# A First Course on Kinetics and Reaction Engineering Unit 17. Reactor Models and Reaction Types

# Overview

The focus of Part II of this course was the modeling of reaction rates. This unit is the introduction to Part III where chemical reaction engineering is the focus. It introduces two primary reaction engineering activities: the design of reactors that are yet to be built and the modeling of reactors that already exist. The purposes and goals for these activities differ, but both utilize reaction engineering at their core. The reactors considered in Part III of the course are the same three ideal reactor types as were used in the generation of kinetics data. However, when these reactor types are used in commercial processes, their operation is not constrained as it was during kinetics studies. In other words, commercial process reactors need not operate at steady state, isothermally, without pressure drop, etc. For this reason, more rigorous design equations are needed in order to accurately model commercial process reactors, and these design equations are derived in this unit. In addition, having spent time examining reaction kinetics in Part II of the course, it is useful to identify typical types of chemical reactions, to consider the "typical" kinetic behavior of chemical reactions and to classify certain atypical behaviors here in this introductory unit. This is so because certain classes of reactions are better suited to certain types of reactors. In addition, if one has a general feel for the kinetic behavior of a reaction, then one can qualitatively assess how a given type of reactor will perform when running that reaction. This can be particularly useful to a practicing engineer who is called upon when something unexpected happens during a reaction process. It allows the engineer to identify likely causes for the unexpected behavior and to rule out other causes without having to write out and solve equations.

# **Learning Objectives**

Upon completion of this unit, you should be able to define, in words, the following terms:

- Auto-thermal reactions
- Auto-catalytic reactions
- · Reactant-inhibited reactions
- · Product-inhibited reactions
- Series reaction networks
- · Parallel reaction networks
- · Series-parallel reaction networks

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- · State the two objectives of reaction engineering
- · List examples of engineering tasks that utilize reaction engineering models
- Explain that reactors must be optimized in the context of the overall chemical process in which they appear

- Identify the mole, energy and momentum balances for ideal batch reactors, ideal CSTRs and ideal PFRs
- Simplify the mole, energy and, if appropriate, momentum balances for cases where the flow reactor (CSTR or PFR) operates at steady state
- Identify input, output, accumulation and generation terms in the mole, energy and momentum balances for ideal batch reactors, ideal CSTRs and ideal PFRs, and describe their physical significance
- · Derive and simplify design equations for reactors that are similar to the ideal reactors
- Describe the effects of temperature, reactant concentration and product concentration upon the rate of a typical reaction
- Discuss the thermal effects associated with exothermic and endothermic reactions, both reversible and irreversible

## Information

Reaction engineering entails the formulation and use of accurate mathematical models of chemical reactors. *The objectives of reaction engineering are (i) to construct accurate mathematical models of real world reactors and (ii) to use those models to perform some engineering task.* There are several such tasks in which the reaction engineering model might be employed. One is to simulate the effect of some change in operating procedure in order to determine how it will affect production, energy consumption, etc. Another is in process simulation and optimization where the reactor is one part of a much larger model and that larger model is being used to find the most efficient and profitable way to operate the overall process. Reaction engineering models can also be used to construct computer programs to control a chemical process so that the reactor operates at the conditions for which it was designed. Those tasks involve modeling of an existing reactor system. Reactor design is an engineering task where the purpose is to specify a new reactor and how it should be operated in order to produce some product or products.

The three idealized reactor models, perfectly mixed batch, CSTR and PFR, can be used to model a surprisingly large number of commercial reactors as long as we remove the restrictions we used when studying kinetics in Part II of this course. Here, in Part III, we will consider reaction engineering using these three idealized model types. Then, in Part IV, we will examine models for some selected reactors that cannot be accurately represented using the ideal reactor models.

Before beginning our study of reaction engineering it is important to put it in the proper context. In this course, we will concentrate primarily on the first of the two objectives mentioned above: construction of accurate mathematical models of reactors that are used for commercial chemical processing. Doing so can create a false impression for first time students because this approach ignores the fact that in almost all cases a commercial chemical reactor is one part of a larger overall process. In a course like this one, our narrow focus can leave the impression that the second objective mentioned above, using the model to perform some engineering task, involves only the reactor model, and that perspective is incorrect. *Chemical processes are operated for the purpose of making a financial profit, and therefore the goal of* 

most of the engineering tasks that use the reaction engineering models is to maximize the rate of profit of the process, not of the reactor. The key point to recognize is that the reactor must efficiently integrate into the overall process; it is not a stand-alone item. For example, it might not be possible to have an absolutely pure feed to the reactor because that would make the cost of reactant purification prohibitive. It might be necessary to limit the temperature of the products so that downstream separation processes can accommodate them. The amount of material to be processed in the reactor may be limited by the capacity of an upstream or downstream process, and so on.

As such, reaction engineering can be thought of as a form of constrained optimization. The optimization involves creating a process that maximizes the rate of financial profit. The constraints come from a variety of sources including safety, cost, operability, ability to integrate into the overall process and so on. For the reactor portion of the overall process, some of the key factors to be considered when performing reaction engineering include operability and reliability of the reactor, energy usage by the reactor, space time yield (rate of product generation per volume of the reactor) and selectivity. Even within this reactor-focused group of factors there are tradeoffs, e. g. getting acceptable selectivity may require lower space time yield. For a general rule of thumb, in reaction engineering *the objective is often to generate the desired product as fast as possible, with the highest selectivity possible, using as little energy as possible and in as small a reactor volume as possible while maintaining reliability, operability, environmental compatibility and safety.* 

Industrial chemical reactors can be large, complex pieces of equipment. Nonetheless, a great many industrial reactors can be modeled with reasonable accuracy as either a perfectly mixed batch reactor, a CSTR or a PFR. For the purpose of analyzing kinetic data the reactors were assumed to be isothermal and in the case of the flow reactors to operate at constant pressure and at steady-state. For the most part, it also was assumed that only a single reaction was taking place. In most cases it would require a lot of effort to make an industrial reactor run isothermally, and rarely is there any compelling reason for doing so. Additionally, it is common for more than one chemical reaction to take place in an industrial reactor. As such, it is necessary to derive the design equations for each of the three ideal reactor types without making these assumptions. The starting point, in each case, is a balance equation, either on the moles of one particular species or on energy, which takes the general form of equation (17.1)

*Mole balance (on an arbitrary species i) for a perfectly mixed batch reactor.* We begin with the balance equation.

**INPUT + GENERATION = OUTPUT + ACCUMULATION** 

By definition, no material enters or leaves the system during a batch reaction, so the input and output terms are zero.

We exclude nuclear reactions, so the only way moles of species *i* can be generated is by chemical reaction. In general, there can be any number of reactions, *j*, and species *i* could be a reactant or a product in any of those reactions. Letting  $r_j$  denote the generalized rate of reaction *j* (as defined in Unit 4), the rate of generation of species *i*, per unit fluid volume, is equal to  $v_{i,j}r_j$  where  $v_{i,j}$  is the stoichiometric coefficient of species *i* in reaction *j*. If we assume that there is a single fluid in which all reactions take place, then the total rate of generation of species per unit fluid volume is equal to  $\sum_{\text{all } j} v_{i,j}r_j$ . The reactor is perfectly mixed, and therefore the rate is the same anywhere within the reaction volume. Therefore, the total generation of moles of species *i* is equal to  $V \sum_{\text{all } j} v_{i,j}r_j$  where we have further assumed that every reaction rate has been normalized per unit fluid volume.

$$V \sum_{j=all \ reactions} v_{i,j} r_j$$
 = ACCUMULATION

Finally, we simply note that the instantaneous accumulation of moles of species *i* is just  $\frac{dn_i}{dt}$ . This leads to the complete mole balance on species *i* in a perfectly mixed batch reactor, equation (17.2), where the equation has been rearranged so that the derivative is on the left hand side. A mole balance of this type can be written for each species present in the system.

$$\frac{dn_i}{dt} = V \sum_{\substack{j=all\\reactions}} v_{i,j} r_j$$
(17.2)

*Energy balance for a perfectly mixed batch reactor.* Once again, we begin with the general balance equation.

INPUT + GENERATION = OUTPUT + ACCUMULATION

While no *mass* enters or leaves the batch reactor during the reaction, it is possible for energy to enter or leave the reactor. Recall that a batch reactor can have a jacket surrounding the reaction volume or it can have a coiled tube submerged within the fluid in the reactor. If a heating medium (for example steam) or a cooling medium (e. g. chilled water) flows within the jacket or coil, heat will move to or from the reactor. Even if neither a jacket nor a coil is used, there can still be heat losses to the surroundings, unless the reactor is perfectly insulated. We define  $\dot{Q}$  to be the net heat input to the reactor, including both deliberate heat exchange and heat losses. This term would also include energy input from electrical heating elements, by radiation, etc.

 $\dot{Q}$  + GENERATION = OUTPUT + ACCUMULATION

Energy can also enter or leave the system in the form of mechanical work that is done on or by any shafts, moving boundaries, etc. We define  $\dot{W}$  to be the net rate at which mechanical work is done by the reactor system on its surroundings through shafts, moving boundaries (including pistons), etc. This means that for the very common case of a closed, constant volume tank with an agitator to mix the contents, the work term will be negative and equal in magnitude to the rate of energy input by the agitator.

$$\dot{Q}$$
 + GENERATION =  $\dot{W}$  + ACCUMULATION

Since we exclude nuclear reactions, there is no way for energy to be generated in the reactor, and so the generation term equals zero. You may be thinking that the heat of reaction generates energy, but actually it only transforms it from chemical potential energy to heat. As such, the heat of reaction will appear momentarily when we consider the accumulation term.

$$\dot{Q} = \dot{W} + \text{ACCUMULATION}$$

Each species within the reactor possesses energy in various forms (kinetic, potential, internal, etc.). If we assume that the reactor is stationary, then overall there is no change in the total kinetic or potential energy of the system. There can be accumulation (or depletion) of internal (chemical) energy within the system, however. If  $\hat{u}_i$  represents the specific molar internal energy of species *i* and  $\Delta \tilde{u}_{mix}$  represents the mass-specific energy of mixing of the entire solution, then the total internal energy of the system is equal to  $m_{tot}\Delta \tilde{u}_{mix} + \sum_{\text{all } i} n_i \hat{u}_i$ , where  $m_{tot}$  represents the total mass of the solution in the reaction volume. Here we will assume that the reacting solution is an ideal solution (gas phase or liquid phase), in which case the first term is equal to zero. The instantaneous accumulation of internal energy is then equal to the

derivative of the internal energy with respect to time,  $\frac{d}{dt}\left(\sum_{\text{all }i} n_i \hat{u}_i\right)$ , which can then be substituted into the energy balance.

$$\dot{Q} = \dot{W} + \frac{d}{dt} \left( \sum_{\substack{i=all\\species}} n_i \hat{u}_i \right)$$

This can be rearranged while also noting that  $\frac{d}{dt}\left(\sum_{\text{all }i}n_{i}\hat{u}_{i}\right) = \sum_{\text{all }i}\frac{d}{dt}\left(n_{i}\hat{u}_{i}\right)$ .

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \frac{d}{dt} (n_i \hat{u}_i)$$

Recall from thermodynamics that  $\hat{u}_i = \hat{h}_i - P\hat{V}_i$ , where  $\hat{h}_i$  is the specific molar enthalpy of species *i*, *P* is the pressure and  $\hat{V}_i$  is the specific molar volume of species *i*.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \frac{d}{dt} \left( n_i \left( \hat{h}_i - P \hat{V}_i \right) \right)$$

The distributive property of multiplication can be applied to the terms within the outer parentheses

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \frac{d}{dt} \left( n_i \hat{h}_i - n_i P \hat{V}_i \right)$$

After taking the derivative of the term in parentheses, the resulting summation over two terms can be split into two summations, one over each of the terms.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left\{ \frac{d}{dt} (n_i \hat{h}_i) - \frac{d}{dt} (n_i P \hat{V}_i) \right\}.$$
$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \frac{d}{dt} (n_i \hat{h}_i) - \sum_{\substack{i=all\\species}} \frac{d}{dt} (n_i P \hat{V}_i)$$

According to the chain rule for differentiation,  $\frac{d}{dt}\left(n_{i}\hat{h}_{i}\right) = n_{i}\frac{d\hat{h}_{i}}{dt} + \hat{h}_{i}\frac{dn_{i}}{dt}$  and

 $\frac{d}{dt}\left(n_{i}P\hat{V}_{i}\right) = \left(n_{i}\hat{V}_{i}\right)\frac{dP}{dt} + P\frac{d}{dt}\left(n_{i}\hat{V}_{i}\right).$  Then, because the total pressure and its derivative with respect to time are each the same in every term in the summations, they can be factored out.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} n_i \frac{d\hat{h}_i}{dt} + \sum_{\substack{i=all\\species}} \hat{h}_i \frac{dn_i}{dt} - \frac{dP}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{V}_i \right) - P \sum_{\substack{i=all\\species}} \frac{d}{dt} \left( n_i \hat{V}_i \right)$$
Next note that 
$$\sum_{\substack{i=all\\species}} \frac{d}{dt} \left( n_i \hat{V}_i \right) = \frac{d}{dt} \left( \sum_{\substack{i=all\\species}} \left( n_i \hat{V}_i \right) \right).$$
 In addition, 
$$\sum_{\substack{i=all\\species}} \left( n_i \hat{V}_i \right) = V$$
 since the solution

has been assumed to be ideal.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} n_i \frac{d\hat{h}_i}{dt} + \sum_{\substack{i=all\\species}} \hat{h}_i \frac{dn_i}{dt} - \frac{dP}{dt}V - P\frac{dV}{dt}$$

Assuming that no phase changes take place during the reaction,  $\frac{d\hat{h}_i}{dt} = \hat{C}_{pi} \frac{dT}{dt}$ , where  $\hat{C}_{pi}$  is the specific molar heat capacity of species *i*.

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$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} n_i \hat{C}_{pi} \frac{dT}{dt} + \sum_{\substack{i=all\\species}} \hat{h}_i \frac{dn_i}{dt} - V \frac{dP}{dt} - P \frac{dV}{dt}$$

Since  $\frac{dT}{dt}$  does has the same value in every term in the summation, it can be factored out.

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{C}_{pi} \right) + \sum_{\substack{i=all\\species}} \hat{h}_i \frac{dn_i}{dt} - V \frac{dP}{dt} - P \frac{dV}{dt}$$

The mole balance design equation, equation (17.2) can then be substituted for  $\frac{dn_i}{dt}$ .

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{C}_{pi} \right) + \sum_{\substack{i=all\\species}} \hat{h}_i \left( V \sum_{\substack{j=all\\rections}} v_{ij} r_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt}$$

Again the volume can be factored out of the summation. At the same time, the distributive property

of multiplication can be applied:  $\hat{h}_i \sum_{\substack{j=all \\ reactions}} v_{i,j}r = \sum_{\substack{j=all \\ reactions}} v_{i,j}\hat{h}_ir$ .

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{C}_{pi} \right) + V \sum_{\substack{i=all\\species}} \sum_{\substack{j=all\\reactions}} \left( v_{i,j} \hat{h}_i r_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt}$$

The summations can be performed in either order.

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{C}_{pi} \right) + V \sum_{\substack{j=all\\reactions}} \sum_{\substack{i=all\\species}} \left( v_{i,j} \hat{h}_i r_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt}$$

Since the generalized rate,  $r_j$ , has the same value in every term in the inner sum, it can be factored out.

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{C}_{pi} \right) + V \sum_{\substack{j=all\\reactions}} r_j \sum_{\substack{i=all\\species}} \left( v_{i,j} \hat{h}_i \right) - V \frac{dP}{dt} - P \frac{dV}{dt}$$

Finally it can be noted that  $\sum_{i=all species} (v_{i,j}\hat{h}_i) = \Delta H_j$ . The result is the energy balance for a perfectly

mixed batch reactor, equation (17.3).

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{C}_{pi} \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt}$$
(17.3)

*Mole balance (on an arbitrary species i) for an ideal CSTR*. An ideal CSTR is quite similar to a perfectly mixed batch reactor. The most significant difference is that mass flows into and out of a CSTR, and consequently additional terms are present in the mole and energy balances. We begin the derivation with the general balance equation.

If the same assumptions are made, the generation term and accumulation terms are the same as they were for the perfectly mixed batch reactor.

INPUT + 
$$V\left(\sum_{\substack{j=all\\reactions}} v_{i,j}r_j\right)$$
 = OUTPUT +  $\frac{dn_i}{dt}$ 

As already noted, mass does flow into and out of a CSTR. If  $\dot{n}_i^0$  and  $\dot{n}_i$  are respectively defined as the inlet and outlet molar flow rates of species *i*, they become the input and output terms.

$$\dot{n}_i^0 + V\left(\sum_{\substack{j=all\\reactions}} \mathbf{v}_{i,j} \mathbf{r}_j\right) = \dot{n}_i + \frac{dn_i}{dt}$$

This equation is not very useful because it mixes moles,  $n_i$ , and molar flow rates, e. g.  $\dot{n}_i$ . First, by definition  $n_i = VC_i$ , where  $C_i$ , is the concentration of *i* in the reaction volume.

$$\dot{n}_i^0 + V\left(\sum_{\substack{j=all\\reactions}} v_{i,j} r_j\right) = \dot{n}_i + \frac{d}{dt} (VC_i)$$

The reactor is perfectly mixed, so the concentration of *i* is the same everywhere within the fluid. Since this same fluid is what leaves the reactor, it, too, must have the same concentration. If we assume that there is a single fluid stream leaving the reactor, then by definition,  $C_i = \frac{\dot{n}_i}{\dot{V}}$  where  $\dot{V}$  is the total volumetric flow rate of the stream leaving the reactor.

$$\frac{d}{dt}\left(\frac{\dot{n}_{i}V}{\dot{V}}\right) = \dot{n}_{i}^{0} - \dot{n}_{i} + V \sum_{\substack{j=all\\reactions}} V_{i,j}r_{j}$$

(Note: the equation above will be used below in deriving the energy balance design equation for an ideal CSTR). For present purposes, the chain rule for differentiation can be applied to the derivative:

$$\frac{d}{dt}\left(\frac{\dot{n}_{i}V}{\dot{V}}\right) = \frac{\dot{n}_{i}}{\dot{V}}\frac{dV}{dt} + \frac{V}{\dot{V}}\frac{d\dot{n}_{i}}{dt} - \frac{\dot{n}_{i}V}{\dot{V}^{2}}\frac{d\dot{V}}{dt}.$$
 Upon substitution, this leads to the final form for the mole

balance design equation on species *i* for a CSTR, equation (17.4), which has been rearranged to put the derivatives on the left hand side of the equation. One must be careful when using this equation not to confuse the reaction volume, *V*, with the total outlet volumetric flow rate of the fluid,  $\dot{V}$ .

$$\frac{\dot{n}_i}{\dot{V}}\frac{dV}{dt} + \frac{V}{\dot{V}}\frac{d\dot{n}_i}{dt} - \frac{\dot{n}_iV}{\dot{V}^2}\frac{dV}{dt} = \dot{n}_i^0 - \dot{n}_i + V\sum_{\substack{j=all\\reactions}} v_{i,j}r_j$$
(17.4)

Energy balance for a CSTR. Once again, we begin with the general balance equation.

#### **INPUT + GENERATION = OUTPUT + ACCUMULATION**

As with the batch reactor, there is no energy generated within the reactor since we exclude nuclear reactions. The accumulation term is also the same as it was for the batch reactor. This implies the same assumption that the reactor is stationary so that its kinetic and potential energies do not change.

INPUT = OUTPUT + 
$$\frac{d}{dt} \left( \sum_{\substack{i=all \\ species}} n_i \hat{u}_i \right)$$

Making the same assumption of a single fluid stream leaving the reactor, the moles of *i* can be replaced:  $n_i = C_i V = \frac{\dot{n}_i V}{\dot{V}}$ .

INPUT = OUTPUT + 
$$\frac{d}{dt} \left( \sum_{\substack{i=all \\ species}} \frac{\dot{n}_i \hat{u}_i V}{\dot{V}} \right)$$

As with the batch reactor, one source of heat flow into the system is by heat transfer, and  $\hat{Q}$  can be used to represent this heat flow with the exact same meaning as for the batch reactor. Similarly,  $\hat{W}$  can be used to represent the rate of any mechanical work done by the system via moving shafts, etc. Again this term is exactly the same as it was for the batch reactor. With a CSTR, there are two additional input and two additional output terms. First, every species flowing into the system has an associated internal energy, and every species flowing from the system carries an associated internal energy with it. *Assuming ideal solutions*, these terms are simply equal to  $\dot{n}_i^0 \hat{u}_i^0$  and  $\dot{n}_i \hat{u}_i$ , and when they are summed for all species, they give the total internal energy entering and leaving the reactor. (We assume that the kinetic and potential energy terms associated with the inlet and outlet streams are nearly equal to each other and consequently cancel each other out. If a stream entered or left the reactor in the form of a high speed jet, one would need to include corresponding difference between the inlet and outlet kinetic energy terms.)

Finally, in order for the fluid to flow into and out of the reactor, it must do flow work (think of it as pushing its way in and out of the reactor) at rates of  $P\dot{V}^0$  and  $P\dot{V}$ , respectively.

$$\dot{Q} + \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \hat{u}_i^0 \right) + P \dot{V}^0 = \dot{W} + \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{u}_i \right) + P \dot{V} + \frac{d}{dt} \left( \sum_{\substack{i=all\\species}} \left( \frac{\dot{n}_i \hat{u}_i V}{\dot{V}} \right) \right)$$

This can be rearranged taking note that the derivative of a sum is the sum of the derivatives.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{u}_i \right) + P\dot{V} - \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \hat{u}_i^0 \right) - P\dot{V}^0 + \sum_{\substack{i=all\\species}} \frac{d}{dt} \left( \frac{\dot{n}_i \hat{u}_i V}{\dot{V}} \right)$$

The substitutions that  $P\dot{V}^0 = \sum_{\text{all }i} \dot{n}_i^0 P \hat{V}_i^0$  and  $P\dot{V} = \sum_{\text{all }i} \dot{n}_i P \hat{V}_i$  can be made.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{u}_i\right) + \sum_{\substack{i=all\\species}} \dot{n}_i P \hat{V}_i - \sum_{\substack{i=all\\species}} \left(\dot{n}_i^0 \hat{u}_i^0\right) - \sum_{\substack{i=all\\species}} \dot{n}_i^0 P \hat{V}_i^0 + \sum_{\substack{i=all\\species}} \frac{d}{dt} \left(\frac{\dot{n}_i \hat{u}_i V}{\dot{V}}\right)$$

Next note that  $\sum_{\text{all }i} (\dot{n}_i \hat{u}_i) + \sum_{\text{all }i} \dot{n}_i P \hat{V}_i = \sum_{\text{all }i} \dot{n}_i (\hat{u}_i + P \hat{V}_i)$  and

$$-\sum_{\text{all }i} (\dot{n}_{i}^{0} \hat{u}_{i}^{0}) - \sum_{\text{all }i} \dot{n}_{i}^{0} P \hat{V}_{i}^{0} = -\sum_{\text{all }i} \dot{n}_{i}^{0} (\hat{u}_{i}^{0} + P \hat{V}_{i}^{0}).$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \dot{n}_i \left( \hat{u}_i + P\hat{V}_i \right) - \sum_{\substack{i=all\\species}} \dot{n}_i^0 \left( \hat{u}_i^0 + P\hat{V}_i^0 \right) + \sum_{\substack{i=all\\species}} \frac{d}{dt} \left( \frac{\dot{n}_i \hat{u}_i V}{\dot{V}} \right)$$

Thermodynamic relationships can then be substituted ( $\hat{u}_i + P\hat{V}_i = \hat{h}_i$  and  $\hat{u}_i^0 + P\hat{V}_i^0 = \hat{h}_i^0$ ).

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \dot{n}_i \left( \hat{h}_i \right) - \sum_{\substack{i=all\\species}} \dot{n}_i^0 \left( \hat{h}_i^0 \right) + \sum_{\substack{i=all\\species}} \frac{d}{dt} \left( \left( \hat{h}_i - P\hat{V}_i \right) \frac{\dot{n}_i V}{\dot{V}} \right)$$

The chain rule can be applied:  $\frac{d}{dt} \left( \left( \hat{h}_i - P\hat{V}_i \right) \frac{\dot{h}_i V}{\dot{V}} \right) = \left( \hat{h}_i - P\hat{V}_i \right) \frac{d}{dt} \left( \frac{\dot{h}_i V}{\dot{V}} \right) + \frac{\dot{h}_i V}{\dot{V}} \frac{d}{dt} \left( \hat{h}_i - P\hat{V}_i \right).$ 

$$\begin{split} \dot{Q} - \dot{W} &= \sum_{\substack{i=all\\species}} \dot{n}_i \left( \hat{h}_i \right) - \sum_{\substack{i=all\\species}} \dot{n}_i^0 \left( \hat{h}_i^0 \right) + \sum_{\substack{i=all\\species}} \left( \left( \hat{h}_i - P\hat{V}_i \right) \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) \right) \\ &+ \sum_{\substack{i=all\\species}} \left( \frac{\dot{n}_i V}{\dot{V}} \frac{d}{dt} \left( \hat{h}_i - P\hat{V}_i \right) \right) \end{split}$$

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The derivative of the difference can be replaced as follows:  $\frac{d}{dt} \left( \hat{h}_i - P \hat{V}_i \right) = \frac{d \hat{h}_i}{dt} - \frac{d}{dt} \left( P \hat{V}_i \right).$ 

$$\begin{split} \dot{Q} - \dot{W} &= \sum_{\substack{i=all\\species}} \dot{n}_i \left( \hat{h}_i \right) - \sum_{\substack{i=all\\species}} \dot{n}_i^0 \left( \hat{h}_i^0 \right) + \sum_{\substack{i=all\\species}} \left( \left( \hat{h}_i - P\hat{V}_i \right) \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) \right) \\ &+ \sum_{\substack{i=all\\species}} \left( \frac{\dot{n}_i V}{\dot{V}} \left( \frac{d\hat{h}_i}{dt} - \frac{d}{dt} \left( P\hat{V}_i \right) \right) \right) \end{split}$$

The distributive property can then be applied inside each of the sums.

$$\begin{split} \dot{Q} - \dot{W} &= \sum_{\substack{i=all\\species}} \dot{n}_i \left( \hat{h}_i \right) - \sum_{\substack{i=all\\species}} \dot{n}_i^0 \left( \hat{h}_i^0 \right) + \sum_{\substack{i=all\\species}} \left( \hat{h}_i \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) \right) - \sum_{\substack{i=all\\species}} \left( P \hat{V}_i \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) \right) \\ &+ \sum_{\substack{i=all\\species}} \left( \frac{\dot{n}_i V}{\dot{V}} \frac{d \hat{h}_i}{dt} \right) - \sum_{\substack{i=all\\species}} \left( \frac{\dot{n}_i V}{\dot{V}} \frac{d}{dt} \left( P \hat{V}_i \right) \right) \end{split}$$

The relationship,  $\frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) = \dot{n}_i^0 - \dot{n}_i + V \sum_{\text{all}_j} V_{i,j} r_j$ , from the derivation of the mole balance design

equation can then be substituted into the third term on the right hand side of the equation.

$$\begin{split} \dot{Q} - \dot{W} &= \sum_{\substack{i=all\\species}} \dot{n}_i \left( \hat{h}_i \right) - \sum_{\substack{i=all\\species}} \dot{n}_i^0 \left( \hat{h}_i^0 \right) + \sum_{\substack{i=all\\species}} \left( \hat{h}_i \left( \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all\\reactions}} V_{i,j} r_j \right) \right) \\ &- \sum_{\substack{i=all\\species}} \left( P \hat{V}_i \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) \right) + \sum_{\substack{i=all\\species}} \left( \frac{\dot{n}_i V}{\dot{V}} \frac{d \hat{h}_i}{dt} \right) - \sum_{\substack{i=all\\species}} \left( \frac{\dot{n}_i V}{\dot{V}} \frac{d}{dt} \left( P \hat{V}_i \right) \right) \end{split}$$

The same term can be expanded using the distributive property:

$$\begin{split} \sum_{\text{all } i} \left( \hat{h}_{i} \left( \dot{n}_{i}^{0} - \dot{n}_{i} + Vj \sum_{\text{all } i} \mathbf{v}_{ij} r_{j} \right) \right) &= \sum_{\text{all } i} \left( \hat{h}_{i} \dot{n}_{i}^{0} \right) - \sum_{\text{all } i} \left( \hat{h}_{i} \dot{n}_{i} \right) + \sum_{\text{all } i} \left( \hat{h}_{i} V \sum_{\text{all } j} \left( \mathbf{v}_{i,j} r_{j} \right) \right) \\ \dot{Q} - \dot{W} &= \sum_{\substack{i=all \\ species}} \dot{n}_{i} \left( \hat{h}_{i} \right) - \sum_{\substack{i=all \\ species}} \dot{n}_{i}^{0} \left( \hat{h}_{i}^{0} \right) + \sum_{\substack{i=all \\ species}} \left( \hat{h}_{i} \dot{n}_{i}^{0} \right) - \sum_{\substack{i=all \\ species}} \left( \hat{h}_{i} \dot{N} \sum_{\substack{j=all \\ species}} \left( \mathbf{v}_{i,j} r_{j} \right) \right) \\ &- \sum_{\substack{i=all \\ species}} \left( P \hat{V}_{i} \frac{d}{dt} \left( \frac{\dot{n}_{i} V}{\dot{V}} \right) \right) + \sum_{\substack{i=all \\ species}} \left( \frac{\dot{n}_{i} V}{\dot{V}} \frac{d \hat{h}_{i}}{dt} \right) - \sum_{\substack{i=all \\ species}} \left( \frac{\dot{n}_{i} V}{\dot{V}} \frac{d \hat{h}_{i}}{dt} \right) - \sum_{\substack{i=all \\ species}} \left( \frac{\dot{n}_{i} V}{\dot{V}} \frac{d \hat{h}_{i}}{dt} \right) - \sum_{\substack{i=all \\ species}} \left( \frac{\dot{n}_{i} V}{\dot{V}} \frac{d \hat{h}_{i}}{dt} \left( P \hat{V}_{i} \right) \right) \end{split}$$

The first and fourth sums on the right hand side cancel each other out. The second and third sums on the right hand side can be combined:  $-\sum_{all i} \dot{n}_i^0 (\hat{h}_i^0) + \sum_{all i} (\hat{h}_i \dot{n}_i^0) = \sum_{all i} (\dot{n}_i^0 (\hat{h}_i - \hat{h}_i^0))$ . Since *V* has the same value in every term in the fifth sum, it can be factored out, and  $\hat{h}_i$  can be moved inside the inner sum. If we assume no phase changes take place,  $\frac{d\hat{h}_i}{dt} = \hat{C}_{pi} \frac{dT}{dt}$ . The chain rule can be used in the last term,  $\frac{d}{dt} (P\hat{V}_i) = P \frac{d}{dt} (\hat{V}_i) + \hat{V}_i \frac{d}{dt} (P)$ .  $\dot{Q} - \dot{W} = \sum_{\substack{i=all \\ species}} (\dot{n}_i^0 (\hat{h}_i - \hat{h}_i^0)) + V \sum_{\substack{i=all \\ species}} \left( \sum_{\substack{j=all \\ reactions}} (v_{i,j}\hat{h}_i r_j) \right) - \sum_{\substack{i=all \\ species}} \left( P\hat{V}_i \frac{d}{dt} (\frac{\dot{n}_i V}{\dot{V}}) \right)$   $+ \sum_{\substack{i=all \\ i=all}} \left( \frac{\dot{n}_i V \hat{C}_{pi}}{\dot{V}} \frac{dT}{dt} \right) - \sum_{\substack{i=all \\ i=all}} \left( \frac{\dot{n}_i V \hat{V}_i}{\dot{V}} \frac{dP}{dt} \right)$ 

Many of the sums include quantities that have the same value in every term in the sum; (in one case after changing the order of the sums) these can be factored out, and the terms can be re-ordered.

$$\begin{split} \dot{Q} - \dot{W} &= \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \left( \hat{h}_i - \hat{h}_i^0 \right) \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \sum_{\substack{i=all\\species}} \left( v_{i,j} \hat{h}_i \right) \right) + \frac{V}{\dot{V}} \left( \frac{dT}{dt} \right) \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{C}_{pi} \right) \\ &- \frac{V}{\dot{V}} \left( \frac{dP}{dt} \right) \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{V}_i \right) - \frac{PV}{\dot{V}} \sum_{\substack{i=all\\species}} \left( \dot{n}_i \frac{d\hat{V}_i}{dt} \right) - P \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) \right) \end{split}$$

If we assume there are no phase changes within the reactor, the enthalpy difference in the first term

on the right side of the equation can be written as  $\hat{h}_i - \hat{h}_i^0 = \int_{T^0}^T \hat{C}_{pi} dT$ . The inner sum of the second term

is, by definition,  $\sum_{\text{all }i} \left( v_{i,j} \hat{h}_i \right) = \Delta H_j \Big|_T$ . As before, the sum in the fourth term on the right side is  $\dot{V} = \sum_{\text{all }i} \dot{n}_i \hat{V}_i$ . The chain rule can be used for the derivative in the last term,  $\frac{d}{dt} \left( \frac{\dot{n}_i V}{\dot{V}} \right) = \frac{V}{\dot{V}} \frac{d\dot{n}_i}{dt} + \frac{\dot{n}_i}{\dot{V}} \frac{dV}{dt} - \frac{\dot{n}_i V}{\dot{V}^2} \frac{d\dot{V}}{dt}$ . A First Course on Kinetics and Reaction Engineering

$$\begin{split} \dot{Q} - \dot{W} &= \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \right|_T \right) + \frac{V}{\dot{V}} \left( \frac{dT}{dt} \right) \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{C}_{pi} \right) \\ &- \frac{V}{\dot{V}} \left( \frac{dP}{dt} \right) \dot{V} - \frac{PV}{\dot{V}} \sum_{\substack{i=all\\species}} \left( \dot{n}_i \frac{d\hat{V}_i}{dt} \right) - P \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{\dot{V}}{\dot{V}} \frac{d\dot{n}_i}{dt} \right) \\ &- P \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{\dot{n}_i}{\dot{V}} \frac{dV}{dt} \right) + P \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{\dot{n}_i V}{\dot{V}^2} \frac{d\dot{V}}{dt} \right) \end{split}$$

The volumetric flow rate can be canceled from the term in blue above. Also, it can be factored outside the summation, along with the derivative,  $\frac{dV}{dt}$ , from the term in red. After doing this, the summation that remains is  $\sum_{\text{all } i} \dot{n}_i \hat{V}_i = \dot{V}$ . This will leave a volumetric flow rate in the numerator and in the denominator, which will cancel. These changes can be made and the equation can be rearranged.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \right|_T \right) + \frac{V}{\dot{V}} \left( \frac{dT}{dt} \right) \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{C}_{pi} \right) - V \left( \frac{dP}{dt} \right)$$
$$- \frac{P}{\frac{dV}{dt}} - \frac{PV}{\dot{V}} \sum_{\substack{i=all\\species}} \left( \dot{n}_i \frac{d\hat{V}_i}{dt} \right) - P \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{V}{\dot{V}} \frac{d\dot{n}_i}{dt} \right) + P \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{\dot{n}_i V}{\dot{V}^2} \frac{d\dot{V}}{dt} \right)$$

The terms whose values are the same in every term can be factored out of the final two terms.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \Big|_T \right) + \frac{V}{\dot{V}} \left( \frac{dT}{dt} \right) \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{C}_{pi} \right) - V \left( \frac{dP}{dt} \right) \right)$$
$$-P \frac{dV}{dt} - \frac{PV}{\dot{V}} \left[ \sum_{\substack{i=all\\species}} \left( \dot{n}_i \frac{d\hat{V}_i}{dt} \right) + \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{d\dot{n}_i}{dt} \right) - \frac{1}{\dot{V}} \frac{d\dot{V}}{dt} \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{V}_i \right) \right]$$

The final sum can be replaced,  $\sum_{\text{all }i} \dot{n}_i \hat{V}_i = \dot{V}$ , and this will leave a volumetric flow rate in the numerator and in the denominator that will cancel.

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \right|_T \right) + \frac{V}{\dot{V}} \left( \frac{dT}{dt} \right) \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{C}_{pi} \right) - V \left( \frac{dP}{dt} \right) \right)$$
$$-P \frac{dV}{dt} - \frac{PV}{\dot{V}} \left[ \sum_{\substack{i=all\\species}} \left( \dot{n}_i \frac{d\hat{V}_i}{dt} \right) + \sum_{\substack{i=all\\species}} \left( \hat{V}_i \frac{d\dot{n}_i}{dt} \right) - \frac{d\dot{V}}{dt} \right]$$

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Next the last derivative can be replaced by first noting that since  $\dot{V} = \sum_{\text{all } i} \dot{n}_i \hat{V}_i$ , then by the chain

$$\begin{aligned} \text{rule, } \frac{d\dot{V}}{dt} &= \sum_{\text{all } i} \dot{n}_i \frac{d\hat{V}_i}{dt} + \sum_{\text{all } i} \hat{V}_i \frac{d\dot{n}_i}{dt} \,. \\ \dot{Q} - \dot{W} &= \sum_{\substack{i=all \\ species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all \\ reactions}} \left( r_j \Delta H_j \right|_T \right) + \frac{V}{\dot{V}} \left( \frac{dT}{dt} \right) \sum_{\substack{i=all \\ species}} \left( \dot{n}_i \hat{C}_{pi} \right) \\ &- V \left( \frac{dP}{dt} \right) - P \frac{dV}{dt} \\ &- \frac{PV}{\dot{V}} \left[ \sum_{\substack{i=all \\ species}} \left( \dot{n}_i \frac{d\hat{V}_i}{dt} \right) + \sum_{\substack{i=all \\ species}} \left( \hat{V}_i \frac{d\dot{n}_i}{dt} \right) - \sum_{\substack{i=all \\ species}} \left( \dot{n}_i \frac{d\hat{V}_i}{dt} \right) \right] \end{aligned}$$

Following the substitution, the four terms in the square brackets cancel each other out and the entire term goes to zero. Specifically, adding the two terms in red gives zero as does adding the two terms in blue. This finally gives the energy balance equation for an ideal CSTR, equation (17.5).

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} dT \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \right|_T \right) + \frac{V}{\dot{V}} \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{C}_{pi} \right) \left( \frac{dT}{dt} \right) - V \left( \frac{dP}{dt} \right) - P \left( \frac{dV}{dt} \right)$$
(17.5)

*Mole balance (on an arbitrary species i) for an ideal PFR*. Unlike the perfectly mixed batch reactor and the CSTR, the composition in an ideal PFR is not uniform. As a consequence, it becomes necessary to write the mole and energy balance equations on a differential element of reactor volume and then take the limit as the size of this element goes to zero. Here, we will *assume that the reactor is cylindrical with a constant diameter, D, and a length, L.* Figure 1 shows such a reactor, highlighting a differentially thick cross section that will be used in formulating the mass and energy balances for the ideal PFR.



### Figure 1 Volume element used in deriving the ideal PFR design equations.

Recall that in a PFR, it is assumed that there is perfect mixing in the radial direction and no mixing in the axial direction. With these assumptions, the environmental variables will be uniform throughout the entire differential element shown in Figure 1 (or, put differently, the differential element shown in Figure 1 is perfectly mixed). The derivation of the mole balance on an arbitrary species *i* begins with the balance equation, applied to the differential element.

**INPUT + GENERATION = OUTPUT + ACCUMULATION** 

The input and output terms are simply the molar flow rate, evaluated at the "front" and "back" of the differential element.

$$\dot{n}_i|_z$$
 + GENERATION =  $\dot{n}_i|_{z+dz}$  + ACCUMULATION

If we assume that there is a single fluid within the reactor in which all reactions take place, then the total rate of generation of species per unit fluid volume is equal to  $\sum_{\text{all } j} v_{i,j} r_j$ . The differential element is perfectly mixed, and therefore the rate is the same anywhere within its volume. Therefore, the total generation of moles of species *i* within the element is equal to the volume of the differential element

times the total rate per volume,  $\frac{\pi D^2(dz)}{4} \sum_{\text{all}_j} v_{i,j} r_j$ , where we have further assumed that every reaction rate has been normalized per unit fluid volume.

$$\dot{n}_i|_z + \frac{\pi D^2(dz)}{4} \sum_{\substack{j=all\\reactions}} v_{i,j}r_j = \dot{n}_i|_{z+dz} + \text{ACCUMULATION}$$

The instantaneous accumulation of moles of *i* is equal to  $\frac{dn_i}{dt}$ , where  $n_i$  represents the number of moles in the differential element. Since the differential element is perfectly mixed, the total moles of *i* in the differential element is equal to the concentration of *i* in the differential element times the volume of the differential element. In a flowing system, the concentration of *i* is equal to the molar flow rate of *i* divided by the volumetric flow rate, just as it was for the CSTR.

$$\dot{n}_{i}\big|_{z} + \frac{\pi D^{2}(dz)}{4} \sum_{\substack{j=all\\reactions}} v_{i,j}r_{j} = \dot{n}_{i}\big|_{z+dz} + \frac{\partial}{\partial t} \left(\frac{\pi D^{2}(dz)}{4} \left[\frac{\dot{n}_{i}\big|_{z}}{\dot{V}}\right]\right)$$

This equation can be rearranged and the constant terms can be factored from the partial derivative.

$$\frac{\dot{n}_i \Big|_{z+dz} - \dot{n}_i \Big|_z}{dz} = \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} v_{i,j} r_j - \frac{\pi D^2}{4} \frac{\partial}{\partial t} \left( \frac{\dot{n}_i \Big|_z}{\dot{V}} \right)$$

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In the limit of an infinitesimally thin volume element,  $\lim_{dz\to 0} \left( \frac{\dot{n}_i \Big|_{z+dz} - \dot{n}_i \Big|_z}{dz} \right) = \frac{\partial \dot{n}_i}{\partial z}.$ 

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} v_{i,j} r_j - \frac{\pi D^2}{4} \frac{\partial}{\partial t} \left(\frac{\dot{n}_i}{\dot{V}}\right)$$

Finally, using the chain rule to differentiate the partial derivative on the right leads to the mole balance design equation for an ideal PFR, equation (17.6).

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} v_{i,j} r_j - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t}$$
(17.6)

Energy balance for a PFR. Once again, we begin with the general balance equation.

## **INPUT + GENERATION = OUTPUT + ACCUMULATION**

As with the batch reactor and the CSTR, energy is not generated in the PFR since we exclude nuclear reactions. Since we have assumed a tubular reactor of fixed diameter, there are no shafts or moving boundaries, and consequently the PFR does not do any work on the surroundings (there is no  $\dot{W}$  term). Heat can flow into the reactor through the reactor wall. We assume that this heat transfer can be described using an overall heat transfer coefficient, U. If we let  $T_e$  denote the temperature exterior to the reactor and let T denote the temperature within the reactor, then the heat input through the wall is equal to the wall area times the heat transfer coefficient times the temperature difference. Applying this to the differential volume element gives  $\dot{Q} = \pi D(dz)U(T_e - T)$ . As with the CSTR, the fluid flowing into and out of the volume element carries internal energy with it and it must do flow work as it enters and leaves. These substitutions can be made for the input, output and generation terms.

$$\sum_{\substack{i=all\\species}} \left(\dot{n}_{i}\hat{u}_{i}\right)\Big|_{z} + P\dot{V}\Big|_{z} + \pi D(dz)U(T_{e} - T) = \sum_{\substack{i=all\\species}} \left(\dot{n}_{i}\hat{u}_{i}\right)\Big|_{z+dz} + P\dot{V}\Big|_{z+dz} + ACCUMULATION$$

The instantaneous accumulation of energy equals the instantaneous accumulation of moles of each species (see the mole balance above) times its specific internal energy. Once again, we assume the reactor is stationary and that the total kinetic energy and potential energy of the flowing fluid remains constant.

$$\sum_{\substack{i=all\\species}} (\dot{n}_i \hat{u}_i) \Big|_z + P\dot{V} \Big|_z + \pi D(dz) U(T_e - T) = \sum_{\substack{i=all\\species}} (\dot{n}_i \hat{u}_i) \Big|_{z+dz} + P\dot{V} \Big|_{z+dz}$$
$$+ \sum_{\substack{i=all\\species}} \frac{\partial}{\partial t} \left( \frac{\pi D^2(dz)}{4} \left( \frac{\dot{n}_i \hat{u}_i}{\dot{V}} \right) \right)$$

Assuming an ideal solution, the volumetric flow rate can be related to the molar specific volumes,

 $\dot{V} = \sum_{i=1}^{n} \dot{n}_i \hat{V}_i$ , and the internal energy can be related to the specific enthalpy ( $\hat{u}_i + P\hat{V}_i = \hat{h}_i$ ) in a manner exactly analogous to the CSTR.

$$\sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{h}_i \right) \Big|_z + \pi D(dz) U(T_e - T) = \sum_{\substack{i=all\\species}} \left( \dot{n}_i \hat{h}_i \right) \Big|_{z+dz} + \frac{\pi D^2(dz)}{4} \sum_{\substack{i=all\\species}} \frac{\partial}{\partial t} \left( \frac{\dot{n}_i}{\dot{V}} (\hat{h}_i - P\hat{V}_i) \right)$$

The equation can then be rearranged.

$$\sum_{\substack{i=all\\species}} \frac{\left(\dot{n}_{i}\hat{h}_{i}\right)\Big|_{z+dz} - \left(\dot{n}_{i}\hat{h}_{i}\right)\Big|_{z}}{dz} = \pi DU(T_{e}-T) - \frac{\pi D^{2}}{4} \sum_{\substack{i=all\\species}} \frac{\partial}{\partial t} \left(\frac{\dot{n}_{i}}{\dot{V}}\left(\hat{h}_{i}-P\hat{V}_{i}\right)\right)$$

For a differentially thin volume element, 
$$\lim_{dz\to 0} \left( \sum_{\text{all } i} \frac{\left( \dot{n}_i \hat{h}_i \right) \Big|_{z+dz} - \left( \dot{n}_i \hat{h}_i \right) \Big|_{z}}{dz} \right) = \sum_{\text{all } i} \left( \frac{\partial}{\partial z} \left( \dot{n}_i \hat{h}_i \right) \right).$$

$$\sum_{\substack{i=all\\species}} \left( \frac{\partial}{\partial z} (\dot{n}_i \hat{h}_i) \right) = \pi DU (T_e - T) - \frac{\pi D^2}{4} \sum_{\substack{i=all\\species}} \frac{\partial}{\partial t} \left( \frac{\dot{n}_i}{\dot{V}} (\hat{h}_i - P\hat{V}_i) \right)$$

This equation can be rearranged, combining all the sums.

$$\pi DU(T_e - T) = \sum_{\substack{i=all\\species}} \left( \frac{\partial}{\partial z} (\dot{n}_i \hat{h}_i) + \frac{\pi D^2}{4} \sum_{\substack{i=all\\species}} \frac{\partial}{\partial t} \left( \frac{\dot{n}_i}{\dot{V}} (\hat{h}_i - P\hat{V}_i) \right) \right)$$

The derivatives inside the sum can be expanded.

$$\pi DU(T_e - T) = \sum_{\substack{i=all\\species}} \left( \hat{h}_i \frac{\partial \dot{h}_i}{\partial z} + \dot{n}_i \frac{\partial \hat{h}_i}{\partial z} + \frac{\pi D^2}{4} \frac{\partial}{\partial t} \left( \frac{\dot{n}_i \hat{h}_i}{\dot{V}} \right) - \frac{\pi D^2}{4} \frac{\partial}{\partial t} \left( \frac{\dot{n}_i P \hat{V}_i}{\dot{V}} \right) \right)$$

If we assume no phase changes take place, then the term in blue is equal to  $\dot{n}_i \hat{C}_{pi} \frac{\partial T}{\partial z}$ .

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \sum_{\substack{i=all\\species}} \left(\hat{h}_i \frac{\partial \dot{n}_i}{\partial z} + \frac{\pi D^2}{4} \frac{\partial}{\partial t} \left(\frac{\dot{n}_i \hat{h}_i}{\dot{V}}\right) - \frac{\pi D^2}{4} \frac{\partial}{\partial t} \left(\frac{\dot{n}_i P \hat{V}_i}{\dot{V}}\right)\right)$$

The chain rule can next be applied to the term in red.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \sum_{\substack{i=all\\species}} \left( \hat{h}_i \left( \frac{\partial \dot{n}_i}{\partial z} + \frac{\pi D^2}{4} \frac{\partial}{\partial t} \frac{\dot{n}_i}{\dot{V}} \right) + \frac{\pi D^2}{4} \left( \frac{\dot{n}_i}{\dot{V}} \frac{\partial \hat{h}_i}{\partial t} - \frac{\partial}{\partial t} \left( \frac{\dot{n}_i P \hat{V}_i}{\dot{V}} \right) \right) \right)$$

The mole balance, equation (17.6), can be rearranged as follows:

$$\frac{\partial \dot{n}_i}{\partial z} + \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} - \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t} = \frac{\partial \dot{n}_i}{\partial z} + \frac{\pi D^2}{4} \frac{\partial}{\partial t} \frac{\dot{n}_i}{\dot{V}} = \frac{\pi D^2}{4} \sum_{\text{all}\,j} V_{i,j} r_j \text{, and substituted for the term in blue.}$$

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \sum_{\substack{i=all\\species}} \left( \hat{h}_i \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} v_{i,j} r_j + \frac{\pi D^2}{4} \left( \frac{\dot{n}_i}{\dot{V}} \frac{\partial \hat{h}_i}{\partial t} - \frac{\partial}{\partial t} \left( \frac{\dot{n}_i P \hat{V}_i}{\dot{V}} \right) \right) \right)$$

This equation can be rearranged, separating the terms of the sum, changing the order of the nested sums, and factoring constants outside the summations.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} \mathbf{v}_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \frac{\partial \hat{h}_i}{\partial t}\right) - \frac{\pi D^2}{4} \sum_{\substack{i=all\\species}} \left(\frac{\partial}{\partial t} \left(\frac{\dot{n}_i P \hat{V}_i}{\dot{V}}\right)\right)$$

As above, 
$$\frac{\partial \hat{h}_i}{\partial z} = \hat{C}_{pi} \frac{\partial T}{\partial z}$$
.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} \mathbf{v}_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^2}{4} \sum_{\substack{i=all\\species}} \left(\frac{\partial}{\partial t} \left(\frac{\dot{n}_i P \hat{V}_i}{\dot{V}}\right)\right)$$

The chain rule can be applied to the final term.

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$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} v_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^2 P}{4} \sum_{\substack{i=all\\species}} \left(\frac{\partial}{\partial t} \left(\frac{\dot{n}_i \hat{V}_i}{\dot{V}}\right)\right) - \frac{\pi D^2}{4} \sum_{\substack{i=all\\species}} \left(\frac{\dot{n}_i \hat{V}_i}{\dot{V}} \frac{\partial P}{\partial t}\right)$$

The terms that do not depend upon the index *i* can be factored outside the final sum, which leaves  $\sum_{\text{all }i} \dot{n}_i \hat{V}_i = \dot{V}$ . The resultant volumetric flow rate appears in the numerator and denominator, and so it can

be canceled.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} v_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t}$$
$$- \frac{\pi D^2 P}{4} \sum_{\substack{i=all\\species}} \left(\frac{\partial}{\partial t} \left(\frac{\dot{n}_i \hat{V}_i}{\dot{V}}\right)\right) - \frac{\pi D^2}{4} \frac{\partial P}{\partial t}$$

Next the chain rule is applied to the term in blue.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} v_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^2 P}{4} \left(\sum_{\substack{i=all\\species}} \left(\frac{1}{\dot{V}} \frac{\partial}{\partial t} (\dot{n}_i \hat{V}_i)\right) - \sum_{\substack{i=all\\species}} \left(\frac{\dot{n}_i \hat{V}_i}{\dot{V}^2} \frac{\partial \dot{V}}{\partial t}\right) - \frac{\pi D^2}{4} \frac{\partial P}{\partial t}$$

The terms that do not depend upon the index *i* can be factored outside the second blue sum.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} v_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^2 P}{4} \left(\sum_{\substack{i=all\\species}} \left(\frac{1}{\dot{V}} \frac{\partial}{\partial t} (\dot{n}_i \hat{V}_i)\right) - \frac{1}{\dot{V}^2} \frac{\partial \dot{V}}{\partial t} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{V}_i\right) - \frac{\pi D^2}{4} \frac{\partial P}{\partial t}$$

The resulting sum in red is just equal to the volumetric flow rate,  $\sum_{\text{all }i} \dot{n}_i \hat{V}_i = \dot{V}$ , which allows additional simplification.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} v_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t}$$
$$- \frac{\pi D^2 P}{4} \left(\sum_{\substack{i=all\\species}} \left(\frac{1}{\dot{V}} \frac{\partial}{\partial t} (\dot{n}_i \hat{V}_i)\right) - \frac{1}{\dot{V}} \frac{\partial \dot{V}}{\partial t}\right) - \frac{\pi D^2}{4} \frac{\partial P}{\partial t}$$

Noting that since  $\dot{V} = \sum_{\text{all }i} \dot{n}_i \hat{V}_i$ , then  $\frac{\partial \dot{V}}{\partial t} = \sum_{\text{all }i} \frac{\partial}{\partial t} (\dot{n}_i \hat{V}_i)$ , and substitution in the term in blue shows

that it cancels the one preceding it.

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \sum_{\substack{i=all\\species}} \mathbf{v}_{i,j} \hat{h}_i\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^2 P}{4} \left(\sum_{\substack{i=all\\species}} \left(\frac{1}{\dot{V}} \frac{\partial}{\partial t} (\dot{n}_i \hat{V}_i)\right) - \sum_{\substack{i=all\\species}} \left(\frac{1}{\dot{V}} \frac{\partial}{\partial t} (\dot{n}_i \hat{V}_i)\right) - \frac{\pi D^2}{4} \frac{\partial P}{\partial t}\right)$$

Noting that the summation in blue above is just the heat of reaction, this, finally, gives the energy balance equation for an ideal PFR, equation (17.7).

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \Delta H_j\right) + \frac{\pi D^2}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^2}{4} \frac{\partial P}{\partial t}$$
(17.7)

*Mechanical energy balance for an ideal PFR*. A third type of balance equation is often needed when modeling plug flow reactors, particularly packed bed catalytic reactors. The flow of a fluid through a tube, particularly one packed with solid particles, requires that some of the flow energy must be expended to overcome friction between the flowing fluid and the stationary solid (reactor walls and packing, if present). The net result is a drop in pressure along the length of the tube. Chemical engineers typically use a mechanical energy balance to model this pressure drop. The complexity of the processes involved is such that these models are usually empirical in nature and include parameters such as the friction factor. This topic is normally covered in chemical energy balance equations. No attempt will be made here to derive the mechanical energy balance equations. However, in the next section two common *steady-state* forms of the mechanical energy balance will be presented without derivation.

Summary and steady-state forms of the balance equations. In deriving the design equations for

a perfectly mixed batch reactor, the following assumptions were made:

- · the reactor is perfectly mixed
- · no mass enters or leaves the reactor during the reaction
- · there is a single fluid volume in which all reactions take place
- the reacting fluid is an ideal solution (gas or liquid)
- · every reaction rate has been normalized per unit fluid volume
- the reactor is stationary
- · no phase changes occur during the reaction

With these assumptions for a perfectly mixed batch reactor, the resulting mole balance is equation (17.2) and the energy balance is equation (17.3).

$$\frac{dn_i}{dt} = V \sum_{\substack{j=all\\reactions}} V_{i,j} r_j$$
(17.2)

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left( n_i \hat{C}_{pi} \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \right) - \frac{dP}{dt} V - P \frac{dV}{dt}$$
(17.3)

It is sometimes helpful to assign physical significance to the terms appearing in these equations. The mole balance is trivial in this regard, the left side of the equation is the accumulation of species *i* in the reactor and the right side is the net generation of species *i* by chemical reaction. In the energy balance, the two terms on the left side are the exchange of energy with the surroundings, either as heat or as work. The first term on the right is the change in sensible heat within the reactor, the second term is the heat absorbed by chemical reaction, and the last two terms are work the fluid must do in expanding or contracting.

The assumptions used in deriving the design equations for a CSTR were as follows:

- perfect mixing
- · every reaction rate has been normalized per unit fluid volume
- the reacting fluid is an ideal solution (gas or liquid)
- · there is a single fluid stream leaving the reactor
- · the reactor is stationary
- no phase changes occur during the reaction
- the kinetic and potential energy of the entering and exiting fluid streams are effectively equal to each other

With these assumptions for an ideal CSTR, the resulting mole balance is equation (17.4) and the energy balance is equation (17.5).

$$0 = \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all\\reactions}} v_{i,j} r_j$$
(17.4)

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \Big|_T \right)$$
(17.5)

If an ideal CSTR operates at steady state, these equations simplify considerably. Specifically, at steady state all the derivatives with respect to time vanish. Thus, equations (17.8) and (19.9) represent the ideal, *steady-state CSTR mole and energy balances*, respectively.

$$0 = \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all\\reactions}} v_{i,j} r_j$$
(17.8)

$$\dot{Q} - \dot{W} = \sum_{\substack{i=all\\species}} \left( \dot{n}_i^0 \int_{T^0}^T \hat{C}_{pi} \, dT \right) + V \sum_{\substack{j=all\\reactions}} \left( r_j \Delta H_j \Big|_T \right)$$
(17.9)

As with the batch reactor, the two terms on the left side of the steady state energy balance are the exchange of energy with the surroundings, either as heat or as work. The first term on the right is the change in sensible heat within the reactor, and the second term is the heat absorbed by chemical reaction.

The assumptions used in deriving the design equations for a PFR were as follows:

- plug flow (perfect radial mixing and no axial mixing)
- · cylindrical reactor with a constant diameter
- · every reaction rate has been normalized per unit fluid volume
- the reacting fluid is an ideal solution (gas or liquid)
- · there is a single fluid stream leaving the reactor
- the reactor is stationary
- · no phase changes occur during the reaction
- · heat transfer with the surrounding can be described using an overall heat transfer coefficient
- · no shafts or moving boundaries
- the kinetic and potential energy of the entering and exiting fluid streams are effectively equal to each other

With these assumptions for an ideal PFR, the resulting mole balance is equation (17.6) and the energy balance is equation (17.7).

$$\frac{\partial \dot{n}_{i}}{\partial z} = \frac{\pi D^{2}}{4} \sum_{\substack{j=all\\reactions}} v_{i,j}r_{j} - \frac{\pi D^{2}}{4\dot{V}} \frac{\partial \dot{n}_{i}}{\partial t} + \frac{\pi D^{2}\dot{n}_{i}}{4\dot{V}^{2}} \frac{\partial \dot{V}}{\partial t}$$
(17.6)  
$$\pi DU(T_{e} - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_{i}\hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^{2}}{4} \sum_{\substack{j=all\\reactions}} \left(r_{j}\Delta H_{j}\right) + \frac{\pi D^{2}}{4\dot{V}} \sum_{\substack{i=all\\species}} \left(\dot{n}_{i}\hat{C}_{pi}\right) \frac{\partial T}{\partial t} - \frac{\pi D^{2}}{4} \frac{\partial P}{\partial t}$$
(17.7)

If an ideal PFR operates at steady state, these equations simplify considerably; equations (17.10) and (17.11) represent the ideal, *steady-state PFR mole and energy balances*, respectively. As with the CSTR, these equations result from setting all of the derivatives with respect to time equal to zero.

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} v_{i,j} r_j$$
(17.10)

$$\pi DU(T_e - T) = \left(\sum_{\substack{i=all\\species}} \dot{n}_i \hat{C}_{pi}\right) \frac{\partial T}{\partial z} + \frac{\pi D^2}{4} \sum_{\substack{j=all\\reactions}} \left(r_j \Delta H_j\right)$$
(17.11)

Here, the term on the left side of the steady state energy balance represents exchange of energy with the surroundings as heat. The first term on the right is the change in sensible heat of the reacting fluid, and the second term is the heat absorbed by chemical reaction.

It was noted above that a mechanical energy balance must be used to model pressure drop. Equation (17.12) is the mechanical energy balance for an unpacked tubular reactor and equation (17.13) is the mechanical energy balance (Ergun equation) for a packed bed tubular reactor. In these equations *G* represents the mass flow divided by the cross sectional area of the tube,  $g_c$  is a gravitational constant (not the acceleration due to gravity), *f* is the friction factor,  $\rho$  is the fluid density,  $\varepsilon$  is the void fraction of the packed bed,  $\Phi_s$  is the "sphericity" of the bed packing,  $D_p$  is the diameter of the bed packing particles, and  $\mu$  is the fluid viscosity.

$$\frac{\partial P}{\partial z} = -\frac{G}{g_c} \left(\frac{4}{\pi D^2}\right) \frac{\partial \dot{V}}{\partial z} - \frac{2fG^2}{\rho D}$$
(17.12)

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[ \frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right]$$
(17.13)

*Typical kinetic behavior and classification of reactions.* Reaction thermodynamics allows one to calculate the heat,  $\Delta H$ , of a chemical reaction at any set of environmental conditions. If the heat of reaction is negative (heat is released by the reaction), the reaction is called an *exothermic reaction*, and if the heat of reaction is positive (heat is absorbed by the reaction), the reaction is called an *endothermic reaction*. To a first approximation, the heat of reaction determines how the equilibrium constant varies with temperature. Recall from Unit 2 that by definition, the equilibrium constant for a reaction, *j*, depends upon the entropy and enthalpy changes for that reaction as given in equation (17.14). If the heat and entropy changes are taken to be constant, the dependence of the equilibrium constant upon temperature can be expressed as in equation (17.15), which can be seen to be of the same form as the Arrhenius equation for the temperature dependence of a rate coefficient. One significant difference is that the activation energy in the Arrhenius equation is a positive number whereas  $\Delta H_j$  can be either positive or negative.

$$K_{j} = \exp\left\{\frac{-\Delta G_{j}}{RT}\right\} = \exp\left\{\frac{\Delta S_{j}}{R}\right\} \exp\left\{\frac{-\Delta H_{j}}{RT}\right\}$$
(17.14)

$$K_{j} = K_{0,j} \exp\left\{\frac{-\Delta H_{j}}{RT}\right\}$$
(17.15)

Rate expressions are typically comprised of concentration terms, one or more rate coefficients, and sometimes one or more equilibrium constants. Quite commonly, the rate coefficients are taken to obey the Arrhenius equation and the equilibrium constants can be modeled using equation (17.15). We have seen that rate expressions can assume wide variety of mathematical forms. Nonetheless, there are some generalizations that can be made and that are found to be true for a majority of reactions. The following is a short list of generalizations about reactions and their rates.

- Typically, the rate of a chemical reaction will increase if the temperature of the reacting system is increased.
- Typically, the rate of a chemical reaction will decrease if the concentration of the reactants decreases.
- Typically, the rate of an irreversible chemical reaction is not strongly affected by the concentration of the products.
- Typically, the rate of a reversible chemical reaction decreases as the concentration of the products increases.
- The equilibrium constant for an exothermic reaction will decrease as the temperature increases.
- The equilibrium constant for an endothermic reaction will increase as the temperature increases.

Again, there are a multitude of rate expressions for chemical reactions, and the statements above are commonly, but not always, true. At this point, several hypothetical chemical reactions will be used, along with corresponding hypothetical rate expressions, to illustrate these generalizations. While the reactions and the rate expressions to be used here are made up, one could find real chemical systems that behave similarly.

Consider first an *irreversible reaction*, using equation (17.16) as the hypothetical reaction and equation (17.17) as the hypothetical rate expression.

$$A + B \rightarrow Y + Z \tag{17.16}$$

$$r_{17.16} = k_{0,17.16} \exp\left\{\frac{-E_{17.16}}{RT}\right\} C_A C_B$$
(17.17)

Supposing this to be a liquid phase reaction that occurs at temperatures near ambient, reasonable values for the rate expression parameters might be  $k_{0,17.16} = 1 \times 10^8 \text{ L} \text{ mol}^{-1} \text{ min}^{-1}$  and  $E_{17.16} = 50 \text{ kJ}$  mol<sup>-1</sup>. The first generalization above suggested that increasing the temperature would increase the rate. In equation (17.17), there is only one term that contains the temperature, namely the exponential term. It is easy to show that increasing *T* increases this term and consequently increases the rate. For example, at 298 K, the exponential term has a value of  $1.72 \times 10^{-9}$ . Increasing the temperature to 313 K increases the exponential term to a value of  $4.53 \times 10^{-9}$ . The second generalization suggests that as the

concentration of a reactant decreases, the rate will decrease. This is easily seen in equation (17.17) because the rate is directly proportional to the concentration of each reactant, and so decreasing  $C_A$  and/ or  $C_B$  will decrease the rate proportionately. The third generalization indicates that the rate of an irreversible reaction is not strongly affected by the concentrations of the products. Here it can be seen that neither  $C_Y$  nor  $C_Z$  appear in the rate expression, so obviously changing either of their values would not affect the rate at all for this irreversible reaction.

Next consider a *reversible reaction*, using equation (17.18) as the hypothetical reaction and equation (17.19) as the hypothetical rate expression.

$$A + B \rightleftharpoons Y + Z \tag{17.18}$$

$$r_{17.18} = k_{17.18} \exp\left\{\frac{-E_{17.18}}{RT}\right\} C_A C_B \left[1 - \frac{C_Y C_Z}{K_{0,17.18} \exp\left\{\frac{-\Delta H_{17.18}}{RT}\right\} C_A C_B}\right]$$
(17.19)

The fourth generalization suggests that for reversible reactions, the rate decreases as the product concentration increases. The rate expression, equation (17.19), involves the difference between two terms (inside the square brackets). The quantity being subtracted can be seen to be proportional to  $C_Y$  and  $C_Z$ . Hence, increasing either  $C_Y$  or  $C_Z$  causes a larger quantity to be subtracted and therefore leads to a smaller rate.

It is simple to illustrate the last two generalizations. As an example, consider the equilibrium constant appearing in the denominator in equation (17.19). Supposing that the equilibrium constant has a value of 0.65 at 298 K and that the (exothermic) heat of reaction is equal to  $-200 \text{ kJ mol}^{-1}$ , it would be found that increasing the temperature to 313 K would decrease the equilibrium constant for this exothermic reaction to 0.014. This is consistent with the fifth generalization above. Similarly, if the equilibrium constant had a value of 0.65 at 298 K and the reaction was endothermic with a heat of reaction equal to +200 kJ mol<sup>-1</sup>, increasing the temperature of the endothermic reaction to 313 K would increase the equilibrium constant to 31.1, consistent with the sixth generalization.

Examining equation (17.19) more closely shows that for an exothermic reaction there is a bit of a trade-off with respect to temperature. Far from equilibrium, where the 1 inside the square brackets is much, much greater than the second term, a higher temperature means that the rate coefficient will be larger, and consequently the rate of reaction will be greater. However, as the temperature is increased, the second term inside the square brackets also becomes greater. With continued increase in temperature, eventually the second term inside the square brackets becomes significant relative to the 1. Further increases in temperature beyond this point still increase the rate coefficient (tending to increase the rate), but they simultaneously increase the second term inside the square brackets (tending to decrease the rate). Eventually the second effect will come to predominate and the rate will decrease to zero as the temperature increases. Put differently, as the temperature increases with an exothermic reaction, the equilibrium conversion becomes smaller and consequently the rate goes to zero at larger

reactant concentrations. As a result, the reaction will not proceed as far as it would at a lower temperature. In contrast, an endothermic reaction is favored by high temperature. In an endothermic reaction a higher temperature means both a larger rate coefficient (faster rate) and a larger equilibrium coefficient (greater conversion).

An *auto-thermal reaction* (or system of reactions) is a special case of an exothermic reaction system. Actually it is probably more accurate to speak of running a reaction auto-thermally than to say the reaction itself is auto-thermal, but the latter usage is commonly encountered. The distinguishing feature of an auto-thermal reaction is that the heat released by the reaction  $(-\Delta H)$  is sufficient to raise the temperature of the fresh reactants to a point where the reaction will proceed spontaneously without the addition of heat from any external source. Many industrial reactions take place at elevated temperatures, and consequently it is necessary to heat the reactants up to the reaction temperature before feeding them into the reactor. For most reactions, this means the reactants must pass through a heat exchanger and steam or some other heating medium must be used to raise their temperature. In the case of an auto-thermal exothermic reaction, it would not be necessary to use any steam or other heating source. Instead, the heat released by the reaction could (with appropriate system engineering) be transferred to the reactants and provide all the heat necessary to heat those reactants to the inlet reactor temperature.

The reaction classifications mentioned so far have all been related to the thermodynamic behavior of the reacting system, and the behavior that has been discussed pertains to "typical" kinetic behavior. In some cases reaction rates are not affected by changes in reactant or product composition as is typically expected. That is, the rates of some reactions do not obey the generalizations with respect to concentration that were given earlier. This represents another basis for classifying reactions. Examples are auto-catalytic reactions, product inhibited reactions and reactant inhibited reactions.

In an *auto-catalytic reaction*, the rate of reaction increases as the concentration of a product increases (contrary to point 3 or 4 above). This doesn't necessarily occur across the full composition spectrum, but for an auto-catalytic reaction there is some range of composition within which an increase in product concentration causes an increase in rate. A very good example of an auto-catalytic process is that of cell growth. If a very simple cell growth process takes place with a yield factor of 0.5, then the cell growth "reaction" can be written as in equation (17.20), where X is used to denote cell mass concentration and S is used to denote substrate (i. e. nutrients or "food") mass concentration. If the Monod equation describes this particular cell growth reaction, then the corresponding rate expression is given in equation (17.21) where the C's represent mass concentrations,  $\mu_{max}$  is a constant (for a given reaction temperature) representing the maximum specific growth rate and  $K_s$  is a second constant (the saturation constant). Typical values of the constants in equation (17.21) might be  $\mu_{max}$  = 1.0 h<sup>-1</sup> and  $K_s$  =  $0.2 \text{ g L}^{-1}$ . Noting that cell mass is the "product" of reaction (17.20), it is easy to see that the reaction is auto-catalytic. If you had a system of pure substrate, no cells would ever grow. The system needs at least one cell initially to metabolize the substrate and eventually divide into two cells. If more cells are present, then the growth will be more rapid because each cell can be metabolizing the substrate and dividing into two cells at the same time. The choice of the name "auto-catalytic" for reactions like this is unfortunate,

though, because the reaction need not involve a catalyst. Also, while the example given here involves a biological process, chemical reactions can also be found that are auto-catalytic.

$$2 \text{ S} \rightarrow \text{X} \tag{17.20}$$

$$r_{17.20} = \frac{\mu_{\max} C_X C_S}{K_s + C_S} \tag{17.21}$$

Another behavior that is not consistent with the generalizations above is the *product inhibited reaction*. A hypothetical example can be constructed again using irreversible reaction (17.16). Generally one would not expect an irreversible reaction to be affected significantly by increasing the product concentration, as long as the reactant concentration remained the same. (This would also be true of a reversible reaction that was very far from reaching equilibrium.) However, if the rate expression for the irreversible reaction (16.16) was like that given in equation (17.22), this generalization would not be obeyed, and the reaction would be called a product inhibited reaction. Supposing that the values of  $k_{17.16}$ and  $k'_{17.16}$  were 0.17 L mol<sup>-1</sup> s<sup>-1</sup> and 8.61 L mol<sup>-1</sup>, respectively, the rate in an equimolar mixture of A and B (1 M each) would be 0.17 mol L<sup>-1</sup> s<sup>-1</sup>, but if the product Y was also present at a 1 M concentration, the rate would decrease by a factor of almost 10 (to 0.018 mol L<sup>-1</sup> s<sup>-1</sup>), even though the reaction is irreversible and the amounts of A and B had not changed.

$$r_{17.16} = \frac{k_{17.16}C_A C_B}{1 + k_{17.16}' C_Y}$$
(17.22)

Some heterogeneous catalytic and other reactions are *reactant inhibited reactions*. Normally, one expects that the rate of reaction will increase if the concentration of reactant is increased (point 2 above), but for a reactant inhibited reaction, the rate of reaction decreases when the concentration of a reactant is increased. A hypothetical example of this behavior might again involve reaction (17.16), but with the kinetics shown in equation (17.23). (The difference between equations (17.22) and (17.23) is the identity of the species whose concentration appears in the denominator, Y versus B, and the power to which that concentration is raised, 1 versus 2.) If  $k_{17.16}$  and  $k'_{17.16}$  have the same numerical values as given above,

then the rate in an equimolar mixture of A and B at 1 M concentration each would be 0.018 mol L<sup>-1</sup> s<sup>-1</sup>. If the concentration of B was doubled ( $C_A$  = 1 M and  $C_B$  = 2 M), the rate would decrease to 0.0096 mol L<sup>-1</sup> s<sup>-1</sup>.

$$r_{17.16} = \frac{k_{17.16}C_A C_B}{1 + k_{17.16}' C_B^2}$$
(17.23)

To this point in the present discussion, only single chemical reactions have been considered. It is very, very common for more than one reaction to be taking place in an industrial reactor. Sometimes the reactants and products involved in each reaction are different from the reactants and products involved in all the other reactions. In this case the reaction system is said to involve an *independent set of reactions*. In other cases, a reactant or product in one reaction is also involved in other reactions. There are many

possible combinations of reactions, but there are three common combinations that are often used in the classification of reaction networks.

If the product of one reaction in a reaction network is the reactant for a subsequent reaction, the reaction network is called a **series reaction network**. Reactions (17.24) and (17.25) schematically represent a series reaction network. For series reactions, such as those given in reactions (17.24) and (17.25), species that are formed in one reaction and consumed in a subsequent reaction are sometimes called intermediate products or intermediate species or just intermediates (not to be confused with the reactive intermediates that appear in reaction mechanisms; here the intermediates are not necessarily highly reactive species). The species names D and U appearing in reactions (17.24) and (17.25) are not arbitrary. It frequently occurs that the intermediate product is the desired (hence represented as D) species that has a high value whereas the final product is undesired (hence U) and has lower value. The number of reactions and intermediates is not limited to two, as illustrated schematically in equation (17.26).

$$A \to D \tag{17.24}$$

$$\mathsf{D} \to \mathsf{U} \tag{17.25}$$

$$A \to B \to C \to D \to \dots \tag{17.26}$$

A second classification of reaction networks is the *parallel reaction network* which is distinguished by having one species serving as the reactant in two or more of the reactions taking place. This is hypothetically illustrated, for two reactions, in equations (17.27) and (17.28), but this should not be taken to mean the number of parallel reactions is limited to two. In these reactions species A is a reactant in both reactions, and so they are parallel reactions. Once again, it is not uncommon for one product to be the desired product and another to be an undesired product.

$$A \to D \tag{17.27}$$

$$A \to U \tag{17.28}$$

A **series-parallel reaction network** is a combination of a series network and a parallel network. Reactions (17.29) and (17.30) hypothetically illustrate a series-parallel reaction network. From the perspective of one species in the network (B in the reactions used here) the reactions appear to be parallel reactions, while from the perspective of a different species (Y in the reactions used here) the reactions appear to be series reactions.

$$A + B \rightarrow Y$$
(17.29)  
$$Y + B \rightarrow Z$$
(17.30)

Finally, it is worth pointing out that in some cases, the number of reactions in a system can become so great that it is effectively impossible to write every one of them down and treat them explicitly. An example is polymerization where a single reactant might form millions of slightly different products. Fortunately, in these cases it is often possible to analyze the associated kinetics and reactors by lumping products into groups and using an effective stoichiometry to represent the whole group of reactions. Also,

in such situations, one often limits the analysis of the reactor to consider only the consumption of the reactant without worrying about which of the millions of products it became a part of.

Hypothetical reactions have been introduced in this unit, in part, for the purpose of illustrating some generalizations about kinetic behavior as well as some cases where the generalizations fail. It is useful for an engineer to develop a qualitative "feel" for how different kinds of reactors perform and to tie that "feel" to its underlying physical origins. This kind of understanding helps when the engineer is called upon to select which type of reactor to use in a new process and how to operate that reactor. This will be illustrated in future units.