

## LECTURE 7a

**Nonisothermal Chemical Reactors**

So far we have dealt with isothermal chemical reactors and were able, by using only as many species mass balances as there are independent reactions to relate reactor size, inlet and outlet composition. However, even for isothermal reactors we need the energy balance to determine what heat duty is necessary in order to keep the reactor isothermal. For nonisothermal reactors (adiabatic and nonadiabatic) we need the energy balance together with the mass balances in order to arrive at reactor design equations.

The energy balance is the principle of conservation of energy or the first law of thermodynamics as applied to our reaction system.

Here we consider only:

Ass1 – homogeneous system

Ass2 – single reaction  $\sum_{j=1}^s \nu_j A_j = 0$

Ass3 – continuous flow reactors operating at steady state

The conservation equation requires:

$$(1) \left( \begin{array}{c} \text{Rate of} \\ \text{input} \end{array} \right) - \left( \begin{array}{c} \text{Rate of} \\ \text{output} \end{array} \right) + \left( \begin{array}{c} \text{Rate of} \\ \text{generation} \end{array} \right) = \left( \begin{array}{c} \text{Rate of} \\ \text{accumulation} \end{array} \right)$$

Apply it to the energy, the control volume being the total volume of the reaction mixture in the reactor.

Because in absence of nuclear reactions, energy cannot be destroyed or created (III)  $\equiv 0$ .

Also, due to assumption of steady state (IV)  $\equiv 0$ .

The energy per unit mass of the inlet stream may have different forms:

$$\underline{E} = \underline{KE} + \underline{PE} + \underline{u} + \underline{O}$$

$$\left( \begin{array}{c} \text{Energy} \\ \text{per unit mass} \\ \text{of a stream} \end{array} \right) = \left( \begin{array}{c} \text{Kinetic} \\ \text{energy per} \\ \text{unit mass} \end{array} \right) + \left( \begin{array}{c} \text{Potential} \\ \text{energy per} \\ \text{unit mass} \end{array} \right) + \left( \begin{array}{c} \text{Internal} \\ \text{energy per} \\ \text{unit mass} \end{array} \right) + \left( \begin{array}{c} \text{Other} \\ \text{energy per} \\ \text{unit mass} \end{array} \right)$$

Among other, energy forms may be surface energy (not important in homogeneous flow), magnetic energy, electric energy, etc.

As we already see from equation (1) only changes in energy play a role. Most often in chemical reactors changes in other energy forms can be neglected since here are no magnetic or electric fields used.

Now we can write:

$$\left( \begin{array}{c} \text{Rate of energy} \\ \text{input} \end{array} \right) = \left( \begin{array}{c} \text{Rate of energy input by} \\ \text{flow of material streams} \end{array} \right) + \left( \begin{array}{c} \text{Rate of heat addition} \\ \text{from the surroundings} \end{array} \right)$$

$$\left( \begin{array}{c} \text{Rate of energy} \\ \text{output} \end{array} \right) = \left( \begin{array}{c} \text{Rate of energy output by} \\ \text{flow of material streams} \end{array} \right) + \left( \begin{array}{c} \text{Rate of work done} \\ \text{by the system} \end{array} \right)$$

$$\left( \begin{array}{c} \text{Rate of energy input or output by} \\ \text{flow of material streams} \end{array} \right) = (\text{Mass flow rate})(\text{Energy per unit mass})$$

Note that due to steady state the overall mass balance indicates a constant mass flow rate

$$\dot{m}_{in} = \dot{m}_{out} = \dot{m} \text{ (kg / s)}$$

$$(2) \quad \left( \begin{array}{c} \text{Rate of energy input by} \\ \text{flow of material streams} \end{array} \right) = \dot{m}(\underline{KE} + \underline{PE} + \underline{u})_{in}$$

$$(3) \quad \left( \begin{array}{c} \text{Rate of energy output by} \\ \text{flow of material streams} \end{array} \right) = \dot{m}(\underline{KE} + \underline{PE} + \underline{u})_{out}$$

$$(4) \quad \left( \begin{array}{c} \text{Rate of heat addition} \\ \text{from the surroundings} \end{array} \right) = \dot{q} \left( \frac{KJ}{s} \right)$$

The work done by the system consists of three parts:

$$\left( \begin{array}{c} \text{Rate of} \\ \text{work done} \\ \text{by the system} \end{array} \right) = \left( \begin{array}{c} \text{Rate of} \\ \text{shaft work} \\ \text{done by the} \\ \text{system} \end{array} \right) + \left( \begin{array}{c} \text{Rate of} \\ \text{work done} \\ \text{to expel} \\ \text{the outflow into} \\ \text{the surroundings} \end{array} \right) - \left( \begin{array}{c} \text{Rate of} \\ \text{work done by} \\ \text{the surroundings} \\ \text{to propel} \\ \text{the inflow into} \\ \text{the system} \end{array} \right) + \left( \begin{array}{c} \text{Rate of} \\ \text{work done} \\ \text{against gravity} \\ \text{or other} \\ \text{body forces} \end{array} \right)$$

$$(5) \quad \dot{w} = \dot{w}_s + \dot{m} \left( \frac{p}{\rho} \right)_{out} - \dot{m} \left( \frac{p}{\rho} \right)_{in} + \dot{m}g(h_{out} - h_{in})$$

Using eqs (2), (3), (4) and (5) in (1) we get

$$0 = \dot{m}(\underline{u} + \underline{KE} + \underline{PE})_{in} + \dot{q} - \dot{m}(\underline{u} + \underline{KE} + \underline{PE})_{out} + \dot{w}_s + \dot{m} \left( \frac{p}{\rho} \right)_{out} - \dot{m} \left( \frac{p}{\rho} \right)_{in}$$

$$(6) \quad \dot{m} \left[ \left( \underline{u} + \frac{p}{\rho} + \underline{KE} + \underline{PE} \right)_{out} - \left( \underline{u} + \frac{p}{\rho} + \underline{KE} + \underline{PE} \right)_{in} \right] = \dot{q} - \dot{w}_s$$

$$\dot{m} \left[ \Delta \underline{E} + \Delta \left( \frac{p}{\rho} \right) \right] = \dot{q} - \dot{w}_s \quad \leftarrow 1^{st} \text{ law}$$

One can readily show that in chemical reactors:

Ass4 – kinetic energy changes are negligible compared to those in internal energy

$$\Delta \underline{KE} \ll \Delta \underline{u}$$

Ass5 – potential energy changes are negligible compared to internal energy changes

$$\Delta \underline{PE} \ll \Delta \underline{u}$$

Recall the definition of enthalpy

$$\underline{H} = \underline{u} + p\underline{v} = \underline{u} + \frac{p}{\rho}$$

Hence equation (6) becomes

$$(7) \quad \dot{m}(\underline{H}_{out} - \underline{H}_{in}) = \dot{q} - \dot{w}_s$$

In almost all chemical reactors there is no considerable shaft work leading to:

Ass6 – negligible shaft work

$$(8) \quad \dot{m}(\underline{H}_{out} - \underline{H}_{in}) = \dot{q}$$

For bookkeeping purposes in chemical reactors we represent

$$(9) \quad \dot{m}\underline{H}_{out} = \sum_{j=1}^s F_j \tilde{H}_j; \quad \dot{m}\underline{H}_{in} = \sum_{j=1}^s F_{j0} \tilde{H}_{j0}$$

$$\left( \text{Mass flow rate} \begin{pmatrix} \text{Enthalpy per unit} \\ \text{mass of mixture} \end{pmatrix} \right) = \sum_{\text{all species}} \left( \text{Molar flow rate} \begin{pmatrix} \text{of species } j \end{pmatrix} \right) \left( \begin{pmatrix} \text{Partial molal enthalpy of} \\ \text{species } j \text{ per mole of } j \text{ at} \\ \text{conditions of the mixture} \end{pmatrix} \right)$$

We will here further assume:

Ass7 – ideal mixtures

$$\tilde{H}_j = H_j$$

$$\left( \begin{pmatrix} \text{partial} \\ \text{molal enthalpy} \end{pmatrix} \right) = \left( \begin{pmatrix} \text{molal} \\ \text{enthalpy} \end{pmatrix} \right)$$

While  $\tilde{H}_j = f(T, P, \text{composition})$ ,  $H_j = f(T, P)$ .

Furthermore, for gases we will assume ideal gases

\*Ass8 – ideal gas  $H_j = f(T)$

This means that molal enthalpies are functions of temperature only.

Note. This assumption must be deleted and effect of pressure considered when dealing with reaction systems such as: ammonia synthesis, high P polymerization, coal conversion, etc.

This means that  $T_s$  – reference (standard) T

$$(10) \quad \left( \frac{\partial H_j}{\partial T} \right)_P = \underbrace{C_{p,j}}_{\text{specific heat for } j} \quad (10a) \quad \tilde{H}_j(T) = \underbrace{\Delta H_{f,j}(T_s)}_{\text{enthalpy of formation at standard conditions}} + \underbrace{\int_{T_s}^T C_{p,j} dT}_{\text{temperature correction}}$$

With eq (9) and assumptions (7) and (8), the reactor energy balance can finally be written as:

$$(11) \quad \sum_{j=1}^s \left[ F_j \tilde{H}_j(T) - F_{j0} \tilde{H}_j(T_0) \right] = \dot{q}$$

where exit temperature is T, inlet temperature is  $T_0$ . The mass balance for any species j is

$$(12) \quad F_j = F_{j_o} + v_j \dot{X}$$

Using eq (12) to eliminate  $F_{j_o}$  in eq (11) we get

$$(13) \quad \sum_{j=1}^s \left\{ F_j \left[ \underset{\sim}{H_j}(T) - \underset{\sim}{H_j}(T_o) \right] + v_j \underset{\sim}{H_j}(T_o) \dot{X} \right\} = \dot{q}$$

Using equation (10a) in eq (13) we get

$$(14) \quad \sum_{j=1}^s F_j \int_{T_o}^T C_{pj} dT + \dot{X} \sum_{j=1}^s v_j \left[ \underset{\sim}{\Delta H_{fj}} + \int_{T_s}^{T_o} C_{pj} dT \right] = \dot{q}$$

Recall that by definition the standard heat of reaction is:

$$\Delta H_R^o = \sum_{j=1}^s v_j \underset{\sim}{\Delta H_{fj}}$$

Heat of reaction at temperature  $T_o$  is

$$\Delta H_R(T_o) = \Delta H_R^o + \sum_{j=1}^s v_j \int_{T_s}^{T_o} C_{pj} dt$$

$$(14a) \quad \underbrace{\sum_{j=1}^s F_j \int_{T_o}^T C_{pj} dT}_{(II)} + \underbrace{\dot{X} \Delta H_R(T_o)}_{(I)} = \underbrace{\dot{q}}_{(III)}$$

Equation (14a) can be interpreted in words as follows:

$$\left( \begin{array}{l} \text{Rate of heat} \\ \text{addition to} \\ \text{the reactor} \end{array} \right) = \left( \begin{array}{l} \text{Rate of heat "absorption"} \\ \text{by reaction at temperature} \\ \text{of feed} \end{array} \right) + \left( \begin{array}{l} \text{Rate of heating the reaction} \\ \text{mixture at exit composition} \\ \text{from feed to exit temperature} \end{array} \right)$$

i.e. change in enthalpy  
caused by reaction · the rate of  
reaction progress

$$(III) = (I) + (II)$$

Had we eliminated by eq (12)  $F_j$  in eq (11) we would obtain an equivalent equation to eq (14a).

$$(14b) \quad \sum_{j=1}^s F_{j_o} \int_{T_o}^T C_{pj} dT + \dot{X} \Delta H_R(T) = \dot{q}$$

$$\left( \begin{array}{l} \text{Heat needed to raise} \\ \text{inlet temperature to} \\ \text{exit temperature } T \end{array} \right) + \left( \begin{array}{l} \text{Heat used by} \\ \text{reaction at exit} \\ \text{temperature } T \end{array} \right) = (\text{Heat added})$$

In reaction engineering problems, additional assumptions are often made.

Ass9: - constant mean specific heat and density can be used, defined by:

$$\rho Q C_{pm}(T - T_o) = \sum_{j=1}^S F_{j_o} \int_{T_o}^T C_{pj} dT$$

Ass10: - heat of reaction is approximately constant

$$\Delta H_R(T) = \Delta H_R(T_o) = \Delta H_R(T_s) = \Delta H_R^o$$

Under the assumptions (9) and (10), equations (14a) or (14b) are reduced to:

$$(15) \quad \rho Q C_{pm}(T - T_o) + \dot{X} \Delta H_R = \dot{q}$$

(I)                      (II)    (III)

Equation (15) is then often interpreted as the “heat balance” causing great disturbance among thermodynamicists.

$$\left( \begin{array}{l} \text{Sensible heat} \\ \text{absorbed by flowing} \\ \text{stream} \end{array} \right) + \left( \begin{array}{l} \text{Heat absorbed} \\ \text{by reaction} \end{array} \right) = (\text{Heat added})$$

By interpreting term (II) as a “generation” term in an energy balance, disservice is done to the clarity of the subject.

However, a user can use equation (15) as long as he recalls what the assumptions under which it was formulated are and makes sure that they are satisfied.

### Applications to Ideal Reactors

**CSTR** – The entire reactor is at temperature T. Hence eq (15) can be used as it is

$$\rho Q C_{pm}(T - T_o) - \dot{X}(-\Delta H_R) = \dot{q}$$

With the mass balance:

$$\dot{X} = \left( \frac{R_j}{v_j} \right) V.$$

**PFR** – Equation (15) as it stands is valid between inlet and outlet. However  $\dot{q}$  then represents total rate of heat addition.

In order to solve the reactor problem we have the mass balance

$$\frac{d\dot{X}}{dV} = \left( \frac{R_J}{v_J} \right) = r$$

where the reaction rate  $r$  is a function of extent  $\dot{X}$  and temperature  $T$  at position  $V$ . Thus we must apply eq (15) to a differential volume resulting in

$$\rho Q C_{pm} \frac{dT}{dV} + \Delta H_R \frac{d\dot{X}}{dV} = \dot{q}_v$$

$\dot{q}_v$  - rate of heat addition per unit reactor volume at position  $V$ .