The Energy Balance over Ideal CSTRs operated at Steady-State

The first law of thermodynamics applied to an open flow system such as the continuous stirred tank reactor yields

$$\dot{Q}_{in} \quad + \quad (\dot{W}_{shaft})_{in} \quad + \quad (\dot{W}_{boundary})_{in} \quad + \quad \frac{d}{dt}\left[H + (\text{kinetic energy}) + (\text{potential energy})\right]_{inlet}$$
$$= \quad \frac{d}{dt}\left[H + (\text{kinetic energy}) + (\text{potential energy})\right]_{exit} \quad + \quad \frac{d}{dt}(\text{energy of the system})$$

If the CSTR operates at steady state then there is no boundary work and no change in the energy of the system. Also, neglecting the kinetic and potential energy terms, the first law can be simplified to

$$\dot{Q}_{in} + (\dot{W}_{shaft})_{in} = \dot{H}_{exit} - \dot{H}_{inlet} \tag{8.1}$$

where $\dot{Q}_{in}$ is the rate at which heat enters the reactor from the surroundings through the reactor walls and $(\dot{W}_s)_{in}$ is the rate at which shaft work is delivered to the reactor.

The rates at which enthalpies entering the reactor and leaving the reactor can be expanded in terms of the molar enthalpies (denoted by h) and the molar flow rates (denoted by F) as

$$\dot{H}_{inlet} = \sum_j h_{j0}F_{j0} \qquad \text{and} \qquad \dot{H}_{exit} = \sum_j h_{jf}F_{jf} \tag{8.2}$$

where the subscripts j denotes the component, 0 denotes the inlet condition and f denotes the exit condition.

Consider a general reaction

$$a\,A + b\,B \;\longrightarrow\; c\,C + d\,D \tag{8.3}$$

taking place in the presence of some inert material, I. For such a system, the expressions for $\dot{H}_{inlet}$ and $\dot{H}_{exit}$, given by (8.2), can be expanded as follows:

$$\dot{H}_{inlet} = h_{A0}F_{A0} + h_{B0}F_{B0} + h_{C0}F_{C0} + h_{D0}F_{D0} + h_{I0}F_{I0} \tag{8.4}$$

$$\dot{H}_{exit} = h_{Af}F_{Af} + h_{Bf}F_{Bf} + h_{Cf}F_{Cf} + h_{Df}F_{Df} + h_{If}F_{If} \tag{8.5}$$

Using (8.4) and (8.5), we can expand (8.1) to

$$\begin{aligned}\dot{Q}_{in} + (\dot{W}_s)_{in} \;=\; & (h_{Af}F_{Af} - h_{A0}F_{A0}) + (h_{Bf}F_{Bf} - h_{B0}F_{B0}) + (h_{Cf}F_{Cf} - h_{C0}F_{C0}) \\ & + (h_{Df}F_{Df} - h_{D0}F_{D0}) + (h_{If}F_{If} - h_{I0}F_{I0})\end{aligned} \tag{8.6}$$

If the conversion of A at the exit is taken as x_{Af} then

$$F_{Af} = F_{A0}(1 - x_{Af}) \tag{8.7}$$

and, in accordance with the stoichiometry of the given reaction, we can write the following:

$$F_{Bf} = F_{B0} - \frac{b}{a}\, F_{A0} x_{Af} \tag{8.8}$$

$$F_{Cf} = F_{C0} + \frac{c}{a}\, F_{A0} x_{Af} \tag{8.9}$$

$$F_{Df} = F_{D0} + \frac{d}{a}\, F_{A0} x_{Af} \tag{8.10}$$

$$F_{If} = F_{I0} \tag{8.11}$$

Using (8.7) to (8.11), we can rewrite (8.6) as

$$\begin{aligned} \dot{Q}_{in} + (\dot{W}_s)_{in} &= F_{A0}(h_{Af} - h_{A0}) + F_{B0}(h_{Bf} - h_{B0}) + F_{C0}(h_{Cf} - h_{C0}) + F_{D0}(h_{Df} - h_{D0}) \\ &\quad + F_{I0}(h_{If} - h_{I0}) + F_{A0} x_{Af} \left(\frac{d}{a}\, h_{Df} + \frac{c}{a}\, h_{Cf} - \frac{b}{a}\, h_{Bf} - h_{Af} \right) \end{aligned} \tag{8.12}$$

Since the heat of reaction at temperature T is defined by

$$\Delta H_R(T) \equiv \frac{d}{a}\, h_D(T) + \frac{c}{a}\, h_C(T) - \frac{b}{a}\, h_B(T) - h_A(T) \tag{8.13}$$

(8.12) takes the following form:

The general energy balance for the CSTR operating at steady state is given by

$$\begin{aligned} \dot{Q}_{in} + (\dot{W}_{shaft})_{in} &= F_{A0}(h_{Af} - h_{A0}) + F_{B0}(h_{Bf} - h_{B0}) \\ &\quad + F_{C0}(h_{Cf} - h_{C0}) + F_{D0}(h_{Df} - h_{D0}) \\ &\quad + F_{I0}(h_{If} - h_{I0}) + F_{A0}\, x_{Af}\, \Delta H_R(T_f) \end{aligned} \tag{8.14}$$

which can be readily used if we know the molar enthalpies of the components involved at the inlet and exit temperatures and the heat of reaction ΔH_R at the exit temperature T_f.

Assuming that the enthalpy changes owing to mixing is neglected and that the component j remains in a single phase throughout the reaction, we can write

$$h_{jf} - h_{j0} = \int_{T_{j0}}^{T_f} C_{pj}\, dT = C_{pj}\, (T_f - T_{j0})$$

where T_f is the exit temperature, T_{j0} is the inlet temperature of the j^{th} component and C_{pj} is the molar heat capacity at constant pressure of the j^{th} component which is assumed to remain a constant.

The above expression allows us to rewrite (8.14) as follows:

The general energy balance for the CSTR operating at steady state is given by

$$\begin{aligned}\dot{Q}_{in} \;+\; (\dot{W}_{shaft})_{in} \;&=\; F_{A0}\,C_{pA}\,(T_f - T_{A0}) + F_{B0}\,C_{pB}\,(T_f - T_{B0}) + F_{C0}\,C_{pC}\,(T_f - T_{C0}) \\ &+ F_{D0}\,C_{pD}\,(T_f - T_{D0}) + F_{I0}\,C_{pI}\,(T_f - T_{I0}) + F_{A0}\,x_{Af}\,\Delta H_R(T_f) \qquad (8.15)\end{aligned}$$

which can be readily used if we know the molar heat capacity at constant pressure for each component and the heat of reaction $\Delta H_R(T_f)$.

Important notes:

- Heat capacities are assumed to be constants.
- The shaft work is normally neglected unless the mixture is highly viscous and the stirring operation draws significant power.
- Changes in total pressure with time is also often neglected.

Special case (i): With molar heat capacities being independent of temperature and the inlet temperatures of all components being the same (say, T_0), (8.15) reduces to the following:

$$\begin{aligned}\dot{Q}_{in} + (\dot{W}_{shaft})_{in} \;&=\; (F_{A0}\,C_{pA} + F_{B0}\,C_{pB} + F_{C0}\,C_{pC} + F_{D0}\,C_{pD} + F_{I0}\,C_{pI})\,(T_f - T_0) \\ &+F_{A0}\,x_{Af}\,\Delta H_R(T_f) \qquad (8.16)\end{aligned}$$

Special case (ii): With the molar heat capacities of all components being the same (say, C_p) in addition to the assumptions made in Special case (i), (8.16) reduces to the following:

$$\begin{aligned}\dot{Q}_{in} + (\dot{W}_{shaft})_{in} \;&=\; (F_{A0} + F_{B0} + F_{C0} + F_{D0} + F_{I0})\;C_p\,(T_f - T_0) \\ &+F_{A0}\,x_{Af}\,\Delta H_R(T_f) \qquad (8.17)\end{aligned}$$

Special case (iii): With the molecular weight of all components being the same (say, MW) in addition to the assumptions made in Special case (ii), (8.17) reduces to the following:

$$\begin{aligned}\dot{Q}_{in} \;&+\; (\dot{W}_{shaft})_{in} \\ &= \dot{m}_{T0}\,\bar{C}_p\,(T_f - T_0) + F_{A0}\,x_{Af}\,\Delta H_R(T_f) \qquad (8.18)\end{aligned}$$

where the total mass flow rate of the feed to the CSTR is given by

$$\dot{m}_{T0} = (\dot{m}_{A0} + \dot{m}_{B0} + \dot{m}_{C0} + \dot{m}_{D0} + \dot{m}_{I0}) \qquad (8.19)$$

and the specific heat capacity (in kJ/kg.K) is related to the molar heat capacity (kJ/kmol.K) by

$$\bar{C}_p = C_p/MW \qquad (8.20)$$

Next, let us take a close look at $\Delta H_R(T_f)$. From the definition of $\Delta H_R(T)$ given by (8.13), we get

$$
\begin{aligned}
\Delta H_R(T_f) &= \frac{d}{a}\, h_D(T_f) + \frac{c}{a}\, h_C(T_f) - \frac{b}{a}\, h_B(T_f) - h_A(T_f) \\
&= \frac{d}{a}\, h_{Df} + \frac{c}{a}\, h_{Cf} - \frac{b}{a}\, h_{Bf} - h_{Af} \\
&= \frac{d}{a}\, h_D^{ref} + \frac{c}{a}\, h_C^{ref} - \frac{b}{a}\, h_B^{ref} - h_A^{ref} \\
&\qquad + \int_{T_{ref}}^{T_f} \left(\frac{d}{a}\, C_{pD} + \frac{c}{a}\, C_{pC} - \frac{b}{a}\, C_{pB} - C_{pA} \right) dT \qquad (8.21)
\end{aligned}
$$

which can be briefed to the simple form

$$\Delta H_R(T_f) = \Delta H_R(T_{ref}) + \int_{T_{ref}}^{T_f} \Delta C_p \, dT \qquad (8.22)$$

where $\Delta H_R(T_{ref})$ is defined by

$$\Delta H_R(T_{ref}) = \frac{d}{a}\, h_D^{ref} + \frac{c}{a}\, h_C^{ref} - \frac{b}{a}\, h_B^{ref} - h_A^{ref} \qquad (8.23)$$

and ΔC_p is defined by

$$\Delta C_p \equiv \frac{d}{a}\, C_{pD} + \frac{c}{a}\, C_{pC} - \frac{b}{a}\, C_{pB} - C_{pA} \qquad (8.24)$$

Therefore, the most general energy balance over the CSTR operating at steady state can be written as

$$
\begin{aligned}
\dot{Q}_{in} \;+\; (\dot{W}_{shaft})_{in} \;=\; & F_{A0} \int_{T_{A,0}}^{T_f} C_{pA}\, dT + F_{B0} \int_{T_{B,0}}^{T_f} C_{pB}\, dT \\
& + F_{C0} \int_{T_{C,0}}^{T_f} C_{pC}\, dT + F_{D0} \int_{T_{D,0}}^{T_f} C_{pD}\, dT \\
& + F_{I0} \int_{T_{I,0}}^{T_f} C_{pI}\, dT + F_{A0}\, x_{Af} \left(\Delta H_R(T_{ref}) + \int_{T_{ref}}^{T_f} \Delta C_p \, dT \right) \qquad (8.25)
\end{aligned}
$$

where $\Delta H_R(T_{ref})$ is the heat of reaction at the reference temperature and ΔC_p is given by (8.24) as

$$\Delta C_p \equiv \frac{d}{a}\, C_{pD} + \frac{c}{a}\, C_{pC} - \frac{b}{a}\, C_{pB} - C_{pA}$$

Important notes: The heat of reaction ΔH_R is independent of the temperature if $\Delta C_p \equiv 0$.

Source: Fogler, H.S., *Elements of Chemical Reaction Engineering*, Second Edition, Prentice-Hall International Editions.