

NON-IDEAL REACTORS

* Temperature changes are a part & parcel of life in the chemical industry.

isothermal

- ① steady state eg. CSTR
- ② unsteady-state eg. batch reactors

non-isothermal

- ③ steady-state
- ④ unsteady-state

We have covered ① & ② thus far.

Let's first look @ ③.

Temperatures \equiv energy flows

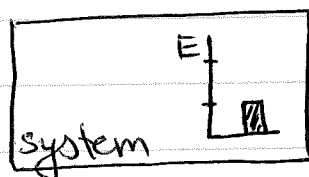
We need an energy balance!

1st law of thermodynamics:

Consider a system that is closed.

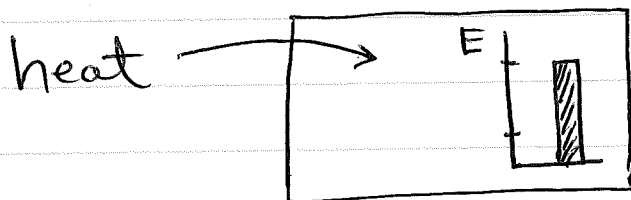
system $\begin{cases} \rightarrow \text{open (material + energy flows)} \\ \rightarrow \text{closed (energy flows)} \\ \rightarrow \text{insulated (completely isolated)} \end{cases}$

The system has an energy content.



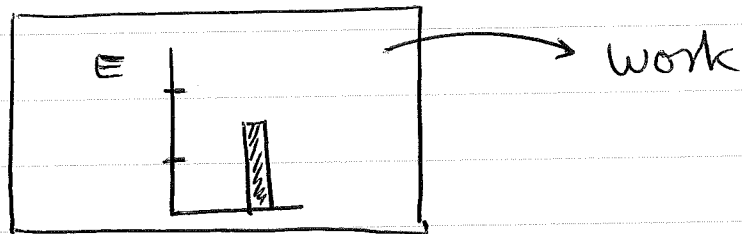
universe

Now, we add heat to this system.



The addition of heat energises the system.

The energised system does work.



By doing work, the energy content of the system drops.

$$\therefore \left\{ \begin{array}{l} \text{heat added} \\ \text{to system} \end{array} \right\} = \left\{ \begin{array}{l} \text{change in} \\ \text{energy} \\ \text{content} \end{array} \right\} + \left\{ \begin{array}{l} \text{work} \\ \text{done} \\ \text{by} \\ \text{system} \end{array} \right\}$$

In this eqn., each quantity is positive.

If you remember, there are 2 types of thermodynamic quantities

→ path functions = work, heat

→ state function = energy, entropy

* path functions are the reason for phenomena like reversible / irreversible work, hysteresis etc.

$$\therefore \left\{ \begin{array}{l} \text{heat added} \\ \text{to system} \end{array} \right\} = \left\{ \begin{array}{l} \text{change in its} \\ \text{energy content} \end{array} \right\} + \left\{ \begin{array}{l} \text{work done} \\ \text{by system} \end{array} \right\}$$

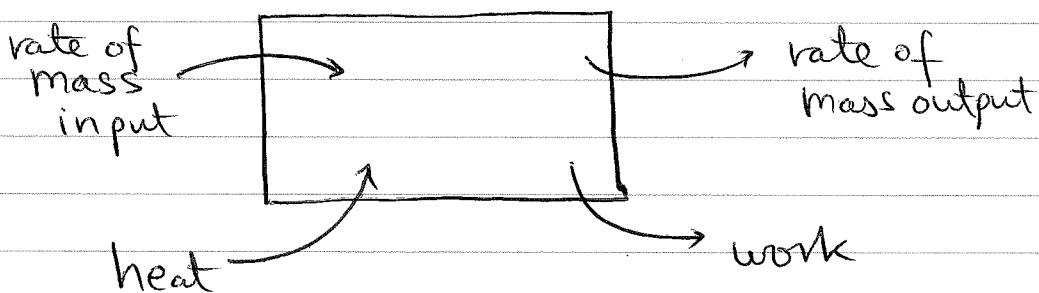
↑ path function
↑ state function
↑ path function

$$\therefore \delta Q = dE + \delta W$$

path fn. $\equiv \delta, \oint$ state fn. $\equiv d, \int$	\Rightarrow	math nomenclature
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$\therefore dE = \delta Q - \delta W$	\rightarrow	$\textcircled{1}$
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For an open system involving material flows,



* mass flows / mole flows can be associated with energy

This time, we incorporate rates in our equation.

$$\left\{ \begin{array}{l} \text{rate of} \\ \text{change of} \\ \text{energy} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of} \\ \text{heat} \\ \text{flow in} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of} \\ \text{work} \\ \text{done} \end{array} \right\} + \left\{ \begin{array}{l} \text{energy} \\ \text{added} \\ \text{due to} \\ \text{mass flow} \\ \text{in} \end{array} \right\} - \left\{ \begin{array}{l} \text{energy} \\ \text{removed} \\ \text{by mass flow} \\ \text{out} \end{array} \right\}$$

$$\therefore \frac{dE}{dt} = \dot{S}Q - \dot{S}W + F_{in}E_{in} - F_{out}E_{out}$$

More generally, $\dot{S}Q$ is written as \dot{Q}

$$\therefore \frac{dE_{sys}}{dt} = \dot{Q} - \dot{W} + F_{in}E_{in} - F_{out}E_{out}$$

$\left(\frac{\text{Joules}}{\text{time}} \right)$ $\left(\frac{\text{moles}}{\text{s}} \right) \left(\frac{\text{J}}{\text{mole}} \right)$

The F_{in} & F_{out} terms can be separated out into all the species.

$$\text{i.e. } F_{in} E_{in} = \sum_{i=1}^n E_i F_i |_{in}$$

$$F_{out} E_{out} = \sum_{i=1}^n E_i F_i |_{out}$$

$$\therefore \frac{dE_{sys}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^n E_i F_i |_{in} - \sum_{i=1}^n E_i F_i |_{out}$$

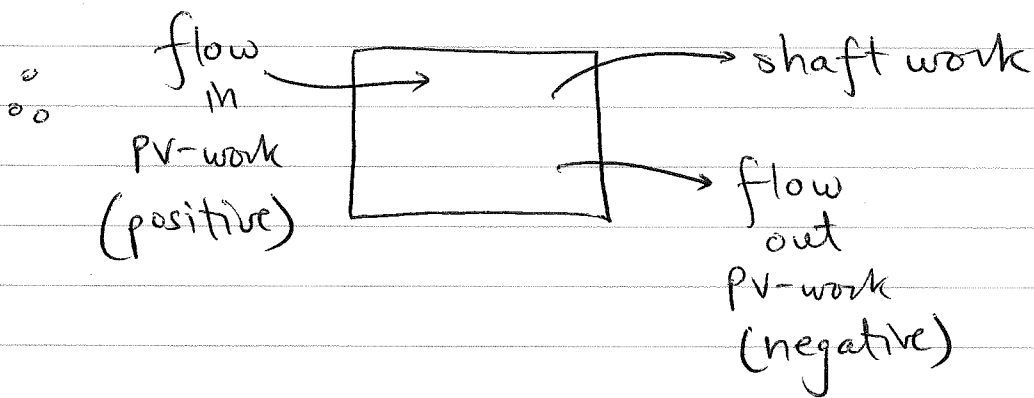
Remember: mole balance = moles/s

energy balance = Joules/s
(or Watts)

Let's take a closer look at each of the terms.

work $\begin{cases} \rightarrow \text{PV-work (due to flow)} \\ \rightarrow \text{shaft work (impeller etc.)} \end{cases}$

Remember the convention \Rightarrow work done by system on surroundings was negative in the energy balance.



$\therefore -\dot{W} = \sum_{i=1}^n F_i P V_i |_{in} - \sum_{i=1}^n F_i P V_i |_{out} - \dot{W}_s$

term as it appears in energy balance

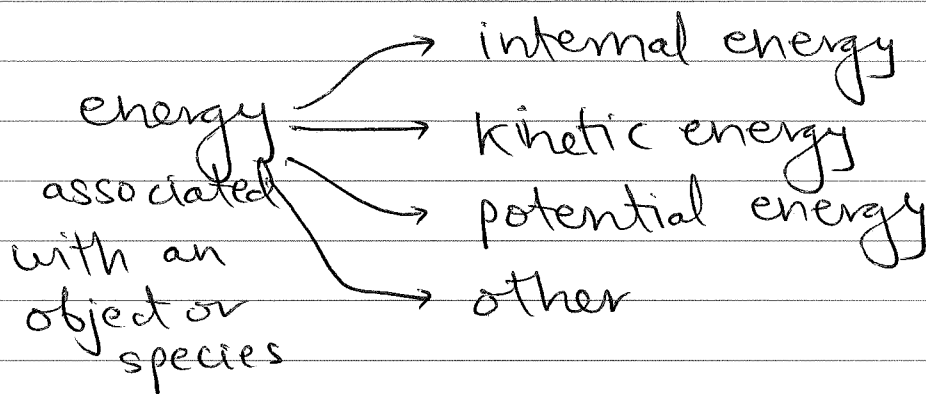
Pascal $\frac{mol}{s}$ m^3/mol

$\therefore \frac{dE_{sys}}{dt} = \dot{Q} + \sum_{i=1}^n F_i P V_i |_{in} - \sum_{i=1}^n F_i P V_i |_{out} - \dot{W}_s$

$+ \sum_{i=1}^n F_i E_i |_{in} - \sum_{i=1}^n F_i E_i |_{out}$

$$\therefore \frac{dE_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n \dot{F}_i (E_i + PV_i) \Big|_{\text{in}} - \sum_{i=1}^n \dot{F}_i (E_i + PV_i) \Big|_{\text{out}}$$

Let's look at E_i



* Generally, kinetic & potential energy terms are negligible (unless you are pumping species to great heights!)

$$\therefore E_i = u_i + \underbrace{\frac{u_i^2}{2} + gz_i}_{\text{negligible}} + \text{other}$$

(Joules/mole)

$\therefore E_i = U_i$ ----- for most cases

$$\therefore E_i + PV_i = U_i + PV_i$$

$\underbrace{\hspace{10em}}$
definition of
enthalpy

$$\therefore \frac{dE_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n \dot{F}_i H_i \Big|_{\text{in}} - \sum_{i=1}^n \dot{F}_i H_i \Big|_{\text{out}}$$

Using the convention we have used thus far,

$$\frac{dE_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n \dot{F}_{i0} H_{i0} - \sum_{i=1}^n \dot{F}_i H_i$$

For steady-state, $\frac{dE_{\text{sys}}}{dt} = 0$
(energetically)

For unsteady-state, $\frac{dE_{\text{sys}}}{dt} \neq 0$

Consider $aA + bB \rightarrow cC + dD$



General energy balance equation:

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^n \dot{F}_{i0} H_{i0} - \sum_{i=1}^n \dot{F}_i H_i$$

Let's look @ the enthalpy terms:

$$\sum_{i=1}^n \dot{F}_{i0} H_{i0} = \dot{F}_{A0} H_{A0} + \dot{F}_{B0} H_{B0} + \dot{F}_{C0} H_{C0} + \dot{F}_{D0} H_{D0}$$

$$\sum_{i=1}^n \dot{F}_i H_i = \dot{F}_A H_A + \dot{F}_B H_B + \dot{F}_C H_C + \dot{F}_D H_D$$

Stoichiometry table

Species	Initial	Change	Final
A	F_{A0}	$-F_{A0} X_A$	$F_{A0}(1-X_A)$
B	$F_{B0} = Q_B F_{A0}$	$-\frac{b}{a} F_{A0} X_A$	$F_{A0}(Q_B - \frac{b}{a} X_A)$
C	$F_{C0} = Q_C F_{A0}$	$\frac{c}{a} F_{A0} X_A$	$F_{A0}(Q_C + \frac{c}{a} X_A)$
D	$F_{D0} = Q_D F_{A0}$	$\frac{d}{a} F_{A0} X_A$	$F_{A0}(Q_D + \frac{d}{a} X_A)$
I	$F_{I0} = Q_I F_{A0}$	0	$Q_I F_{A0}$

there
could be
inerts present

make these substs.
in the energy balance

$$\therefore \sum_{i=1}^n F_{i0} H_{i0} = F_{A0} H_{A0} + Q_B F_{A0} H_{B0} + Q_C F_{A0} H_{C0} + Q_D F_{A0} H_{D0} + Q_I F_{A0} H_{I0}$$

$$\& \sum_{i=1}^n F_i H_i = F_{A0} (1 - X_A) H_A + F_{A0} \left(Q_B - \frac{b}{a} X_A \right) H_B + F_{A0} \left(Q_C - \frac{c}{a} X_A \right) H_C + F_{A0} Q_I H_I + F_{A0} \left(Q_D - \frac{d}{a} X_A \right) H_D$$

$$\therefore \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i \Rightarrow \text{let's look @ individual terms for simplicity}$$

species A: $F_{A0} H_{A0} = \text{in}$ } subtraction gives:
 $F_{A0} (1 - X_A) H_A = \text{out}$

$$= F_{A0} H_{A0} - [F_{A0} H_A - F_{A0} X_A H_A]$$

$$= F_{A0} H_{A0} - F_{A0} H_A + F_{A0} X_A H_A$$

$$= F_{A0} [H_{A0} - H_A] + F_{A0} X_A H_A \rightarrow \textcircled{1}$$

species B: difference = $Q_B F_{A0} H_{B0} - [F_{A0} (Q_B - \frac{b}{a} X_A) H_B]$

$$= Q_B F_{A0} H_{B0} - [Q_B F_{A0} H_B - \frac{b}{a} F_{A0} X_A H_B]$$

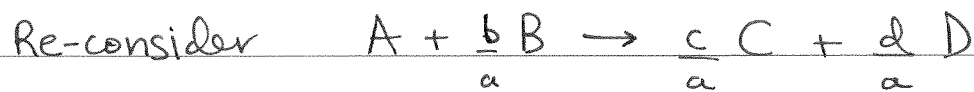
$$= Q_B F_{A0} (H_{B0} - H_B) + \frac{b}{a} F_{A0} X_A H_B \rightarrow \textcircled{2}$$

Similarly: species C = $Q_C F_{A0} (H_{C0} - H_C) - \frac{c}{a} F_{A0} X_A H_C \rightarrow \textcircled{3}$

species D = $Q_D F_{A0} (H_{D0} - H_D) - \frac{d}{a} F_{A0} X_A H_D \rightarrow \textcircled{4}$

$$\begin{aligned} \therefore \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i &= F_{A0} [H_{A0} - H_A] + F_{A0} X_A H_A \\ &+ F_{A0} Q_B [H_{B0} - H_B] + \frac{b}{a} F_{A0} X_A H_B \\ &+ F_{A0} Q_C (H_{C0} - H_C) + \left\{ -\frac{c}{a} F_{A0} X_A H_C \right\} \\ &+ F_{A0} Q_D (H_{D0} - H_D) + \left\{ -\frac{d}{a} F_{A0} X_A H_D \right\} \\ &+ F_{A0} Q_I (H_{I0} - H_I) \end{aligned}$$

$$\begin{aligned} \therefore \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i &= F_{A0} \left[(H_{A0} - H_A) + Q_B (H_{B0} - H_B) + Q_C (H_{C0} - H_C) \right. \\ &\left. + Q_D (H_{D0} - H_D) + Q_I (H_{I0} - H_I) \right] \\ &+ F_{A0} X_A \left[H_A + \frac{b}{a} H_B - \frac{c}{a} H_C - \frac{d}{a} H_D \right] \end{aligned}$$



What is ΔH_{rxn} ?

$\Delta H_{rxn} =$ enthalpies of products
- enthalpies of reactants

include stoichiometry!

$$\therefore \Delta H_{rxn} = \frac{c}{a} \Delta H_f^C + \frac{d}{a} \Delta H_f^D - \frac{b}{a} \Delta H_f^B - \Delta H_f^A$$

One can approximate this as:

$$\Delta H_{rxn} = \frac{c}{a} H_c + \frac{d}{a} H_D - \frac{b}{a} H_B - H_A$$

or, more specifically:

we'll look @ this
in more detail later

$$\Delta H_{rxn}(T) = \frac{c}{a} H_c(T) + \frac{d}{a} H_D(T) - \frac{b}{a} H_B(T) - H_A(T)$$

$$\begin{aligned} \therefore \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i &= F_{A0} \sum_{i=1}^n Q_i (H_{i0} - H_i) \\ &\quad - F_{A0} X_A \Delta H_{rxn}(T) \end{aligned}$$

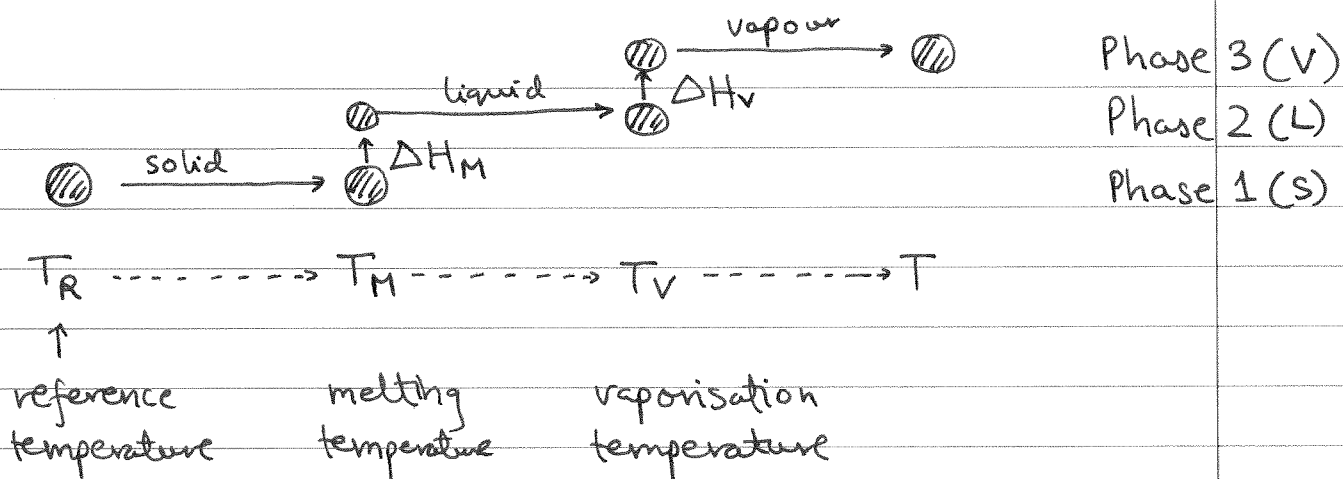
$$\begin{aligned} \therefore \frac{dE_{sys}}{dt} &= \dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^n Q_i (H_{i0} - H_i) \\ &\quad - F_{A0} X_A \Delta H_{rxn}(T) \end{aligned}$$

↳ $H_{i0} @ T_{i0}$, $H_i @ T$

So far we have looked @ work (PV & shaft work) and the enthalpy of reaction.

However, enthalpies are temperature-dependent.

★ Let us dissect this dependence a little further.



for any species

$$H_i(T) = H_i^\circ(T_R) + C_{p_i}^s (T_M - T_R) + \Delta H_{M_i} + C_{p_i}^l (T_V - T_M) + \Delta H_{v_i} + C_{p_i}^v (T - T_V)$$

reference enthalpy (standard enthalpy)

$C_{p_i}^s$ \equiv heat capacity of solid i

$C_{p_i}^l$ \equiv heat capacity of liquid i

$C_{p_i}^v$ \equiv heat capacity of vapour i

C_p can be a function of temperature too!

a more general form of enthalpy is:

$$H_i(T) = H_i^\circ(T_R) + \int_{T_R}^{T_M} C_{p_i}^s dT + \Delta H_{M_i} + \int_{T_M}^{T_V} C_{p_i}^l dT + \Delta H_{v_i} + \int_{T_V}^T C_{p_i}^v dT$$

Phase changes are rare in the industry.

In this course, as well as an overwhelming number of real-life cases, we do not consider phase changes.

$$\therefore H_i(T) = H_i^\circ(T_R) + \int_{T_R}^T C_p dT$$

the phase of the reaction

Generally, $C_p = \alpha + \beta T + \gamma T^2 + \dots$

you can derive these expressions from a source like Perry's Handbook

Therefore,

$$H_{i0} - H_i = \left\{ H_i^\circ(T_R) + \int_{T_R}^{T_{i0}} C_{pi} dT \right\} - \left\{ H_i^\circ(T_R) + \int_{T_R}^T C_{pi} dT \right\}$$

@ T

Why T_{i0} ? Because different species can enter the system @ different temperatures.

$$\begin{aligned}
 \therefore H_{i0} - H_i &= H_i^\circ(T_R) + \int_{T_R}^{T_{i0}} C_{p_i} dT - H_i^\circ(T_R) - \int_{T_R}^T C_{p_i} dT \\
 &= \int_{T_R}^{T_{i0}} C_{p_i} dT - \int_{T_R}^T C_{p_i} dT \\
 &= - \int_{T_{i0}}^T C_{p_i} dT
 \end{aligned}$$

$$\begin{aligned}
 \therefore \frac{dE_{\text{sys}}}{dt} &= \dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^n \phi_i \left\{ - \int_{T_{i0}}^T C_{p_i} dT \right\} \\
 &\quad - F_{A0} X_A \Delta H_{\text{rxn}}(T)
 \end{aligned}$$

$$\therefore \frac{dE_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^n \phi_i \int_{T_{i0}}^T C_{p_i} dT - F_{A0} X_A \Delta H_{\text{rxn}}(T)$$

Let us treat ΔH_{rxn} similarly.

$$\Delta H_{\text{rxn}} = \frac{c}{a} H_c(T) + \frac{d}{a} H_d(T) - \frac{b}{a} H_b(T) - H_a(T)$$

$$\text{But } H_c(T) = H_c^\circ(T_R) + \int_{T_R}^T C_{p_c} dT$$

no inerts here!

$$\therefore \Delta H_{rxn} = \left[\frac{c}{a} H_C^\circ(T_R) + \frac{d}{a} H_D^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \right]$$

$$+ \left[\frac{c}{a} \int_{T_R}^T C_{pC} dT + \frac{d}{a} \int_{T_R}^T C_{pD} dT - \frac{b}{a} \int_{T_R}^T C_{pB} dT - \int_{T_R}^T C_{pA} dT \right]$$

$$\therefore \Delta H_{rxn} = \Delta H_{rxn}^\circ(T_R) + \int_{T_R}^T \left(\frac{c}{a} C_{pC} + \frac{d}{a} C_{pD} - \frac{b}{a} C_{pB} - C_{pA} \right) dT$$

let's define this as $\Delta C_{p_{rxn}}$

$$\therefore \Delta H_{rxn} = \Delta H_{rxn}^\circ(T_R) + \int_{T_R}^T \Delta C_{p_{rxn}} dT$$

$$\therefore \frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_S - F_{A0} \sum_{i=1}^n \dot{Q}_i \int_{T_{i0}}^T C_{pi} dT$$

applies to all systems

$$- F_{A0} X_A \left\{ \Delta H_{rxn}^\circ(T_R) + \int_{T_R}^T \Delta C_{p_{rxn}} dT \right\}$$

Remember, since enthalpy is a state function,

we can solve the energy balance by merely looking at the entry & exit streams.

Let's consider some simplifications:

① → If steady-state, $\frac{dE_{\text{sys}}}{dt} = 0$

→ If adiabatic, $\dot{Q} = 0$

→ Assume \dot{W}_s is negligible (good assumption for PFRs)

→ Also assume C_p is constant & independent of temperature for all species.

For such a system,

$$0 = -F_{A0} \sum_{i=1}^n Q_i C_{pi} (T - T_{i0}) - F_{A0} X_A \left[\Delta H_{rxn}^{\circ}(T_R) + \Delta C_{p,rxn} (T - T_R) \right]$$

Remember, this includes inerts

no inerts involved

$$\therefore F_{A0} \sum_{i=1}^n Q_i C_{pi} (T - T_{i0}) = -F_{A0} X_A \left[\Delta H_{rxn}^{\circ}(T_R) + \Delta C_{p,rxn} (T - T_R) \right]$$

$$\therefore X_A = \frac{\sum_{i=1}^n Q_i C_{pi} (T - T_{i0})}{-\left[\Delta H_{rxn}^{\circ}(T_R) + \Delta C_{p,rxn} (T - T_R) \right]}$$

Since this conversion is derived from the energy balance,

$$X_A^{EB} = \frac{\sum_{i=1}^n Q_i C_{pi} (T - T_{i0})}{-\left[\Delta H_{rxn}^{\circ}(T_R) + \Delta C_{pmn}(T - T_R) \right]}$$

For a PFR that is operated adiabatically & with similar assumptions in case (1) discussed previously:

$$F_{A0} \frac{dX_A}{dV} = -r_A(X_A, T) \quad \dots \text{mass balance}$$

We need to solve these equations simultaneously to design our reactor.

Let us look @ an actual example.

Consider an elementary, gas-phase rxn.



Assumptions = adiabatic, no shaft work, all species enter at same temperature, temperature independence of C_p 's, liquid-phase

* Also assume negligible thermal expansivity.

→ i.e. $v \approx v_0$.

2 design equations:

$$EB \Rightarrow X_A^{EB} = \frac{\sum_{i=1}^n Q_i C_{pi} (T - T_{i0})}{-\left[\Delta H_{rxn}^\circ (T_R) + \Delta C_{p,rxn} (T - T_R) \right]} \rightarrow \textcircled{A}$$

$$MB \Rightarrow F_{A0} \frac{dX_A^{MB}}{dV} = -r_A \rightarrow \textcircled{B}$$

Also, $-r_A = k C_A$

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

Let's simplify the two equations

$$\therefore X_A^{EB} = \frac{\sum_{i=1}^n Q_i C_{pi} (T - T_{i0})}{-\left[\Delta H_{rxn}^\circ (T_R) + \Delta C_{p,rxn} (T - T_R) \right]}$$

$$\therefore X_A^{EB} = \frac{(C_{PA} + C_{PB} Q_B) (T - T_0)}{-\left[\Delta H_{rxn}^\circ (T_R) + (C_{PB} - C_{PA}) (T - T_R) \right]} \rightarrow \textcircled{1}$$

Algebraic eqn.

The material balance becomes:

$$F_{A0} \frac{dX_A^{MB}}{dV} = -r_A$$

$$\therefore F_{A0} \frac{dX_A^{MB}}{dV} = k C_A$$

due to negligible expansivity

$$\therefore v_0 C_{A0} \frac{dX_A^{MB}}{dV} = \left\{ A \exp\left(-\frac{E_a}{RT}\right) \right\} C_{A0} (1 - X_A^{MB})$$

$$\therefore v_0 \frac{dX_A^{MB}}{dV} = \left\{ A \exp\left(-\frac{E_a}{RT}\right) \right\} (1 - X_A^{MB})$$

you can either be given this expression

$$\text{or } k = k_R \exp\left(\frac{E_a}{RT_R} - \frac{E_a}{RT}\right)$$

reference point

$$\therefore \frac{dX_A^{MB}}{dV} = \left\{ A \exp\left(-\frac{E_a}{RT}\right) \right\} (1 - X_A^{MB}) \rightarrow (2)$$

There are 2 types of problems

Type 1 : * You are given v_0 & V i.e. T & ^{inlet} flow conditions.

* You are also given all the other parameters

* You don't know the exit temperature

Goal : Solve for X_A

The solutions to X_A^{MB} & X_A^{EB} must be equivalent

$$\therefore X_A^{EB} = \frac{(C_{PA} + C_{PB} Q_B) (T - T_0)}{-\Delta H_{rxn}^\circ(T_R) - (C_{PB} - C_{PA})(T - T_R)}$$

$$\therefore X_A = \frac{(C_{PA} + C_{PB} Q_B) T - (C_{PA} + C_{PB} Q_B) T_0}{-\Delta H_{rxn}^\circ(T_R) - (C_{PB} - C_{PA}) T + (C_{PB} - C_{PA}) T_R}$$

$$\begin{aligned} \therefore (C_{PA} + C_{PB} Q_B) T - (C_{PA} + C_{PB} Q_B) T_0 &= -\Delta H_{rxn}^\circ(T_R) X_A \\ &\quad - (C_{PB} - C_{PA}) T X_A + (C_{PB} - C_{PA}) T_R X_A \end{aligned}$$

$$\begin{aligned} \therefore T \{ (C_{PA} + C_{PB} Q_B) + (C_{PB} - C_{PA}) X_A \} &= -\Delta H_{rxn}^\circ(T_R) X_A \\ &\quad + (C_{PA} + C_{PB} Q_B) T_0 + (C_{PB} - C_{PA}) T_R X_A \end{aligned}$$

$$\therefore T = \frac{-\Delta H_{rxn}^{\circ}(T_R) X_A + (C_{PA} + \theta_B C_{PB}) T_0 + X_A (C_{PB} - C_{PA}) T_R}{(C_{PA} + C_{PB} \theta_B) + (C_{PB} - C_{PA}) X_A} \quad (3)$$

The generic form is:

$$T = \frac{-\Delta H_{rxn}^{\circ}(T_R) X_A + \sum_{i=1}^n \theta_i C_{Pi} T_0 + X_A \Delta C_{P_{rxn}} T_R}{\sum_{i=1}^n \theta_i C_{Pi} + \Delta C_{P_{rxn}} X_A}$$

Subst. this value of T into the MB.

$$\text{i.e. } \frac{dX_A}{dT} = \left[A \exp\left(\frac{-E_a}{RT}\right) \right] (1 - X_A)$$

$$\therefore dT = \frac{dX_A}{\left\{ A \exp\left(\frac{-E_a}{RT}\right) \right\} (1 - X_A)}$$

$$\therefore T = \int_0^{X_{Af}} \frac{dX_A}{\left\{ A \exp\left(\frac{-E_a}{RT}\right) \right\} (1 - X_A)}$$