4 Dec 12
1430–1530

Prof. Shankar
Lec. ~~30~~ ~~12~~ 4/12/2012

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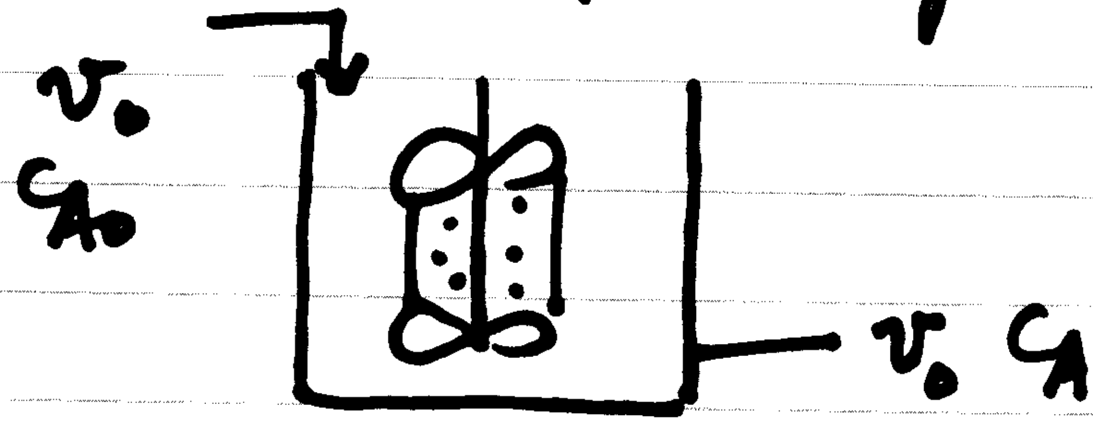
Advanced Reaction Engineering

Time Dependent operations

Deactivating Catalysts



$$v_0 C_{A0} - v_0 C_A + r_A V = V \frac{dC_A}{dt}$$

$\psi = C_A / C_{A0}$; $\theta = t/\tau_d$

τ_d: Characteristic Time for deactivation

$$1-\psi+\frac{r_A V}{v_0 C_{A0}} = \frac{V}{\tau_d}\frac{d\psi}{d\theta} v_0$$

$$1-\psi+\frac{r_A \tau_r}{C_{A0}} = \frac{\tau_r}{\tau_d}\frac{d\psi}{d\theta}.$$

$$\tau_r << \tau_d$$

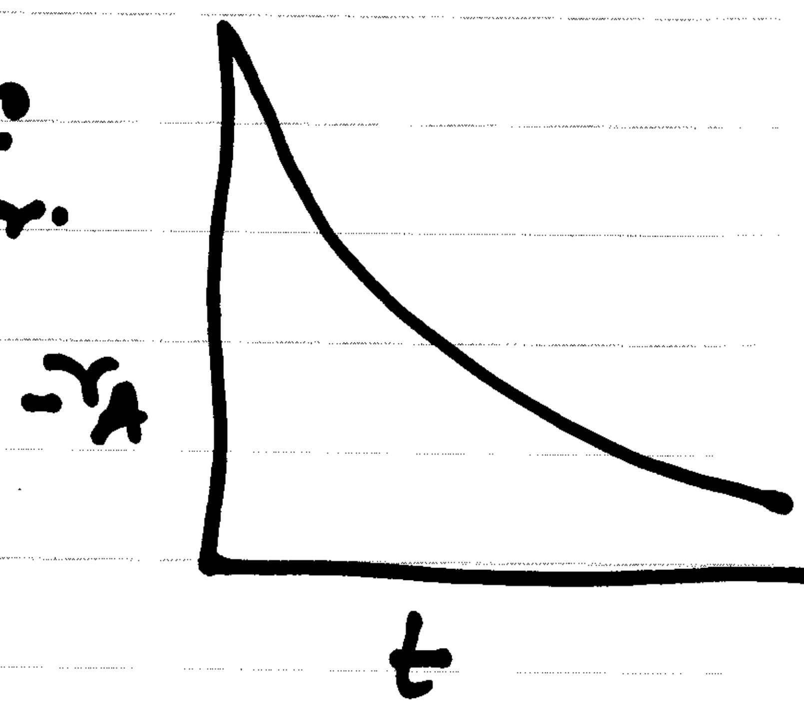
$$A \rightarrow \text{Products}$$

$$1-\psi + r_A \frac{\tau_r}{C_{A0}} = 0 \qquad \text{QSSA}$$

$$(-)\, r_A(t) = [1-\psi(t)] \frac{C_{A0}}{\tau_r}.$$

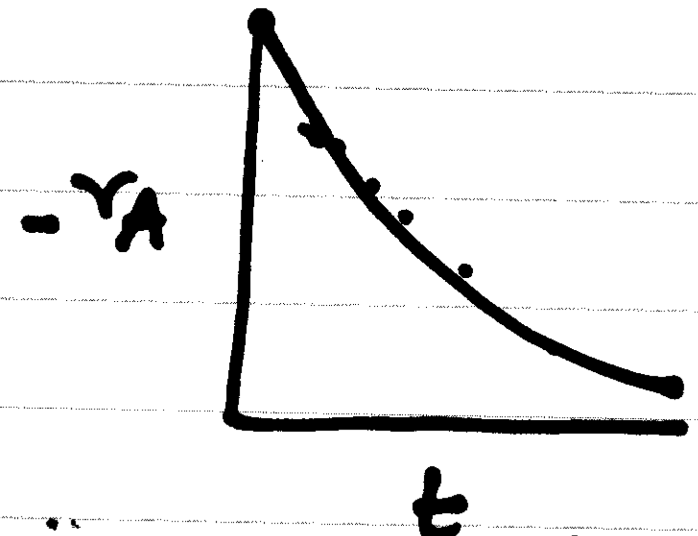
must in video

$\psi(t)$; $r_A(t)$



$$a = \frac{r_A(t)}{r_A(0)}$$

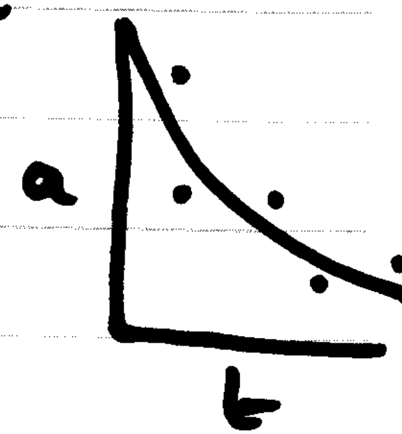
↖ Standard state



$$r_A(t) = (a)\, r_A(0)$$

$$= (-)\, k_0(T)\, f(c)\, (a)$$

most in vitro

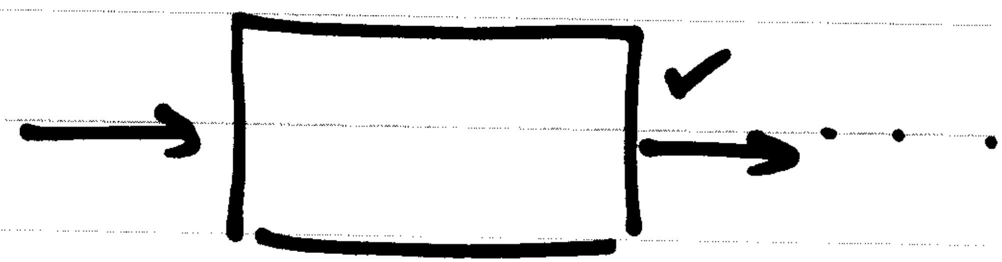


$$r_a = k_d\, a^m\, C_A^n\, C_B^p.$$

$$-r_A = \underbrace{k(T)\cdot(a)}\cdot f(C)$$

$$r_d = k_d\, a^m \cdot C_A^n \cdots$$

$$-\frac{da}{dt} = r_d$$



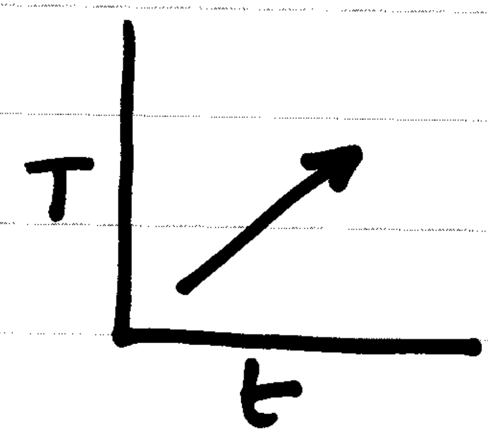
$$k(T)\, a\{\cdots\} = \text{Constant}$$

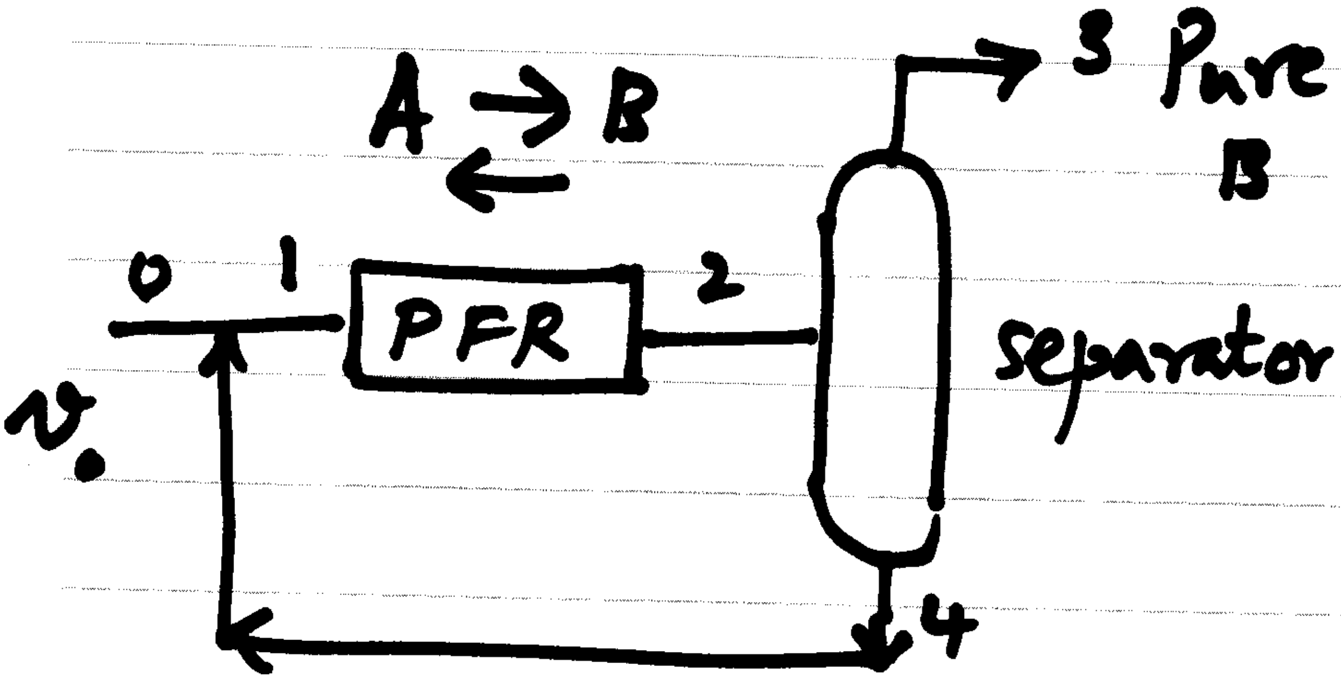
$$k(T) \cdot a(T, t, C_A \cdots) = \text{Constant}$$

$$a = A e^{-k_d t}$$

$$k_d = k_{d0} \exp(-E_d/RT).$$

$$k(T) = A_0 \exp\left[-E/RT\right]$$



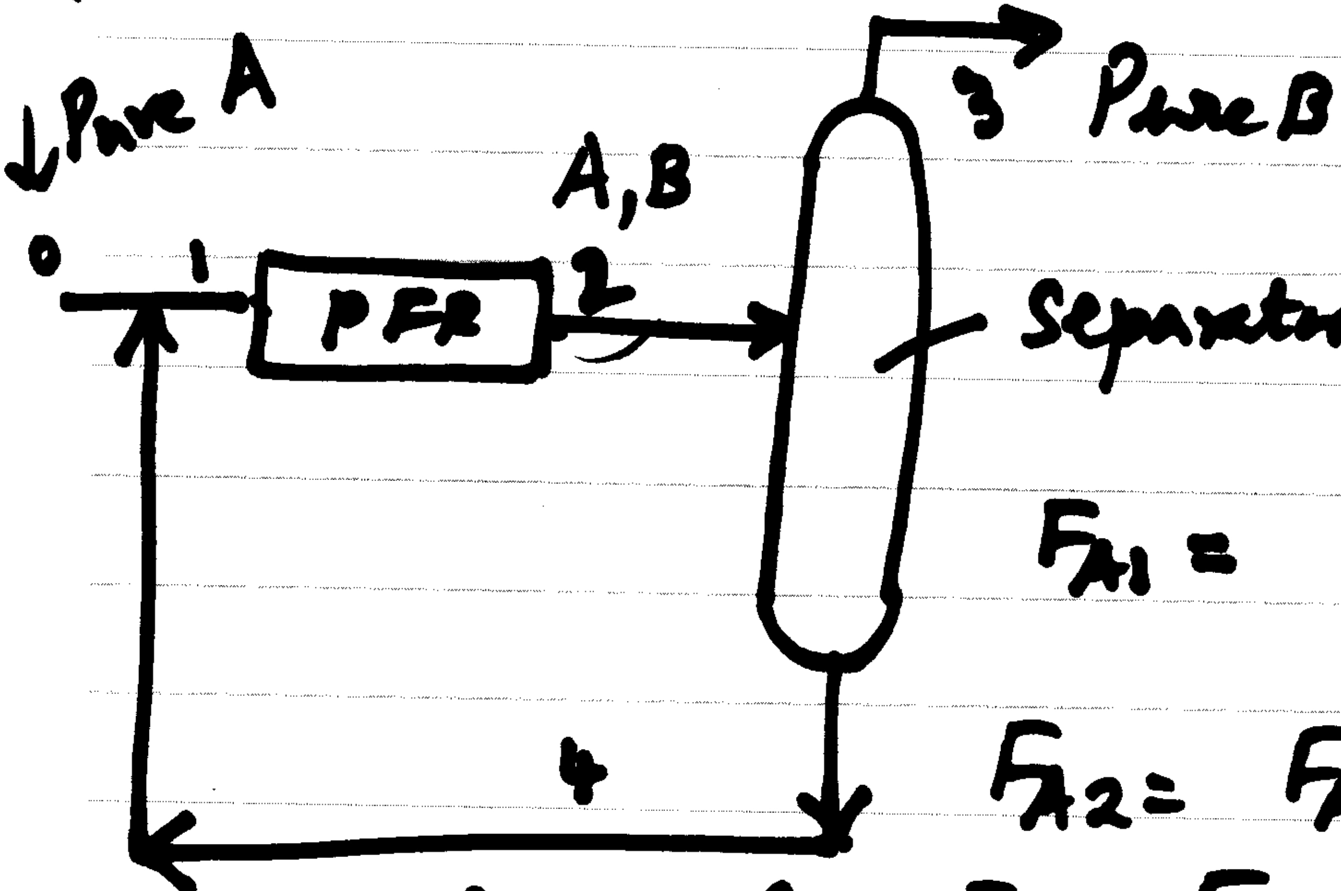


$$k = \exp\left[8.8 - \frac{5000}{T(K)}\right]$$

$$k_d = \exp\left[1.3 - \frac{2500}{T(K)}\right]$$

$$K = \exp\left[-19.5 + \frac{10000}{T(K)}\right].$$

Catalyst	T K	Feed F_{A0} lit/s	A at Reactor exit %
Fresh	450)	0.39	25
Spent	477	0.38	362
Regenerated	450	0.28	19



$F_{A1} = F_{A0} + F_{A4}$

$F_{A2} = F_{A1}(1 - Y_2) = F_{A4}$

C_{A4} = Pure A = C_{A0} $\quad F_{A1} = F_{A0} + F_{A1}(1 - Y_2) \Rightarrow \frac{F_{A0}}{Y_2}$

Y_2 is conversion at position 2 with respect to F_{A1} at position 1

$$C_{A4} = C_{A0} \Rightarrow C_{A1} = C_{A0}$$

$$v_4 = \frac{F_{A4}}{C_{A4}} = \frac{F_{A2}}{C_{A4}} = \frac{F_{A1}}{C_{A0}}(1-y_2)$$

$$= \frac{F_{A0}}{y_2 C_{A0}}(1-y_2) = \frac{v_0}{y_2}(1-y_2).$$

$$v_1 = v_0 + v_4 = v_0 + \frac{v_0}{y_2}(1-y_2) = \frac{v_0}{y_2}$$

$$F_{A1} = F_{A0}/y_2$$

Design Eqn PFR

$$\frac{dF_A}{dV} = r_A$$

$C_{A2} = C_{A0}(1-y_2)$

$C_{B2} = C_{A0}\, y_2$

C_A (at any position) $= C_{A0}(1-y)$

$C_B(\cdots) = C_{A0}\, y$

$C_{A1} = C_{A0}.$

$$C_{A2} = \frac{F_{A2}}{v_2} = \frac{F_{A1}(1-y_2)}{v_1}$$

$$= \frac{F_{A1}(1-y_2)y_2}{v_0}$$

$$= \frac{F_{A0}\cdot(1-y_2)y_2}{y_2\, v_0}$$

$= C_{A0}(1-y_2).$

$$F_A = F_{A_1}(1-y)$$

$$\frac{dF_A}{dV} = k_2 \alpha C_B - k_1 \alpha C_A.$$

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

$$-F_{A_1}\frac{dy}{dV} = k_2 \alpha C_{A0}\, y - k_1 \alpha C_{A0}(1-y)$$

α - activity

$$\frac{F_{A0}}{y_2}\frac{dy}{dV} = k_{(1)} \alpha C_{A0}(1-y) - k_2 \alpha C_{A0}\, y$$

$$\boxed{\frac{v_0}{y_2}\frac{dy}{dV} = k_{(1)} \alpha (1-y) - k_{(2)} \alpha y}$$

$$\frac{v_0}{y_2}\frac{dy}{dV} = k_{(1)}\alpha(1-y) - k_{(2)}\alpha y.$$

$$(k_{(1)}\alpha V) = -\frac{v_0}{y_2\beta}\ln(1-\beta y_2)$$

K_e = Eq. Constant

$$\beta = (K_e+1)/K_e$$

Fresh Catalyst

$$k_{(1)} \propto V = -\frac{v_0 \ln(1-\beta y_2)}{y_2 \beta}$$

$$\beta = \frac{K_e+1}{K_e} = \frac{8.5+1}{8.5}.$$

$K_e(450K) = 8.5$ from data given

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Fresh Catalyst Contd.

$$k_{(2)}(\alpha)V = \frac{-0.39}{0.75} \ln\left[1 - 1.117 \times 0.75\right]$$

$$(k_{(1)} \alpha V)_F = 0.847 \quad \text{(fresh catalyst).}$$

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Mol. Fraction at position 2 of A

$$\frac{F_{A1}(1-y_2)}{F_{A1}(1-y_2)+F_{A1}y_2} = (1-y_2) = 0.25$$

~~1 - 0.25 = 0.75~~

$$1-y_2 = 0.25$$

$$y_2 = 0.75$$

Spent: 477 K

Eq. Constant at 477 K. = 6.

$\beta = (6+1)/6 = 1.16$

$$\left(k_{(1)} \alpha V\right)_{477} = -\frac{v_1}{\beta y_2} \ln(1-\beta y_2)$$

$$= \frac{-0.38}{1.16(0.678)} \ln(1-1.16 \times 0.678)$$

$$\left(k_{(1)} \alpha V\right)_{477} = 0.75$$

$$\frac{(k_1 \alpha V)_{477}}{(k_{(1)} \alpha . V)_{450}} = \frac{0.75}{0.847} = 0.88$$

$$\frac{(k_1 \alpha)_{477}}{(k_1 \alpha)_{450}} = (0.88)$$

Activity of Spent Catalyst at

477 K = (0.88) $\frac{k_{(1)}(450\,K)}{k_{(1)}\text{ at }477\,K.}$

Spent Cat.

$$\frac{(\alpha)_{477}}{(\alpha_{450})_{f.}} = \frac{0.88}{2.66} = (0.33)$$

$(2.25)(0.33) \simeq 0.74$

Regenerated Catalyst.

$$\left(k_{(1)}\alpha V\right)_{Reg} = \frac{-V_0 \ln(1-\beta y_2)}{y_2 \beta}$$

$$= \frac{-0.28 \ln(1-1.117\times 0.81)}{(0.81)(1.117)}$$

$$\left(k_{(1)}\alpha . V\right)_{Reg} = 0.727$$

Req.

$$\frac{(k_1 \alpha V)_{Req}^{(450)}}{(k_1 \alpha V)_{Fresh}^{450}} = \frac{0.727}{0.847} = 0.858$$

Reg Cat ankts > 2.25 times S/pub

0.727 > 0.71

So Criteria II is Satisfied.