Batch reactors:

$$\boxed{\frac{dN_A}{dt} = r_A V}$$

$$\therefore \frac{dN_{A0}(1-X)}{dt} = r_A V$$

$$\therefore -N_{A0}\frac{dX}{dt} = r_A V$$

$$\therefore N_{A0}\frac{dX}{dt} = (-r_A)\cdot V$$

look at the signs, $-r_A$ is positive
Expectedly, X increases with time
(N_A decreases with time)

Flow reactors

⇒ CSTRs here, $F_A = F_{A0}(1-X)$

Design equation of a CSTR:

$$F_{A0} - F_A = -r_A \cdot V$$

$$\therefore \boxed{F_{A0} X = -r_A \cdot V}$$

PFRs (& PBRs):

$$\frac{dF_A}{dV} = r_A \quad \left\{ \text{OR } \underset{\text{if PBR}}{\frac{dF_A}{dW} = r_A'} \right\}$$

$$\therefore \frac{d\{F_{A0}(1-X)\}}{dV} = r_A$$

$$\therefore -F_{A0}\frac{dX}{dV} = r_A$$

$$\boxed{\therefore F_{A0}\frac{dX}{dV} = -r_A}$$

For PBR:

$$\boxed{F_{A0}\frac{dX}{dW} = -r_A'}$$

Let us apply our knowledge of the design equations to design some reactors.

Consider the following system:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

* elementary rxns,
* liquid-phase
* constant volume
* isothermal

This reaction takes place in a batch reactor.

Start with the design equation:

$$\frac{dN_i}{dt} = r_i V$$ units? $\frac{mol}{time}$!

$$\frac{d(C_i V)}{dt} = r_i V$$

$$\therefore \frac{dC_i}{dt} = r_i$$

+ve for products

-ve for reactants

$$\therefore \frac{dC_A}{dt} = -k_1 C_A \quad \ldots\ldots \quad -r_A = k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

$$\therefore \frac{dC_A}{C_A} = -k_1 dt$$

$$\ln C_A = -k_1 t + a$$

At $t=0$, $C_A = C_{A0}$, $C_B = 0$, $C_C = 0$ .... initial conditions

$$\therefore \quad \ln C_{A0} = -k_1 \cdot (0) + a$$

$$\therefore \quad a = \ln C_{A0}$$

$$\therefore \quad \ln C_A = -k_1 t + \ln C_{A0}$$

$$\therefore \quad \ln\left(\frac{C_{A0}}{C_A}\right) = k_1 t$$

$$\therefore \quad \frac{C_{A0}}{C_A} = \exp(k_1 t)$$

$$\boxed{\therefore \quad C_A = C_{A0} \exp(-k_1 t)}$$

Thus,

$$\frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B$$

$$\therefore \quad \frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$$

$$\therefore \quad \exp(k_1 t) \frac{dC_B}{dt} + k_2 \exp(k_1 t) C_B = k_1 C_{A0}$$

$$\therefore \quad \exp(k_1 t)\frac{dC_B}{dt} + \underbrace{k_2 \exp(k_1 t)\, C_B} = k_1 C_{A0}$$

to satisfy product rule

$$* \quad \therefore \quad \exp(k_1 t)\frac{dC_B}{dt} + k_1 \exp(k_1 t)\, C_B + (k_2 - k_1)\exp(k_1 t)\, C_B = k_1 C_{A0}$$

$$\therefore \quad \frac{d}{dt}\Big[\underbrace{C_B \exp(k_1 t)}_{\text{Let} = y}\Big] + (k_2 - k_1)\exp(k_1 t)\, C_B = k_1 C_{A0}$$

$$\therefore \quad \frac{dy}{dt} + (k_2 - k_1)\, y = k_1 C_{A0}$$

$$\therefore \quad \frac{dy}{dt} = k_1 C_{A0} + (k_1 - k_2)\, y$$

$$\therefore \quad \frac{dy}{k_1 C_{A0} + (k_1 - k_2)\, y} = dt$$

$$\therefore \quad \frac{\ln\left[k_1 C_{A0} + (k_1 - k_2)\, y\right]}{k_1 - k_2} = t + b$$

At $t = 0$, $y = C_B \exp(k_1 t) = 0$

$$\therefore \quad \frac{\ln(k_1 C_{A0})}{k_1 - k_2} = b$$

$$\therefore \frac{\ln\left[k_1 C_{A0} + (k_1 - k_2) y\right]}{k_1 - k_2} = \frac{\ln(k_1 C_{A0})}{k_1 - k_2} + t$$

$$\therefore \ln\left[\frac{k_1 C_{A0} + (k_1 - k_2) y}{k_1 C_{A0}}\right] = (k_1 - k_2) t$$

$$\therefore 1 + \left(\frac{k_1 - k_2}{k_1 C_{A0}}\right) C_B \exp(k_1 t) = e^{(k_1 - k_2) t}$$

$$\therefore \frac{(k_1 - k_2)}{k_1 C_{A0}} C_B \exp(k_1 t) = \exp\left[(k_1 - k_2) t\right] - 1$$

$$\therefore C_B = \left(\frac{k_1 C_{A0}}{k_1 - k_2}\right) \left[\frac{\exp\left[(k_1 - k_2) t\right]}{\exp(k_1 t)} - \exp(-k_1 t)\right]$$

$$\boxed{\therefore C_B = \left(\frac{k_1 C_{A0}}{k_1 - k_2}\right) \left[\exp(-k_2 t) - \exp(-k_1 t)\right]}$$

$$\therefore \frac{dC_c}{dt} = k_2 C_B$$

$$\therefore \frac{dC_c}{dt} = \left(\frac{k_1 k_2 C_{A0}}{k_1 - k_2}\right) \left[\exp(-k_2 t) - \exp(-k_1 t)\right]$$

$$\therefore \frac{dC_c}{dt} = \left(\frac{k_1 k_2 C_{A0}}{k_1 - k_2}\right)\left\{\exp(-k_2 t) - \exp(-k_1 t)\right\}$$

$$\therefore C_c = \left(\frac{k_1 k_2 C_{A0}}{k_1 - k_2}\right)\left[\frac{\exp(-k_2 t)}{-k_2} + \frac{\exp(-k_1 t)}{k_1}\right] + \gamma$$

$$\therefore C_c = \left(\frac{\cancel{k_1 k_2} C_{A0}}{k_1 - k_2}\right)\left[\frac{-k_1 \exp(-k_2 t) + k_2 \exp(-k_1 t)}{\cancel{k_1 k_2}}\right] + \gamma$$

At $t = 0$, $C_c = 0$

$$\therefore 0 = \frac{C_{A0}}{k_1 - k_2}\left[k_2 - k_1\right] + \gamma$$

$$\therefore 0 = -C_{A0} + \gamma$$

$$\gamma = C_{A0}$$

$$\boxed{\therefore C_c = C_{A0} + \frac{C_{A0}}{k_1 - k_2}\left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right]}$$

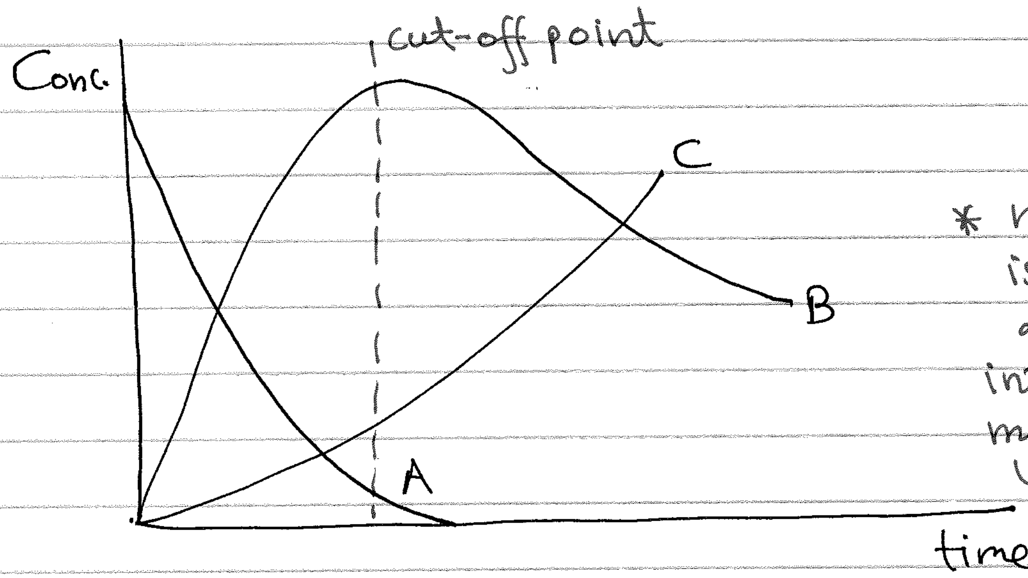
if C is undesired, B is desired (optimisat^n):

$\frac{dC_B}{dt}$ the expression, set = 0 & solve for $\underline{t}$.

$$\therefore \quad C_A = C_{A0}\left[\exp(-k_1 t)\right]$$

$$C_B = \frac{k_1 C_{A0}}{k_1 - k_2}\left[\exp(-k_2 t) - \exp(-k_1 t)\right]$$

$$C_C = C_{A0} + \frac{C_{A0}}{k_1 - k_2}\left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right]$$



* non-isothermal design introduces more variables

Common design question: when do I stop the batch?

important if B is desired product & C is unwanted product.

example: <u>oxidation of alcohols & carbonyl compounds</u>

alcohols → aldehydes → carboxylic acid (desired)

alcohols → ketones → carboxylic acid

Design of flow reactors

① CSTR : $\boxed{F_{A0} - F_A = (-r_A) \cdot V}$

OR

$$\boxed{F_{A0} X = (-r_A) \cdot V}$$

Common design question:

* Given F_{A0} (flow characteristics) & reaction information, how large should the vessel be?

$$F_{A0} X = (-r_A) \cdot V$$

$$\therefore \quad V = \frac{F_{A0} X}{-r_A}$$ ..... size of CSTR

OR $$X = \frac{(-r_A) \cdot V}{F_{A0}}$$ ..... conversion for a given CSTR

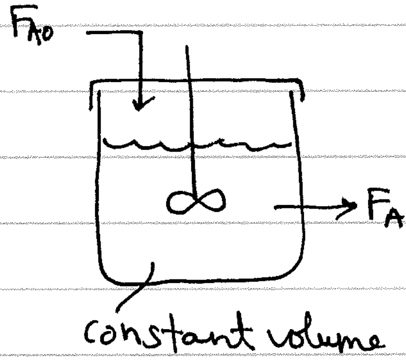
* your boss could ask you any of these questions

* keep track of units

Example on sizing a CSTR

Consider $A \rightarrow B$

$$-r_A = kC_A$$



Design eqn. for a CSTR:

$$F_{A0} - F_A = (-r_A) \cdot V$$

$$\therefore (C_{A0} - C_A)\upsilon = (-r_A) \cdot V$$

$$\therefore (C_{A0} - C_A)\upsilon = (kC_A)V$$

$$\therefore C_{A0} = C_A + \frac{kV}{\upsilon}C_A$$

$$\boxed{\therefore C_{A0} = C_A\left[1 + \frac{kV}{\upsilon}\right]} \quad \ldots \boxed{\underbrace{\frac{V}{\upsilon}}_{\text{residence time}} = \tau}$$

These are plug-&-chug problems

* Arguably the easiest problems in reactor design.

$$C_{A0} = C_A\left[1 + \frac{kV}{v}\right] \xrightarrow{\text{OR}} X = \frac{C_A k V}{C_{A0} v}$$

$\left\{ \begin{array}{l} \text{2 eqns.} \\ \text{2 unknowns} \end{array} \right\}$

Variables: $\underbrace{C_{A0},\ C_A,\ k,\ v,\ V}$

I can give you any 4 & ask you to find the 5th variable (also X)

Solving CSTR problems graphically

Let's rewrite the equation:

$$F_{A0} - F_A = (-r_A)\,V$$

$$\therefore \quad F_{A0}X = (-r_A)\,V$$

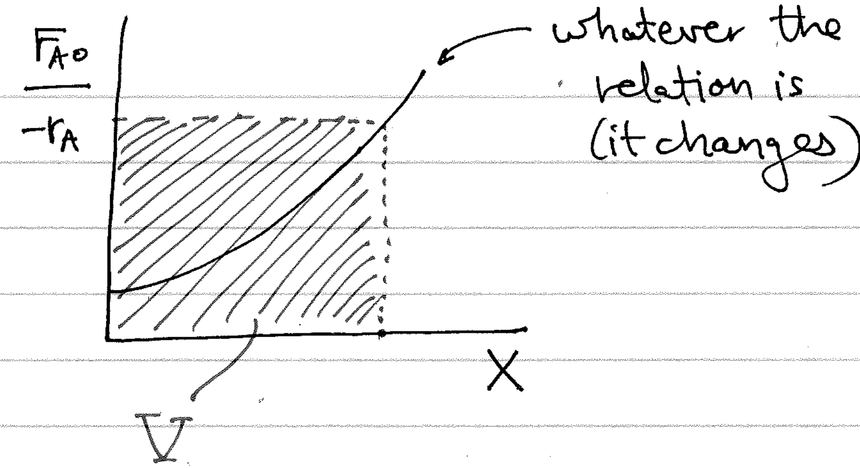
$$\therefore \quad \underbrace{V = \frac{F_{A0}X}{(-r_A)}}_{\text{let's rewrite this eqn.}}$$

$$\boxed{V = \left(\frac{F_{A0}}{-r_A}\right) \times X}$$

area of a rectangle — length — breadth

essential for graphical design

$\therefore$



What is the implication?

$$F_{A0} \equiv \underbrace{C_{A0}}_{\text{you can set this}} \times \underbrace{v}_{\text{you can set this}}$$

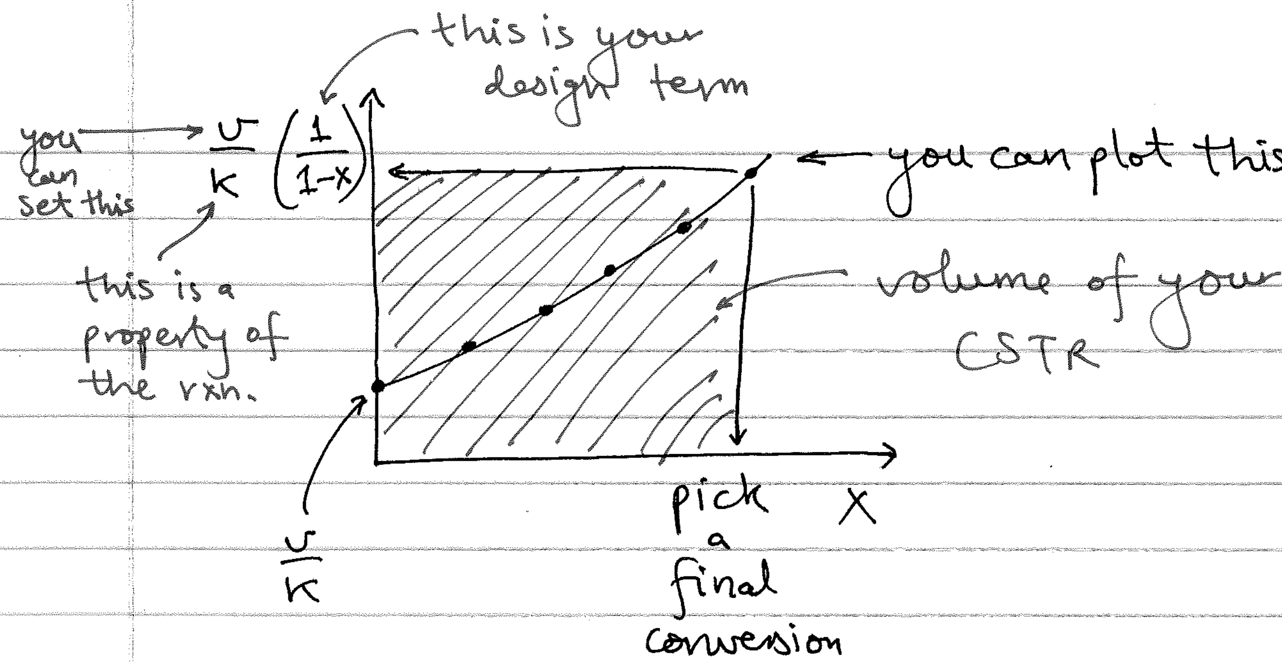
$$X = \frac{F_{A0} - F_A}{F_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = 1 - \frac{C_A}{C_{A0}}$$

$$\frac{F_{A0}}{-r_A} = \frac{C_{A0}v}{kC_A} = \frac{v}{k}\left(\frac{C_{A0}}{C_A}\right)$$

But $X = 1 - \frac{C_A}{C_{A0}} \Rightarrow \frac{C_A}{C_{A0}} = 1 - X$

$$\therefore \frac{C_{A0}}{C_A} = \frac{1}{1-X}$$

$$\therefore \frac{F_{A0}}{-r_A} = \frac{v}{k}\left(\frac{1}{1-X}\right)$$



Let's look at a 2nd order rxn.

$$-r_A = kC_A^2$$

$$\therefore \quad \frac{F_{A0}}{-r_A} = \frac{C_{A0}v}{kC_A^2} = \frac{v}{k}\frac{C_{A0}}{C_A^2}$$

Also, $\frac{C_{A0}}{C_A} = \frac{1}{1-X}$ ---- from the definition of conversion

$$\therefore \quad \left(\frac{C_{A0}}{C_A}\right)^2 = \left(\frac{1}{1-X}\right)^2$$

$$\therefore \quad \frac{F_{A0}}{-r_A} = \frac{v}{k}\frac{C_{A0}}{C_A^2} = \frac{v}{kC_{A0}}\left(\frac{C_{A0}}{C_A}\right)^2$$

$$\therefore \quad \frac{F_{A0}}{-r_A} = \frac{v}{kC_{A0}}\left(\frac{1}{1-X}\right)^2$$