

# A First Course on Kinetics and Reaction Engineering

## Unit 24. Multiple Steady States in CSTRs

### Overview

The design equations for a steady state CSTR are non-linear. Temperature appears in an exponential term in the design equations, and if the reaction is anything other than first order, the molar flow rates also appear in terms that are non-linear. In general, non-linear equations can have more than one solution. For example, a quadratic equation has two roots. Quite often in science and engineering problems, an equation may have multiple roots, but only one of the roots makes sense physically. When this type of equation is solved, the root that makes physical sense is chosen as the correct solution of the equation. Unit 24 shows that in the case of steady state CSTR, the equations can have more than one root, and more than one of those roots can make sense physically. That is, a CSTR with fixed inlet conditions may be capable of attaining more than one steady state outlet condition.

### Learning Objectives

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

- stable steady state
- unstable steady state
- bifurcation point

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:

- Analyze CSTRs where multiple steady states are possible and identify the preferred stable steady state for operational purposes
- Specify a start up procedure for a CSTR that will lead to the attainment of the desired stable steady state when multiple steady states are possible

### Information

Let's look at a very simple example where irreversible reaction (24.1) takes place adiabatically in a steady state CSTR. Suppose that reaction (24.1) is first order in A and that it has an exothermic heat of reaction that is essentially constant with temperature. Let's assume that the reaction takes place in a solvent, and because the solvent is present in excess, the heat capacity of the fluid in the reactor can be taken to equal that of the solvent. For simplicity, let's also assume that the heat capacity of the solvent is essentially constant with temperature.



For the situation just described (after simplification), the mole balance design equation for A is given by equation (24.2) that for R is given by equation (24.3), and the energy balance is given by equation (24.4). The inlet molar flow rate of A, the pre-exponential factor, the activation energy, the gas constant, the solvent flow rate, the heat capacity, the feed temperature and the heat of reaction are all known

constants for this problem, so the only unknowns are the outlet molar flow rate of A, the outlet molar flow rate of R and the outlet temperature. Thus, we have three equations and three unknowns.

$$\dot{n}_A^0 - \dot{n}_A = \frac{k_0 V}{\dot{V}} \exp\left\{\frac{-E}{RT}\right\} \dot{n}_A \quad (24.2)$$

$$\dot{n}_R = \frac{k_0 V}{\dot{V}} \exp\left\{\frac{-E}{RT}\right\} \dot{n}_A \quad (24.3)$$

$$\dot{n}_{solvent}^0 \hat{C}_{p,solvent} (T - T^0) = -\frac{k_0 V}{\dot{V}} \exp\left\{\frac{-E}{RT}\right\} \dot{n}_A \Delta H(T) \quad (24.4)$$

$$\text{Heat absorbed} = \text{Heat released} \quad (24.5)$$

Instead of solving these equations algebraically, let's use a different approach. Let's guess a temperature,  $T$ . Having done so, we can solve equation (24.2) for the outlet molar flow rate of A, and once we know that, we can solve equation (24.3) for the outlet molar flow rate of R. If the temperature we guessed corresponds to a solution to the design equations, then if we substitute it into equation (24.4), along with the value we calculated for the outlet molar flow rate of A, equation (24.4) should be satisfied. If equation (24.4) is not satisfied, then the temperature we guessed and the outlet molar flow rates we calculated do not correspond to a steady state of the system. Looking at equation (24.4) we can see that the right hand side is just the heat released by the reaction. Since we're considering an adiabatic system, the heat released by the reaction has to all be absorbed in heating the feed from the inlet temperature to the internal reactor temperature, and that's just what the energy balance says. Hence, in words, we could write the energy balance as in equation (24.5).

For illustrative purposes, let's solve the design equations graphically using the procedure just described. We'll guess a temperature, calculate the molar flow rates of A and R, calculate the "heat absorbed" term, calculate the "heat generated" term, and then plot the latter 2 quantities versus the temperature we guessed. Repeating this process with many guesses for the temperature will lead to the curves plotted in Figure 24.1.

It can be seen in Figure 24.1, that there are three places where the two curves intersect, that is, there are three temperatures where the left hand side of equation (24.4) is equal to the right hand side of equation (24.4). Each of these three temperatures represents a different solution to the design equations. In addition, all three solutions make physical sense. This phenomenon is known a multiplicity of steady states. In this case, there are three possible steady states for the CSTR system. You might wonder which one is "the correct one." The answer is that all three are correct; the procedure used to start up the reactor, or the details of the last transient phase of operation will determine which of these steady states the reactor goes to.

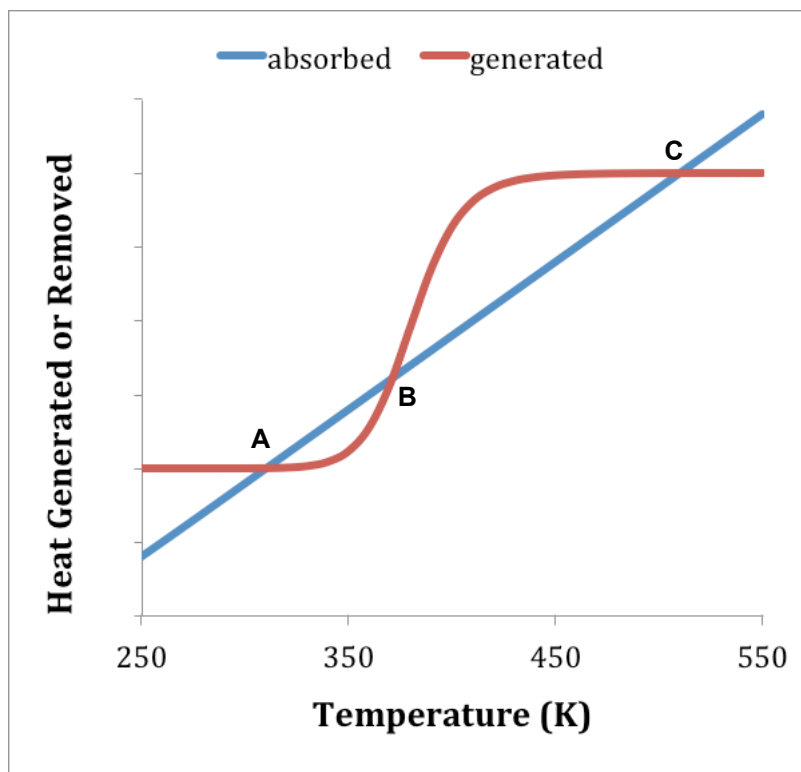


Figure 24.1 Plot of the two sides of equation (24.5) as a function of temperature.

The three solutions to the design equations could have been found using algebra; it wasn't necessary to use the graphical approach above. However, the graph can be used to analyze the stability of each of the steady states. Strictly speaking, the analysis that follows is not rigorous; it applies the results from the steady-state design equations to transient situations. Despite its lack of rigor, the analysis is highly illustrative of the concept of stability of a steady state. By that we mean how sensitive the system is to being perturbed slightly from a given steady state.

First suppose that the CSTR system was operating at the steady state denoted in Figure 24.1 by an A. If the CSTR system was perturbed slightly so that the temperature was a little greater than the steady state value (if we move slightly to the right of point A in the graph) then the heat absorption term would become greater than the heat generation term. Since more heat would be absorbed than was being generated, the temperature would decrease back to the steady state point A. Similarly, if the CSTR system was perturbed to a temperature slightly less than the steady state value at A, the heat generation would be greater than the heat absorption. Since heat would be generated faster than it was absorbed, the temperature would rise back to the steady state value at point A. Thus, we have seen that in response to a small perturbation away from steady state A, the system will return to steady state A. We therefore say that steady state A is a *stable steady state*.

You can do the same kind of analysis on the steady state labeled C in Figure 24.1, and you will find that steady state C is also a stable steady state. However, the steady state labeled B is different. If a

CSTR system operating at steady state B was perturbed slightly so that the temperature was a little greater than the steady state value, then the heat absorption term would become less than the heat generation term. Since more heat would be generated than was being absorbed, the temperature would increase, moving the system even farther from steady state B. Indeed, instead of returning to steady state B following a small positive perturbation of the temperature, the system would undergo a transient that would take it to steady state C. Similarly, if a system operating at steady state B was perturbed slightly so that the temperature was a little less than the steady state value, the heat absorption term would become larger than the heat generation term. Since more heat was being absorbed than was being generated, the temperature would decrease even more, and the system would eventually move to steady state A. Hence, we say that steady state B is an *unstable steady state*. You would not find a real reactor operating at this steady state, because as soon as any small perturbation occurred, it would move to one of the stable steady states.

Figure 24.1 was developed for one specific set of CSTR operating conditions. The curves shown in the figure will change if these operating conditions are changed. For example, in creating Figure 24.1, the feed was assumed to be at a specified temperature. Figure 24.2 shows the heat absorbed and heat generated in the same CSTR system with the only difference being that the feed temperature was higher than in Figure 24.1. It can be seen that the CSTR system only displays a single steady state when a higher feed temperature is used. Note that the reactions involved for the two systems are the same; the kinetics and thermochemistry are not changed. The only change is in a single operating parameter, in this case the feed temperature.

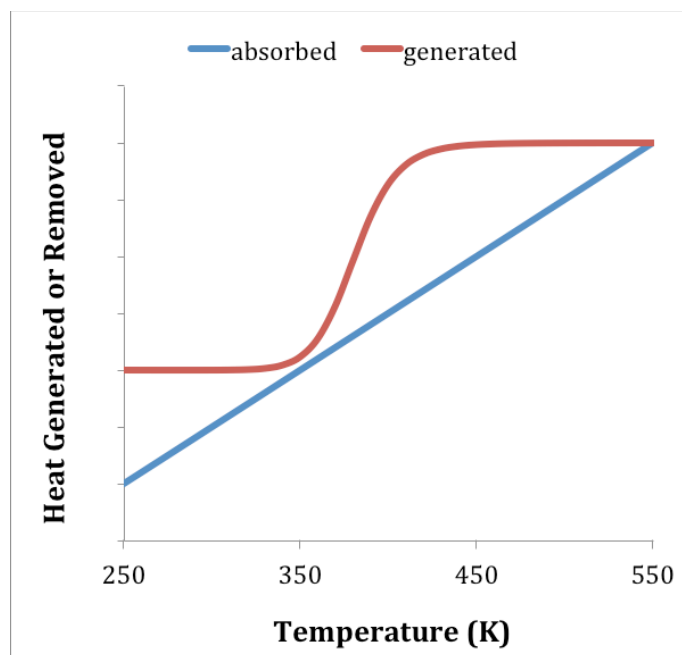


Figure 24.2 Heat generation and absorption in the same CSTR system as in Figure 24.1 except that the feed temperature is greater.

Comparing Figure 24.1 and Figure 24.2, we can surmise that given a CSTR and a specific chemical reaction system, multiple steady states may or may not be possible depending upon the operating parameters of the reactor system. If one started with the system shown in Figure 24.2 and slowly decreased the feed temperature, there would initially be only one solution. At some point, however, multiple solutions would suddenly become possible. This point is known as a bifurcation point. Put differently, a *bifurcation point* is the location where a single valued function splits (bifurcates) into multiple solutions as a parameter is varied.

There are many, many different kinds of bifurcations, and a large body of mathematics has been developed for the analysis of bifurcations. The mathematics can become quite complicated; it is beyond the scope of an introductory course in reaction engineering. Nonetheless, it has been mentioned here for two reasons. First, you should know that multiple steady states are possible, but their existence is not guaranteed. The operating parameters for a reactor will determine whether multiple steady states are possible. Second, you should be aware that there are more advanced mathematical methods available that can be used to identify whether multiple steady states are possible and to characterize the steady states if they are possible. No attempt will be made here to teach how bifurcation analysis is performed; other sources should be consulted.

The purpose of this unit was to make you aware that CSTRs can have more than one steady state and to introduce you to the concept of stability of steady states. Here we used a non-rigorous analysis to illustrate the stability of a steady state. There are rigorous mathematical methods that can be used to assess the stability of steady states. Such methods go beyond the scope of the present course; they are often discussed in more advanced courses on reaction engineering. If an engineer is asked to specify a start-up procedure for a CSTR, it is important to fully analyze that procedure to make sure it will lead to the desired, stable steady state.

Finally, one should note that the two stable steady states of the system considered here are very different. This is quite often the case. Here, at steady state A there is almost no reaction taking place. The outlet temperature is nearly equal to the inlet temperature, and the computed values of the outlet molar flow rates are nearly equal to the inlet values. At steady state C, in contrast, the temperature is much higher than the inlet temperature and the conversion of A to R is substantial. Even though everything about the system (feed temperature, feed composition, feed rate, etc.) is identical, the reaction never gets going in one case while it goes nearly to completion in the other. Obviously, if this process was being used in a chemical plant, the desired steady state would be the one where conversion is high.