

A First Course on Kinetics and Reaction Engineering

Unit 18. Reaction Engineering of Batch Reactors

Overview

Unit 18 describes some of the more common reaction engineering tasks that involve batch reactors, and it identifies some generic reaction engineering objectives that can be used in the absence of more complete information about other process constraints and economics. Important goals of Unit 18 are to learn how to *qualitatively* analyze a batch reactor and to begin to develop a “feel” for how perfectly mixed batch reactors behave over the course of one or more reactions. Eventually, of course, calculations will be necessary, but being able to set up and solve the design equations is not enough to make one a good reaction engineer. It is equally important to acquire an intuitive, physical understanding of why the temperature, pressure, composition, etc. change in the way they do for a given combination of reaction, reactor and reactor operating procedure. This unit shows that it is possible to predict, at least qualitatively, many things about reactor performance without ever solving the design equations. If you aspire to be a good and competent reaction engineer, you should strive to be able to perform the kind of analysis presented here (as well as a rigorous quantitative analysis that does use the design equations).

Learning Objectives

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

- batch reactor productivity
- turnaround time
- temporal variations
- spatial variations

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- instantaneous selectivity parameter for parallel reactions
- overall selectivity parameter for parallel reactions

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:

- Distinguish between reactor design problems and other reaction engineering problems
- List the typical steps in the operational procedure of a batch reactor
- List factors that might favor the selection of a batch reactor over other reactor types
- List disadvantages of batch reactors compared to other reactor types
- Explain, on physical grounds without using any equations, why composition and temperature vary as they do during the course of a specified single reaction, series reaction network or parallel reaction network taking place in a perfectly mixed batch reactor being operated in a known and specified manner.
- Predict how (qualitatively) composition and temperature will vary during the course of a specified single reaction, series reaction network or parallel reaction network taking place in an isothermal or adiabatic perfectly mixed batch reactor.

- Analyze (qualitatively) the effect a change in the mode of operation of a perfectly mixed batch reactor has upon its concentration and temperature as a function of processing time.
- Recommend a preferred mode of perfectly mixed batch operation for a given reaction or reaction network on the basis of a qualitative analysis.

Information

Before discussing reaction engineering of perfectly mixed batch reactors, it is useful to consider their typical operational procedure. By definition, reaction does not take place continuously in a batch reactor. Before reaction can take place, the reactor must first be cleaned (or, in some cases, sterilized) to remove anything “left behind” by the last reaction that was run. Then the reactants must be prepared and charged into the reactor. From this point on, the operation is much like a cooking recipe. A prescribed series of steps is followed, and reaction may take place during every step. A simple example might be that after the reactants are charged, the reactor is heated to a specified temperature, held at that temperature for a specified length of time, and then cooled back to room temperature. Of course, the operational protocol, i. e. the “recipe,” could be more complicated or could involve any number of steps. An important point to note is that once the reactants (and catalyst, if any) are placed in the reactor, reaction can occur. The operator can't tell the reactants to wait until the temperature reaches a certain value before they begin to react. Consequently, an engineering analysis of a batch reactor must include every step in the process. Once the protocol has been followed, the final operational step is to drain the reactor, sending the products on to the next stage of processing (this could be another reaction, purification, storage, etc.). It is very important to recognize that the *productivity of the reactor*, that is the amount of product it produces per hour, must be calculated taking the so-called *turnaround* time into account. That is, one must include the time needed to clean, fill and drain the reactor, not just the length of time reaction takes place.

It is very important to gain an understanding of the manner in which the environmental variables change, both *spatially* (i. e. with location) and *temporally* (i. e. with time), during the use of a batch reactor. In the definition of a batch reactor it was stipulated that the reactor is perfectly mixed. Therefore, at any instant of time the environmental variables (temperature, pressure and composition) do not vary spatially. If, at any one instant of time, the environmental variables were simultaneously measured at fifty different locations, the fifty measures of temperature would be the same, the fifty measures of pressure would be the same and the fifty measures of composition would be the same. The environmental variables do change over time, that is they do vary temporally. Obviously, if a reaction is taking place in a batch system (where no material enters or leaves during reaction), then the amounts of the reactants must decrease and the amounts of the products must increase. Similarly, the temperature and/or the pressure might vary temporally. Thus, near the start of a batch, the concentration of the reactants would be expected to be high everywhere in the reactor, and at a later time concentration of the reactants would be lower everywhere in the reactor.

The reaction engineering of batch reactors can be divided into two broad categories of problems: reactor design and reactor engineering. In batch reactor design, the engineer typically knows what

reaction is going to be run, the desired rate of production of the product, the desired selectivity (if there is more than one reaction), etc. What isn't known, and thus constitutes the problem, are the specifications for the reactor (it's volume, heat transfer area, etc.) along with the exact protocol that will be used in operating it. As mentioned in Unit 17, the possible solutions to this type of problem are constrained by a number of economic, safety and operability/reliability factors. In the second type of problem, the engineer usually does know the specifications of the reactor, and the problem is one of modeling how that reactor will perform. Thus, the key difference is that in reactor design, the specifications of the reactor and how it is operated are one of the things the engineer is trying to determine while in other reaction engineering problems, the specifications of the reactor are known.

In either case, often the goal of the engineer is to optimize the overall process (of which the reactor may only be one part) so as to maximize the rate of profit generated by the process. This is important for young engineers to recognize: the objective is not to design the most technically elegant or sophisticated reactor system, but to maximize the rate at which the overall process makes profit. It should be further noted that the reactor conditions at which the overall process makes the greatest rate of profit may not be the same as the reactor conditions at which the reactor process alone would make the greatest rate of profit. While this is an important point, it is also beyond the scope of this course. Here we will only focus on the reactor process, and if we do consider economics, we will implicitly assume that the goal is to maximize the profits of the reactor process, independent of the rest of the chemical plant.

In the absence of economic data, batch reactor design can be guided by the following general objectives.

- The reactor volume should be as small as possible.
- Each run should be of the shortest possible duration.
- The conversion should be as large as possible.
- The selectivity should be as large as possible.
- The heating or cooling demand should be as small as possible.

In most cases, it won't be possible to satisfy all these criteria simultaneously, and it will be necessary for the reaction engineer to seek the best compromise among them. At the same time, if these principles are guiding the design, instead of economics, that suggests that the design is preliminary in nature, and these guidelines may suffice.

When faced with a reactor design problem, one of the choices the engineer must make is which type of reactor to use. A batch reactor might be preferred over other types of reactors in situations where a large number of different products must be made. Batch reactors offer good flexibility because in principle a different reaction could be run in each batch. Batch reactors are also used when the desired amount of product is too small to warrant continuous production. An example of this is the manufacture of small market, niche chemicals and value-added products such as perfumes, specialty drugs, etc. A third circumstance where a batch reactor might be preferred is for reactions that require many reaction steps or stages. That is, for reactions where the "recipe" is long and involved. In this sense, batch reactors offer

greater operational flexibility than the flow reactors (CSTRs and PFRs) with respect to varying processing conditions during the reaction or reactions.

There are some disadvantages to the use of batch reactors, as well. Their operation is often more labor intensive due to the need for filling, cleaning, draining, etc. This can contribute significantly to the operating costs for batch reactors. A related issue is that of product consistency. The operators need to be well-trained so that the quality (purity, etc.) of the product is the same from batch to batch. The non-continuous nature of batch operation can also be a disadvantage under some circumstances. Generally speaking, batch reactors are well suited to the production of value-added chemical products, and they are less advantageous for the manufacture of commodity chemicals.

Qualitative Analysis of Batch Reactors. In general, when a chemical reaction takes place within a reactor, the composition, temperature and pressure will vary spatially and temporally, but with a perfectly mixed batch reactor the situation is less complicated. Since the reactor is perfectly mixed, there aren't any spatial variations. Therefore, all that needs to be considered in a qualitative analysis is how the concentrations and temperature vary over time. For the present we will consider "typical" reactions, as described in Unit 17. Recall the following generalizations about the kinetics and thermodynamics of "typical" chemical reactions:

- 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 one or more 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.

These generalizations were made for single reactions, both irreversible and reversible, that might occur independently or that might occur as a part of simple reaction networks, including series, parallel and series parallel networks. Recall, also, that not all reactions behave "typically." The approach to qualitative analysis presented here also can be use with atypical reactions, such as those that were identified in Unit 17.

First let's recognize that the driving force for a chemical reaction is reducing the free energy of the system. Put differently, a chemical reaction always proceeds toward chemical reaction equilibrium. As a consequence, a single chemical reaction will never change direction spontaneously. To do so, the

reaction would have to go beyond equilibrium and then turn around and go back*. Since the reaction will never change directions, *the concentrations of the reactants will continually decrease over time and the concentrations of the products will continually increase over time* until equilibrium is reached. As equilibrium is reached, the concentrations will stop changing over time.

The temperature within the reactor is affected by two factors. The first is the occurrence of the chemical reaction and the other is the transfer of heat through the walls of the reactor and/or through a coil immersed in the reactor. As reaction takes place, heat is either released (if the reaction is exothermic) or consumed (if the reaction is endothermic). Since the direction of the reaction does not change, heat will either be continually released or continually consumed over time until equilibrium is reached. If heat is released by the reaction, the question arises “what becomes of this heat?,” and if heat is consumed by the reaction the question is “what is the source of this heat?” In both cases, the answer is the same.

Please excuse the wording in this paragraph; it is written as if the system can make decisions, and while this seems foolish, it is helpful in understanding the heat-related processes. The first thing the heat released by reaction will try to do is to leave the reactor through the heat transfer surfaces (reactor or coil walls). Similarly, if heat is consumed by reaction, the reaction will first try to obtain that heat from the heat transfer surfaces. However, the rate at which heat can be supplied or removed through the heat transfer surfaces is limited by the properties of those surfaces and by the difference in temperature between the reacting fluid and the fluid on the other side of the heat transfer surface. If an exothermic reaction is releasing heat faster than the heat transfer surface can remove it, the “extra” heat that can’t get out through the heat transfer surfaces must be “stored” within the reactor. The way this heat is “stored” in this case, is by raising the temperature of the fluid in the reactor, i. e. it becomes sensible heat. (At some later time, this “stored” heat could be taken out of “storage” by exposing the fluid in the reactor to a heat transfer surface that is colder than the reactor fluid.) Similarly, if an endothermic reaction is consuming heat faster than the heat transfer surfaces can supply it, it obtains the “extra” heat it needs (beyond what the heat transfer surfaces can supply) by taking it out of “storage.” That is, the fluid in the reactor cools, and the heat that is released by the cooling is used by the reaction. Thus if an exothermic reaction releases heat faster than it can be removed, the temperature rises and if an endothermic reaction consumes heat faster than it can be supplied, the temperature decreases.

The amount of heat released or consumed by the reaction will vary over the processing time because the rate of the reaction will be varying. Additionally, since the temperature of the fluid within the reactor may vary over time, the rate of heat transfer may vary over the processing time. As a result, it is possible that for the first part of the processing time (while the rate is greater) the fluid temperature might be increasing (say because the reaction is releasing heat faster than the heat transfer surfaces can remove it), and then for the second part of the processing time (when the rate has become smaller) the fluid temperature might be decreasing (because now the heat transfer surfaces are removing it faster

* If a batch reactor was run to the point of reaching thermodynamic equilibrium, and then heating or cooling was continued, the reaction could change direction. In a reactor where multiple reactions are taking place, this could conceivably occur for one of the reactions. However, when only a single reaction is occurring, as assumed in this unit, the processing of the batch would normally end when equilibrium was reached, if not sooner.

than the reaction is generating it). This leads to a spectrum of possible modes of reactor operation. When the heat transfer rate exactly matches the heat of reaction over the entire course of the reaction, the reactor operates **isothermally**. When the reactor operates isothermally, the temperature does not change over time. Alternatively, if the reactor is perfectly insulated so that there is no heat transfer, the reactor operates **adiabatically**. *When the reactor operates adiabatically and the reaction is exothermic, the temperature will increase steadily over time until equilibrium is reached. When the reactor operates adiabatically and the reaction is endothermic, the temperature will decrease steadily over time until equilibrium is reached.* As equilibrium is reached, the temperature will stop changing over time. Otherwise (neither isothermal nor adiabatic operation), the instantaneous change in temperature will be determined by the instantaneous difference between the heat released by reaction and the heat transferred out of the system.

Thus, we see that before we can perform a qualitative analysis of a single reaction taking place in a batch reactor we need to determine or know how the reactor is being operated (isothermal, adiabatic, or neither). Here we will concentrate on isothermal operation and adiabatic operation. If the reactor is being operated isothermally, that's all we need to know. If the reactor is being operated adiabatically, we also need to know whether the reaction is exothermic or endothermic and whether it is reversible or irreversible. (If the reactor was neither isothermal nor adiabatic, we would need additional information on the rate of heat transfer relative to the heat of reaction.) Limiting ourselves to isothermal or adiabatic operation, we find that there are three possibilities:

- Isothermal operation – the concentrations of the reactants decrease steadily over time until equilibrium is reached, the concentrations of the products increase steadily over time until equilibrium is reached, and the temperature does not change over time.
- Adiabatic operation involving an exothermic reaction – the concentrations of the reactants decrease steadily over time until equilibrium is reached, the concentrations of the products increase steadily over time until equilibrium is reached, and the temperature increases steadily over time until equilibrium is reached.
- Adiabatic operation involving an endothermic reaction – the concentrations of the reactants decrease steadily over time until equilibrium is reached, the concentrations of the products increase steadily over time until equilibrium is reached, and the temperature decreases steadily over time until equilibrium is reached.

To perform a qualitative analysis of a single reaction taking place in a perfectly mixed batch reactor we begin by considering what changes occur in the concentrations and temperatures during a very small interval of time at the start of the reaction. These changes in the concentrations and the temperature during the first small interval of time affect the rate of the reaction, and so, in the next small interval of time, the rate will be different than it was in the first interval. As a consequence, the concentration and temperature changes during the second small interval of time will be larger or smaller than they were during the first interval. Additionally, if the reaction is reversible and if the temperature changes during the

first interval, then the maximum possible conversion is affected (that is, the equilibrium conversion changes if the temperature changes). Consequently, the maximum possible conversion during the second interval will be different than it was during the first interval. We can continue considering small intervals of time in this way until we reach the point of chemical equilibrium. We will see that in some cases it is useful to remember that eventually the reaction stops because equilibrium has been reached. This sometimes allows us to infer intermediate behavior that must occur at some point after the first few brief intervals of time mentioned above. Thinking through a few cases in this way hopefully will clarify how the analysis is performed.

The case of isothermal operation of a perfectly mixed batch reactor is particularly straightforward. During the first few moments of operation the concentrations of the reactants decrease slightly, the concentrations of the products increase slightly and the temperature remains constant. Referring to the kinetic behavior of a typical reaction, we now consider how these changes will affect the rate during the next few moments:

- The decrease in reactant concentrations during the first brief interval of processing will result in a smaller rate of reaction during the second brief interval of processing.
- The increase in product concentration during the first brief interval of processing will result in a smaller rate of reaction during the second brief interval of processing (if the reaction is reversible) or it will result in no change in the rate of reaction during the second brief interval of processing (if the reaction is irreversible).
- The temperature does not change during the first brief interval of processing, and this will result in no change in the rate of reaction during the second brief interval of processing.

Therefore, during the next (second) brief interval of reactor operation, the rate of reaction will be smaller than it was during the first interval.

Continuing with the analysis, during the second brief interval of operation, the concentrations of the reactants will again decrease, the concentrations of the products will again increase, and the temperature will not change. However, since the rate of reaction is smaller during this second interval of operation, the decrease in the reactant concentrations and the increase in the product concentrations will not be as large as they were during the first interval of operation. The third and later intervals of operation will follow the same

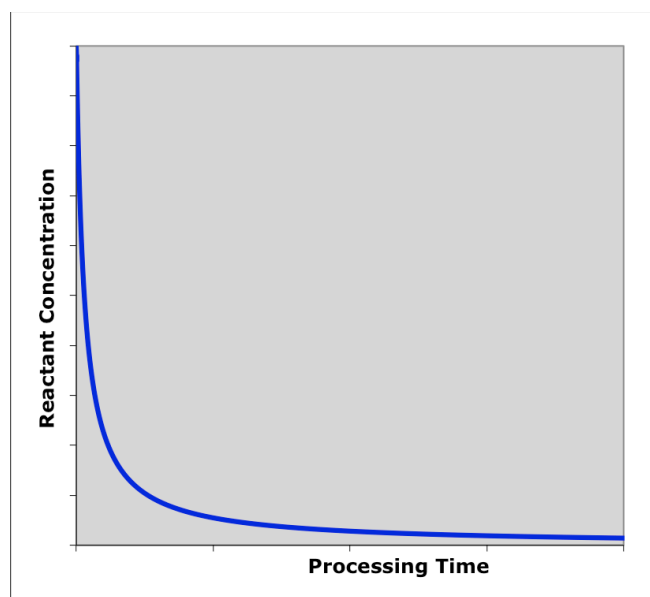


Figure 18.1 Concentration of reactant as a function of processing time in an isothermal batch reactor.

pattern as the second interval. That is, the concentrations of the reactants will continually decrease, but the amount by which they decrease will become smaller and smaller in each successive interval of operation. If you plotted the reactant concentration versus time, it would be steepest initially (the biggest change was during the first interval of operation) and would become less steep as time progressed (the change becomes smaller and smaller with each successive interval). Another way to say this is to say that the curve would display a shape that is concave upward. Eventually the reaction would reach equilibrium. At this point the concentrations of the reactants would no longer change over time. The plot would asymptotically approach a horizontal line. Similarly, a plot of the product concentrations would increase continuously until reaching equilibrium, being steepest initially (concave downward) and eventually reaching a horizontal asymptote at equilibrium. This reactant behavior is shown in Figure 18.1, and product behavior is shown in Figure 18.2.

Notice that according to the definition of a reaction rate with respect to a species, the slope of either Figure 18.1 or Figure 18.2 at any point in time is proportional to the rate of reaction at that time. This is consistent with the analysis above. The rate was greatest at the start, and accordingly the magnitudes of the slopes of the curves are greatest at time zero. In each successive interval of processing time, the rate decreases, and the magnitudes of the slopes of the curves get smaller and smaller as the processing time increases. Eventually, the reaction reaches equilibrium and the rate becomes zero. Correspondingly, the curves asymptotically approach a horizontal line

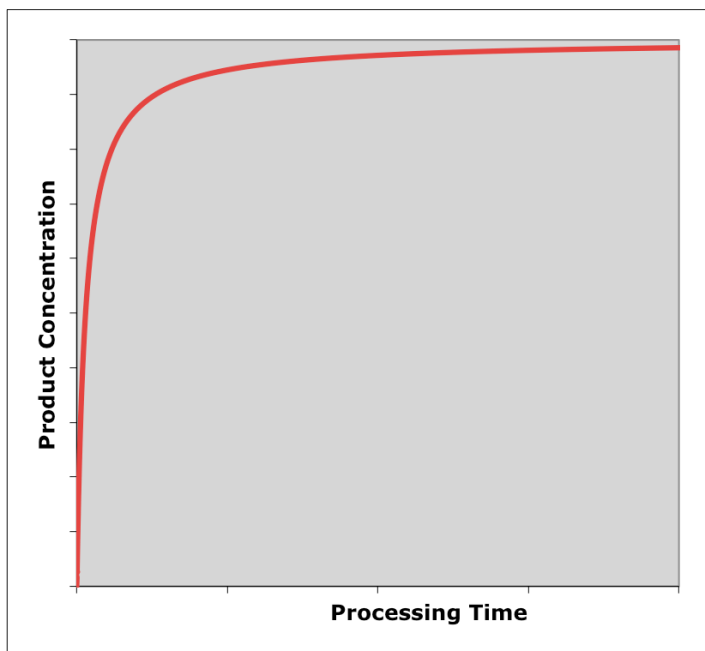


Figure 18.2 Concentration of product as a function of processing time in an isothermal batch reactor.

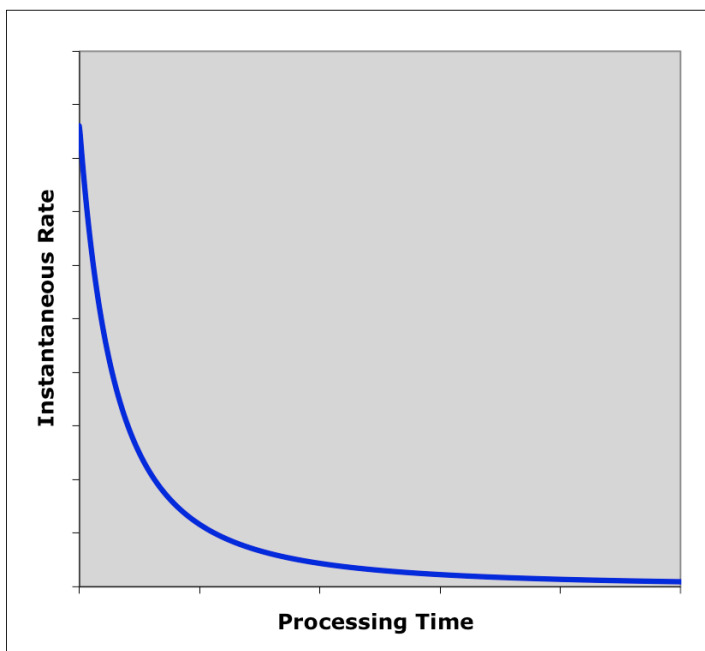


Figure 18.3 Instantaneous rate of reaction as a function of processing time in an isothermal batch reactor.

with slope of zero. Indeed, one could plot the instantaneous rate of reaction as a function of the processing time, and the result would look as shown in Figure 18.3.

Instead of plotting concentrations versus time (as in Figures 18.1 and 18.2), one might prefer to plot the conversion of one reactant versus time. At the beginning of the reaction, the conversion would equal zero, so the plot would start at the origin. The rate is greatest at the start of the reaction and decreases over time as just discussed.

Consequently the conversion will increase most steeply at the start of the reaction. The slope of the plot will then decrease as the time increases, eventually approaching a horizontal asymptote as equilibrium is reached. This behavior is depicted in Figure 18.4.

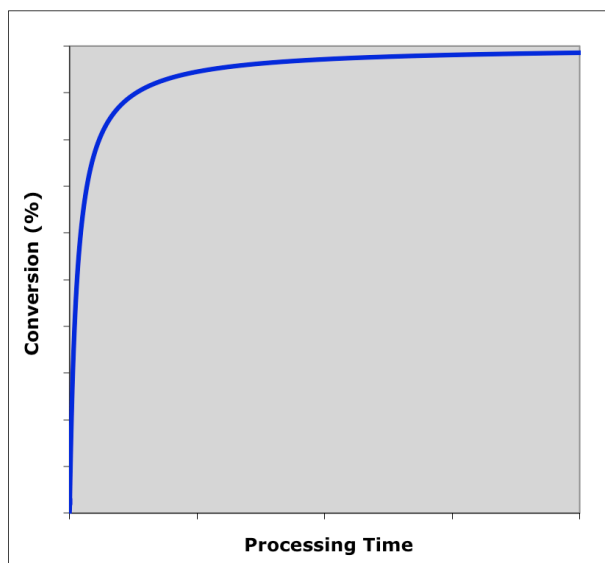


Figure 18.4 Conversion of reactant as a function of processing time in an isothermal batch reactor.

The isothermal case that was just presented is quite straightforward because, by definition, the temperature does change. Remember, that in order for the reactor to remain isothermal, one must remove exactly as much heat from the reactor as is being released by the reaction. We've already seen that the rate of reaction changes continuously over the processing time, so this means that the amount of heat that needs to be removed will change continuously over the course of the reaction. Stop reading for a moment and think about how difficult it would be to do this with a commercial sized batch reactor*. When one is conducting experiments for the purpose of finding an appropriate rate expression for a given reaction, it is usually worth the effort required to keep the reactor isothermal because it greatly simplifies the subsequent data analysis. Also the laboratory reactors used in the study of kinetics are generally small and the amount of heat to be removed is manageable. In contrast, 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. Thus, it is quite common for the temperature to vary in industrial reactors. An adiabatic reactor (perfectly insulated) represents a limiting case of these temperature variations.

A qualitative analysis of any non-isothermal reactor, including an adiabatic reactor, will entail changes in temperature as well as changes in reactant and product concentrations. To illustrate, consider the case of an *irreversible, exothermic reaction*. We've already noted above that in this case the temperature will increase as the reaction proceeds. This is easy to understand given the preceding

* It is unlikely that one would be able to vary the temperature of the heat transfer fluid in the coils or jacket of the reactor to just match the instantaneous heat being released by reaction. The flow rate of the heat transfer fluid could be varied (and this might lead to variations in its average temperature) to effect a variable rate of heat transfer. Additionally, one might design a reactor with multiple coils present, in which case the rate of heat transfer could be varied by changing the number of coils being used at different times during processing. With either of these approaches, it would be quite difficult to precisely match the instantaneous heat release.

discussion: the reactor is insulated so that the heat released by the reaction is not removed. It “has nowhere to go,” so it is “stored” within the chemicals inside the reactor in the form of sensible heat. Put differently, the heat released by the reaction causes the temperature of the fluid within the reactor to rise.

Now consider again what happens during a brief interval of time at the start of the reaction for the irreversible, exothermic case. As before, the concentrations of the reactants decrease and the concentrations of the products increase, but now the temperature also increases during this first brief interval of processing. Referring to the kinetic behavior of a typical reaction, we now consider how these changes will affect the rate during the next brief interval of processing:

- The decrease in reactant concentrations during the first brief interval of processing contributes to reducing the of reaction during the second brief interval of processing.
- The increase in product concentration during the first brief interval will result in no change in the rate of reaction during the second brief interval of processing (since we’re considering an irreversible reaction).
- The increase in temperature during the first brief interval of processing will contribute to increasing the rate of reaction during the second brief interval of processing.

Thus, in this case, we have competing forces where the decreasing reactant concentration is trying to decrease the rate while the increasing temperature is trying to increase the rate. Recall from our study of kinetics that concentrations typically appear in rate expressions as a term that is raised to a small power (e. g. first or second order reactions), while the reciprocal of the temperature typically appears inside and exponential term (e. g. as in the Arrhenius expression). Generally, due to the exponential dependence inherent in the Arrhenius expression, temperature effects are greater in magnitude than concentration effects, and so, in the present case the net effect of the three factors listed above is expected to be that the rate of reaction will be greater during the next brief interval of processing.

So, during the second brief interval of time, the reactant concentrations will decrease by more than they did during the first interval. That is, a plot of reactant concentration versus processing time will have a negative slope (reactant concentration decreases with time) that initially becomes steeper as the processing time increases (it is initially concave down). We know, however, that this can’t continue forever, because eventually the reactants will run out, and at that time, the rate will equal zero. Knowing that the rate initially increases with time and that eventually it must approach zero

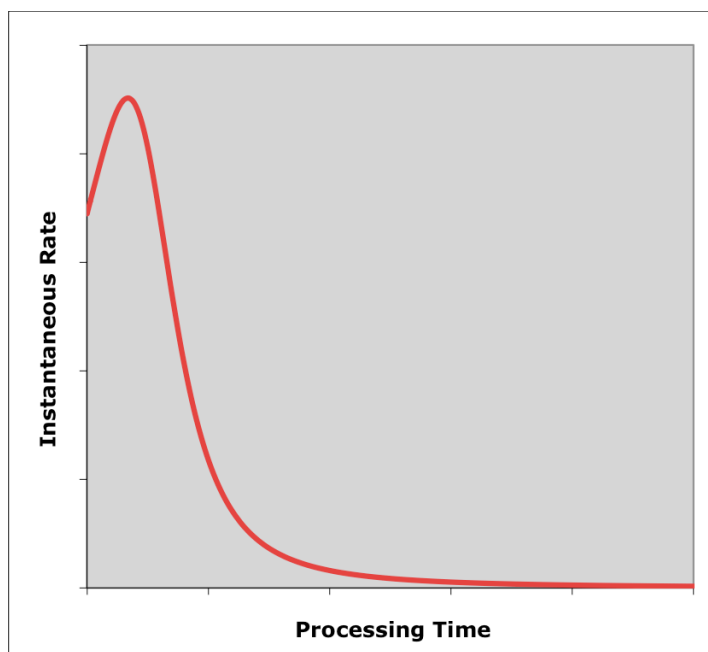


Figure 18.5 Instantaneous rate of an exothermic reaction as a function of processing time in an adiabatic batch reactor.

asymptotically after longer processing times, we can infer that the rate must pass through a maximum. This is actually easy to understand. At any processing time prior to the maximum in the rate, the effect of the increase in temperature upon the rate predominates over the effect of the decrease in concentration. At any processing time after the maximum in the rate, the reactant concentrations have become sufficiently small that the effect of their decrease predominates over the effect of the increase in temperature. The point of maximum rate corresponds to the brief time interval where the increase in rate corresponding to the increase in temperature is exactly offset by the decrease in rate corresponding to the decrease in reactant concentration. Figure 18.5 gives an example of a plot of instantaneous rate versus processing time for an irreversible, exothermic reaction taking place in an adiabatic batch reactor.

It has already been noted that the instantaneous rate is proportional to the slope of a plot of concentration versus processing time. If the instantaneous rate passes through a maximum as the processing time increases, as just inferred, then it follows that a plot of concentration versus time will exhibit an inflection point at the same time that the rate reaches its maximum value. As always for a single reaction, a plot of reactant concentration will steadily decrease from time zero. Here, unlike the isothermal case, it will initially be concave down, becoming steeper as time increases. There will be an inflection point at some intermediate processing time, and from that point onward it will be concave upward (become less steep with increasing time), as it was from the start in the isothermal case.

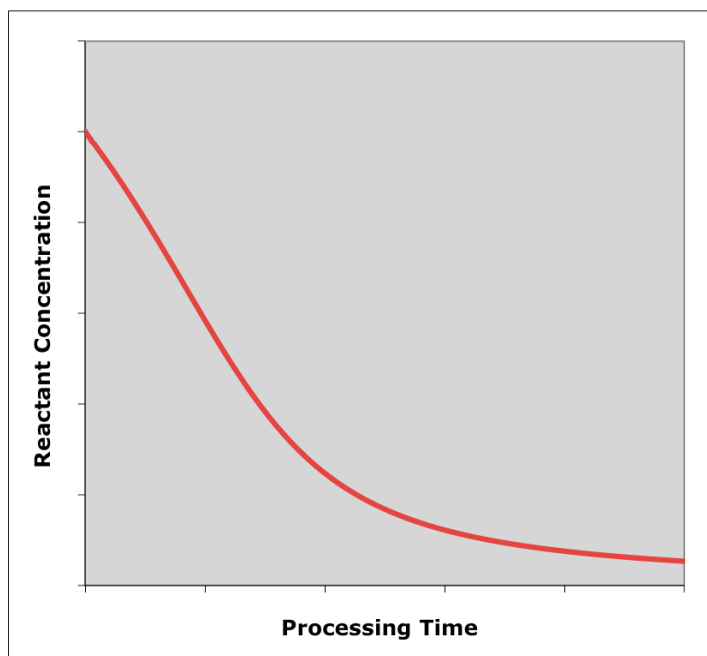


Figure 18.6 Reactant concentration as a function of processing time for an exothermic reaction taking place in an adiabatic batch reactor. At very short times the curve is slightly concave down; at longer times it becomes concave up.

Eventually it will asymptotically approach a horizontal line as the reaction reaches equilibrium. Figure 18.6 presents an example of a plot of reactant concentration versus processing time for an irreversible, exothermic reaction taking place in an adiabatic batch reactor.

Notice that while the rate passed through a maximum, the reactant concentration decreased steadily and the product concentration increased steadily. Similarly, it is important to note that the temperature will not pass through a maximum. The reaction is exothermic and the reaction is adiabatic, so as long as the reaction continues to take place, the temperature will continue to rise. The slope of a plot of temperature versus processing time will depend on several factors including the instantaneous heat capacity of the fluid, but to a first approximation, we expect that the increase in temperature during an interval of processing time will be proportional to the rate of reaction during that interval. Hence, while

a plot of temperature versus processing time will increase monotonically, its slope may initially become steeper with time, and then later its slope will become less steep with time. That is, a plot of the temperature versus the processing time may also display an inflection point. Figure 18.7 gives an example of a plot of the temperature versus processing time for an irreversible, exothermic reaction taking place in an adiabatic batch reactor.

The analysis of an irreversible, *endothermic* reaction taking place adiabatically in a perfectly mixed batch reactor is again straightforward. During the first brief interval of processing time the concentration of reactants decrease, the concentration of products increase and the temperature decreases. In the

same manner as was illustrated above, it can be seen that as a consequence of these changes the rate of reaction will be smaller during the second interval of processing than it was during the first interval. As a consequence, during the second brief interval of processing the changes in concentrations and temperature will be smaller than they were during the first interval. Hence, plots of the reactant and product concentrations versus processing time will be similar to those for an isothermal reaction (Figures 18.1 and 18.2). The reactant concentration plot will continually decrease with a shape that is concave upward, and it will asymptotically approach a horizontal line at long processing times. The product concentration plot will continually increase with a shape that is concave downward, and it will asymptotically approach a horizontal line at long processing times. The temperature will behave like the reactant concentration, continually decreasing with a shape that is concave upward and approaching a horizontal asymptote at long processing times.

The two adiabatic cases just presented both assumed irreversible reactions. If the reaction in either case were reversible, the behavior would be very similar to the irreversible reaction. In fact, the only difference would be that when the reaction was irreversible, the horizontal asymptote in the reactant concentration would correspond to a reactant concentration of zero whereas with a reversible reaction, the asymptote would correspond to the non-zero equilibrium concentration of reactant.

It is, however, interesting to compare adiabatic operation to isothermal operation when the reaction is reversible. Recall from thermodynamics that for an exothermic reaction, the equilibrium constant will decrease as the temperature increases. It was seen above that for an exothermic reaction the temperature will increase with processing time during adiabatic operation. Consequently, if the same

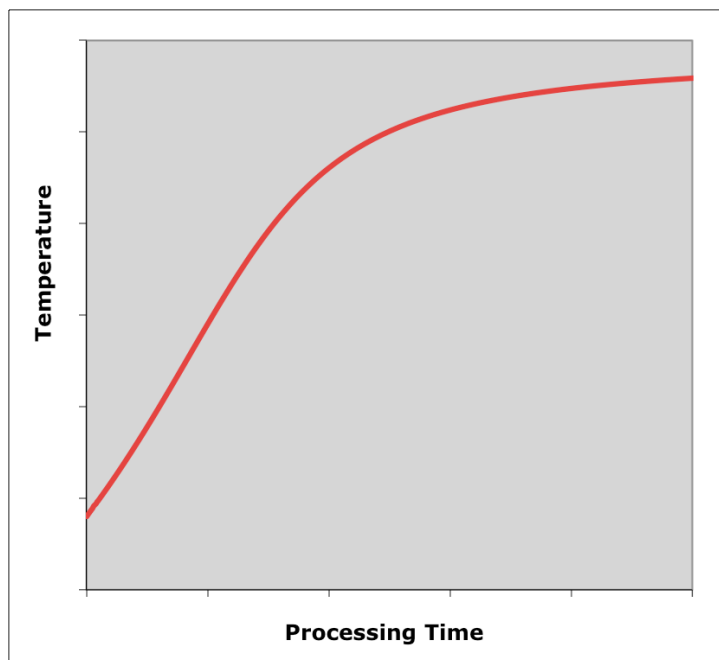


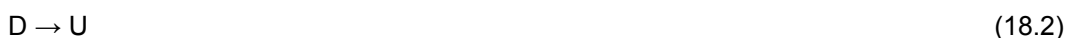
Figure 18.7 Reaction temperature versus processing time for an exothermic reaction taking place in an adiabatic batch reactor. At very short times the curve is slightly concave up; at longer times it becomes concave down.

reversible, exothermic reaction took place in two identical batch reactors starting at the same identical conditions, the isothermal reactor would ultimately achieve a larger reactant conversion than the adiabatic reactor. This happens because the final temperature in the adiabatic reactor is higher and consequently the corresponding final (equilibrium) conversion is lower as compared to the isothermal reactor. Using analogous reasoning, if the same reversible, endothermic reaction took place in two identical batch reactors starting at the same identical conditions, the isothermal reactor again would ultimately achieve a larger reactant conversion than the adiabatic reactor. This time the reason would be that the final temperature in the adiabatic reactor is lower and consequently the corresponding final (equilibrium) conversion (for an endothermic reaction) is lower than that in an isothermal reactor.

Similar analyses can be performed when multiple reactions are taking place. As might be imagined, however, the number of possibilities increases greatly. In fact, there are so many possible combinations of reaction types and reaction thermochemistries, that it makes little sense to attempt to generalize behavior. Basically, if one is told how exothermic or endothermic the reactions are relative to each other, the relative rates of the reactions involved, and the nature of the kinetics (i. e. “typical” or “atypical”), then an analysis can be performed in the same manner as above.

As noted in Unit 17, some reaction networks fall into the classification of serial reactions or the classification of parallel reactions. It is worthwhile to examine the qualitative performance of an *isothermal* batch reactor when each of these types of reaction network is taking place. This will permit a focus upon a new aspect of the analysis associated with how the concentrations change. Specifically, by considering irreversible reactions taking place isothermally, the effect of operational methods upon the *selectivity* of the reaction network can be highlighted.

We will begin by considering the series reactions given in equations (18.1) and (18.2). Those reactions use hypothetical reagents with S representing the starting reagent, D representing the desired product and U representing undesired product. When an engineer deals with series reactions, quite often a primary objective is to increase the selectivity for one product relative to the others. By the end of this unit it should become clear that it is relatively easy to obtain a high selectivity for the final products (denoted by U here). It is more challenging to obtain a high selectivity for an intermediate product (denoted by D here), and that is what motivated the nomenclature (D & U) being used here.



With that background, we can immediately proceed to a qualitative analysis of how the system will perform, remembering again that in the analysis presented here, the series reactions are assumed to be irreversible and taking place in an isothermal batch reactor. Looking at the system, we notice immediately that from the perspective of the starting reactant, S, there isn't any difference from when only one reaction was taking place. We immediately expect the concentration of S as a function of the batch processing time to vary in the exact same manner as was described earlier. Specifically, the concentration of S will have its greatest value at the start of the batch process, and it will decrease monotonically to zero over time. (It goes to zero because we have assumed the reactions to be irreversible.) For an irreversible reaction (where products have a negligible effect upon the rate) in a isothermal reactor (where the

temperature is constant and therefore doesn't affect the rate), the slope of a plot of the concentration of S as a function of processing time will be the steepest at the start of the batch and will become less steep steadily, giving the plot a shape that is concave upward.

The concentration of D as a function of processing time will be different because D participates in two reactions. *At very short reaction times*, the concentration of S is relatively high so the rate of production of D via reaction (18.1) is high, and at the same time, the concentration of D is relatively low, so the rate of reaction (18.2) is low. Consequently D is generated by reaction (18.1) faster than it is consumed by reaction (18.2), and its concentration increases over time. Clearly, however, these trends cannot continue for the duration of the reaction. Eventually, *after sufficient processing time*, the reactant S begins to run out and therefore the rate of generation of D by reaction (18.1) decreases. By this time, the concentration of D has grown relatively large, and so its consumption by reaction (18.2) continues at a higher rate. Thus, because D is now being produced more slowly, and consumed more rapidly, its concentration stops rising and begins to fall. That is, we can predict that the concentration of D will pass through a maximum as the batch processing continues. Eventually, at long processing times, the rate of production of D becomes negligible (because essentially all the S has been consumed) but its consumption continues. During this period it is as if reaction (18.2) is the only reaction taking place. Hence, the concentration of D is expected to decrease continuously with a slope that becomes less and less steep until eventually, it is completely consumed and its concentration becomes zero.

By now, you should be able to predict how the concentration of U will vary as a function of batch processing time. Initially it increases very slowly because there isn't any D present. Then, as the concentration of D builds, the rate of reaction (18.2) becomes faster and consequently the slope of the concentration of D versus processing time becomes larger. Later, as the concentration of D again becomes smaller, the slope of a plot of the concentration of U versus time passes through an inflection point, after which its slope becomes continually smaller. The inflection point occurs at the same time that the concentration of D reaches its maximum value. Finally it approaches a horizontal asymptote of constant equilibrium concentration. Here since the reactions were both assumed to be irreversible, the concentrations of S and D asymptotically approach equilibrium values of zero, while that of U approaches the equilibrium concentration corresponding to complete conversion.

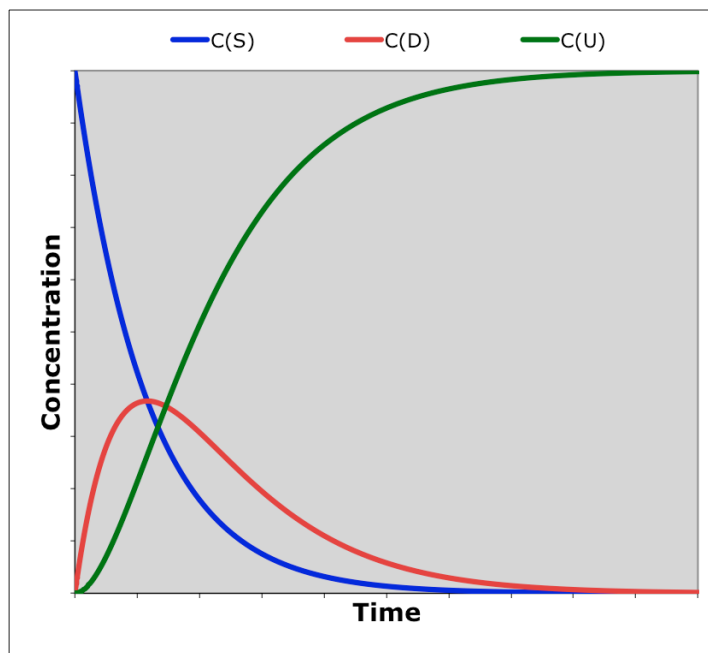


Figure 18.8 Species concentrations as a function of processing time for series reactions taking place in an isothermal batch reactor.

Figure 18.8 shows a typical plot of the concentrations of S, D and U as a function of batch processing time. We find again that we were able to qualitatively describe the performance of the batch reactor in considerable detail without ever writing or solving a design equation. A simple consideration of the physical consequences of the chemical events, along with an understanding of how reaction rates typically respond to changes in composition was all that was needed. Generally, the batch processing time at which the concentration of D reaches a maximum as well as the concentration at that maximum will depend upon the relative rates of the two reactions, which is determined in large part by the rate coefficients for the two reactions. The faster reaction (18.2) is, as compared to reaction (18.1), and hence the greater is the ratio of the rate coefficients (of reaction (18.2) to reaction (18.1)), the smaller the maximum concentration of D will be and the smaller will be the processing time at which it is observed. Intuitively this makes sense because if reaction (18.2) is quite fast, it tends to consume the desired product D as soon as it is formed.

Very often, in commercial series reactions it is the intermediate product (D in this case) that is most valuable. From the behavior observed here it is apparent that the *design engineer can affect the selectivity for the intermediate D in series reactions by adjusting the reaction time*. That is to say, the engineer can specify that the process be stopped at the time when the concentration of D is at its optimum value. (The optimum concentration of D is that which maximizes the rate of profit, and this might not correspond exactly to the maximum concentration of D). *The selectivity for the intermediate D in series reactions can also be affected if the relative values of the rate coefficients can be changed*. This might be possible if the activation energies of the two reactions are unequal, in which case a change in temperature will affect one rate coefficient more than the other. Thus, by raising or lowering the temperature, it may be possible to increase the rate of reaction (18.1) relative to that of reaction (18.2). Sometimes, however, the thermal stability of the reactants and/or products limits the temperature range in which the reaction can be run, and thereby limits this approach to controlling the selectivity.

The other case we will consider here is that of irreversible parallel reactions taking place isothermally in a perfectly mixed batch reactor. Reactions (18.3) and (18.4) can be used for illustration purposes, and the nomenclature will retain the same meaning, with S representing the starting reagent, D representing the desired product and U representing undesired product.



In fact, there is almost nothing new to consider in this case that wasn't already considered earlier for a single reaction. Each reaction can be considered separately, leading to the same qualitative analysis as was presented for a single isothermal reaction in that unit. Specifically, looking at either reaction, we expect that the concentration of S will have its greatest value at the start of the batch process, it will decrease monotonically to zero over time, and the slope will be the steepest at the start of the batch and its magnitude will decrease steadily to zero, giving the plot a shape that is concave upward. Similarly, for either of the two products D or U, we expect the concentration to start at zero and increase monotonically with a slope that is steepest at the beginning and that continually decreases so that the curve eventually reaches a final asymptotic value. Figure 18.9 shows one possibility for the performance of a batch reactor

when irreversible parallel reactions take place isothermally within it, and the behavior can be seen to be as expected.

There is one subtle difference compared to a single reaction. During any brief interval of time, the concentration of S will decrease in part, due to reaction (18.3) and in part due to reaction (18.4). Consequently, at the end of the brief interval of time, the rate of each of the two reactions will be smaller, assuming that the reactions exhibit “typical” kinetic behavior. The subtle difference is that the rate of either reaction in the end of the interval is affected by the occurrence of the other reaction during the interval. That is, suppose reaction (18.3) was much, much, much slower than reaction (18.4).

After the first brief interval, even though reaction (18.3) might have hardly taken place at all, its rate would still be much smaller at the end of the interval because the concentration of S would have dropped due to reaction (18.4). Had reaction (18.3) somehow taken place in the absence of reaction (18.4), its rate would not have been as small at the end of the interval, because only reaction (18.3) would be contributing to the decrease in the concentration of S.

Varying the reaction time was an effective means of altering the selectivity for series reactions (Figure 18.8), but Figure 18.9 shows that this is not necessarily true for parallel reactions. Further qualitative analysis would show that if the reactions are of equal order, then the processing time has no effect at all upon the selectivity. If the orders of the reactions differ, then reaction time can have an effect upon selectivity, but generally it is not nearly as significant as for series reactions. The relative magnitude of the rate coefficients has the most significant effect upon the selectivity of parallel reactions when the kinetics are the same. *Hence, if the activation energies of the reactions are unequal and the chemicals involved are stable over a range of temperature, the design engineer may try to affect the selectivity in parallel reactions by varying the reactor temperature so as to increase the rate coefficient for the desired reaction relative to that for the undesired reaction.*

Defining an instantaneous selectivity parameter can be useful when dealing with parallel reactions. The selectivity parameter is simply the rate of generation of the desired product to that of the undesired product, as given in equation (18.5). The symbol S_{DU} is used here to denote the instantaneous selectivity for D relative to U. (The overall selectivity parameter is just the final ratio of D to U.) The rate expressions can be substituted into equation (18.5) and a design engineer can use the resulting expression to guide the specification of the reactor operating procedure so as to maximize the selectivity. As just noted, if the

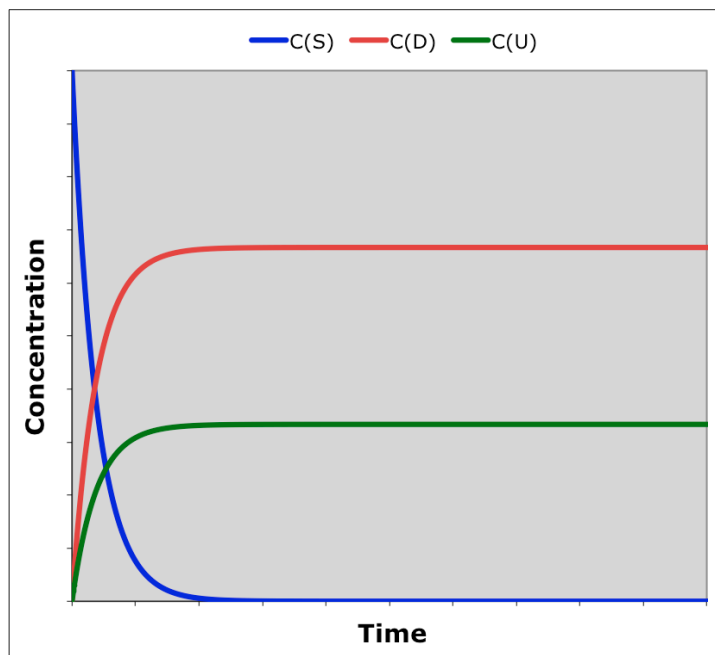


Figure 18.9 Species concentrations as a function of processing time for parallel reactions taking place in an isothermal batch reactor.

reactions are of the same order, then the instantaneous selectivity parameter becomes equal to the ratio of the rate coefficients, as given in equation (18.6), and the only way to affect the instantaneous selectivity is by altering the ratio of the rate coefficients. The only way to alter the ratio of the rate coefficients is by changing the temperature, and even so, that will only work if the activation energies for the two rate coefficients are different. In other cases the reaction orders may not be equal, and that will lead to an expression for the instantaneous selectivity parameter that includes both rate coefficients and concentrations. In such cases, the engineer might be able to improve selectivity by varying the amounts charged to the reactor and by optimizing the processing time in addition to varying the temperature.

$$S_{D/U} = \frac{r_D}{r_U} \quad (18.5)$$

$$S_{D/U} = \frac{k_D}{k_U} \quad (\text{equal reaction orders}) \quad (18.6)$$

One objective of this unit is to begin to build an intuitive “feel” for, and physical understanding of, how and why perfectly mixed batch reactors perform as they do. Many students who are very, very adept at “solving batch reactor problems” never acquire this feel because they rely exclusively on the design equations. It is very helpful to one’s understanding, especially when first learning the subject, to always examine the results from solving the equations with the goal of being able to explain the trends and behavior in physical terms (without resorting to the equations). Units 19 and 20 describe how to solve the design equations for perfectly mixed batch reactors, but as you progress to those units, you are encouraged to additionally perform a qualitative analysis of each problem you encounter. Doing so will serve as a check on your quantitative answers, but it will also help you to continue to develop a physical understanding and feel for batch reactors.

The qualitative analyses that were presented here all involved “typical” reactions. However, once one knows how to perform such an analysis, it can be applied to “unusual” reactions in just the same way. Having this ability, one should also be able to compare the effect of changing an operating parameter (e. g. compare a system using two different starting temperatures). When faced with the assignment of designing a reactor system for a new reaction, one can use this type of analysis to postulate the most effective mode of operation before undertaking the formal design (that is, before writing and solving sets of equations). One can also qualitatively analyze operation that is neither isothermal nor adiabatic, using those two situations as limiting cases. Finally, if one is a student and one must solve the reactor design equations as a homework or exam problem, one can qualitatively predict the result, and if the mathematical solution does not agree with the qualitative prediction, one would know to double check both analyses and find the error that caused them to differ.