REB, The Course
Class 8 Learning Activity Solution

Consider the reaction, A → Z, which is irreversible, autocatalytic and endothermic. Suppose that reaction occurs isothermally and sketch the concentration of A as a function of reaction time. Assuming the system initially contains only A, describe the shape of the curve noting slope, curvature, inflection points, etc and explain them on a physical basis. Then discuss the differences you would expect if the reaction occurred adiabatically.

Since the reaction occurs isothermally, only the concentrations of A and Z affect the rate. The change in the two concentrations are linked through the stoichiometry; as A decreases, Z increases. At the start of the process the concentration of A will be positive and decreasing while the concentration of Z will be zero and increasing.

After a brief interval of time, the concentration of A will have decreased while that of Z increased. In a typical reaction, these changes would cause the reaction rate to decrease, but here the rate will increase because the reaction is autocatalytic. That means that the concentration of A will initially be decreasing with a concave downward curvature, as sketched in Figure 1.

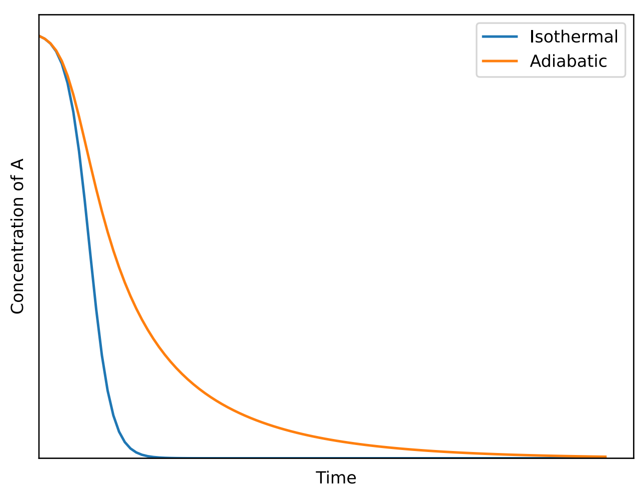

Figure 1. Concentration of A versus reaction time for isothermal and adiabatic operation.

That initial trend cannot continue indefinitely. If it did, the concentration of A would eventually reach negative infinity. Instead, the curve must pass through an inflection point where the curvature changes from concave downward to concave upward. That trend can then continue for as long as required until eventually the concentration of A asymptotically goes to zero as shown in Figure 1. (If the reaction had not been irreversible, it would asymptotically approach its equilibrium value).

The physical reason for the inflection point is easy to understand. The change in the concentration of A is caused by the reaction, and two factors affect the rate of the reaction. In this case, those factors oppose each other. As the concentration of A decreases, the associated rate factor decreases, and as the concentration of Z increases, the associated rate factor increases.

Initially, the rate factor associated with the concentration of Z predominates and the rate increases as the reaction progresses. This clearly cannot continue indefinitely because eventually all of the A will be consumed and the rate must go to zero. Hence, the inflection point occurs when the rate factor associated with the concentration of A and that associated with the concentration of Z become equal. After that time, the factor associated with the concentration of A predominates, and the rate decreases as the reaction continues.

If the reaction occurred adiabatically, there would be a third factor affecting the rate, namely the temperature. Since the reaction is endothermic, if the reaction occurred adiabatically, the temperature would decrease as the reaction progresses. As a consequence, the rate factor associated with the temperature, that is the Arrhenius rate coefficient, would decrease as the reaction progresses.

Since the reaction is autocatalytic, the rate factor associated with the concentration of Z must still predominate initially. However, because the factor associated with the concentration of A and the Arrhenius factor both decrease, the overall increase in the rate will be less than during isothermal operation. This will result in the concentration of A versus time curve shifting to higher temperatures as shown in Figure 1. The extent of the shift will depend on the heat of reaction. As the heat of reaction approaches zero, the adiabatic curve will become equal to the isothermal curve.