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STEADY STATE NON-ISOTHERMAL DESIGN

Chapter 8

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Introduction

After this chapter you will be able to focus on
HEAT EFFECTS in Chemical reactors

- ❑ Seldom does reaction occur non-isothermally
- ❑ Isothermal principles still valid
- ❑ Temperature variation along a PFR or heat removal from a CSTR

IF YOU CANNOT STAND THE HEAT, GET OUT OF
THE KITCHEN – HARRY TRUMAN

How we will go about it?

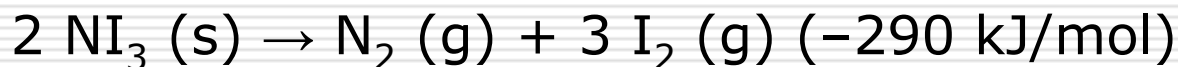
- ❑ Understand Energy Balance and how it will be used for reactor design
- ❑ Develop Energy Balance for application to different types of reactors
- ❑ Energy Balance and adiabatic reactors
- ❑ Energy Balance and PFR's / PBR' with heat exchange

PHASE - 1

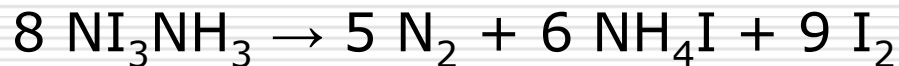
Rationale

Nitrogen tri-iodide is unstable, and reacts exothermically when agitated

The decomposition of NI_3 proceeds as follows to give nitrogen gas and iodine

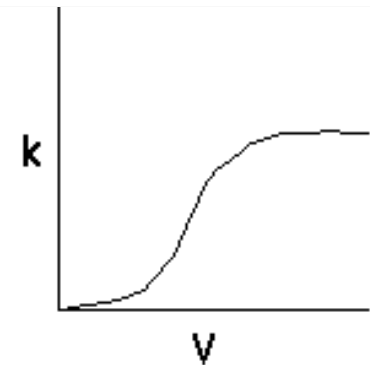
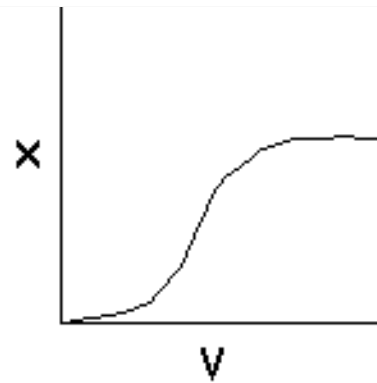
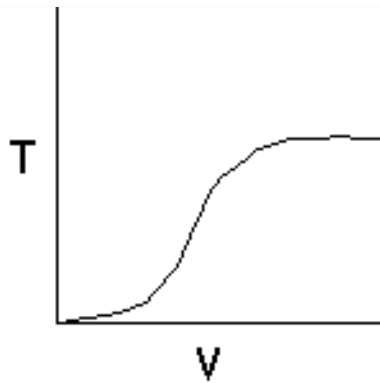


However, the dry material is a contact explosive, decomposing approximately as follows



Rationale

Let's calculate the volume necessary to achieve a conversion, X , in a PFR for a first-order, exothermic reaction carried out adiabatically. For an adiabatic, exothermic reaction the temperature profile might look something like this:



Rationale

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



$$r_A = -k_i \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] C_A$$

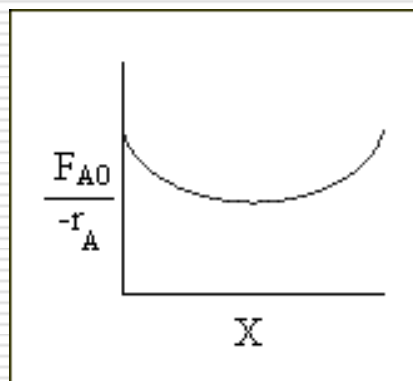
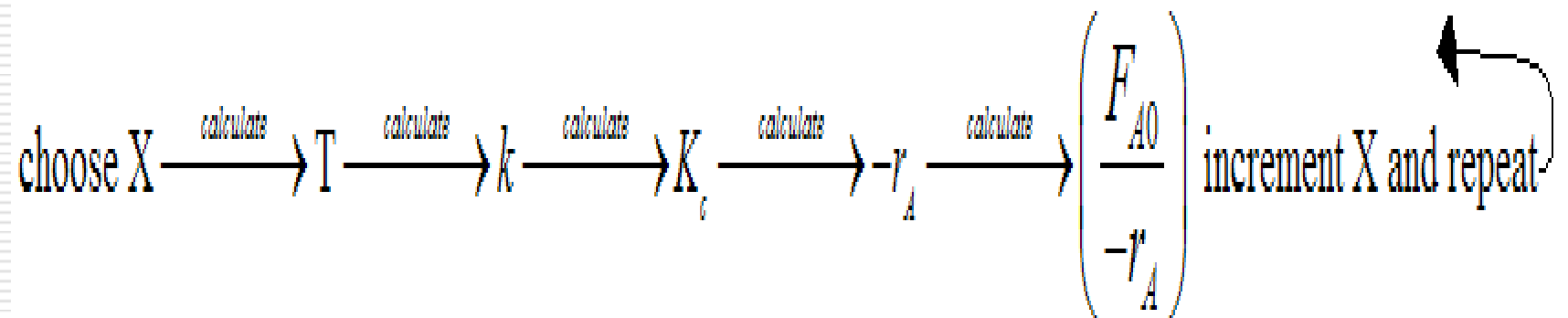
To solve this equation we need to relate **X** and **T**. We will use the **Energy Balance** to relate X and T

For an adiabatic reaction, $A \rightarrow B$ the energy balance can be written in the form

$$\frac{dX}{dV} = \frac{k_i \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]}{F_{A0}} C_{A0} (1-X)$$

$$T = T_0 + \frac{(-\Delta H_{rx})X}{C_{pA}}$$

Rationale

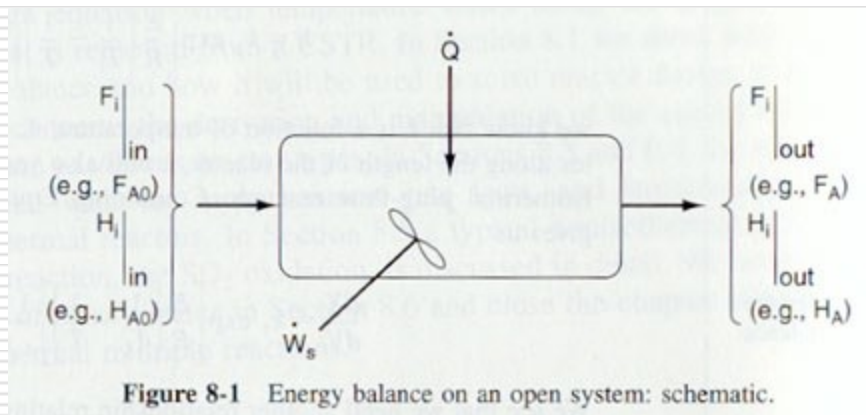


Energy Balance (Open / Closed Systems)

$$\begin{array}{c} \left[\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of energy} \\ \text{within the} \\ \text{system} \end{array} \right] = \left[\begin{array}{c} \text{rate of flow} \\ \text{of heat to} \\ \text{the system} \\ \text{from the} \\ \text{surroundings} \end{array} \right] - \left[\begin{array}{c} \text{rate of work} \\ \text{done by} \\ \text{the system} \\ \text{on the} \\ \text{surroundings} \end{array} \right] + \left[\begin{array}{c} \text{rate of energy} \\ \text{added to the} \\ \text{system by mass} \\ \text{flow into the} \\ \text{system} \end{array} \right] - \left[\begin{array}{c} \text{rate of} \\ \text{energy leaving} \\ \text{system by mass} \\ \text{flow out of} \\ \text{the system} \end{array} \right] \\ \frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W} + F_{\text{in}} E_{\text{in}} - F_{\text{out}} E_{\text{out}} \end{array}$$

$$Q_{1-2} = E_2 - E_1 + W_{1-2}$$

Energy Balance



$$E_i = U_i$$

$$\dot{W} = \dot{W}_s + \sum F_{i0} P_{i0} \tilde{V}_{i0} - \sum F_i P_i \tilde{V}_i$$

$$H_i = U_i + P_i \tilde{V}_i$$

$$\dot{Q} - \dot{W}_s + \sum F_{i0} E_{i0}|_{IN} - \sum F_i E_i|_{OUT} = \frac{dE_{system}}{dt}$$

$$\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = \frac{dE_{system}}{dt}$$

Let us get it in usable form!!

$$\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = 0$$

Dissecting Flowrates and Enthalpies

To achieve this goal, we write the molar flow rates in terms of conversion and the enthalpies as a function of temperature.

For the generalized reaction:

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$F_A = F_{A0}(1-X), \quad F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$F_i = F_{A0}(\Theta_i + \nu_i X)$$

$$\nu_A = -1, \quad \nu_B = -\frac{b}{a}, \quad \nu_C = \frac{c}{a}, \quad \nu_D = \frac{d}{a}$$

Dissecting Flowrates and Enthalpies

- First expand inlet and outlet summation terms
- Substitute molar flowrates into the above

$$\dot{Q} - \dot{W}_s + F_{A0} \sum \Theta_i (H_{i0} - H_i) - \Delta H_{RX}(T) F_{A0} X = 0$$

****Dot above Q and W (rate)**

$\Delta H_{RX} \rightarrow$ Heat of reaction at Temperature T (at the outlet of system)

$$(d/a)H_D(T) + (c/a)H_C(T) - (b/a)H_B(T) - H_A(T)$$

ALL WE NEED TO DO IS TAKE CARE OF ENTHALPIES

Dissecting Flowrates and Enthalpies

- ❑ Neglect Phase change and enthalpy changes during mixing
- ❑ Partial Molar enthalpies = Molal Enthalpies of pure components

$$H_i = H_i^\circ(T_R) + \int_{T_R}^T C_{pi} dT$$



What is the expression for H_{i0} ?

$$Q - W_s + F_{A0} \sum_i \Theta_i C_{pi} (T - T_{i0}) - \Delta H_{Rx}(T) F_{A0} X = 0$$

Dissecting Flowrates and Enthalpies

$$\Delta H_{RX} = (d/a)H_D(T) + (c/a)H_C(T) - (b/a)H_B(T) - H_A(T)$$

$$H_i = H_i^\circ(T_R) + \hat{C}_{Pi}(T - T_R)$$



What happens on substitution?

$$\Delta H_R(T) = \Delta H_R^\circ(T_R) + \Delta \hat{C}_P(T - T_R)$$

$$\sum v_i \hat{C}_{Pi} = \Delta \hat{C}_P = \frac{d}{a} \hat{C}_{PD} + \frac{c}{a} \hat{C}_{PC} - \frac{b}{a} \hat{C}_{PB} - \hat{C}_{PA}$$

Test yourself

- Calculate the following for the reaction (with inerts)



$$\Delta H_{RX}^{\circ}$$

$$\Delta C_p$$

$$\Delta H_{RX}(400)$$

$$H_A^{\circ}(298) = -100 \text{ kcal/mol } A$$

$$H_B^{\circ}(298) = -40 \text{ kcal/mol } B$$

$$H_C^{\circ}(298) = -30 \text{ kcal/mol } C$$

$$H_I^{\circ}(298) = -100 \text{ kcal/mol } I$$

$$\tilde{C}_{pA} = 80 \text{ cal/mol } ^{\circ}\text{C}$$

$$\tilde{C}_{pB} = 20 \text{ cal/mol } ^{\circ}\text{C}$$

$$\tilde{C}_{pC} = 30 \text{ cal/mol } ^{\circ}\text{C}$$

$$\tilde{C}_{pI} = 190 \text{ cal/mol } ^{\circ}\text{C}$$

Final Energy Balance with Dissected Enthalpies

$$\dot{Q} - \dot{W}_s - F_{A0} \int_{T_R}^T \sum \Theta_i C_{Pi} dT - F_{A0} X \left[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_P dT \right] = 0$$

In most systems reactants enter at same temperature, $T_{i0} \sim T_0$. This equation can relate temperature and conversion

Simple for adiabatic reactors and difficult for non-adiabatic systems

$$\dot{Q} - \dot{W}_s - F_{A0} X \left[\Delta H_R^\circ(T_R) + \Delta \hat{C}_P (T - T_R) \right] = F_{A0} \sum \Theta_i \tilde{C}_{Pi} (T - T_{i0})$$

Adiabatic Operation

$W = 0$ and $Q = 0$

Can you write the X vs T relationship?

$$T = T_0 - \frac{X[\Delta H_R^\circ(T_R) + \Delta \hat{C}_P(T_0 - T_R)]}{\sum \Theta_i \tilde{C}_{Pi} + X\Delta \hat{C}_P} = T_0 - \frac{X[\Delta H_R(T_0)]}{\sum \Theta_i \tilde{C}_{Pi} + X\Delta \hat{C}_P}$$

Couple this with the differential mole balance

$$F_{A0}dX/dV = -r_A(X, T)$$

To find T , X and concentration profiles along the reactor

Adiabatic Reactor Algorithm

Consider the reversible gas phase elementary reaction



$$-r_A = k \left[C_A - \frac{C_B}{K_c} \right]$$

What is K_c ?

at equilibrium

$$-r_A = 0$$

$$K_c = \frac{C_{B_e}}{C_{A_e}} = \frac{C_{A0} X_e \frac{T_e}{T} y}{C_{A0} (1 - X_e) \frac{T_0}{T} y} = \frac{X_e}{1 - X_e}$$

$$X_e = \frac{K_c}{1 + K_c}$$

Adiabatic Reactor Algorithm



Choose X



Calculate T

$$T = T_0 - \frac{\Delta H_{RX} X}{\sum \theta_i C_{pi}}$$

Calculate k

$$k = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

Calculate T

$$K_c = K_{c2} \exp \left[\frac{\Delta H_{RX}}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right]$$

Calculate T/T₀

Adiabatic Reactor Algorithm

Calculate C_A

$$C_A = \frac{C_{A0}(1-X)\left(\frac{T_0}{T}\right)}{1+\varepsilon X}$$

Calculate $-r_A$

$$-r_A = k\left(C_A - \frac{C_B^2}{K_c}\right)$$

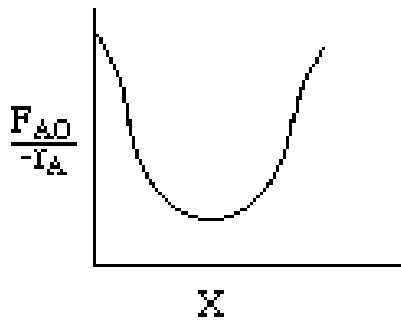
Calculate C_B

$$C_B = \frac{C_{A0}X\left(\frac{T_0}{T}\right)}{1+\varepsilon X}$$

Increment X and then repeat calculations

Adiabatic Reactor Algorithm

When finished, plot $\frac{F_{A0}}{-r_A}$ vs. X or use some numerical technique to find V



**Levenspiel Plot for an
exothermic, adiabatic reaction.
Reactor Sizing**

We can now use the techniques developed in Chapter 2 to size reactors and reactors in series to compare and size CSTRs and PFRs.

