# Lecture 19: Batch Reactor Energy Balance

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We can look up internal energies of formation per mole at $T_{ref}$ and $p_{ref}$.

$$\underline{U}_f(T_{ref}, p_{ref})$$

Because the internal energy is a state function, the change in the internal energy between state point 1 and state point 2 is independent of the path. Therefore, we can imagine a path that moves us from the reference state to an arbitrary state at T and p in two steps. In the first step, we expand or compress the material isothermally at $T_{ref}$ from $\underline{V}(T_{ref}, p_{ref})$ to $\underline{V}(T, p)$. The internal energy change associated with this process is

$$\int_{\underline{V}(T_{ref}, p_{ref})}^{\underline{V}(T,p)} \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{T_{ref}} d\underline{V}$$

where the partial derivative given above is a material property of the system. In the second step, we heat or cool the material isochorically at a constant volume of $\underline{V}(T, p)$ from $T_{ref}$ to $T$. The internal energy change associated with this process is

$$\int_{T_{ref}}^{T} \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}(T,p)} dT$$

where the partial derivative given above is a material property of the system, commonly called the constant volume heat capacity. Therefore, we can compute the internal energy at any arbitrary temperature and pressure as follows

$$\underline{U}(T,p) = \int_{T_{ref}}^{T} \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}(T,p)} dT + \int_{\underline{V}(T_{ref}, p_{ref})}^{\underline{V}(T,p)} \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{T_{ref}} d\underline{V} + \underline{U}_f(T_{ref}, p_{ref})$$

Frequently the dependence of the internal energy on the molar volume is assumed to be negligible, leaving

$$\underline{U}(T) = \int_{T_{ref}}^{T} C_V dT + \underline{U}_f(T_{ref}, p_{ref})$$

**Assumption 1: the internal energy is not a function of molar volume.**

The internal energy of a mixture per mole is a function of the partial molar internal energies of each component.

$$\underline{U}_{mix}(T) = \sum_{i=1}^{N_c} x_i \overline{U}_i$$

If we assume that we have an ideal mixture then the partial molar internal energy of component i can be approximated by the molar internal energy of pure component i.

$$\underline{U}_{mix}(T) = \sum_{i=1}^{N_c} x_i \underline{U}_i$$

**Assumption 2: The mixture is an ideal mixture.**

This pure component internal energy has already been derived above. If we neglect volume dependence, then we have

$$\underline{U}_{mix}(T) = \sum_{i=1}^{N_c} x_i \left( \int_{T_{ref}}^{T} C_{V,i} dT + \underline{U}_{f,i}(T_{ref}, p_{ref}) \right)$$

The mole fraction is defined in terms of the number of moles or the concentration.

$$x_i = \frac{N_i}{\sum_{i=1}^{N_c} N_i} = \frac{N_i}{N_T} = \frac{C_i}{C_T}$$

$$\underline{U}_{mix}(T) = \frac{1}{C_T} \sum_{i=1}^{N_c} C_i \left( \int_{T_{ref}}^{T} C_{V,i} dT + \underline{U}_{f,i}(T_{ref}, p_{ref}) \right)$$

The total energy of a system with a given concentration in a given volume is

$$VC_T \underline{U}_{mix}(T) = V \sum_{i=1}^{N_c} C_i \left( \int_{T_{ref}}^{T} C_{V,i} dT + \underline{U}_{f,i}(T_{ref}, p_{ref}) \right)$$

Let’s examine the time derivative of the energy in this system.

$$\frac{d\left(VC_T \underline{U}_{mix}\right)}{dt} = VC_T \frac{d\underline{U}_{mix}}{dt} + V\underline{U}_{mix} \frac{dC_T}{dt} + C_T \underline{U}_{mix} \frac{dV}{dt}$$

We need to evaluate all the derivatives on the RHS.

$$\frac{d\underline{U}_{mix}}{dt}=\frac{1}{C_T}\sum_{i=1}^{N_c}\left(C_i\frac{d\underline{U}_i}{dt}+\underline{U}_i\frac{dC_i}{dt}\right)-\frac{1}{{C_T}^2}\sum_{i=1}^{N_c}\left(C_i\underline{U}_i\right)\frac{dC_T}{dt}$$

Let’s examine the derivative of the molar internal energy of pure component i first.

$$\frac{d\underline{U}_i}{dt}=\frac{d}{dt}\int_{T_{ref}}^{T}C_{V,i}dT+\frac{d}{dt}\underline{U}_{f,i}(T_{ref},p_{ref})$$

The second derivative is zero, since the internal energy of formation of component i is a constant.

The first derivative requires Leibniz’s rule for differentiation under the integral sign.

$$\frac{d}{dz}\int_{a(z)}^{b(z)}f(z,x)dx=\int_{a(z)}^{b(z)}\frac{df(z,x)}{dz}dx+f(z,b(z))\frac{db(z)}{dz}-f(z,a(z))\frac{da(z)}{dz}$$

For our case this becomes,

$$\frac{d}{dt}\int_{T_{ref}}^{T}C_{V,i}dT=\int_{T_{ref}}^{T}\frac{dC_{V,i}}{dt}dT+C_{V,i}\left(T\right)\frac{dT}{dt}-C_{V,i}\left(T_{ref}\right)\frac{dT_{ref}}{dt}$$

So that

$$\frac{d\underline{U}_i}{dt}=\int_{T_{ref}}^{T}\frac{dC_{V,i}}{dt}dT+C_{V,i}\left(T\right)\frac{dT}{dt}$$

The last term is zero since the reference temperature is constant. The first term is also zero because the temperature dependence inside the integral is really only a dummy variable of integration and not explicit time dependence.

$$\int_{T_{ref}}^{T}\frac{dC_{V,i}}{dt}dT=\int_{T_{ref}}^{T}\frac{dC_{V,i}\left(T'\right)}{dt}dT'=0$$

Thus we can write the time derivative of the internal energy as

$$\frac{d\underline{U}_i}{dt}=C_{V,i}\left(T\right)\frac{dT}{dt}$$

If the heat capacity is constant,

$$\frac{d\underline{U}_i}{dt} = C_{V,i}\frac{dT}{dt}$$

**Assumption 3: The heat capacity is constant.**

The other required derivative comes from the molar balance.

$$\frac{dC_i}{dt} = \nu_i r$$

Substituting into the derivative of the mixture internal energy, we have

$$\frac{d\underline{U}_{mix}}{dt} = \frac{1}{C_T}\sum_{i=1}^{N_c}\left(C_i C_{V,i}(T)\frac{dT}{dt} + \underline{U}_i \nu_i r\right) - \frac{1}{C_T{}^2}\sum_{i=1}^{N_c}\left(C_i \underline{U}_i\right)\frac{dC_T}{dt}$$

$$\frac{d\underline{U}_{mix}}{dt} = \frac{1}{C_T}\sum_{i=1}^{N_c}\left(C_i C_{V,i}(T)\frac{dT}{dt} + \underline{U}_i \nu_i r\right) - \frac{1}{C_T}\underline{U}_{mix}\frac{dC_T}{dt}$$

We also need to know the change in the total number of moles with time.

$$\frac{dC_T}{dt} = \sum_{i=1}^{N_c}\frac{dC_i}{dt} = \left(\sum_{i=1}^{N_c}\nu_i\right)r$$

Substituting these expressions into the expression for the total internal energy above we have,

$$\frac{d\left(VC_T\underline{U}_{mix}\right)}{dt} = V\sum_{i=1}^{N_c}\left(C_i C_{V,i}(T)\frac{dT}{dt} + \underline{U}_i \nu_i r\right) - V\underline{U}_{mix}\left(\sum_{i=1}^{N_c}\nu_i\right)r + V\underline{U}_{mix}\left(\sum_{i=1}^{N_c}\nu_i\right)r + C_T\underline{U}_{mix}\frac{dV}{dt}$$

The terms that are a function of the change in moles cancel.

$$\frac{d\left(VC_T\underline{U}_{mix}\right)}{dt} = V\sum_{i=1}^{N_c}\left(C_i C_{V,i}(T)\frac{dT}{dt} + \underline{U}_i \nu_i r\right) + C_T\underline{U}_{mix}\frac{dV}{dt}$$

If the reactor volume is constant

$$V\frac{d\left(C_T\underline{U}_{mix}\right)}{dt} = V\sum_{i=1}^{N_c}\left(C_i C_{V,i}(T)\frac{dT}{dt} + \underline{U}_i \nu_i r\right)$$

**Assumption 4: The reactor volume is constant.**

For the batch reactor, our balance is of the form

accumulation = in – out + generation

The in and out terms are zero in the batch reactor. We will consider it to be of fixed volume and well insulated. While it may not be intuitive, there is no generation term in the energy balance. We will see why this is shortly. So our balance is acc = 0,

$$V\frac{d\left(C_T\underline{U}_{mix}\right)}{dt}=0$$

**Assumption 5: The reactor volume is well-insulated and runs adiabatically.**

Then we have

$$V\sum_{i=1}^{N_c}\left(C_iC_{V,i}(T)\frac{dT}{dt}+\underline{U}_i\nu_i r\right)=0$$

$$\sum_{i=1}^{N_c}\left(C_iC_{V,i}(T)\right)\frac{dT}{dt}=-\sum_{i=1}^{N_c}\left(\underline{U}_i\nu_i\right)r$$

We recognize that the internal energy of reaction appears in this equation,

$$\Delta U_R=\sum_{i=1}^{N_c}\left(\nu_i\underline{U}_i\right)$$

so we have

$$\sum_{i=1}^{N_c}\left(C_iC_{V,i}(T)\right)\frac{dT}{dt}=-\Delta U_R r$$

which can be written as

$$C_TC_{V,mix}\frac{dT}{dt}=-\Delta U_R r$$

where

$$C_{V,mix}=\frac{1}{C_T}\sum_{i=1}^{N_c}\left(C_iC_{V,i}(T)\right)=\sum_{i=1}^{N_c}\left(x_iC_{V,i}(T)\right)$$

This is the energy balance for a reaction in a batch reactor having all of the five assumptions made above, namely:

Assumption 1:  the internal energy is not a function of molar volume.
Assumption 2:  The mixture is an ideal mixture.
Assumption 3:  The heat capacity is constant.
Assumption 4:  The reactor volume is constant.
Assumption 5:  The reactor is well-insulated and runs adiabatically.