Catalyst Deactivation

Book: *Chemical Reaction Engineering*, O. Levenspiel, 3rd Edition, Wiley and Sons (Chapter 21)
Chemical Engineering Kinetics, J. M. Smith, (Chapter 11), 2nd and 3rd Edition

Pore mouth (shell poisoning)

- If the adsorption (or reaction) causing <u>poisoning is very fast</u>, the <u>outer part of a catalyst pellet</u> will be completely <u>deactivated</u> while the central portion retains its un-poisoned activity

- The layer of poisoned catalyst starts to grow at the outer surface and continues to grow in thickness till all the pellet is deactivated

- This type of poisoning is described by the "progressive shell model"

- The effect of pore mouth poisoning can be obtained by <u>equating the rate of diffusion through the outer, deactivated layer to the rate of reaction on the inner fully active part of the pellet</u>

- The rate of diffusion into one pellet is = $\boxed{R = D_e 4\pi r^2 \dfrac{dC}{dr}}$

- Integrating between r_s and r_c where this equation is applicable we have,

$$\boxed{\int_{r_s}^{r_c} \frac{dr}{r^2} = \frac{D_e 4\pi}{R} \int_{C_s}^{C_c} dC}$$

$$\left(\frac{1}{r_c} - \frac{1}{r_s}\right) = -\frac{D_e 4\pi}{R}(C_c - C_s)$$

$$\boxed{R = \frac{4\pi D_e r_s r_c}{r_s - r_c}(C_s - C_c)}$$
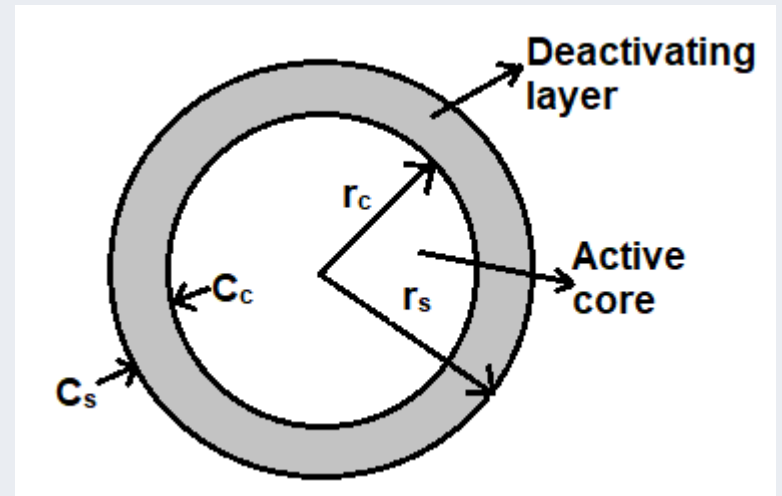
r_c = radius of un-poisoned central portion
r_s - r_c =thickness of completely poisoned catalyst

- Rate of reaction (first order reaction) in the inner core is = $m_p \eta k C_c$

where m_p = mass of active core of pellet

$$\therefore \quad \boxed{\frac{4\pi D_e r_s r_c}{r_s - r_c}(C_s - C_c) = m_p \eta k C_c}$$

$$\frac{4\pi D_e r_s r_c}{r_s - r_c}C_s - \frac{4\pi D_e r_s r_c}{r_s - r_c}C_c = \left(\frac{4}{3}\pi r_c^3 \rho_p\right)\eta k C_c$$

$$\boxed{C_c = \frac{\dfrac{D_e r_s r_c C_s}{(r_s - r_c)}}{\dfrac{D_e r_s r_c}{(r_s - r_c)} + \dfrac{1}{3}r_c^3 \rho_p \eta k}}$$

Now, $\quad R = \frac{4\pi D_e r_s r_c}{r_s - r_c}(C_s - C_c)$

Replacing the value of C_c in the above equation we have,

$$R = \frac{4\pi D_e r_s r_c}{r_s - r_c}\left(C_s - \frac{\dfrac{D_e r_s r_c C_s}{(r_s - r_c)}}{\dfrac{D_e r_s r_c}{(r_s - r_c)} + \dfrac{1}{3}r_c^3 \rho_p \eta k}\right)$$

$$R = \frac{4\pi D_e r_s r_c}{r_s - r_c}\left(C_s - \frac{D_e r_s C_s}{D_e r_s + \dfrac{1}{3}r_c^2 \rho_p \eta k(r_s - r_c)}\right)$$

$$R = \frac{4\pi D_e r_s r_c}{r_s - r_c} \left(\frac{\cancel{D_e r_s C_s} + \frac{1}{3} r_c^2 \rho_p \eta k (r_s - r_c) C_s - \cancel{D_e r_s C_s}}{D_e r_s + \frac{1}{3} r_c^2 \rho_p \eta k (r_s - r_c)} \right)$$

$$R = 4\pi D_e r_s r_c \left(\frac{\frac{1}{3} r_c^2 \rho_p \eta k C_s}{D_e r_s + \frac{1}{3} r_c^2 \rho_p \eta k (r_s - r_c)} \right)$$

Now , rate for whole pellet on unit mass basis, $r_p = \dfrac{R}{\frac{4}{3}\pi r_s^3 \rho_p}$

$$r_p = \frac{\pi D_e r_s \frac{4}{3} r_c^3 \rho_p \eta k C_s}{D_e r_s + \frac{1}{3} r_c^2 \rho_p \eta k (r_s - r_c)} \times \frac{1}{\frac{4}{3}\pi r_s^3 \rho_p}$$

$$r_p = \frac{D_e r_c^3 \eta k C_s}{D_e r_s^3 + \frac{1}{3} r_c^2 \rho_p \eta k (r_s - r_c) r_s^2}$$

$$\boxed{r_p = \frac{k C_s}{\left(\dfrac{r_s}{r_c}\right)^3 \dfrac{1}{\eta} + \left(\dfrac{k \rho_p}{D_e} \cdot \dfrac{r_s^2}{3}\right)\left(\dfrac{r_s - r_c}{r_c}\right)}}$$

Fraction of total surface un-poisoned is

$$1 - \alpha = \frac{\frac{4}{3}\pi r_c^3 \rho_p S_g}{\frac{4}{3}\pi r_s^3 \rho_p S_g} = \left(\frac{r_c}{r_s}\right)^3$$

Replacing this value in the rate equation we have,

$$r_p = \frac{kC_s}{\frac{1}{(1-\alpha)} \cdot \frac{1}{\eta} + (3\phi_s^2)\left[\frac{1 - \frac{r_c}{r_s}}{\frac{r_c}{r_s}}\right]}$$

$$r_p = \frac{kC_s}{\frac{1}{(1-\alpha)} \cdot \frac{1}{\eta} + (3\phi_s^2)\left[\frac{1 - (1-\alpha)^{1/3}}{(1-\alpha)^{1/3}}\right]}$$

Now, $\qquad a = \dfrac{r_p}{r_p(\alpha=0)}$

$$a = \frac{\dfrac{kC_s}{\frac{1}{(1-\alpha)} \cdot \frac{1}{\eta} + (3\phi_s^2)\left[\frac{1 - (1-\alpha)^{1/3}}{(1-\alpha)^{1/3}}\right]}}{\dfrac{kC_s}{\frac{1}{\eta} + 0}}$$

$$a = \frac{1}{\frac{1}{(1-\alpha)} + (3\eta\phi_s^2)\left[\frac{1 - (1-\alpha)^{1/3}}{(1-\alpha)^{1/3}}\right]}$$

(i) If <u>intrinsic rate is very slow</u>, $\underline{\phi_s \text{ is low, } \eta \rightarrow 1}$ (diffusion resistance in the inner core of active catalyst will be negligible) ;$\phi_s$is low but not as small as would be expected as $\underline{\eta \text{ is a function of}}$

ϕ_c $\left[\phi_c = \dfrac{r_c}{3}\sqrt{\dfrac{k\rho_p}{D_e}}\right]$ and therefore of α and not ϕ_s
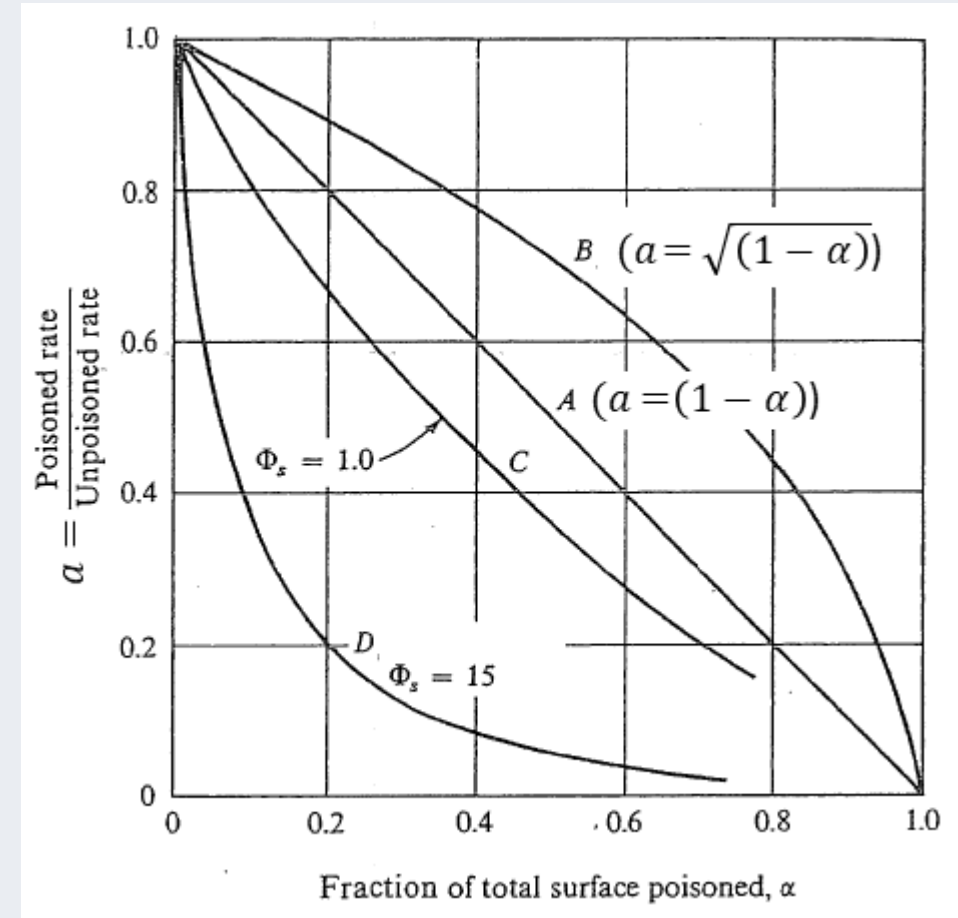
The second term in the denominator tends to reduce a; when the second term is negligible, $a = 1 - \alpha$

For the conditions of $\eta \rightarrow 1$, ϕ_s will be of the order of 1 and $\phi_c = \dfrac{1}{3}$; then the second term is small and curve is shown by **C**

(ii) If the <u>main reaction is fast</u> (ϕ_c >5), the effectiveness factor is given by

$$\boxed{\eta = \frac{1}{\phi_c} = \frac{r_s}{r_c}\cdot\frac{1}{\phi_s} = \frac{1}{(1-\alpha)^{1/3}}\cdot\frac{1}{\phi_s}}$$

$\therefore$ $$\boxed{a = \cfrac{1}{\cfrac{1}{(1-\alpha)} + (3\phi_s)\left[\cfrac{1-(1-\alpha)^{1/3}}{(1-\alpha)^{2/3}}\right]}}$$

Fraction of total surface poisoned, α

A—Uniform poisoning and slow main reaction $\eta \rightarrow 1$
B—Uniform poisoning and fast main reaction $\eta \leqslant 0.2$
C—Pore-mouth poisoning and slow main reaction $\Phi_s = 1.0$
D—Pore-mouth poisoning and fast main reaction $\Phi_s = 15$

- For $\phi_c \geq 5$, ϕ_s is even larger

- For $\frac{r_c}{r_s} = \frac{1}{3}$, $\phi_s \geq 15$,

- A sharp drop in activity is observed in this case

- The <u>reactant molecule cannot penetrate far into the active part</u> (large diffusional resistances) <u>of the catalyst before reaction occurs</u> (fast reaction)

- Thus both poisoning and main reaction compete for sites on the same outer surface

- <u>As the outer surface is poisoned, rate falls dramatically</u>

- For pore mouth poisoning finding a <u>relation between a and t and hence α and t</u>, means <u>finding a relation between</u> $(\frac{r_c}{r_s})$ <u>and t for a shell model</u>

- This is developed in a later chapter on gas-solid non-catalytic reactions where the product is also a solid

Design

- When <u>reacting fluid flows through a batch of deactivating catalysts the conversion drops progressively</u> during the run and <u>steady state conditions cannot be maintained</u>

- If conditions change slowly with time, then the <u>average conversion during a run can be found by calculating the steady-state conversion at various times and summing over time</u>

$$\overline{X_A} = \frac{\int_0^{t_{run}} X_A(t)dt}{t_{run}}$$

When conversion drops too low, the run is terminated, and the catalyst is either discarded or regenerated

Example

The isomerization of $A \rightarrow R$ is carried out in a packed bed reactor (Feed pure A, F_{Ao} = 5 kmol/h, W = 1 ton catalyst, P = 3 atm, T = 730 K). The catalyst deactivates, so it is planned to make 120 day runs and the regenerate the catalyst.

The rate of the reaction with C_A in mol/m³ is $\quad -r_A = 0.2 C_A^2 a \quad$ (mol A /kg cat.h)

Rate of deactivation is given by

(a) $-\dfrac{da}{dt} = 8.3125 \times 10^{-3} \quad$ day⁻¹ (poisoning by feed impurity)

(b) $-\dfrac{da}{dt} = 10^{-3}(C_A + C_R)a \quad$ day⁻¹ (poisoning by reactant and product to influence pore diffusion)

(c) $-\dfrac{da}{dt} = 3.325\, a^2 \quad$ day⁻¹ (fairly strong pore diffusion resistance)

(i) Plot conversion and activity versus time for the run

(ii) Find $\overline{X_A}$ for 120 day run

For a PFR,

$$\tau = \frac{W C_{Ao}}{F_{Ao}} = \int_{C_{Ao}}^{C_A} \frac{dC_A}{(-r_A)}$$

$$C_{Ao} = \frac{p_{Ao}}{RT} = \frac{3}{0.082 \times 1000 \times 730} = 5.0117 \times 10^{-5} \text{ mol/cm}^3 = 50.117 \text{ mol/m}^3$$

$$\tau = \frac{W C_{Ao}}{F_{Ao}} = \frac{1000 \times 50.117}{5000} = 10.02 \text{ kg.h/m}^3$$

$$\tau = \int_{C_{Ao}}^{C_A} \frac{dC_A}{(-r_A)} = \int_{C_{Ao}}^{C_A} \frac{dC_A}{0.2C_A^2 a} = \frac{1}{0.2a}\left[\frac{1}{C_A} - \frac{1}{C_{Ao}}\right]$$

$$\tau = \frac{1}{0.2a}\left[\frac{1}{C_A}\left\{1 - \frac{C_A}{C_{Ao}}\right\}\right] = \frac{1}{0.2aC_{Ao}(1-X_A)}X_A$$

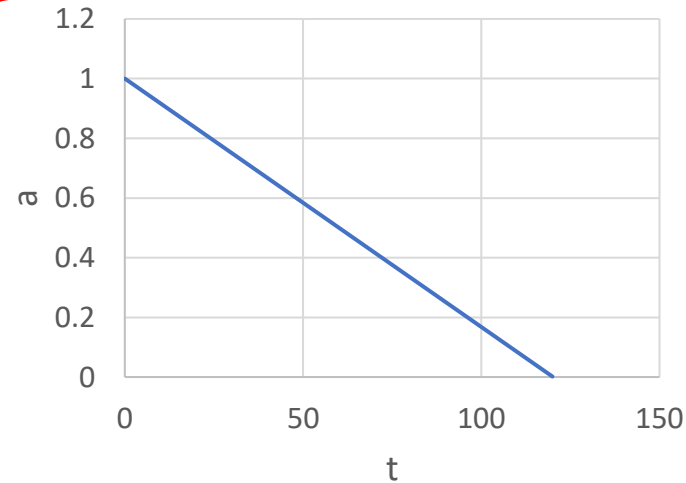$$\frac{X_A}{(1-X_A)} = (10.02 \times 0.2 \times 50.117)a = 100.44a$$

$$X_A = \frac{100.44a}{(1 + 100.44a)}$$

(a) $\quad -\frac{da}{dt} = 8.3125 \times 10^{-3}$

$$-\int_1^a da = 8.3125 \times 10^{-3}\int_0^t dt$$

$$1 - a = 8.3125 \times 10^{-3}\, t$$

$$\boldsymbol{a = 1 - 8.3125 \times 10^{-3}\, t}$$
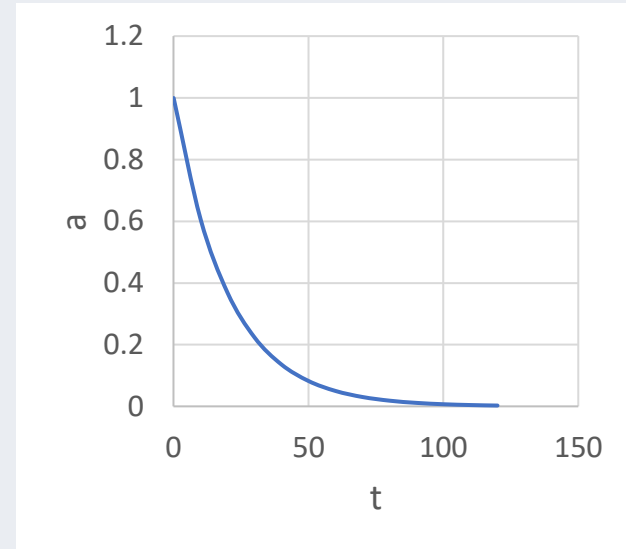
(b) $-\dfrac{da}{dt} = 10^{-3}(C_A + C_R)a$

$$-\int_1^a \frac{da}{a} = 10^{-3}(50.117)\int_0^t dt$$

$$ln\frac{1}{a} = 0.05\, t$$

$$\boldsymbol{a = e^{-0.05t}}$$
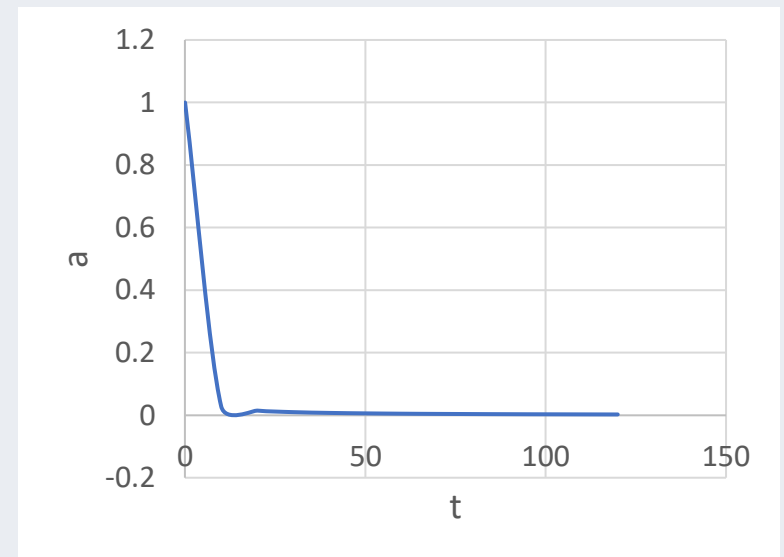
Initially,
$C_A = C_{Ao}$
$C_R = 0$

(c) $-\dfrac{da}{dt} = 3.325\, a^2$

$$-\int_1^a \frac{da}{a^2} = 3.325\int_0^t dt$$

$$\left[\frac{1}{a} - 1\right] = 3.325\, t$$

$$\frac{1}{a} = 1 + 3.325\, t$$

$$\boldsymbol{a = \dfrac{1}{1 + 3.325\, t}}$$

Now, $X_A = \dfrac{100.44a}{(1+100.44a)}$

(a) $a = 1 - 8.3125 \times 10^{-3}\, t$

(b) $a = e^{-0.05t}$

(c) $a = \dfrac{1}{1 + 3.325\, t}$

For a 120 day period,

t	X_A	X_A	X_A
0	0.990142	0.990142	0.990142
10	0.989258	0.98385	0.745712
20	0.988199	0.973649	0.598071
30	0.98691	0.957285	0.49923
40	0.985304	0.931474	0.428425
50	0.983248	0.891829	0.37521
60	0.980524	0.83335	0.333754
70	0.976742	0.752047	0.300548
80	0.971138	0.647841	0.273351
90	0.961975	0.527363	0.250668
100	0.944287	0.403612	0.231461
110	0.895835	0.291019	0.214987
120	0.200703	0.199338	0.200703
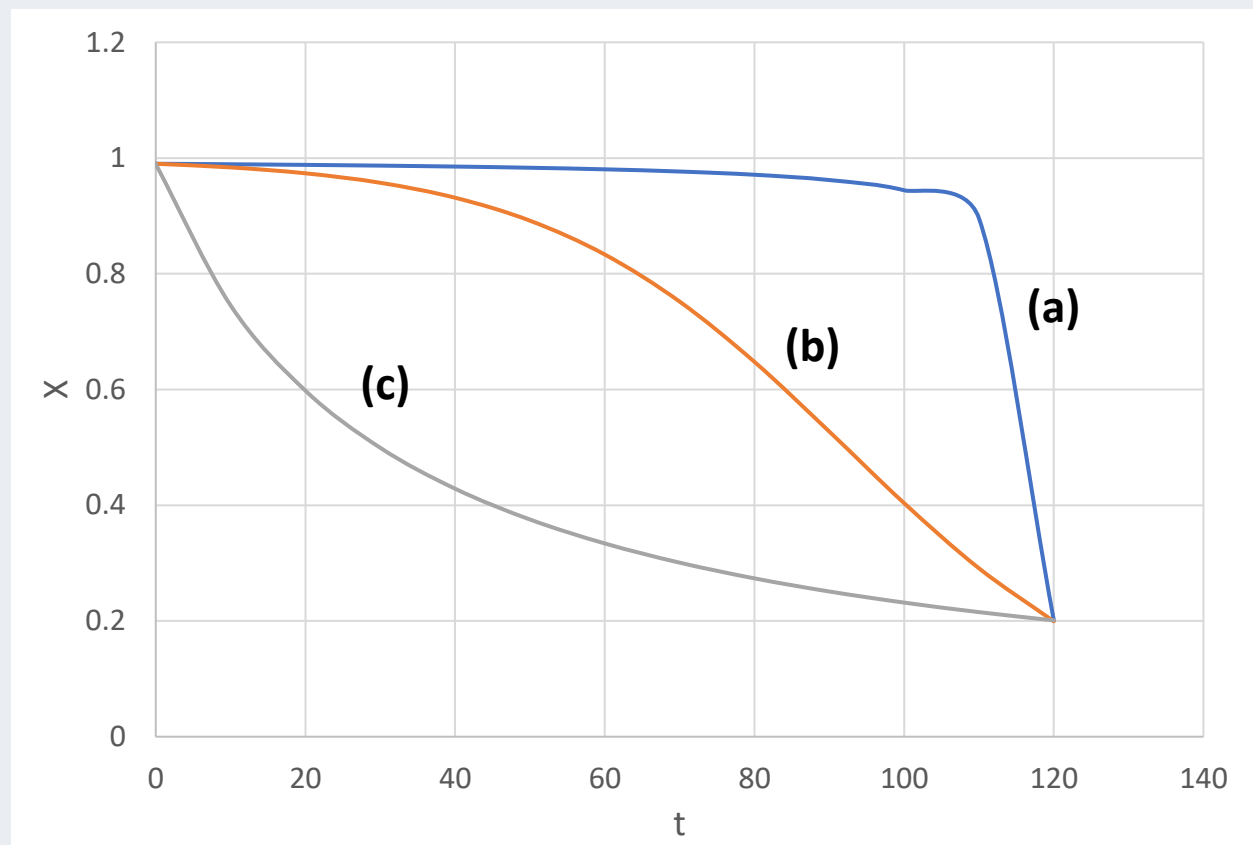
$$\overline{X_A} = \frac{\int_0^{t_{run}} X_A(t)dt}{t_{run}} = \frac{area\ under\ the\ curve}{t_{run}}$$

(a) $\overline{X_A} = \dfrac{113.977}{120} = \mathbf{0.9498}$

(b) $\overline{X_A} = \dfrac{87.9276}{120} = \mathbf{0.7327}$

(c) $\overline{X_A} = \dfrac{48.2626}{120} = \mathbf{0.4022}$

The two important and real problems with deactivating catalysts are:

Operational problem: This means how to operate the reactor and finding the best temperature progression during the run since temperature is the most important variable affecting reaction and deactivation
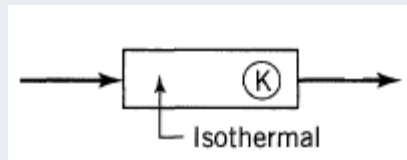
Regeneration problem: When to stop the run and either discard or regenerate the catalyst

For the operational problem, let us consider

$$-r_A = kC_A^n a = \left(k_o e^{-E/RT}\right) C_A^n a$$

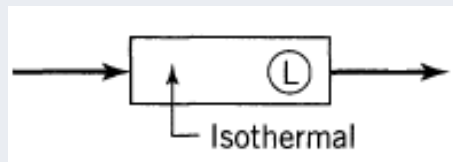$$-\frac{da}{dt} = k_d a^d = \left(k_{do} e^{-E_d/RT}\right) a^d$$

For slow deactivation, a batch of catalysts can be used and the reactor can be run in one of the following ways:
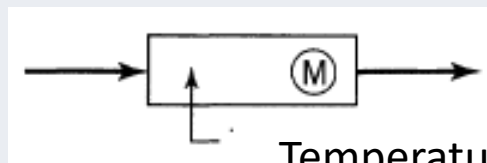
(I) Constant flow

X_A decreases with time as catalyst deactivates
F_R decreases with time

(II) Flow decreases with time so as to keep X_A constant

X_A and composition stay constant
F_R decreases with time

(III) Constant molar flow

X_A and F_R are kept constant

Temperature is boosted to keep X_A constant

- The performance equations are obtained by solving

$$\frac{W}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{\left(k_o e^{-E/RT}\right) C_A^n a}$$

$$-\int_1^a \frac{da}{a^d} = k \int_0^t dt$$

For the three operating conditions:

For (I), a decreases with t, and so does X_A

For (II), a decreases with t, feed rate is lowered so that at any time, $\frac{F_{Ao}}{a} = f_{Ao,constant}$, X_A is constant

For (III), $\frac{W}{F_{Ao}} = \frac{1}{ka C_{Ao}} \int_0^{X_A} \frac{dX_A}{(1-X_A)^n}$ The LHS and the integral term is constant, so $ka C_{Ao}$ should remain constant as temperature is varied

For <u>no pore diffusion resistance</u>, change T such that

ka = constant   for all liquid systems

$\frac{ka}{T^n}$ = constant   for ideal gases with nth order reaction

For <u>strong resistance to pore diffusion</u>,   change T such that

$ka D_e$ = constant   for all liquid systems

$\frac{ka D_e}{T^{n+1}}$ = constant   for ideal gases with nth order reaction

(i) If <u>deactivation is very temperature sensitive compared to reaction</u>, the optimal policy is to <u>raise temperature with time so as to keep conversion from the reactor unchanged</u> – use method (III) ending the run at maximum allowable temperature (T^*)
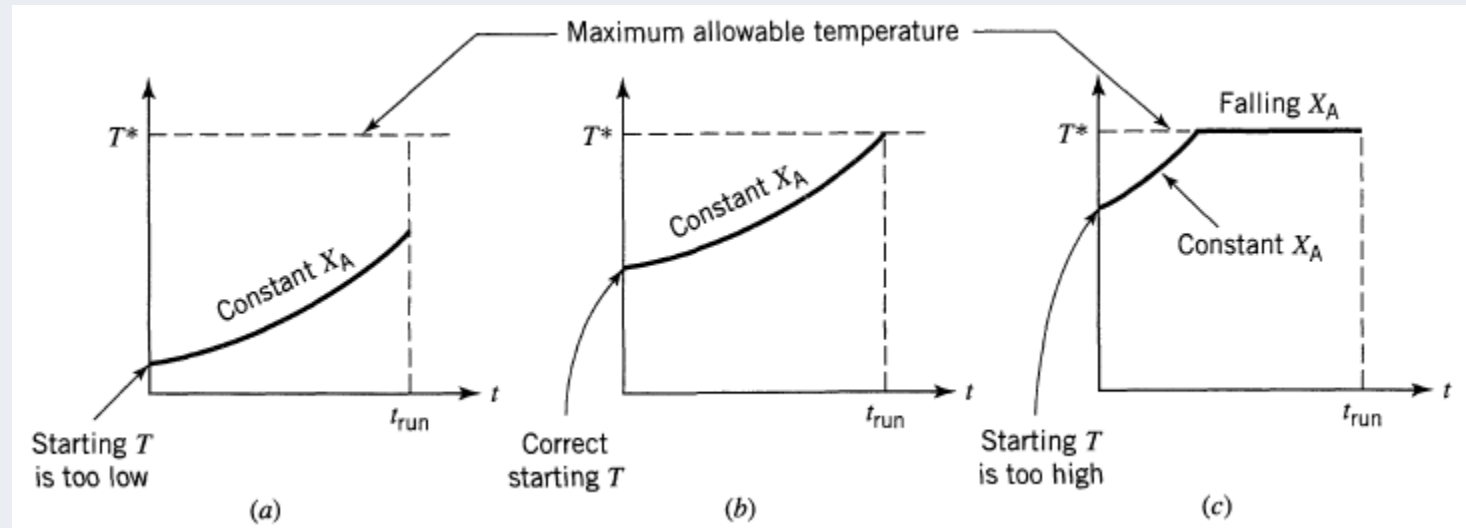
(ii) If <u>deactivation is less temperature sensitive</u>, then one can <u>use either method (I) or (II)</u> but run is <u>made at maximum allowable temperature (T^*)</u>

(iii) If <u>deactivation is concentration dependent</u>, the catalyst <u>activity varies with position in reactor</u>. It is required that temperature varies with position along the reactor as well as time – difficult situation to analyze

(iv) For <u>catalysts that deactivate rapidly</u>, packed bed reactors are not practical and <u>moving bed reactors with solid flow systems are required</u>