REB, The Book
Example 5.5.1 Solution

Consider the typical reaction, A → Z, which is irreversible and exothermic. Suppose that reaction is run in an adiabatic reactor starting with pure A. Sketch the concentration of A, and the temperature versus reaction time. Describe the shape of each graph noting slopes, curvature, inflection points, etc. Then explain the shape on a physical basis.

Analysis and Discussion

Generally the reaction rate is affected by composition and temperature. Here the reaction is irreversible and the kinetics are typical, so the only important concentration is that of the reactant, A. The reaction is exothermic and the reactor is adiabatic, so the temperature will increase due to reaction, and consequently the temperature is also important.

At the start of the reaction, the concentration of A and the temperature will both have positive values. The corresponding rate will be positive, so initially the concentration of A is decreasing because it is a reactant, and the temperature is increasing because the reaction is exothermic and the reactor is adiabatic.

So after a very brief interval of time, the concentration of A will have decreased and the temperature will have increased. The curvature of the reactant concentration vs. time and temperature vs. time graphs will depend upon whether the reaction rate at the end of the small interval of time is greater of less than the initial rate. However, the decrease in reactant concentration and the increase in temperature have opposing effects on the rate. Decreasing reactant concentration decreases the composition term in the rate expression while increasing the temperature increases the rate through the Arrhenius term.

In a qualitative analysis it isn’t possible to know whether the concentration decrease will have the greater effect leading to a rate decrease or whether the temperature increase will have the greater effect leading to a rate increase. Both possibilities must be considered.

If the decrease in reactant concentration predominates over the increase in temperature the rate will decrease. That means that the concentration of A will decrease less during the next brief interval of time so that initially (over these brief time intervals) the concentration of A is decreasing with a concave upward shape. At the same time, the temperature will increase less during the second brief interval than during the first, so initially the temperature is increasing with a concave downward shape. These trends can continue for as long as required until eventually both the concentration and the temperature will asymptotically approach constant values as shown in Figure 1.

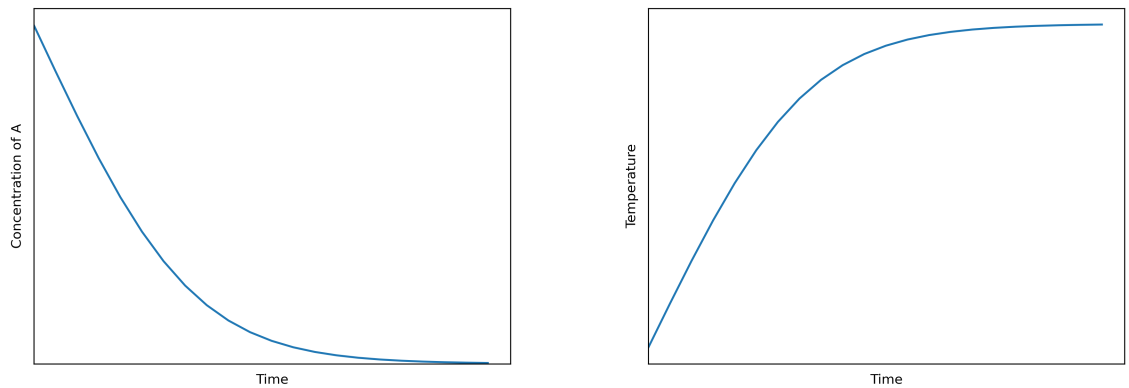

Figure 1. Concentration (left) and temperature (right) profiles during the adiabatic conversion of A to Z under conditions where the concentration dependence of the rate predominates over the temperature dependence.

The other possibility is that the increase in temperature predominates over the decrease in reactant concentration and the rate increases. In this case the concentration initially decreases with a concave downward shape and the temperature initially increases with a concave upward shape. This can be seen at lower times in the concentration and temperature profiles shown in Figure 2. Those trends cannot continue indefinitely because they would lead an infinite negative concentration and an infinite positive temperature. Very clearly, and as shown in the figure, the curves must pass through an inflection point where their curvatures invert. The trends after the inflection point can continue for as long as required until eventually both the concentration and the temperature will asymptotically approach constant values.

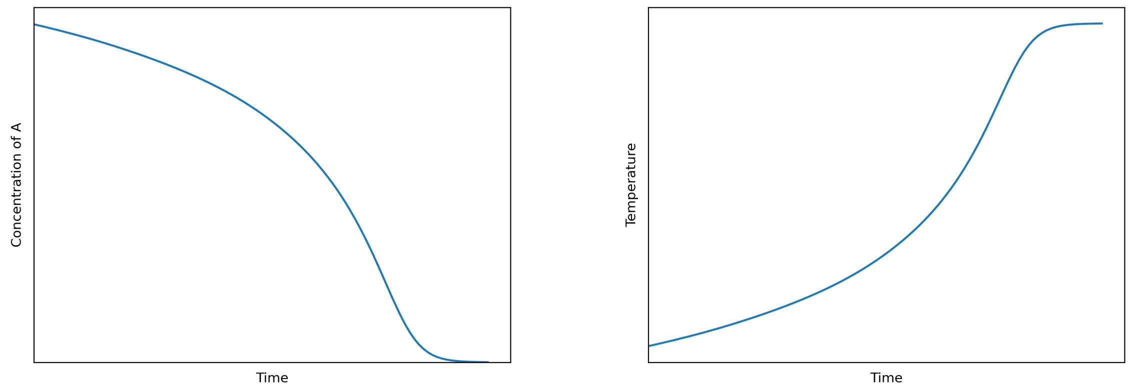

Figure 2. Concentration (left) and temperature (right) profiles during the adiabatic conversion of A to Z under conditions where the temperature dependence of the rate initially predominates over the concentration dependence.

The physical reason for the inflection point can be understood by considering the rate as a function of reaction time, shown in Figure 3. Initially the increase in temperature predominates over the decrease in reactant concentration and the rate increases. That cannot continue indefinitely, however, because eventually the reactant will run out and at which point the rate must equal zero. So as the reaction proceeds, the temperature effect becomes less and less predominant until a point is reached where the effects of the decreasing concentration and increasing temperature become equal. At that point, the rate reaches a maximum. The reaction time where the maximum rate occurs coincides with the times where the inflection points occur in the concentration and temperature profiles (Figure 2). At times beyond that point, the concentration term predominates over the temperature term. From this point on, the analysis is the same as first possibility considered above wherein the concentration term predominated from the start. Specifically the concentration decreases with a concave upward shape, the temperature increases with a concave downward shape, and they both asymptotically approach constant values at sufficiently large reaction times.

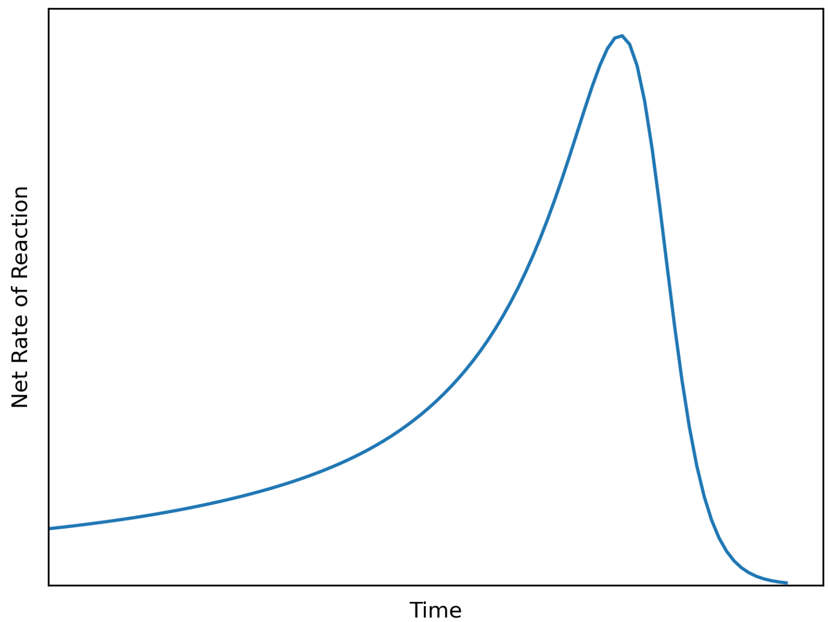

Figure 3. Rate profile during the adiabatic conversion of A to Z under conditions where the temperature dependence of the rate initially predominates over the concentration dependence.

A qualitative analysis is not always conclusive when used to predict the behavior of a system. That was seen here where two possible behaviors were identified depending on whether concentration effects on the rate or temperature effects on the rate predominate initially. In this case, one would expect the heat of reaction to play a significant role in determining which effect predominates. If the heat of reaction was equal to zero, the reaction would become isothermal (no heat released or absorbed) and there would not be a temperature effect. The greater the heat of reaction, then, the more likely that the temperature effect would predominate over the concentration effect.

Even though qualitative analysis may not offer a unique prediction of reactor behavior, it can still be extremely helpful for understanding the actual observed behavior of a reactor or the behavior predicted by a quantitative analysis. For example, if a reaction engineer was studying or modeling an reaction system like that considered here, and the engineer observed concentration and temperature profiles like those shown in Figure 2, the qualitative analysis presented here provides valuable physical insight into why the system performs as it does.