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 \( \sum_{j=1}^{s} v_j A_j = 0 \)

**Ass3** – continuous flow reactors operating at steady state

The conservation equation requires:

\[
(1) \quad \left( \text{Rate of input} \right) - \left( \text{Rate of output} \right) + \left( \text{Rate of generation} \right) = \left( \text{Rate of accumulation} \right)
\]

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 \((\text{III}) = 0\).

Also, due to assumption of steady state \((\text{IV}) = 0\).

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

\[
E = KE + PE + u + Q
\]
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:

\[
\begin{align*}
\text{Rate of energy input} & = \left( \text{Rate of energy input by flow of material streams} \right) + \left( \text{Rate of heat addition from the surroundings} \right) \\
\text{Rate of energy output} & = \left( \text{Rate of energy output by flow of material streams} \right) + \left( \text{Rate of work done by the system} \right) \\
\text{Rate of energy input or output by flow of material streams} & = \left( \text{Mass flow rate} \right) \left( \text{Energy per unit mass} \right)
\end{align*}
\]

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

\[ \dot{m}_m = \dot{m}_{out} = \dot{m} \ (kg / s) \]

(2) \[ \text{Rate of energy input by flow of material streams} = \dot{m}(KE + PE + u)_{in} \]

(3) \[ \text{Rate of energy output by flow of material streams} = \dot{m}(KE + PE + u)_{out} \]

(4) \[ \text{Rate of heat addition from the surroundings} = \dot{q} \ (kJ / s) \]
The work done by the system consists of three parts:

\[
\begin{pmatrix}
\text{Rate of work done by the system} \\
\text{Rate of work done to expel the outflow into the surroundings} \\
\text{Rate of work done by the surroundings to propel the inflow into the system} \\
\text{Rate of work done against gravity or other body forces}
\end{pmatrix}
\]

\[
\dot{W} = \dot{W}_s + m \left( \frac{P}{\rho} \right)_{out} - \dot{m} \left( \frac{P}{\rho} \right)_{in} - \dot{m} \left( h_{out} - h_{in} \right)
\]

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

\[
0 = \dot{m} \left( u + KE + PE \right)_{in} + \dot{q} - \dot{m} \left( u + KE + PE \right)_{out} + \dot{W}_s + \dot{m} \left( \frac{P}{\rho} \right)_{out} - \dot{m} \left( \frac{P}{\rho} \right)_{in}
\]

\[
\dot{m} \left[ \left( u + \frac{P}{\rho} + KE + PE \right)_{out} - \left( u + \frac{P}{\rho} + KE + PE \right)_{in} \right] = \dot{q} - \dot{W}_s
\]

\[
\dot{m} \left[ \Delta E + \Delta \left( \frac{P}{\rho} \right) \right] = \dot{q} - \dot{W}_s \quad \text{[1st law]}
\]

One can readily show that in chemical reactors:

**Assumption 4** – kinetic energy changes are negligible compared to those in internal energy

\[\Delta KE \ll \Delta u\]

**Assumption 5** – potential energy changes are negligible compared to internal energy changes

\[\Delta PE \ll \Delta u\]

Recall the definition of enthalpy

\[H = u + pv = u + \frac{P}{\rho}\]

Hence equation (6) becomes

\[
\dot{m} \left( H_{out} - H_{in} \right) = \dot{q} - \dot{W}_s
\]

In almost all chemical reactors there is no considerable shaft work leading to:
Ass6 – negligible shaft work

\[ m(H_{\text{out}} - H_{\text{in}}) = \dot{q} \]

For booking purposes in chemical reactors we represent

\[ \dot{m}H_{\text{out}} = \sum_{j=1}^{s} F_j \tilde{H}_j, \quad \dot{m}H_{\text{in}} = \sum_{j=1}^{s} F_{j\circ} \tilde{H}_{j\circ} \]

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

We will here further assume:

Ass7 – ideal mixtures

\[ \tilde{H}_j = H_j \]

\( \text{partial molal enthalpy} = \left( \frac{\text{molal enthalpy}}{\text{molal}} \right) \)

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

\[ \left( \frac{\partial H_j}{\partial T} \right)_p = \frac{C_{p_j}}{\text{specific heat for } j} \quad \text{(10a)} \]

\[ H_j(T) = \Delta H_{f_j}^{\circ}(T_s) \quad + \quad \int_{T_s}^{T} C_{p_j} \, dT \]

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

\[ \sum_{j=1}^{s} \left[ F_j H_j(T) - F_{j\circ} H_j(T_\circ) \right] = \dot{q} \]

where exit temperature is \( T \), inlet temperature is \( T_\circ \). The mass balance for any species \( j \) is
Using eq (12) to eliminate $F_{j0}$ in eq (11) we get

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

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

$$\sum_{j=1}^{s} F_j \int_{T_e}^{T} C_{pj} dT + \hat{X} \sum_{j=1}^{s} v_j \left[ \Delta H_{fj} + \int_{T_e}^{T} C_{pj} dT \right] = \hat{q}$$

Recall that by definition the standard heat of reaction is:

$$\Delta H^o_R = \sum_{j=1}^{s} v_j \Delta H_{fj}$$

Heat of reaction at temperature $T_o$ is

$$\Delta H_R(T_o) = \Delta H^o_R + \sum_{j=1}^{s} v_j \int_{T_e}^{T} C_{pj} dt$$

$$\sum_{j=1}^{s} F_j \int_{T_e}^{T} C_{pj} dT + \hat{X} \Delta H_R(T_o) = \hat{q}$$

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

\[
\begin{align*}
\text{(Rate of heat addition to the reactor)} &= \text{(Rate of heat "absorption" by reaction at temperature of feed)} \\
&\quad + \text{(Rate of heating the reaction mixture at exit composition from feed to exit temperature)}
\end{align*}
\]

$$\text{(III)} = \text{(I)} + \text{(II)}$$

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

$$\sum_{j=1}^{s} F_j \int_{T_e}^{T} C_{pj} dT + \hat{X} \Delta H_R(T) = \hat{q}$$
In reaction engineering problems, additional assumptions are often made.

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

\[
\rho Q_{mp}(T - T_o) = \sum_{j} \int_{T_o}^{T} F_{j0} C_{pj} dT
\]

**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) \[ \rho Q_{mp}(T - T_o) + \dot{X} \Delta H_R = \dot{q} \]

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

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

\[
\rho Q_{mp}(T - T_o) - \dot{X}(-\Delta H_R) = \dot{q}
\]

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

\[
\frac{d\hat{X}}{dV} = \left( \frac{R_j}{v_j} \right) = r
\]

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

\[
\rho QC_{fr} \frac{dT}{dV} + \Delta H_r \frac{d\hat{X}}{dV} = \dot{q}_v
\]

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