`CP303 — Set #7 (January-May 2012)`

The Energy Balance over Ideal Batch Reactors

Consider a batch reactor where the following general reaction is taking place in the presence of an inert material I:

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

The first law of thermodynamics, when applied to the reacting mixture at time t, gives the following energy balance:

$$\dot{Q}_{in} + (\dot{W}_{shaft})_{in} + (\dot{W}_{boundary})_{in} = dE(t)/dt \tag{7.1}$$

where $\dot{Q}_{in}$ is the rate at which heat enters the reacting mixture from the surroundings at time t, $(\dot{W}_{shaft})_{in}$ is the rate at which shaft work is delivered to the reacting mixture at time t, $(\dot{W}_{boundary})_{in}$ is the rate at which boundary work is delivered to the reacting mixture at time t, and $E(t)$ is the energy content of the reacting mixture at time t.

In general, $E(t)$ includes the internal energy, kinetic energy, potential energy, and any other energies such as electric energy or magnetic energy or light. However, in most of the chemical reactor situtaions, kinetic, potential and "'other"' energy terms are negligible in comparision with the internal energy, heat transfer and work terms, and hence they are omitted. Therefore, (7.1) can be written as

$$\dot{Q}_{in} + (\dot{W}_{shaft})_{in} + (\dot{W}_{boundary})_{in} = dU(t)/dt \tag{7.2}$$

where $U(t)$ is the internal energy content of the reacting mixture at time t, which can be expnaded to the following:

$$U(t) = N_A\,u_A + N_B\,u_B + N_C\,u_C + N_D\,u_D + N_I\,u_I \tag{7.3}$$

where N_A, N_B, N_C, N_D and N_I are the respective number of moles of A, B, C, D and inert I at time t, and u_A, u_B, u_C, u_D and u_I are the respective molar internal energies.

We want to convert the molar internal energies in (7.3) to molar entahlpies, which could be done using the definition of molar enthalpy, given by $h \equiv u + P_T\,\bar{v}$, where P_T is the total pressure of the system and $\bar{v}$ is the molar volume of the substance concerned. Using the above, (7.3) can be expanded to the following:

$$\begin{aligned} U(t) &= N_A\,(h_A - P_T\,\bar{v}_A) + N_B\,(h_B - P_T\,\bar{v}_B) + N_C\,(h_C - P_T\,\bar{v}_C) + N_D\,(h_D - P_T\,\bar{v}_D) \\ &\qquad + N_I\,(h_I - P_T\,\bar{v}_I) && (7.4) \\ &= N_A\,h_A + N_B\,h_B + N_C\,h_C + N_D\,h_D + N_I\,h_I \\ &\qquad - P_T\,[N_A\,\bar{v}_A + N_B\,\bar{v}_B + N_C\,\bar{v}_C + N_D\,\bar{v}_D + N_I\,\bar{v}_I] && (7.5) \\ &= N_A\,h_A + N_B\,h_B + N_C\,h_C + N_D\,h_D + N_I\,h_I - P_T\,V_T && (7.6) \end{aligned}$$

where V_T is the total volume of the reacting mixture under ideal mixing conditions, given by $V_T = N_A\,\bar{v}_A + N_B\,\bar{v}_B + N_C\,\bar{v}_C + N_D\,\bar{v}_D + N_I\,\bar{v}_I$.

Let us write down the number of moles of A, B, C, D and I at time t in (7.6) as functions of the respective intital number of moles, N_{A0}, N_{B0}, N_{C0}, N_{D0} and N_{I0}, and conversion of A at time t, defined as $x_A \equiv (N_{A0} - N_A)/N_{A0}$.

Definition of x_A gives the following:

$$N_A = N_{A0}(1 - x_A) \tag{7.7}$$

and the stoichiometry of the given reaction gives the following:

$$\begin{aligned} N_B &= N_{B0} - \frac{b}{a}\, N_{A0}x_A && (7.8)\\ N_C &= N_{C0} + \frac{c}{a}\, N_{A0}x_A && (7.9)\\ N_D &= N_{D0} + \frac{d}{a}\, N_{A0}x_A && (7.10)\\ N_I &= N_{I0} && (7.11) \end{aligned}$$

Using (7.7) to (7.11), $U(t)$ of (7.6) is expanded to the following:

$$\begin{aligned} U(t) &= N_{A0}h_A + N_{B0}h_B + N_{C0}h_C + N_{D0}h_D + N_{I0}h_I \\ &\qquad + N_{A0}\, x_A \left(\frac{d}{a}\, h_D + \frac{c}{a}\, h_C - \frac{b}{a}\, h_B - h_A \right) - P_T\, V_T \end{aligned} \tag{7.12}$$

Using the definition of heat of reaction for a mole of A reacting at temperature T, expressed by

$$\Delta H_{RA}(T) \equiv \frac{d}{a}\, h_D(T) + \frac{c}{a}\, h_C(T) - \frac{b}{a}\, h_B(T) - h_A(T)\,, \tag{7.13}$$

(7.12) is reduced to the following:

$$U(t) = N_{A0}h_A + N_{B0}h_B + N_{C0}h_C + N_{D0}h_D + N_{I0}h_I + N_{A0}\, x_A\, \Delta H_{RA}(T) - P_T\, V_T \tag{7.14}$$

Using (7.14) in (7.2), we get the following:

$$\begin{aligned} \dot{Q}_{in} \;&+\; (\dot{W}_{shaft})_{in} \;+\; (\dot{W}_{boundary})_{in} \\ &= \frac{d}{dt}\Big(N_{A0}h_A + N_{B0}h_B + N_{C0}h_C + N_{D0}h_D + N_{I0}h_I + N_{A0}\, x_A\, \Delta H_{RA}(T) - P_T\, V_T \Big) \\ &= N_{A0}\frac{dh_A}{dt} + N_{B0}\frac{dh_B}{dt} + N_{C0}\frac{dh_C}{dt} + N_{D0}\frac{dh_D}{dt} + N_{I0}\frac{dh_I}{dt} \\ &\qquad + N_{A0}\, \frac{d}{dt}\Big[x_A\, \Delta H_{RA}(T) \Big] \;-\; P_T\, \frac{dV_T}{dt} \;-\; V_T\, \frac{dP_T}{dt} \end{aligned} \tag{7.15}$$

For a variable-volume batch reactor, $(\dot{W}_{boundary})_{in} = -P_T\, dV_T/dt$. For a constant-volume batch reactor, $(\dot{W}_{boundary})_{in} = 0$ and $dV_T/dt = 0$. Therefore, in either cases, (7.15) reduces to the following:

$$\begin{aligned} \dot{Q}_{in} + (\dot{W}_{shaft})_{in} &= N_{A0}\frac{dh_A}{dt} + N_{B0}\frac{dh_B}{dt} + N_{C0}\frac{dh_C}{dt} + N_{D0}\frac{dh_D}{dt} + N_{I0}\frac{dh_I}{dt} \\ &\qquad + N_{A0}\, \frac{d}{dt}\Big[x_A\, \Delta H_{RA}(T) \Big] - V_T\, \frac{dP_T}{dt} \end{aligned} \tag{7.16}$$

Molar enthalpies in (7.16) are not directly measurable quantities. Therefore, let us convert the molar enthapies to functions of temperature using the procedure explained below.

Neglecting the enthalpy changes owing to mixing and assuming component j remains in a single phase throughout the reaction, we can write $h_j(T)$, the molar enthapy of component j at temperature T, as

$$h_j(T) - h_j(T_{ref}) = \int_{T_{ref}}^{T} C_{pj}\, dT = C_{pj}\,(T - T_{ref}) \tag{7.17}$$

where T_{ref} is the reference temperature at which $h_j(T_{ref})$, the reference molar enthalpy of component j, is taken to be known, and C_{pj} is the molar heat capacity at constant pressure of the component j which is assumed to be a constant throughout. Differentiating (7.17), we get

$$\frac{dh_j}{dt} = C_{pj}\,\frac{dT}{dt} \tag{7.18}$$

Using (7.18), we can rewrite (7.16) as follows:

$$\begin{aligned} \dot{Q}_{in} + (\dot{W}_{shaft})_{in} &= \Big(N_{A0}C_{pA} + N_{B0}C_{pB} + N_{C0}C_{pC} + N_{D0}C_{pD} + N_{I0}C_{pI}\Big)\,\frac{dT}{dt} \\ &\quad + N_{A0}\,\frac{d}{dt}\Big[x_A\,\Delta H_{RA}(T)\Big] \;-\; V_T\,\frac{dP_T}{dt} \end{aligned} \tag{7.19}$$

which is the energy balance over a constant or variable volume batch reactor for a system with components having constant heat capacities, written in terms of rate of change of temperature of the reacting mixture.

Next, let us take a close look at the heat of reaction term, $\Delta H_{RA}(T)$, in (7.19). It is given at temperature T, and can be related to $\Delta H_{RA}(T_{ref})$, the heat of reaction at the reference temperature T_{ref}, as follows:

Combining (7.13) and (7.17), we get the following:

$$\begin{aligned} \Delta H_{RA}(T) &= \frac{d}{a}\,\left[h_D(T_{ref}) + C_{pD}(T - T_{ref})\right] + \frac{c}{a}\,\left[h_C(T_{ref}) + C_{pC}(T - T_{ref})\right] \\ &\quad -\frac{b}{a}\,\left[h_B(T_{ref}) + C_{pB}(T - T_{ref})\right] - \left[h_A(T_{ref}) + C_{pA}(T - T_{ref})\right] \\ &= \left[\frac{d}{a}\,h_D(T_{ref}) + \frac{c}{a}\,h_C(T_{ref}) - \frac{b}{a}\,h_B(T_{ref}) - h_A(T_{ref})\right] \\ &\quad \left(\frac{d}{a}\,C_{pD} + \frac{c}{a}\,C_{pC} - \frac{b}{a}\,C_{pB} - C_{pA}\right)(T - T_{ref}) \end{aligned} \tag{7.20}$$

which gives

$$\Delta H_{RA}(T) = \Delta H_{RA}(T_{ref}) + \Delta C_p\,(T - T_{ref})\;, \tag{7.21}$$

where

$$\Delta H_{RA}(T_{ref}) = \frac{d}{a}\,h_D(T_{ref}) + \frac{c}{a}\,h_C(T_{ref}) - \frac{b}{a}\,h_B(T_{ref}) - h_A(T_{ref}) \tag{7.22}$$

and

$$\Delta C_p \equiv \frac{d}{a}\,C_{pD} + \frac{c}{a}\,C_{pC} - \frac{b}{a}\,C_{pB} - C_{pA} \tag{7.23}$$

Differentiating (7.21), we get

$$\frac{d}{dt}[\Delta H_{RA}(T)] = \Delta C_p \, \frac{dT}{dt} \; . \tag{7.24}$$

Substituting (7.24) in (7.19), we get the following:

The general energy balance over a constant or variable volume batch reactor for a system with components having constant heat capacities is given by

$$\begin{aligned} \dot{Q}_{in} \;&+\; (\dot{W}_{shaft})_{in} \\ &= \Big(N_{A0}C_{pA} + N_{B0}C_{pB} + N_{C0}C_{pC} + N_{D0}C_{pD} + N_{I0}C_{pI} + N_{A0}\, x_A \, \Delta C_p\Big) \, \frac{dT}{dt} \\ &\qquad + N_{A0}\,\frac{d\,x_A}{dt}\,\Delta H_{RA}(T) \;-\; V_T\,\frac{dP_T}{dt} \end{aligned} \tag{7.25}$$

where

$$\Delta C_p \equiv \frac{d}{a}\, C_{pD} + \frac{c}{a}\, C_{pC} - \frac{b}{a}\, C_{pB} - C_{pA} \tag{7.23}$$

Important Notes:

- Heat capacities are assumed to be constants.
- Components are assumed to remain in single phase throughout the reaction.
- The heat of reaction ΔH_{RA} is independent of the temperature if $\Delta C_p \equiv 0$.
- 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.

See page 5 for some special cases of (7.25).

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

Special case(i): Molar heat capacities of all components are the same (say, C_p)

$$\begin{aligned}
N_{A0}C_{pA} \;+\; N_{B0}C_{pB} \;+\; N_{C0}C_{pC} \;+\; N_{D0}C_{pD} \;+\; N_{I0}C_{pI} \;+\; N_{A0}\,x_A\,\Delta C_p & \\
&= (N_{A0}+N_{B0}+N_{C0}+N_{D0}+N_{I0})\,C_p + N_{A0}\,x_A\left(\frac{d}{a}+\frac{c}{a}-\frac{b}{a}-1\right)C_p \\
&= N_{T0}\,C_p + N_{A0}\,x_A\left(\frac{d}{a}+\frac{c}{a}-\frac{b}{a}-1\right)C_p \\
&= N_{T0}\,(1+\epsilon_A\,x_A)\,C_p \qquad (7.26)
\end{aligned}$$

where

$$N_{T0} = N_{A0}+N_{B0}+N_{C0}+N_{D0}+N_{I0} \qquad (7.27)$$

and

$$\epsilon_A = \frac{N_{A0}}{N_{T0}}\left[\frac{(c+d+\cdots)-(a+b+\cdots)}{a}\right] \qquad (7.28)$$

Combining (7.25) and (7.26), we get the following:

$$\dot{Q}_{in} + (\dot{W}_{shaft})_{in} = N_{T0}\,(1+\epsilon_A\,x_A)\,C_p\,\frac{dT}{dt} + \; N_{A0}\,\frac{d\,x_A}{dt}\,\Delta H_{RA}(T) \;-\; V_T\frac{dP_T}{dt} \qquad (7.29)$$

Special case(ii): Molar heat capacities of all components are the same (say, C_p) and the molecular weight of all components are the same (say, MW)

$$\begin{aligned}
N_{A0}C_{pA} \;+\; N_{B0}C_{pB} \;+\; N_{C0}C_{pC} \;+\; N_{D0}C_{pD} \;+\; N_{I0}C_{pI} \;+\; N_{A0}\,x_A\,\Delta C_p & \\
&= (N_{A0}+N_{B0}+N_{C0}+N_{D0}+N_{I0})\,C_p + N_{A0}\,x_A\left(\frac{d}{a}+\frac{c}{a}-\frac{b}{a}-1\right)C_p \\
&= (N_A+N_B+N_C+N_D+N_I)\,C_p \qquad \text{when using (7.7) to (7.11)} \\
&= (m_A+m_B+m_C+m_D+m_I)\;\frac{C_p}{MW} \\
&= m_T\,\bar{C}_p \qquad (7.30)
\end{aligned}$$

where the total mass of the reacting mixture in the reactor at time t is given by

$$m_T = (m_A+m_B+m_C+m_D+m_I) = \text{ constant} \qquad (7.31)$$

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

$$\bar{C}_p = \frac{C_p}{MW} \qquad (7.32)$$

Combining (7.25) and (7.30), we get the following:

$$\dot{Q}_{in} + (\dot{W}_{shaft})_{in} = m_T\,\bar{C}_p\,\frac{dT}{dt} + \; N_{A0}\,\frac{d\,x_A}{dt}\,\Delta H_{RA}(T) \;-\; V_T\frac{dP_T}{dt} \qquad (7.33)$$