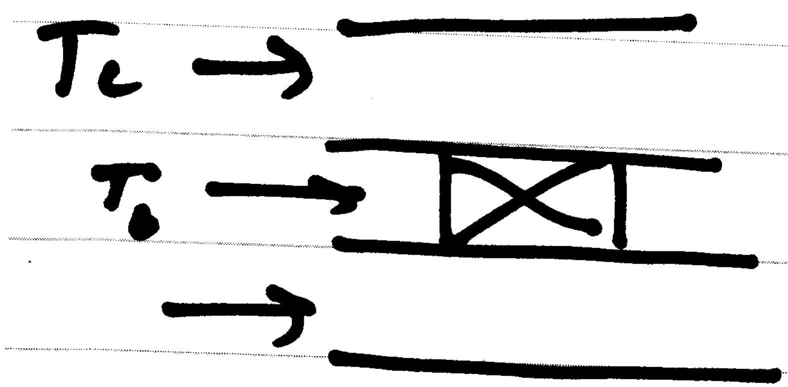
$$X = \left(\frac{K}{K+1}\right) \; ; \quad K: \text{equilibrium constant}$$

$$\frac{d\ln K}{dT} = \Delta H / RT^2 \Rightarrow \frac{dK}{dT} = K \frac{\Delta H}{RT^2}$$

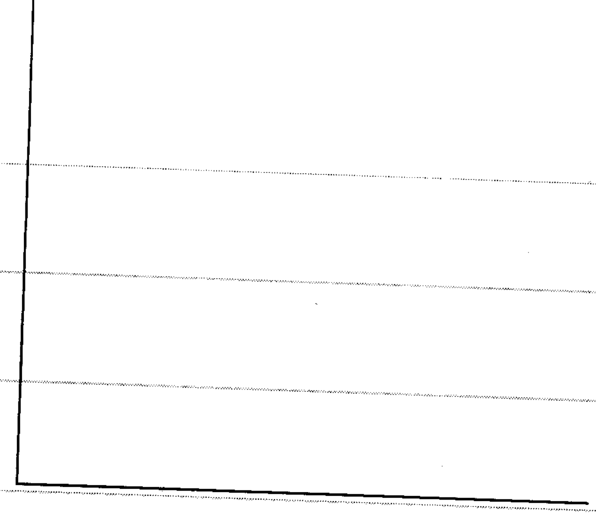
Practical Situations

1) Rate processes for Reaction are very rapid.

2) Endothermic Reaction → only at the rate which heat is supplied.



$A \rightleftharpoons B$



Exo +ve

-ve

$$v\hat{C}_p \frac{dT_0}{dV} = \underbrace{(r_1 - r_2)(-\Delta H_1^*)}_{\text{heat generation}} + \frac{4h}{D}(T_c - T). \quad \text{— (1)}$$

heat addition

= -ve +ve

$$\frac{dF_A}{dV} = r_2 - r_1$$

$$F_{A0}\frac{dX}{dV} = r_1 - r_2 \quad \text{— (2)}$$

$$\frac{dK}{dT} =$$

$$vC_p \frac{dT}{dV} = \left(F_{A0} \frac{dx}{dV}\right)(-\Delta H_1^*) + \frac{4h}{D}(T_c - T). \quad -(4)$$

$$\frac{dx}{dV} = \frac{dx}{dT} \cdot \frac{dT}{dV} = \frac{K}{(K+1)} \frac{\Delta H}{RT^2} \cdot \frac{dT}{dV}$$

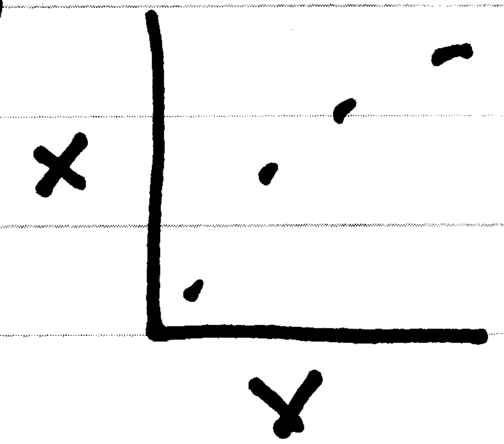
$$x = \frac{K}{K+1}$$

$$\frac{dx}{dT} = \left[\frac{1}{K+1} - \frac{1}{(K+1)^2}\right] \frac{dK}{dT} = \frac{1}{(K+1)^2} \cdot K\left(\frac{\Delta H}{RT^2}\right)$$

$$\left(F_{A0}\,\frac{dx}{dV}\right) = r_1 - r_2 \quad (2)$$

$$\nu C_p \frac{dT}{dV} = (r_1 - r_2)(-\Delta H^*) + \frac{4h}{D}(T_c - T) \quad -(1)$$

$$= \left(F_{A0}\frac{dx}{dV}\right)(-\Delta H^*) + \frac{4h}{D}(T_c - T). \quad -(3)$$



$$v C_p \frac{dT}{dv} = \left[F_{A0} \frac{K}{(K+1)^2} \frac{\Delta H'}{RT^2} \frac{dT}{dv} \right] (-\Delta H_r^*)$$

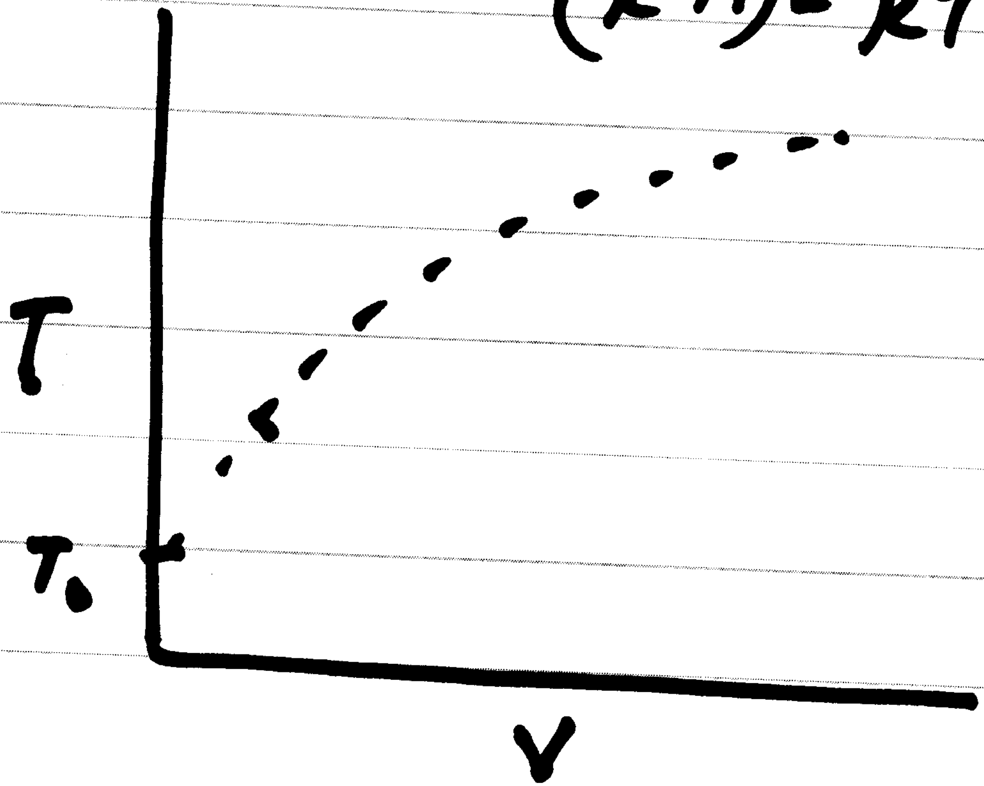
$$+ \frac{4h}{D} (T_c - T).$$

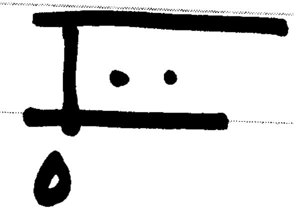
$$\frac{dT}{dv} \left\{ v C_p + F_{A0} \cdot (\Delta H)^2 \frac{K}{(K+1)^2} \frac{1}{RT^2} \right\} = \frac{4h}{D} (T_c - T)$$

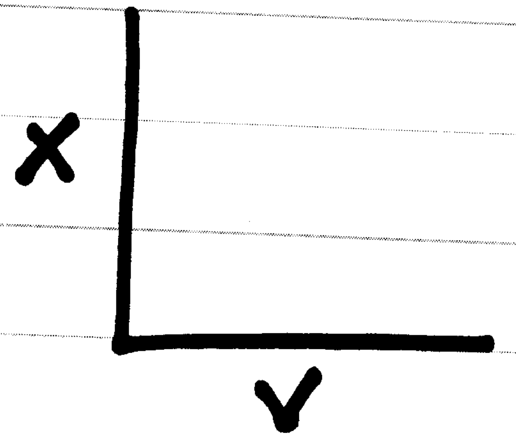
$$\frac{dT}{dv} = f(T, T_c, D, F_{A0}, v).$$

$$\frac{dT}{dv}\left\{ v\,C_p + F_{A0}(\Delta H)^2 \frac{K}{(K+1)^2}\frac{1}{RT^2} \right\} = \frac{4h}{D}(T_c - T)$$

$$X = \frac{K}{K+1}$$





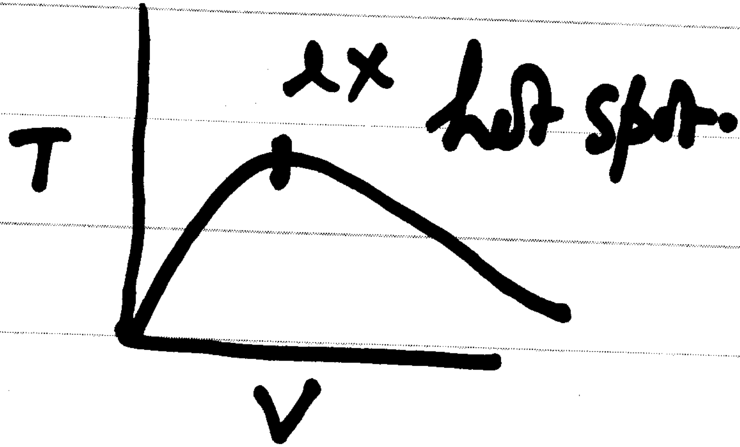


$$A \underset{2}{\overset{1}{\rightleftharpoons}} B$$

$$v C_p \frac{dT}{dV} = \overbrace{(r_1 - r_2)(-\Delta H^{r})}^{I} + \overbrace{\frac{4h}{D}(T_c - T)}^{II}.$$

$$\left(F_{A0} \frac{dX}{dV}\right)(-\Delta H^{r}) + \frac{4h}{D}(T_c - T)$$

Endothermic



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$B + C = MB + HCl$ 1

$MB + C = DB + HCl$ 2

$F_B = F_{B0}(1 - X_1)$ (1)

$F_M = F_{B0}(X_1 - X_2) + \cancel{F_{M0}}$ (2)

$F_D = F_{B0} X_2$ (3)

$\cancel{F_C} = F_{C0} - F_{B0}(X_1 + X_2 + X_2)$ (4)

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$$-r_B = k' C_B \cdot C_{Cl_2}$$

$$k' C_{Cl_2} = k$$

$$= k C_B.$$

Material Balance for DB

$I/p - O/p + G = \cancel{Acc}$ CSTR at SS

$$0 - F_{B0} X_2 + k_2 C_{MB} V = 0$$

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Balance for Benzene

$$F_{B0} - F_{B0}(1-X_1) - k_1 C_B V = 0$$

$$F_{B0} X_1 = k_1 C_B V$$

$$C_B = \frac{F_B}{v} = \frac{F_{B0}(1-X_1)}{v_0} = C_{B0}(1-X_1)$$

$$C_{NB} = F_{NB}/v_0 = \frac{F_{B0}(X_1-X_2)}{v_0} = C_{B0}(X_1-X_2)$$

From Benzene Balance

$$F_{B0} x_1 - V k_1 C_{B0} (1 - x_1) = 0$$

$$v_0 C_{B0} X_1 = k_1 C_{B0} (1 - x_1) V$$

$$\cancel{C_B} \; X_1 = k_1 \tau (1 - x_1)$$

$$X_1 = \frac{k_1 \tau}{1 + k_1 \tau}$$

$$-F_{B0}X_2 + k_2 C_{B0}(X_1 - X_2)V = 0$$

$$-\cancel{v_0}\,\cancel{C_{B0}}\,X_2 + k_2\,\cancel{C_{B0}}\,(X_1 - X_2)\frac{V}{v_0}$$

$$X_2 = k_2\tau(X_1 - X_2)$$

$$X_2 = \frac{k_2\tau\,.\,X_1}{(1 + k_2\tau)}$$

$$\frac{F_{C0}}{F_{B0}} = X_1 + X_2 + \cancel{X_3}$$

$$\frac{F_{B0}}{F_{C0}} = 1.4$$

$$\frac{1}{1.4} = X_1 + X_2$$

$$\frac{k_1}{k_2} = 8$$

$$0.71 = \frac{k_1\tau}{1+k_1\tau} + \frac{k_2\tau}{1+k_2\tau} \cdot \frac{k_1\tau}{1+k_1\tau}$$

$$0.71 = \frac{8k_2\tau}{1+8k_2\tau} \cdot \frac{k_2\tau}{1+k_2\tau} \cdot \frac{8k_2\tau}{1+8k_2\tau}$$

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$$0.71 = \frac{k_1\tau}{1+k_1\tau} + \frac{k_2\tau}{1+k_2\tau} \cdot \frac{k_1\tau}{1+k_1\tau}$$

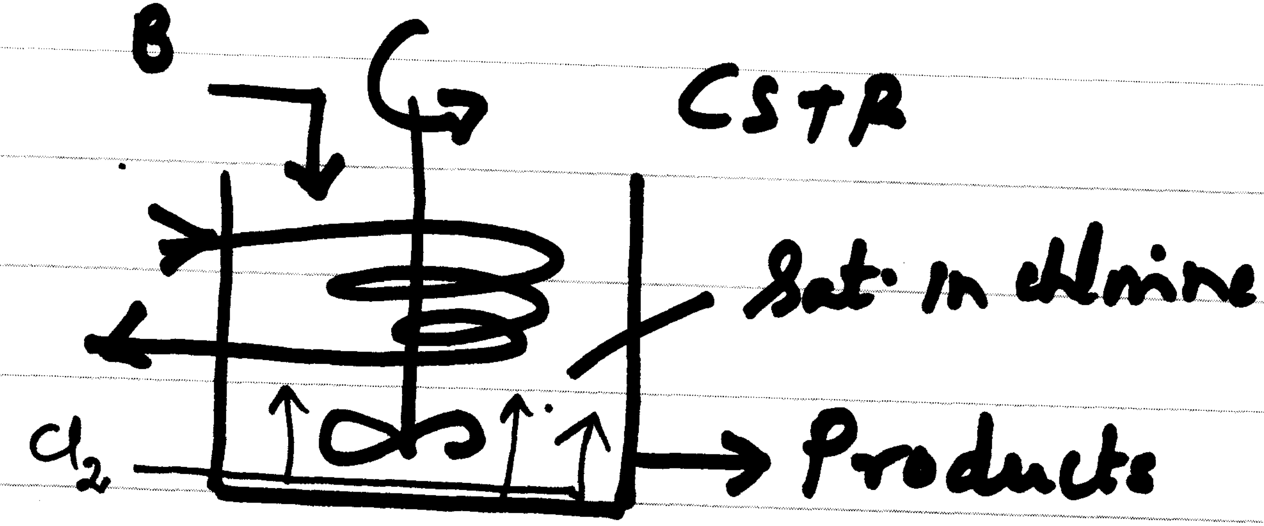
$$\frac{k_1}{k_2} = 8$$

$k_2\tau = 0.22;$

$k_1\tau \simeq$ ~~200~~ 1.76

$x_1 = 0.63 \quad x_2 = 0.18$

$F_B, \; F_{DB}; \; F_{MB}$



$$B + Cl_2 \overset{1}{=} MB + HCl \qquad \frac{F_{C0}}{F_{B0}} = \frac{1}{1.4}.$$

$$MB + Cl_2 \overset{2}{=} DB + HCl. \qquad k_1\tau = 8k_2\tau$$

1) Find the temperature which maximises yield of MB

2) What is the heat load that the coil must handle

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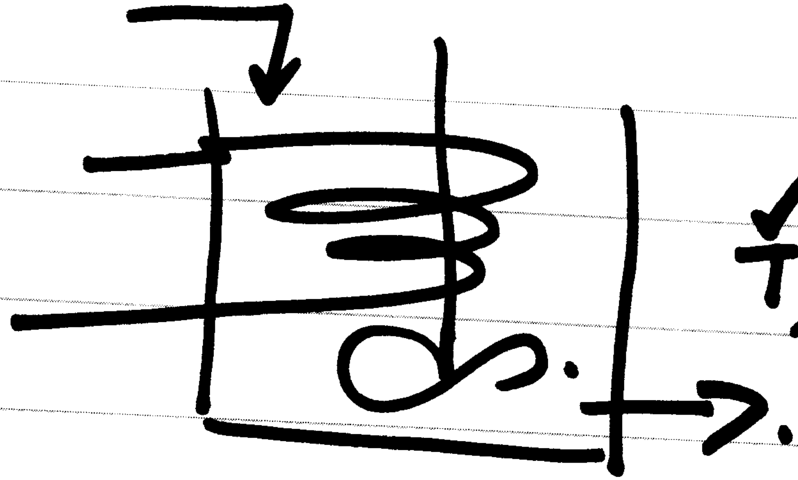
$$F_{MB} = F_{B0}(X_1 - X_2)$$

$$= F_{B0}\left\{ \frac{k_1 \tau}{1+k_1\tau} - \frac{k_1 \tau}{1+k_1\tau} \cdot \frac{k_2\tau}{1+k_2\tau} \right\}.$$

$$\frac{d}{d\tau}(X_1 - X_2) = 0 \quad \text{find the condition}$$

$$\frac{E_1}{E_2} = \frac{k_2\tau\,(1+k_1\tau)}{(1+k_2\tau)} \Rightarrow (k_2 \to T \qquad \underline{\underline{\text{choose } T.}}$$



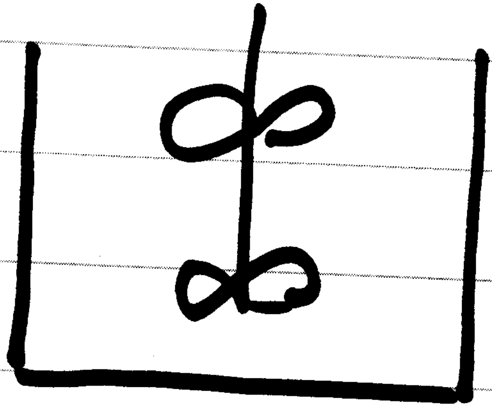
T, τ

$$V C_p \cancel{\frac{dT}{dt}} = v_0 C_p (T_0 - T) + \sum_{i=1}^{2} r_i(-\Delta H_i) V + Q - \cancel{W_s}$$

$$(Q) = v_0 C_p (T - T_0) - \sum_{i=1}^{2} r_i(-\Delta H_i) V.$$

Multiple rxn.

CSTR



$$-r_M = k_i M + \sum_{i=1}^{n} k_p M P_i$$

$$r_p = k_p P_n M.$$

$M \rightarrow P_1$ initiation

$P_1 + M = P_2$ Polymer

$P_n + M = P_{n+1}$ Polymer

$$\boxed{P_n ? \; ; \; X}$$

Monomer Balance

$$v_0(M_0 - M) + r_M V = 0$$

$$M_0 - M - \tau \left\{ k_i M + \sum_{i=1}^{n} k_p M P_i \right\} = 0 \quad - (1)$$

$$M_0 - M - k_i \tau M - M(k_p \tau P_1 + k_p \tau P_2 + \dots k_p \tau P_n)$$

$$= 0 \quad \dots . (2).$$

Balance for P_1

$$\cancel{P_0} - P_1 + k_1 \tau M - k_p \tau M P_1 = 0$$

$$\cancel{-P_1 + k_1 \tau}$$

$$P_1 (1 + k_p \tau M) = k_i M \tau$$

$$P_1 = \frac{k_i M \tau}{(1 + k_p M \tau)} = \frac{k_i}{k_p} \frac{(k_p M \tau)}{(1 + k_p \tau M)}$$

$\underline{P_2}$

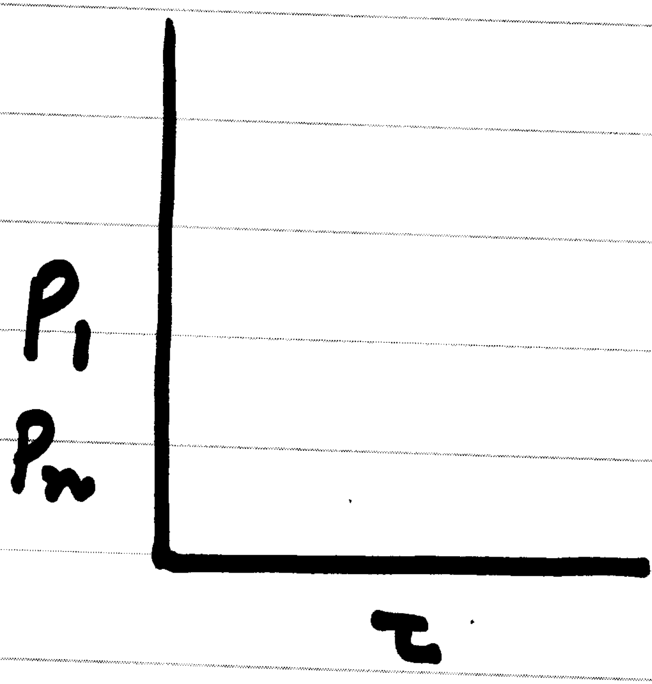
$$-P_2 + k_p \tau M P_1 - k_p \tau P_2 M = 0$$

$$P_2 (1 + k_p \tau M) = k_p P_1 M \tau .$$

$$P_2 = \frac{k_p P_1 M \tau .}{(1 + k_p \tau M)}$$

$$P_2 = P_1 \frac{k_p M \tau}{(1 + k_p M \tau)} = \frac{k_i}{k_p} \frac{(k_p M \tau)^2}{(1 + k_p M \tau)^2}$$

$$P_n = \frac{k_i}{k_p} \frac{(k_p M \tau)^n}{(1 + k_p M \tau)^n}$$



Monomer Balance

$$X - (1-X)\, k_i \tau \left\{ 1 + k_p \tau M_0 (1-X) \right\} = 0$$

✓ X is determined from this eqn.