

1 Ideal, Non-Isothermal Reactors

- So far \rightarrow In the analysis of various ideal reactors, we have considered Isothermal operations.
 - \rightarrow Under these conditions, since ~~the reactor~~ T remains constant, we were able to neglect energy considerations.
 - \rightarrow The basic rate laws and design eq. that were considered for isothermal reactors are still valid for Non-Isothermal operation.
- We now \rightarrow have to consider situations where T varies as the rxn proceeds or where heat is supplied or removed from a chemical reactor.
- For Non-Isothermal reactors, one must consider Two key questions:

1. How can one relate the T of the reacting system to the degree of conversion
2. How does this T change influence the subsequent performance of the system.

- We have seen \rightarrow that T has a great influence on the rxn rate via the Arrhenius relationship: $k = Ae^{-E_a/RT}$

- In order to answer the above questions we must consider:

1. Material balance eq. \rightarrow same as the Isothermal reactors
2. Energy balance eq.

• The design of non-isothermal reactors require simultaneous solution to the above eq.

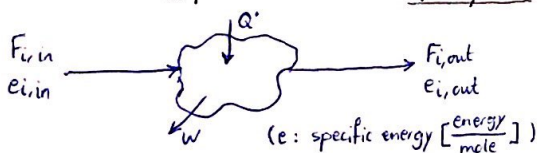
1.1 The General Energy Balance

- The general energy balance for chemical reactors can be obtained by applying the first law of thermodynamics. For Closed systems.

$dE = \delta Q - \delta W$ δQ : heat flow to the system
 $(\Delta E = Q - W)$ δW : work done by the system on the surroundings.

(δ signifies that Q and W are not exact differentials of a state function)

- We can now apply the 1st law to an open system:



[rate of accumulation of energy in the system] = [rate of heat flow to the system] - [rate of work done by the system] + [rate of energy added by flow into the system] - [rate of energy leaving by flow out of the system]

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W} + \sum_i F_{i,in} e_{i,in} - \sum_i F_{i,out} e_{i,out}$$

"General Energy balance eq."

- Work Term (\dot{W})

$$\dot{W} = - \sum_i F_{i,in} (Pv_i)_{in} + \sum_i F_{i,out} (Pv_i)_{out} + \dot{W}_s$$

= flow work = work necessary to get the mass into and out of system. $v_i \triangleq$ specific volume = $[m^3/mol]$

$\dot{W}_s \triangleq$ shaft work e.g. by stirrer (CSTR) or turbine (PFR)

$$\Rightarrow \frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_i F_{i,in} (e_i + Pv_i)_{in} - \sum_i F_{i,out} (e_i + Pv_i)_{out}$$

- Specific energy (e_i)

$$e_i = u_i + \frac{v_i^2}{2} + gz_i + \text{other}$$

u_i : internal energy, $\frac{v_i^2}{2}$: kinetic energy, gz_i : potential energy, other: electric or magnetic energy. $v_i \triangleq$ velocity

for most reactors, the kinetic, potential, and other energy terms are negligible. $\Rightarrow e_i \approx u_i$

$$\Rightarrow \frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_i F_{i,in} (u_i + Pv_i)_{in} - \sum_i F_{i,out} (u_i + Pv_i)_{out}$$

- now

$$h = u + Pv$$

In most circumstances, the shaft work, \dot{W}_s , can also be negligible

$$\Rightarrow \frac{dE_{sys}}{dt} = \dot{Q} + \sum_i F_{i,in} h_{i,in} - \sum_i F_{i,out} h_{i,out}$$

"Simplified General Energy balance"

1.2 Non-Isothermal CVBR

For a batch reactor $F_{i,in} = F_{i,out} = 0$
 hence, the energy balance becomes: $\frac{dE_{sys}}{dt} = \dot{Q}$ [J/s]
 neglecting the kinetic, potential, and other energy terms:
 thus: $\frac{dU_{sys}}{dt} = \frac{d}{dt} (U_{thermal} + U_{chemical}) = \dot{Q}$

E_{sys} $\hat{=}$ total energy of the system
 U_{sys} $\hat{=}$ CVBR's entire volume

$E_{sys} = U_{sys}$
 $\Rightarrow \frac{dU_{thermal}}{dt} + \frac{dU_{chemical}}{dt} = \dot{Q}$ (I)

Sensible Heat $\frac{dU}{dt}$: $\frac{dU_{thermal}}{dt} = \frac{d(mu)}{dt} = m \frac{du}{dt}$ [J/s]
 $(\frac{du}{dT})_V = C_V' \Rightarrow \frac{dU_{thermal}}{dt} = m C_V' \frac{dT}{dt}$

u $\hat{=}$ specific internal energy of reacting mixture on a mass basis [J/kg]
 m $\hat{=}$ mass of reacting mixture (constant)
 C_V' $\hat{=}$ constant volume heat capacity on a mass basis for the reacting mixture

Chemical React $\frac{dU}{dt}$: $\frac{dU_{chemical}}{dt} = (\Delta U_{R,j})(-r_j)V_R$ [J/s]
 $\Delta U_R^o = \Delta H_R^o - [P + (\frac{\partial U}{\partial V})_T] (\sum v_i V_i)$ [mol/m³.s]

V_R $\hat{=}$ reactor volume [m³]
 ΔU_R $\hat{=}$ internal energy change of rxn (negative for exothermic rxns) [J/mol]
 v_i $\hat{=}$ molar volume
 v_i $\hat{=}$ stoichiometric coeff. (positive for products)

for liquids: $\Delta U_R \approx \Delta H_R$
 for ideal gases: $(\frac{\partial U}{\partial V})_T = 0 \Rightarrow \Delta U_R = \Delta H_R - P \sum v_i V_i \Rightarrow \Delta U_R = \Delta H_R - (\sum v_i) RT$

thus: (I) $\Rightarrow m C_V' \frac{dT}{dt} + (\Delta U_{R,j})(-r_j)V_R = \dot{Q} \Rightarrow \frac{dT}{dt} = \frac{\dot{Q}}{m C_V'} - \frac{(\Delta U_{R,j})(-r_j)V_R}{m C_V'}$ (II)

+ for adiabatic op. $\dot{Q} = 0$
 + the heat flow to the reactor is generally expressed as:
 $\dot{Q} = U_o A (T_a - T)$

U_o $\hat{=}$ overall heat transfer coef.
 A $\hat{=}$ heat exchange area
 T_a $\hat{=}$ ambient or jacket T
 T $\hat{=}$ rxn T

$\Rightarrow \frac{dT}{dt} = \frac{U_o A (T_a - T)}{m C_V'} - \frac{(\Delta U_{R,j})(-r_j)V_R}{m C_V'}$ (III) "General Energy balance"

Note we can replace $m C_V'$ by $\sum N_i C_{V,i}$ where $C_{V,i}$ are on mole basis.

The general mole balance eq. for CVBR is given by:

$-r_j = \frac{-1}{V_R} \frac{dN_j}{dt} = \frac{N_{j0}}{V_R} \frac{dX_j}{dt}$ or $\frac{dN_j}{dt} = -V_R (-r_j)$ or $\frac{dX_j}{dt} = \frac{V_R}{N_{j0}} (-r_j)$ (IV)

Eqs II and IV are a system of O.D.E.s which must be solved simultaneously to obtain X_j (or N_j) and T as a function of t .
 To do this \rightarrow we need to express the rate function $(-r_j)$ in terms of N_j and T .

Note that for adiabatic op. (No heat transfer into or out of the system) $\dot{Q} = 0$
 hence, the first term of eq II is dropped.
 This is the situation where we have no external heating or cooling.

- Ex. I "Non-Isothermal batch reactor"

Decomposition of Phosphine (gas phase, ideal gas) $PH_3 \rightarrow \frac{1}{4} P_4 + \frac{3}{2} H_2$

$-r_{PH_3} = k_1 C_{PH_3}$, $\log k_1 = -\frac{15263}{T} + 2 \log T + 12.136$

Feed: pure phosphine @ 672°C / CVBR reactor / initial $P = 1$ atm / $V_R = 2$ m³

$\Delta H_{R,228} = 5665$ cal/mol / $T_{jacket} = 700$ °C / heat transfer area = 10 m² / $U_o = 0-15$ cal/m².k.s

comp.	C_p [cal/mol.k]
P_4	$5.5 + 0.0016T$
PH_3	$6.7 + 0.0063T$
H_2	$7.2 + 0.0009T$

What is the conversion and reactor T after 10 min?

- ex. 1 solution (Material Balance eq.)

for CVBR: $-r_A = \frac{-1}{V} \frac{d(N_A V)}{dt} = \frac{-1}{V} \frac{dN_A}{dt} = \frac{N_{A0}}{V} \frac{dX_A}{dt} \Rightarrow \frac{N_{A0}}{V} \frac{dX_A}{dt} = k_1 C_A$

$\Rightarrow \frac{dX_A}{dt} = \frac{V}{N_{A0}} k_1 C_A = k_1 \frac{V}{N_{A0}} \frac{N_{A0}(1-X_A)}{V} = k_1(1-X_A)$ ($-\frac{18263}{T} + 2 \log T + 12.13$)

thus, our MBE becomes: $\frac{dX_A}{dt} = k_1(1-X_A)$, where $k_1 = 10$

In the case of a Non-Isothermal reactor, k_1 is no longer a constant, since it changes with the rxn T

- ex. 1 solution (Energy Balance eq.)

$\frac{dT}{dt} = \frac{U_0 A (T_0 - T)}{m C_p} - \frac{(\Delta U_R)(-r_A)V}{m C_p}$

$m C_p = \sum_i N_i C_{p,i}$, for ideal gases: $C_p = C_v + R$

$\sum_i N_i C_{p,i} = \sum_i N_i (C_{p,i} - R) = \sum_i N_i C_{v,i} - R \sum_i N_i$

Note that N_i can be related to N_{A0} and X_A

Construct the stoichiometric table

Comp.	initially	at time t	in terms of X_A
A	N_{A0}	N_A	$N_{A0}(1-X_A)$
B	-	N_B	$\frac{1}{4} N_{A0} X_A$
C	-	N_C	$\frac{3}{2} N_{A0} X_A$
Total	N_{A0}	-	$N_{A0}(1 + \frac{3}{4} X_A)$

$m C_p = N_{A0} \left[(1-X_A) C_{p,A} + \frac{X_A}{4} C_{p,B} + \frac{3X_A}{2} C_{p,C} - R(1 + \frac{3}{4} X_A) \right]$

where $C_{p,i}$ are given by: $C_{p,i} = \alpha_i + \beta_i T$

ΔU_R Term: for gas phase rxns (of ideal gases): $\Delta U_R = \Delta H_R - (\sum_i \nu_i) RT$

$\sum_i \nu_i = \frac{3}{2} + \frac{1}{4} - 1 = \frac{3}{4}$

$\Delta H_R = \Delta H_{R,298} + \int_{298}^T (\Delta C_p) dT$, where $\Delta C_p = \Delta \alpha + (\Delta \beta) T$

$\Delta \alpha = \sum_i \nu_i \alpha_i$
 $\Delta \beta = \sum_i \nu_i \beta_i$

$\Delta H_R = \Delta H_{R,298} + \Delta \alpha (T-298) + \frac{\Delta \beta}{2} (T^2 - 298^2)$

thus, $\Delta U_R = \Delta H_{R,298} + \Delta \alpha (T-298) + \frac{\Delta \beta}{2} (T^2 - 298^2) - \frac{3}{4} RT$

$(-r_A)V$ term: $-r_A = k_1 C_A = \frac{k_1 N_{A0} (1-X_A)}{V} \Rightarrow (-r_A)V = k_1 N_{A0} (1-X_A)$, where $N_{A0} = \frac{P_0 V}{RT_0}$

- ex. 1 solution (Finalization)

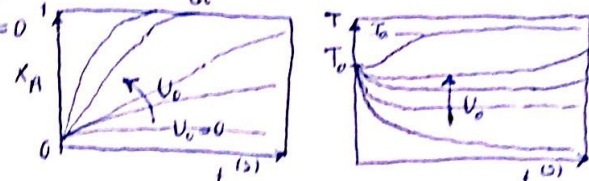
MBE: $\frac{dX_A}{dt} = k_1(1-X_A)$

EBE: $\frac{dT}{dt} = \frac{U_0 A (T_0 - T) - [\Delta H_{R,298} + \Delta \alpha (T-298) + \frac{\Delta \beta}{2} (T^2 - 298^2) - \frac{3}{4} RT] k_1 (1-X_A)}{(1-X_A)(\alpha_A + \beta_A T) + \frac{X_A}{4} (\alpha_B + \beta_B T) + \frac{3X_A}{2} (\alpha_C + \beta_C T) - R(1 + \frac{3}{4} X_A)}$

in above eqs.: $k_1 = 10^{-\frac{18263}{T} + 2 \log T + 12.13}$

Now we have to O.D.C.s of the form $\frac{dT}{dt} = f_1(X_A, T)$, $\frac{dX_A}{dt} = f_2(X_A, T)$

solve numerically with $X_A=0, T=T_0$ @ $t=0$



- Ex. 2 Exothermic, liquid phase CVBR with cooling

$A \rightarrow B$, $-r_A = 4.03 \times 10^5 \exp(-\frac{5624}{T}) C_A$ [$\frac{mol}{m^3 \cdot s}$], $V_R = 0.2 m^3$, $T_0 = 285 K$, $T_c = 280 K$ (cooling water T)

$\Delta U_R = -0.21 \times 10^6 \frac{J}{mol}$ (constant), $C_v = 4.2 \times 10^3 \frac{J}{kg \cdot K}$ (constant), $\rho = 1050 \frac{kg}{m^3}$ (constant), $N_{A0} = 150 \frac{mol}{m^3}$

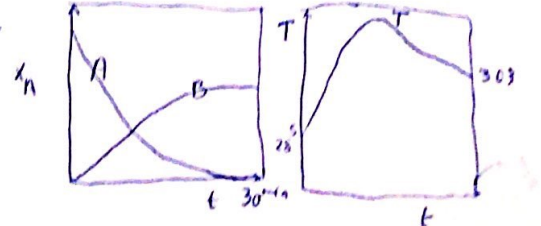
$U_c = 170 \frac{W}{m^2 \cdot K}$, $A = 2 m^2$

- Solution

Energy balance: $\frac{dT}{dt} = \frac{U_0 A (T_c - T)}{m C_p} - \frac{(\Delta U_R)(-r_A)V_R}{m C_p}$

Comp. balance: $\frac{dN_A}{dt} = -V_R (-r_A)$

rate eq: $-r_A = 4.03 \times 10^5 \exp(-\frac{5624}{T}) \frac{N_A}{V_R}$



- From the examples
 - T profiles in batch reactors:
 - Note that with exothermic rxns, sometimes it is necessary to provide sufficient cooling.
 - For highly exothermic rxns, as conversion increases, the T is increased, which in turn results in a higher rate of rxn which further increases the rxn T. This can lead to an explosion if sufficient cooling is not provided.
 - T vs. X_R in batch reactors:

