(1) Opt. T for chemical reactors

- By operating chemical reactors $\rightarrow$ Optimize T so for a fixed reactor V, x_A is maximized.
  at an opt. T, we can $\qquad$ " " " " required x_A, the reactor V is minimized.

1.1 CSTR

- consider the design eq. for a CSTR:
$$-r_A = \frac{F_{A_0} - F_{AE}}{V} = \frac{F_{A_0} x_{AE}}{V}$$

$$V = \frac{F_{A_0} x_{AE}}{-r_{AE}} \qquad \text{"for a given } x_{AE}, \text{ to minimize V, we must maximize } (-r_{AE})\text{"}$$

$$x_{AE} = \frac{(-r_A) V}{F_{A_0}} \qquad \text{" " " V, we must maximize } (-r_{AE}) \text{ to maximize } x_{AE}\text{"}$$

- The optimum operating T for a CSTR
  $\rightarrow$ involves the determination of a single T at which $(-r_A)$ is max, $T_E = T_{opt}$.
  $$T = T_{opt}. \quad \text{where} \quad \frac{\partial (-r_A)}{\partial T} = 0$$
  $\rightarrow$ The value of T_{opt} depends on the type of rate expression.

1.1.1 $T_{opt} = \infty$

- In this case, operate the reactor at the max allowable T, T_{max}.

- e.g. $-r_{AE} = k C_{AE}^n$ $\rightarrow$ where it is used for liquid phase rxn, irreversible, with Arrhenius rate expression.
  $$\rightarrow -r_{AE} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot C_{A_0}^n (1-x_{AE})^n$$
  $$\rightarrow \frac{\partial}{\partial T}(-r_{AE}) = A \left(\frac{E}{RT^2}\right) \cdot \exp\left(-\frac{E}{RT}\right) \cdot C_{A_0}^n (1-x_{AE})^n = 0 \quad @ \ T = T_{opt}$$

$$\Rightarrow \frac{1}{T^2} \cdot \exp\left(\frac{-E}{RT}\right) = 0 \quad , \quad E > 0 \quad \Rightarrow \quad T_{opt} = \infty$$
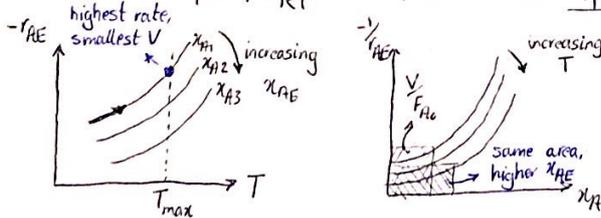

1.1.2 There is a single max in $(-r_A)$ vs. T curve which is independent of x_{AE}.

- e.g. gas phase rxn, power-law kinetics, any stoichiometry, arrhenius rate expression, irreversible.
- for example $\rightarrow A \rightarrow 2B$, $-r_A = k C_A^n$, consider a constant P, ideal gas case
  $$\rightarrow -r_{AE} = k \left(\frac{1-x_{AE}}{1+x_{AE}} \cdot \frac{P}{RT}\right)^n = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot \left(\frac{1-x_{AE}}{1+x_{AE}}\right)^n \left(\frac{P}{R}\right)^n \cdot \frac{1}{T^n}$$
  $$\rightarrow \frac{\partial}{\partial T}(-r_{AE}) = A \cdot \left(\frac{1-x_{AE}}{1+x_{AE}}\right)^n \left(\frac{P}{R}\right)^n \left(\frac{T^n \frac{E}{RT^2} \cdot \exp\left(-\frac{E}{RT}\right) - n T^{n-1} \cdot \exp\left(-\frac{E}{RT}\right)}{T^{2n}}\right) = 0 \quad @ \ T = T_{opt}$$

$$\Rightarrow \frac{E T^n}{RT^2} = n T^{n-1} \quad \Rightarrow \quad T_{opt} = \frac{E}{nR}$$
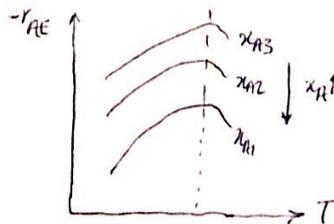
– e.g. reversible power-law rxns (exothermic) – Langmuir-Hinshelwood rate functions

– for example → $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ liquid phase rxn, feed pure A at C_{A_0}, k_1 and k_{-1} follow arrhenius expressions

$\rightarrow -r_A = k_1 C_A - k_{-1} C_B = k_1 C_{A_0}(1-x_{AE}) - k_{-1} C_{A_0} x_{AE} = k_1 C_{A_0}\left[1 - x_{AE} - \frac{k_{-1}}{k} x_{AE}\right]$

$\rightarrow$ recall the eq. constant $K = \frac{k_1}{k_{-1}} = \frac{A_1 \exp(-E_1/RT)}{A_{-1}\exp(-E_{-1}/RT)}$ $\implies -r_{AE} = A_1 \exp\left(-\frac{E_1}{RT}\right) \cdot C_{A_0}\left[1 - x_{AE} - \frac{x_{AE}}{K}\right]$

– Before we proceed
$\rightarrow$ how K varies with T.
$\rightarrow$ Van't Hoff eq.: $\frac{d \ln K}{dT} = \frac{\Delta H_R^o}{RT^2}$

$\rightarrow$ but $K = \frac{A_1}{A_{-1}} \cdot \exp\left(\frac{E_{-1} - E_1}{RT}\right) \implies \ln K = \ln \frac{A_1}{A_{-1}} + \frac{E_{-1} - E_1}{RT}$

$\rightarrow$ so: $\frac{d \ln K}{dT} = \frac{E_1 - E_{-1}}{RT^2} \implies \underline{\Delta H_R^o = E_1 - E_{-1}}$

endothermic : $\Delta H_R^o > 0$
exothermic : $\Delta H_R^o < 0$

– for endothermic: $T\uparrow \implies K\uparrow$

– for enothermic: $T\uparrow \implies K\downarrow$

reversible, exo

reversible, endo.
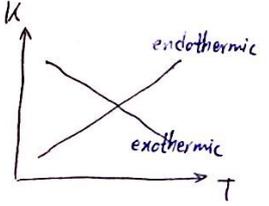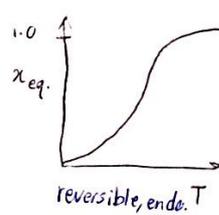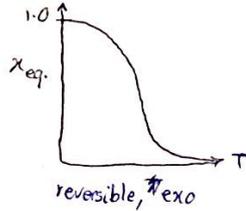
– back to our rate expression
$\rightarrow$ for endothermic
$\rightarrow T\uparrow \implies \exp\left(-\frac{E_1}{RT}\right)\uparrow$
$\rightarrow T\uparrow \implies K\uparrow$
$\rightarrow$ thus, $(-r_{AE})$ keeps increasing with increasing T
$\rightarrow T_{opt.} = \infty$, hence operate at $T = T_{max}$
$\rightarrow$ If we fix x_{AE}, increasing T would increase $(-r_{AE}) \implies$ smaller V

$\rightarrow$ for exothermic
$\rightarrow$ let us now proceed to obtain T_{opt}.
$\rightarrow -r_{AE} = A_1 C_{A_0}\left[(1-x_{AE})\cdot\exp\left(-\frac{E_1}{RT}\right) - \frac{A_{-1}}{A_1}\cdot x_{AE}\cdot\exp\left(-\frac{E_{-1}}{RT}\right)\right]$

$\rightarrow \frac{\partial}{\partial T}(-r_{AE}) = A_1 C_{A_0}\left[\frac{E_1}{RT^2}(1-x_{AE})\cdot\exp\left(-\frac{E_1}{RT}\right)\right.$
$\left. - \frac{A_{-1}}{A_1}\cdot\frac{E_{-1}}{RT^2}\cdot\exp\left(-\frac{E_{-1}}{RT}\right)\right] = 0$ @ $T = T_{opt}$.
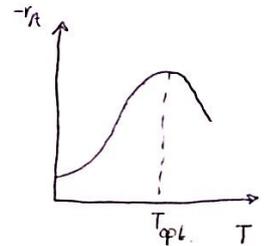
$\implies A_1 E_1 (1-x_{AE})\cdot\exp\left(-\frac{E_1}{RT}\right) = A_{-1}E_{-1} x_{AE} \exp\left(-\frac{E_{-1}}{RT}\right)$

$\implies \frac{A_{-1}E_{-1} x_{AE}}{A_1 E_1 (1-x_{AE})} = \exp\left(\frac{E_{-1} - E_1}{RT}\right) \implies T_{opt.} = \dfrac{E_{-1} - E_1}{R \ln \dfrac{A_{-1}E_{-1} x_{AE}}{A_1 E_1 (1-x_{AE})}}$
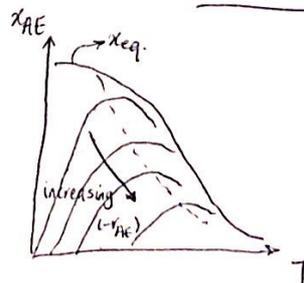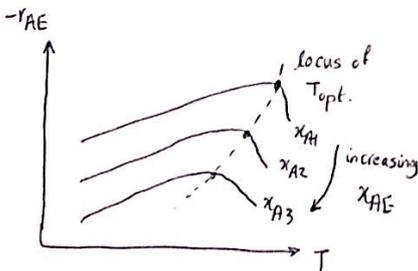
1.2 PFRs

- Recall the design eq. for PFR: $-r_A = -\dfrac{dF_A}{dV}$ $\Rightarrow$ $V = F_{A_0}\displaystyle\int_0^{x_{AE}} \dfrac{dx_A}{-r_A}$

- to minimize the reactor V, we have to maximize the rate at every point inside the reactor.
- But note that for a PFR, the x_A varies along the length of the reactor.
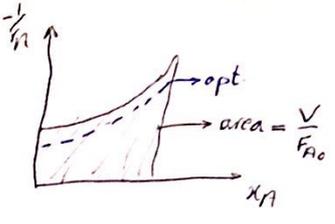
- case 01 → $T_{opt.} = \infty$
  - → optimal operation: $T = T_{max}$ (isothermal)

- case 02 → T_{opt} independent of x_A
  - → optimal operation: $T = T_{opt.}$ ($\sim$)

- case 03 → $T_{opt.}$ depends on x_A
  - → optimal operation: Optimum Temperature Progression (OTP)
  - → In this situation we maintain a T profile in the PFR which is opt. (i.e. Reactor T varies along the reactor length as x_A changes)
  - → e.g. → Reversible exothermic rxn
    - → note that at low x_A, $T_{opt.}$ maybe be very high, so we may have to operate the reactor isothermally @ $T = T_{max}$ until such point in the reactor, the $T_{opt.}$ corresponding to a higher x_A is less than T_{max}. (right figure)
  - → Interstage cooling for exothermic reversible rxn:

Distance along PFR's
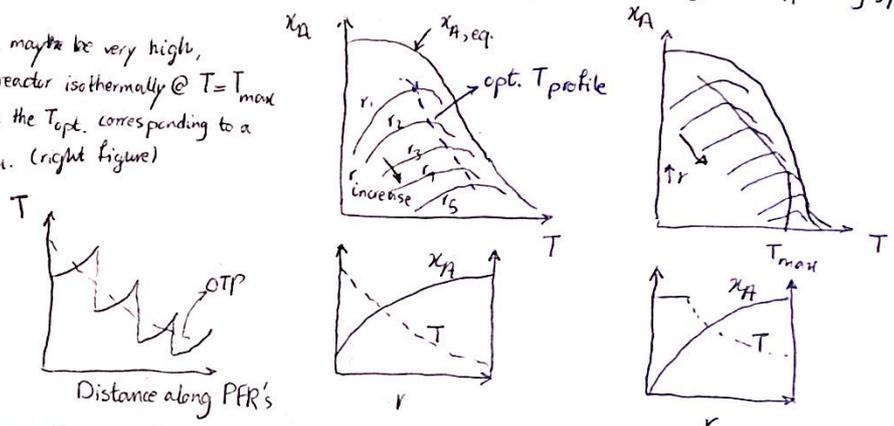
- Ex. → "Example of Optimal T progression for a PFR"
  - → liquid phase rxn: $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, $-r_A = k_1 C_A - k_2 C_B$ $[\text{mol}/\text{m}^3 \cdot \text{s}]$
  - → Feed pure A, $C_{A_0} = 1.0 \text{ mol}/\text{m}^3$, $F_{A_0} = 1.0 \text{ mol}/\text{s}$
  - → $k_1 = A_1 \exp(-E_1/RT)$, $A_1 = 5\times10^4$, $E_1/R = 4000\,k$, $k_2 = A_2 \exp(-E_2/RT)$, $A_2 = 5\times10^8$, $E_2/R = 8000\,k$
  - → The rxn is to be carried out in a PFR. what is the V requirement for 80% conversion of A if:
  - → a. operate isothermally @ $T = 375\,k$
  - → b. operate with OTP
  - → c. operate $\sim$ $\sim$ with $T_{max} = 450\,k$

- Solution of a. →
$$V = F_{A_0}\int_0^{x_A=0.8} \frac{dx_A}{-r_A} = F_{A_0}\int_0^{0.8} \frac{dx_A}{k_1 C_{A_0}(1-x_A) - k_2 C_{A_0} x_A} \quad \text{(for isothermal, } k_1 \text{ and } k_2 \text{ are constant)}$$

$$\Rightarrow V = \frac{F_{A_0}}{k_1 C_{A_0}}\int_0^{0.8} \frac{dx_A}{1 - x_A - \frac{k_2}{k_1}x_A} = \frac{F_{A_0}}{k_1 C_{A_0}}\int_0^{0.8} \frac{dx_A}{1 - (\frac{k_1+k_2}{k_1})x_A} = \frac{F_{A_0}}{k_1 C_{A_0}}\left[\frac{-k_1}{k_1+k_2}\ln\left(1 - (\frac{k_1+k_2}{k_2})x_A\right)\right]_0^{0.8}$$

$$\Rightarrow V = \frac{-F_{A_0}}{(k_1+k_2)C_{A_0}}\ln\left(1 - \frac{k_1+k_2}{k_1}x_A\right) , \quad x_A = 0.8$$

→ @ $T = 375\,k$: $k_1 = 1.16545$, $k_2 = 0.27166$ ↳ $\boxed{V = 2.994 \text{ m}^3}$

- Solution of b. → $T_{opt.} = \dfrac{E_2 - E_1}{R\ln\dfrac{A_2 E_2 x_A}{A_1 E_1 (1-x_A)}} = \dfrac{4000}{\ln\dfrac{(5\times10^8)(8000)\,x_A}{(5\times10^4)(4000)(1-x_A)}}$ $\Rightarrow T_{opt.} = \dfrac{4000}{\ln\dfrac{20000\,x_A}{1-x_A}}$

→ $k_1 = A_1\exp(-E_1/RT) = 5\times10^4\cdot\exp\left(\frac{-4000}{4000}\ln\frac{20000\,x_A}{1-x_A}\right) = 5\times10^4\cdot\exp\left(\frac{20000\,x_A}{1-x_A}\right)^{-1}$ $\Rightarrow k_1 = 2.5\left(\frac{1-x_A}{x_A}\right)$

→ likewise: $k_2 = 1.25\left(\dfrac{1-x_A}{x_A}\right)^2$

→ $V = F_{A_0}\displaystyle\int_0^{0.8} \frac{dx_A}{k_1 C_{A_0}(1-x_A) - k_2 C_{A_0} x_A} = \frac{F_{A_0}}{C_{A_0}}\int_0^{0.8} \frac{dx_A}{2.5\frac{(1-x_A)^2}{x_A} - 1.25\frac{(1-x_A)^2}{x_A}} = \frac{F_{A_0}}{1.25\,C_{A_0}}\int_0^{0.8} \frac{x_A\,dx_A}{(1-x_A)^2}$

$$\Rightarrow V = \frac{F_{A_0}}{1.25\,C_{A_0}}\left[\frac{1}{1-x_A} + \ln(1-x_A)\right]_0^{0.8} = \frac{F_{A_0}}{1.25\,C_{A_0}}(5 + \ln 0.2 - 1 - \ln 1) \Rightarrow \boxed{V = 1.912 \text{ m}^3}$$

(9)

- Solution
of c.

$T_{max} = 950^k$ $\Rightarrow$ @ $T_{max} = T_{opt}$ $\Rightarrow$ $950 = \dfrac{4000}{\ln \frac{20000\, x_A}{1-x_A}}$ $\xRightarrow[\text{for } x_A]{\text{solving}}$ $\underline{x_A = 0.226}$

$\hookrightarrow$ operate isothermally @ $T=950^k$ until $x_A = 0.226$, then follow OTP :

$$V_{tot} = V_{iso.} + V_{OTP} = \dfrac{-F_{Ao}}{(k_1+k_2)\, C_{Ao}} \ln \left(1 - \dfrac{k_1+k_2}{k_1}(0.266)\right) + \dfrac{F_{Ato}}{1.25\, C_{Ao}} \left[5 + \ln 0.2 - \dfrac{1}{1-0.266} - \ln(1-0.266)\right]$$

$$= 0.061 + 1.870 \Rightarrow \underline{V_{tot.} = 1.931 \ m^3}$$