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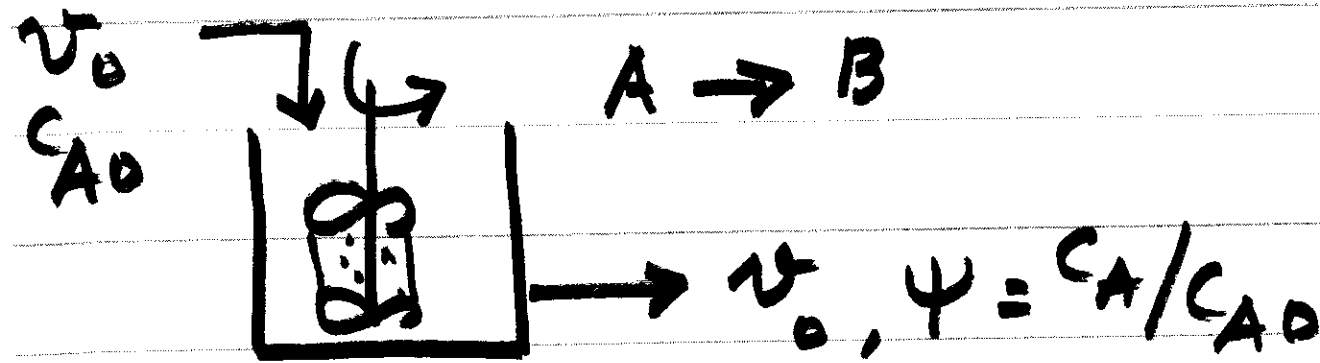
L11

Advanced Reaction Engineering.

Deactivating Catalytic Systems.

check 6

catalyst Deactivation



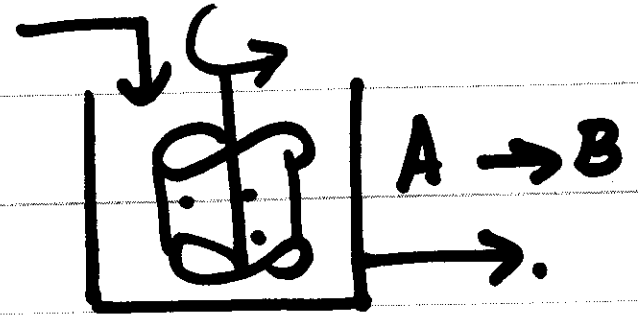
$$v_0 C_{A0} - v_0 C_A + r_A V = V \frac{dC_A}{dt}$$

$$\text{Let } \psi = C_A / C_{A0}; \quad \theta = t / \tau_d \quad \tau_r = V / v_0$$

τ_d is a characteristic time for deactivation

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

$$1 - \psi + \frac{\gamma_A \tau_r}{C_{A0}} = \left(\frac{\tau_r}{\tau_d} \right) \frac{d\psi}{d\theta}$$



$$\psi = 0(1); \quad \theta = 0(1); \quad \gamma_A \tau_r / C_{A0} = 0(1)$$

So if $\tau_r / \tau_d \ll 1$ then RHS can be

deleted

$$1 - \psi + \frac{\gamma_A \tau_r}{C_{A0}} = \frac{\tau_r}{\tau_d} \frac{d\psi}{d\theta} = 0 \quad \frac{QSSA}{v/v_0 = \tau_r}$$

$$(-\gamma_A) = (1 - \psi) C_{A0} / \tau_r$$

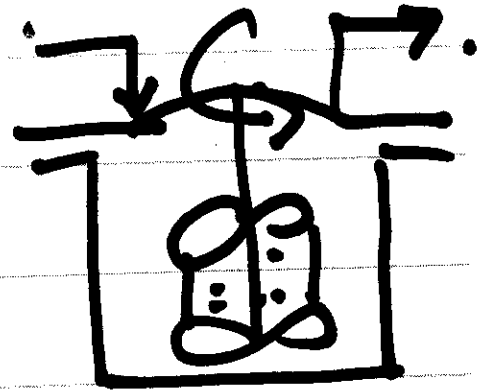
$$\psi = C_A / C_{A0}$$

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

$$-r_A = (1 - \psi) \frac{C_{A0}}{\tau_r}$$

Since catalyst is deactivation.

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



$$\psi = C_A / C_{A0}$$

$$\tau_r = V / v_0$$



First order Rxn $X = \frac{k\tau_r}{(1+k\tau_r)}$

Second Order Reaction

in a PFR

$$\frac{dc_A}{d\tau} = -kC_A^2$$

Integration $C_A =$

$$\frac{C_{A0}}{(1+kC_{A0}\tau)}$$

$$X = 1 - \frac{C_A}{C_{A0}} = \frac{kC_{A0}\tau}{(1+kC_{A0}\tau)}$$

$$-r_A = +kC_A^2 =$$

$$+ \frac{kC_{A0}^2}{(1+kC_{A0}\tau)^2}$$

For a First order Reaction $(k_{r0}) \cdot \underline{a}(t)$

CSTR

$$-r_A = k_r C_A; \quad -r_A(t) = k_r(t) C_A$$

$$= k_r C_{A0} (1-x)$$

$$\text{where } x = \frac{k\tau}{1+k\tau}$$

$$= k_r C_{A0} \left[1 - \frac{k_r \tau}{1+k_r \tau} \right]$$

$$-r_A = \frac{k_r C_{A0}}{1+k_r \tau}$$

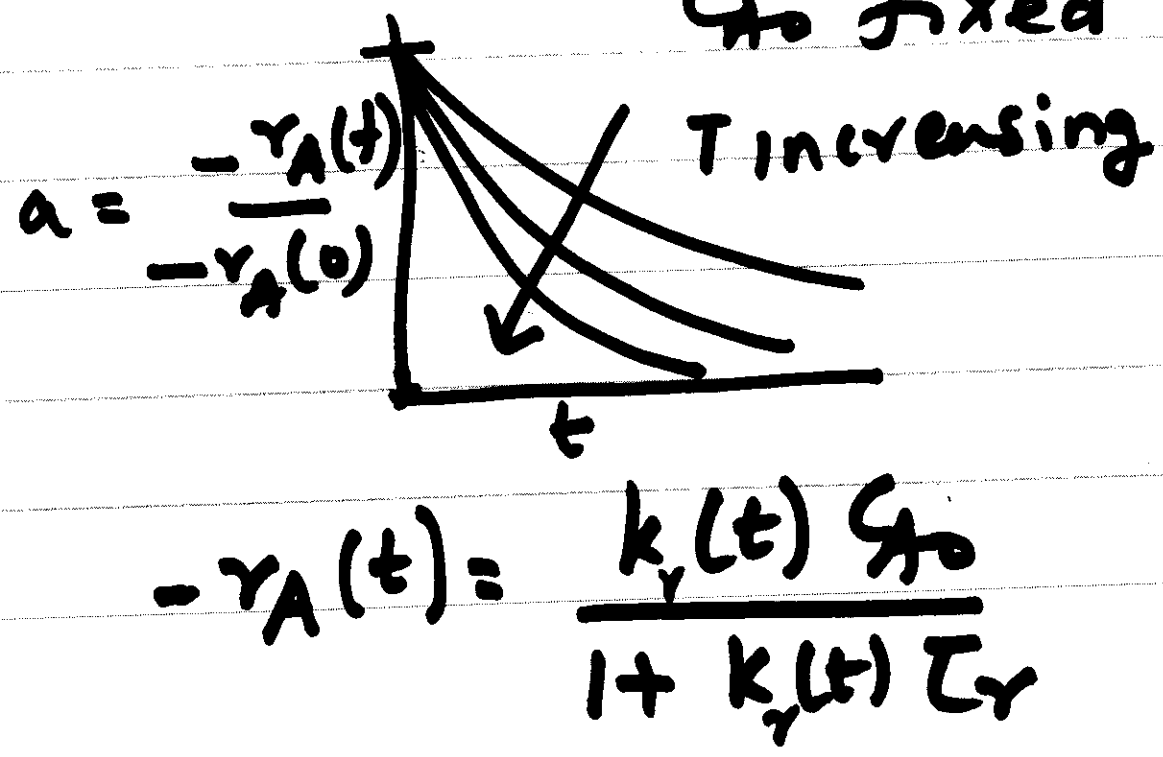
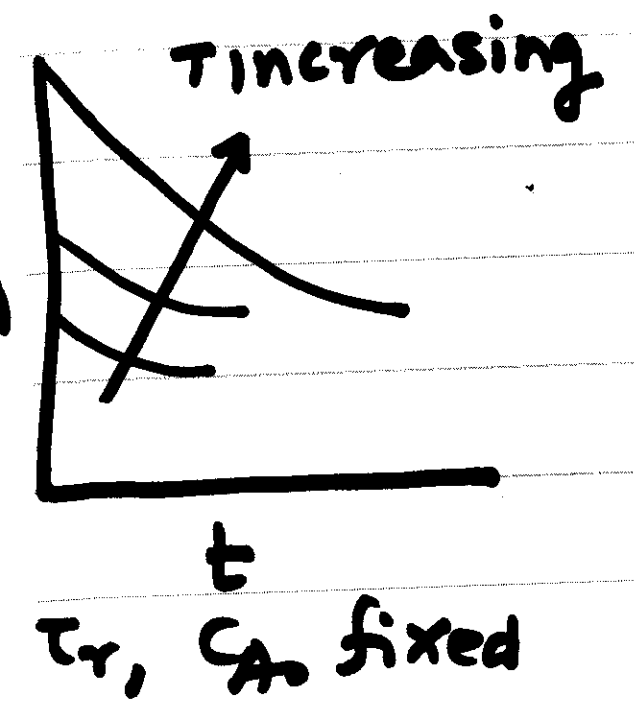
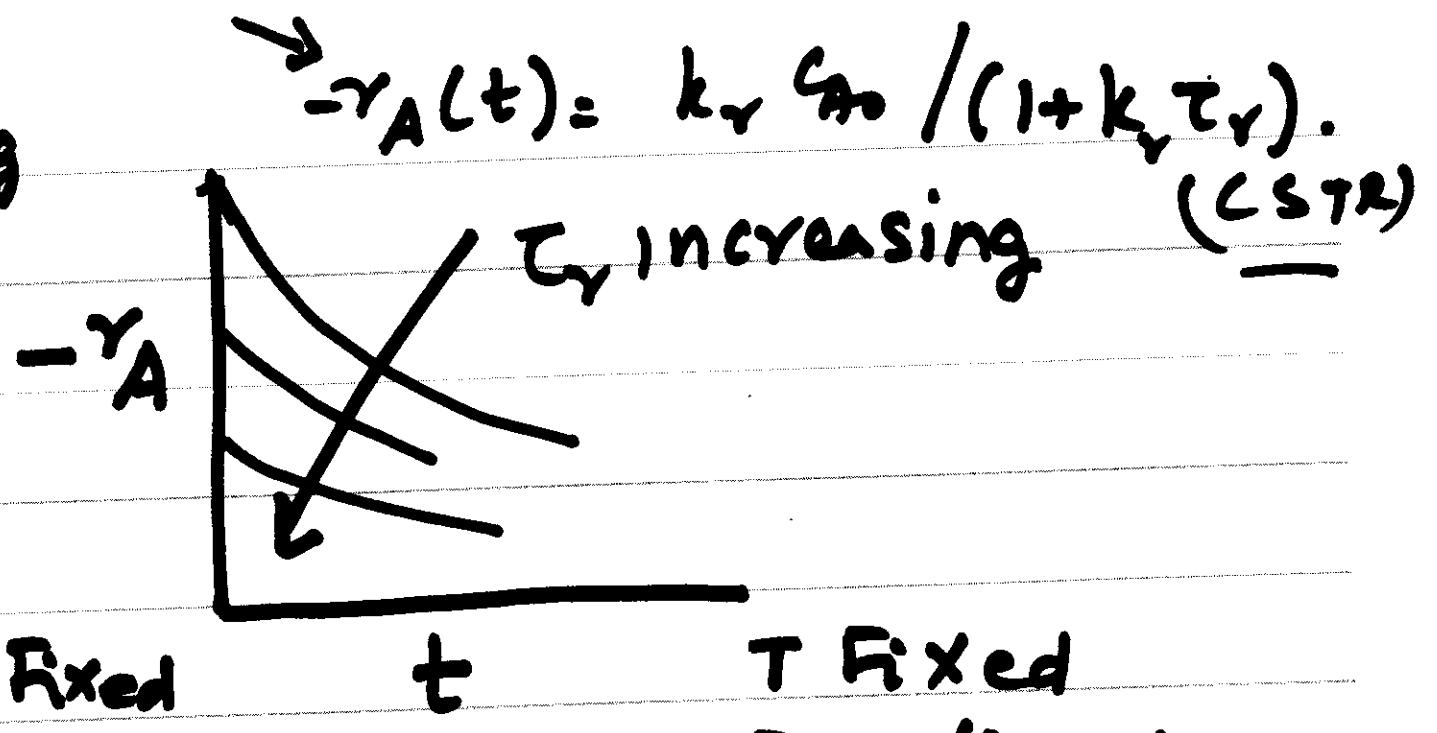
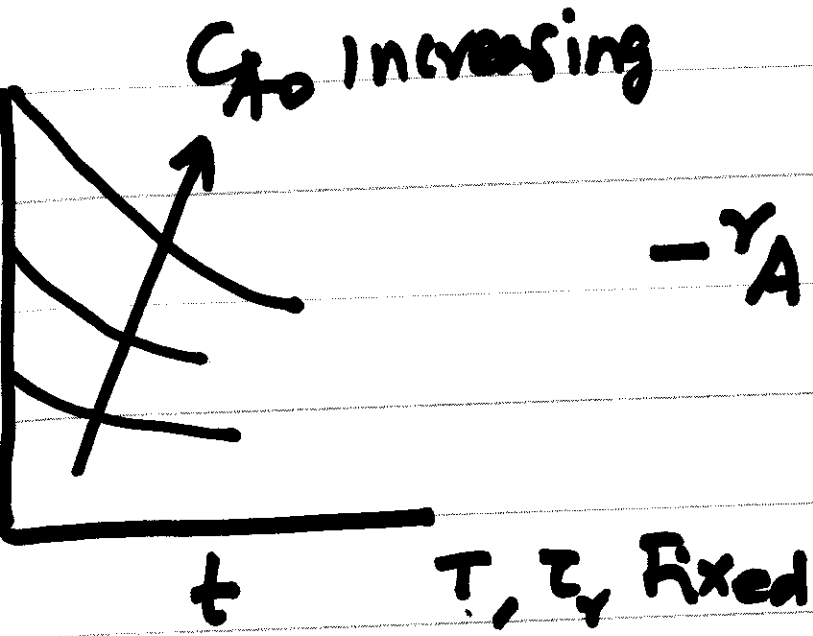
First order

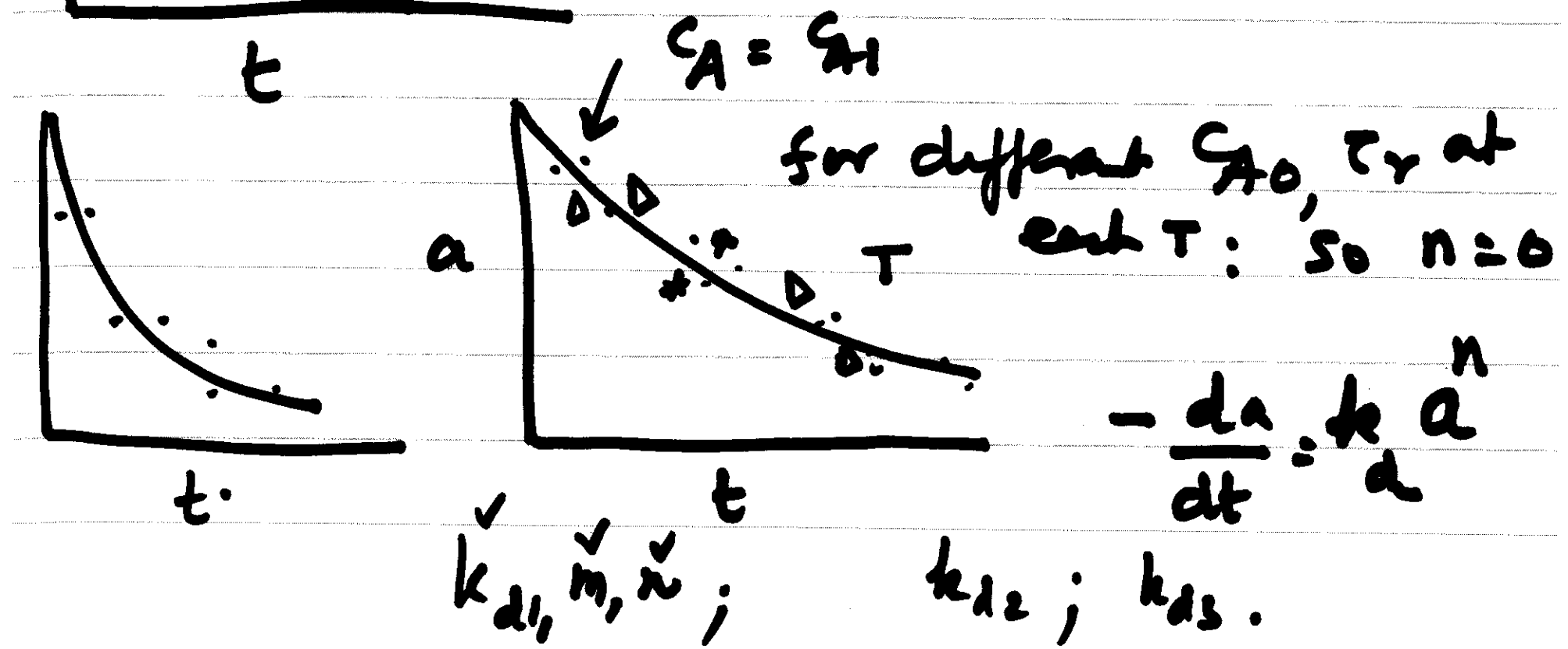
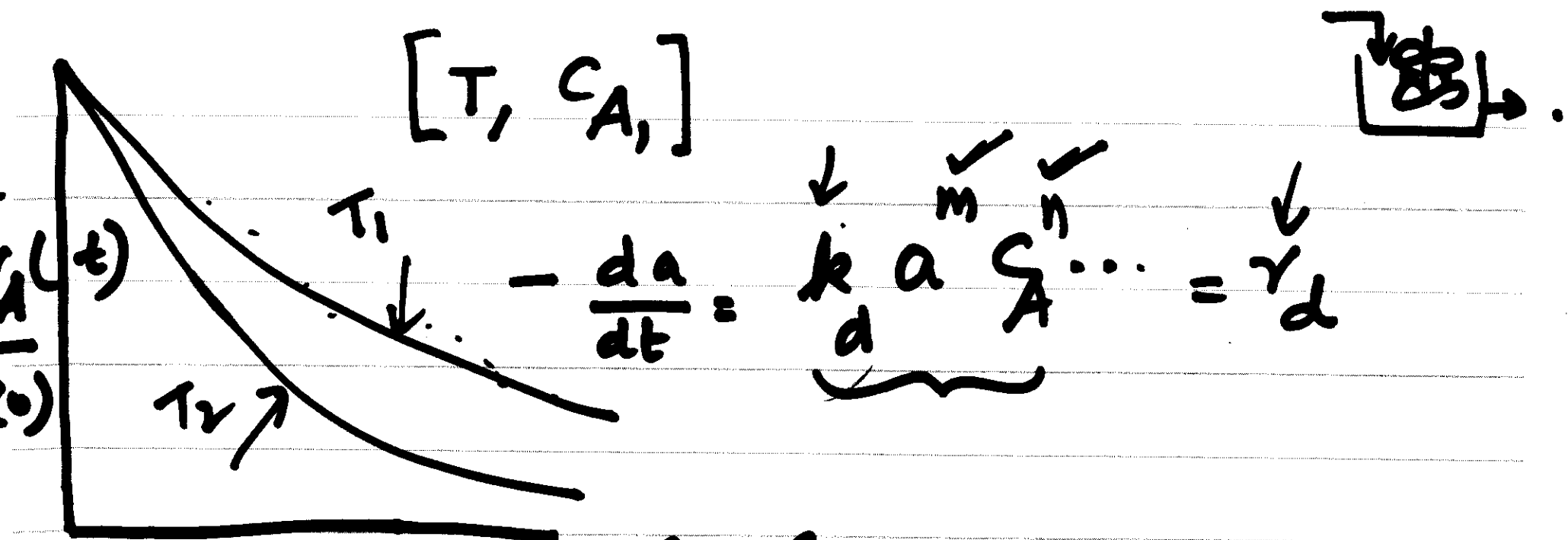
$$-r_A(t) = \frac{k_r(t) C_{A0}}{(1+k_r(t) \tau)}$$

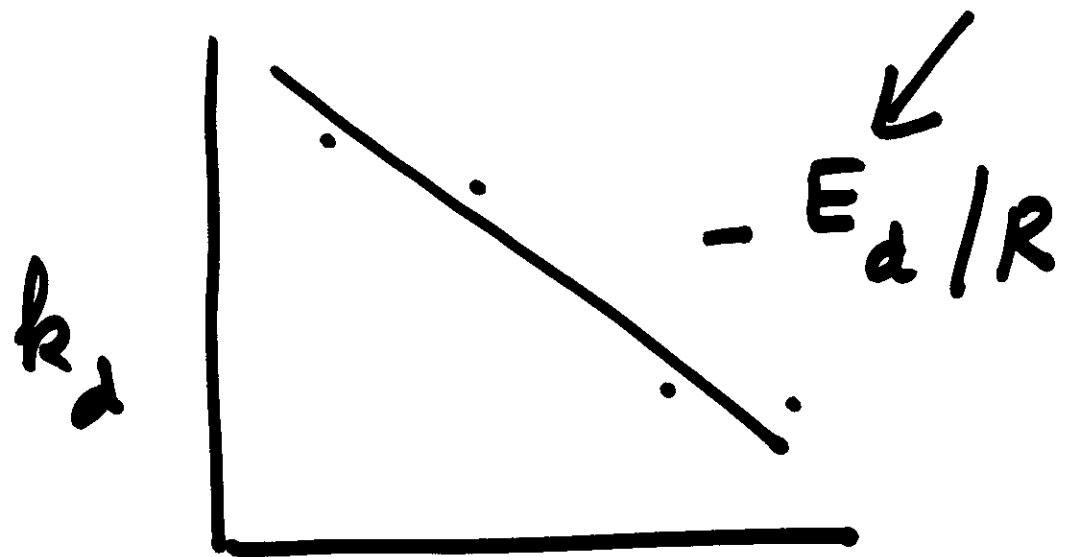
First order Reaction

$$\frac{-r_A(t)}{-r_A(0)} = \left[\frac{k_v(t) C_{A0}}{1 + k_v(t) \tau_r} \right] \cdot \left[\frac{1 + k_{v0} \tau_r}{k_{v0} \cdot C_{A0}} \right]$$

k_{v0} is rate constant of reaction at $t=0$







Activation
Energy

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

$\neq m, n, E_d, k_{d0}.$

$$-r_A(t) = \underbrace{k_r}_{k_r} k_{r0}(\tau) a(t) f(c)$$

$$- \frac{da}{dt} = r_d = k_d a^m \phi(c)$$

$$-r_A(t) = k_{r0}(\tau) e^{-k_d t} f(c) \quad \text{for } m=1$$

$$\phi(c) = 1$$

For first order reaction:

$$-r_A(t) = \frac{k_{r0} C_{A0} \cdot a}{1 + k_{r0} \tau \cdot a}$$

CSTR
[k_{r0} · a]
constant

In order to keep $-r_A(t) \leftarrow$

constant ensure that

$$\underbrace{k_r \cdot a}_{\downarrow} = \text{Constant} = \frac{k_r e^{-k_d t}}{\downarrow} = \text{Constant}$$

$$k_r = A_{r0} \exp(-E/RT)$$

$$-\frac{da}{dt} = k_d a$$

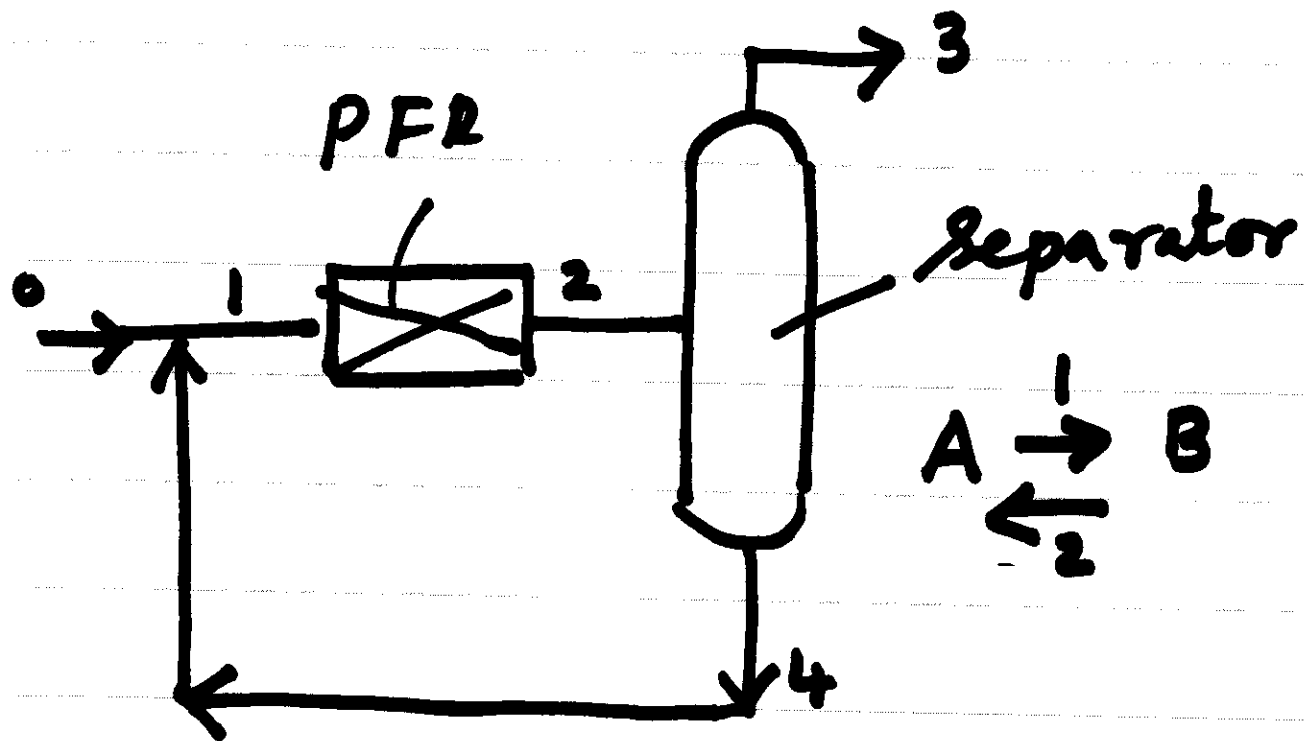
$$k_d = k_{d0} \exp(-E_d/RT)$$

$$T \rightarrow k_d \rightarrow$$

$$T \rightarrow k_{r0} \rightarrow$$

So

$$\underbrace{A_{r0} \exp\left[-\frac{E}{RT}\right]}_{\uparrow} \exp\left[-\frac{k_d t}{\uparrow}\right] = \text{Constant}$$



Activation Energy for Rxn 1 = $15000 \frac{\text{Cal}}{\text{mol}}$

Equilibrium Constant at 450 K = 8.5

Equilibrium Constant at 477 K = 6.0

Catalyst is proprietary
Catalyst Deactivates.

A regeneration process is available

Performance of fresh catalyst, Spent

Catalyst and regenerated catalyst is

available. We can accept the regeneration
process under certain conditions

Catalyst	T (K)	Feed (lit/s) v_0	A at reactor exit %. ($\frac{I}{I_0}$)v_0
Fresh	450	0.39	25 ✓
spent	477	0.38	32.2
Regenerated	450	0.28	19.0

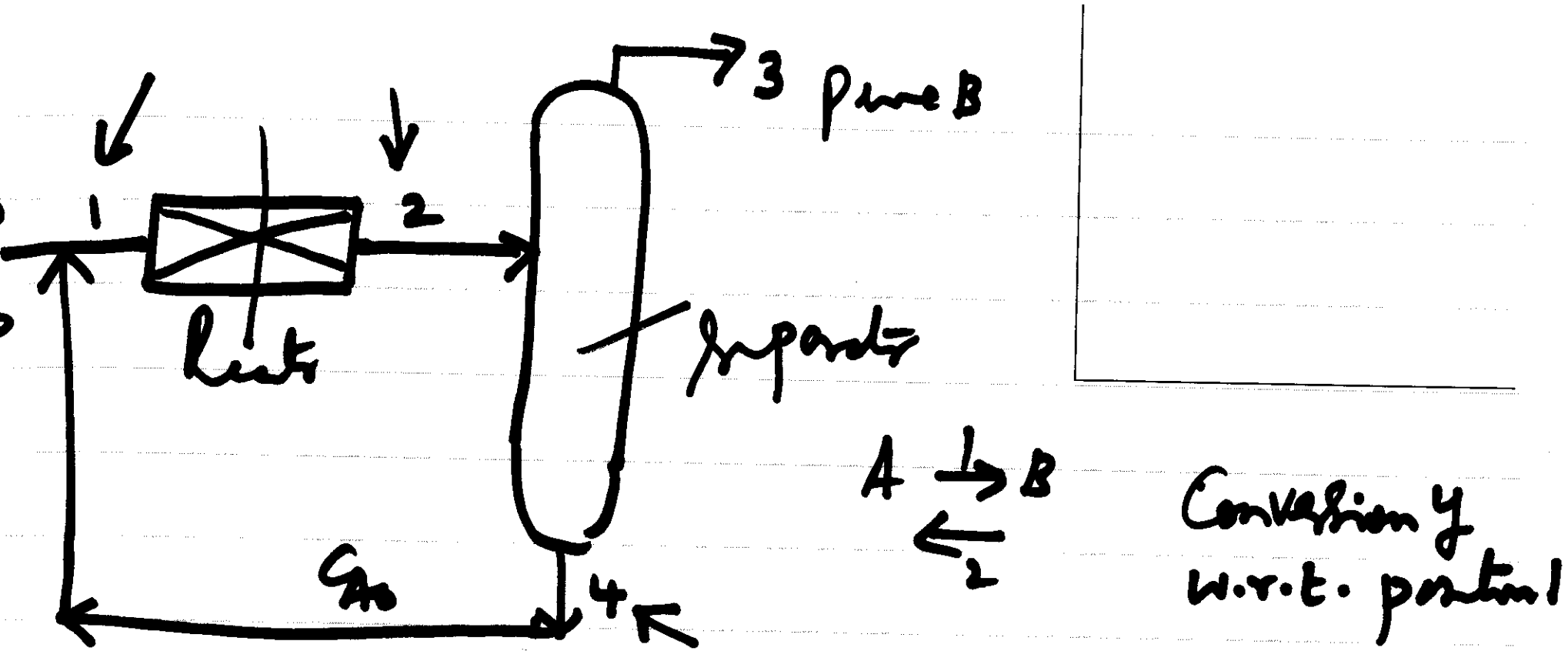
Criteria - I:

activity of Regenerated Catalyst
is 90 % of fresh Catalyst.

OR

Criteria II: Activity of regenerated

Catalyst is 2.25 times activity of
spent Catalyst.



We have to derive the design eqns for the reactor; then on we can evaluate the performance data given.

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

Let y_2 be conv w.r.t. position 1

$$F_{A2} = F_{A1}(1-y_2)$$

$$F_{B2} = F_{A1}y_2$$

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

$$F_{A1}y_2 + F_{A1}(1-y_2)$$

$$\frac{F_{A1}(1-y_2)}{F_{A1}} = 0.25 \quad (\text{mol. fraction at 2})$$

$$y_2 = 0.75$$

$$F_{A1} = F_{A0} + F_{A4}$$
$$= F_{A0} + F_{A1}(1-y_2)$$

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

$C_{A4} = C_{A0}$ since B is fully recovered

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

$$= v_0(1-y_2)/y_2$$

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

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

$$C_A \text{ (at any position)} = \frac{F_A}{v}$$

$$= \frac{F_{A1}(1-y)}{v_1} = C_{A1}(1-y) = C_{A0}(1-y) \downarrow \\ = C_{A0}(1-y)$$

$$C_B = \frac{F_B}{v} = \frac{F_{A1}y}{v_1} = C_{A1}y = C_{A0}y$$

Note $v = v_1$ (since volume flow in reactor does not change)

$$F_B = F_{A0} \gamma$$

$$\frac{dF_B}{dV} = r_B$$

$$\frac{d\gamma}{dV} = (k_{(1)} C_A - k_{(2)} C_B) \alpha \quad \downarrow \quad \text{Catalyst activity.}$$

$$= k_{(1)} \alpha C_{A0} (1 - \gamma) - k_{(2)} \alpha C_{A0} \gamma$$

$$\frac{F_{A0}}{y_2} \frac{d\gamma}{dV} = k_{(1)} \alpha C_{A0} \left(1 - \gamma - \frac{\gamma}{K_e} \right)$$

$$= \alpha k_{(1)} C_{A0} [1 - \beta \gamma]; \quad \beta = \frac{(K_e + 1)}{K_e}$$

$$\frac{v_0}{y_2} \frac{dy}{dv} = \frac{k \alpha}{(1)} (1 - \beta y)$$

Integrating

$$\int \frac{k \alpha}{(1)} dv = - \frac{v_0}{y_2 \beta} \ln(1 - \beta y_2)$$

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

Note this form of the design eqn is able to utilise performance data supplied.

Fresh Catalyst

$$\checkmark y_2 = 0.75; T = 450 \text{ K}$$

putting numbers

$$\beta = \frac{K_e + 1}{K_e} = \frac{9.5}{8.5} = 1.117 \checkmark \text{ at } 450.$$

$K_e \text{ at } 450 = 8.5$

$$v_0 = 0.39 \text{ ht/s}$$

$$k_{(1), 450} = \frac{-0.39}{0.75} \ln [1 - (1.117)(0.75)]$$
$$= 0.847 \checkmark$$

Activity of spent catalyst

$$\frac{k_{(1)}(477)}{k_{(1)}(450)} = \frac{e^{-15000/(R)(477)}}{e^{-15000/(R)(450)}}$$

$$\frac{k_{(1)}(477)}{k_{(1)}(450)} = 2.66 ; \quad 1 - y_2 = 0.322 \checkmark$$

$$y_2 = 0.678 \checkmark$$

$$\alpha k_{(0)}^{(v)}(477) = \frac{-0.38}{(0.678)(7/6)} [1 - 1.166 \times 0.678]$$

$$= 0.750 \checkmark \quad \nearrow \beta$$

$$\beta = \frac{K_e + 1}{K_e} = \frac{7}{6}$$

$$k_{(1)} \left(\frac{\alpha v}{477} \right) = \frac{0.75}{0.847} = \underline{\underline{0.88}}$$

$$(1) \left(\frac{\alpha v}{450} \right)$$

$$\text{So } \left[\frac{\left(\frac{\alpha v}{477} \right)}{\left(\frac{\alpha v}{450} \right)} \right] = \frac{[0.88] [k_{(1)}]_{450}}{(k_{(1)})_{477}} = \frac{0.8}{2.66}$$

Note that spent catalyst activity is $\underline{\underline{0.33}}$ only 33% of fresh catalyst. So the need to change catalyst.

Activity of Regenerated Catalyst

$$(k_{(1)} \propto V)_{450} = \frac{-V_0 \ln(1 - \beta y_2)}{y_2 \beta}$$

$$(k_{(1)} \propto V)_{450} = \frac{-0.28 \ln(1 - (1.117)(0.81))}{(0.81)(1.117)}$$

$$(K_1 \propto V)_{450, Reg} = \underline{\underline{0.727}}$$

$$(k_1 \propto V)_{Reg, 450}$$

$$= \frac{0.727}{0.847} = \underline{\underline{0.858}}$$

$$(K_1 \propto V)_{450, Fresh}$$

Concn I is not reduced

So activity of Reg Catalyst = 0.858

As per Criteria I which

Specifies that Reg Cat should be

90% fresh Cat activity. So Criteria I
is not satisfied.

Criteria - II

Activity of Reg Cat. 0.858 ✓

Activity spent catalyst = (0.33 ✓)

Activity of reg catalyst should be greater than (2.25) activity of spent catalyst

Accordingly criteria II is satisfied.