REB, The Book
Example 5.5.2 Solution

Suppose the irreversible series reactions given in equations (1) and (2) take place in the liquid phase in an isothermal reactor. Only reagent A is present initially, and the kinetics of both reactions are typical. On a single set of axes, sketch the concentrations of A, D, and U versus reaction time. Describe the shape of each curve noting slopes, curvature, inflection points, etc. Then interpret the results in physical terms.

$$A \rightarrow D \qquad (1)$$

$$D \rightarrow U \qquad (2)$$

Analysis and Discussion

Generally the reaction rate is affected by composition and temperature, but the reactor in this system operates isothermally so temperature is not important. The reactions are irreversible and the kinetics are typical, so only the concentrations of the reactants, A and D, are important in terms of the qualitative analysis, but the assignment narrative requests that the concentration of U be included as well.

It is worth noting that because the rate of reaction (1) depends only on the concentration of A, it will track with it. That is, if at some reaction time the concentration of A is increasing with a concave upward shape, the rate of reaction (1) will also be increasing with a concave upward shape at that point. The same relationship holds between the concentration of D and the rate of reaction (2).

At the start of the reaction, the concentration of A will have a positive value while the concentrations of both D and U will equal zero. The initial rate of reaction (1) will be positive, but because the initial concentration of D is zero, the initial rate of reaction (2) will equal zero. So to summarize, the concentration of A will start with a positive value that is decreasing. The concentration of D will start at zero, and it will be increasing because it is being produced by reaction (1). The concentration of U will start at zero and will not be changing initially because the rate of reaction (2) is zero initially.

After a very brief interval of time the concentration of A will have decreased due to its participation in reaction (1). At the end of that brief interval, the concentration of A will be smaller than its initial value, and since the rate of reaction (2) tracks with the concentration of A, the rate of reaction (1) will be smaller than the its initial rate. Consequently, at the start of the next brief interval of time, the rate of reaction 1 will be smaller than at the start of the first interval, and therefore, the concentration of A will decrease by less during the second interval than it did during the first interval. In other words, the concentration of A will initially decrease with a shape that is concave upward. This trend can continue for as long as required until eventually the concentration of A will asymptotically approach zero as shown in Figure 1.

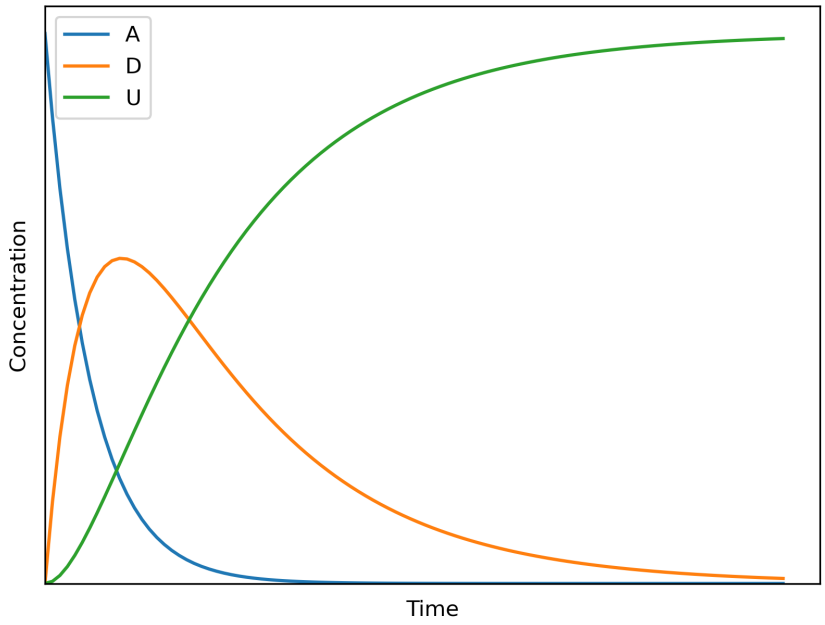

Figure 1. Concentrations of A, D, and U as functions of reaction time.

Since the rate of reaction (1) tracks with the concentration of A, the rate of reaction (1) decreases continuously by smaller and smaller amounts. The concentration of D, and hence the rate of reaction (2) starts at zero. So during the first very brief interval of time, the concentration of D will increase because it is being produced by reaction (1) and not being consumed by reaction (2). At the start of the next brief interval of time,

less D will be generated by reaction (1) due to its decreasing rate, and more will be consumed by reaction (2), due to its increasing rate. The net effect is that the concentration of D will increase during the second time interval, but by less than during the first interval.

In other words, the concentration of D initially will be increasing from zero with a curvature that is concave downward. The concentration of D cannot continue to increase indefinitely because eventually all of the D must be converted to U. Instead, the concentration of D must pass through a maximum where it changes from increasing to decreasing. In addition, it must pass through an inflection point where its shape changes from being concave downward to concave upward. That trend can then continue for as long as required until eventually the concentration of D asymptotically approaches zero as shown in Figure 1.

The physical reason for the maximum in the concentration of D can be understood by considering how the rates vary over time. During the period where the concentration of D is increasing with a concave downward curvature, the rate of reaction (2) is greater than the rate of reaction (1), but the difference is getting smaller and smaller leading to the concave downward curvature. The maximum in the concentration of D occurs at the reaction time where the two rates become equal.

This is consistent with the change in the concentration of U which is only produced by reaction (2). Up to the time where D reaches a maximum. the rate of reaction (2), which tracks the concentration of D, is increasing, so the concentration of U increases by larger and larger amounts. It starts at zero and increases with a concave up curvature up to the time where D reaches a maximum. Beyond the maximum, the rate of reaction (2) is decreasing, so the concentration of U increases by smaller and smaller amounts. That is, at the point where D reaches a maximum and the rates of reactions (1) and (2) become equal, the concentration of U passes through an inflection point. After that, the concentration of U is increasing with a concave downward curvature. That trend can continue for as long as required until eventually the concentration of U asymptotically approaches the initial concentration of A as shown in Figure 1. (It approaches the initial concentration of A due to the one-to-one stoichiometry an irreversibility of the reactions.)

It remains to provide the physical reason for the change in the shape of the curve for the concentration of D from concave down to concave up after the maximum in the D concentration. The reason is more subtle, and cannot be seen directly in Figure 1. The concentrations in Figure 1 correspond to reaction rates that become equal when the concentration of D reaches its maximum value as shown in Figure 2.

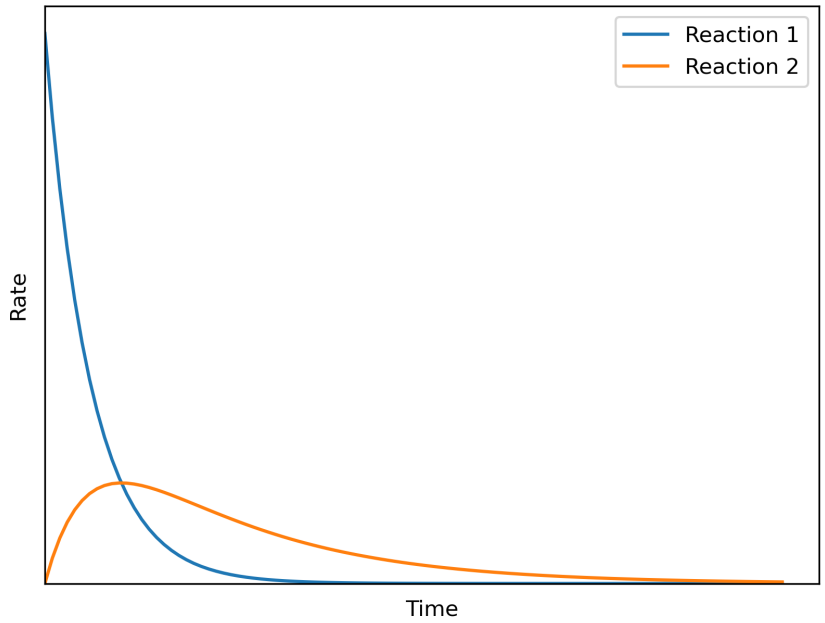

Figure 2. Rates of reactions (1) and (2) as functions of reaction time.

Immediately after the maximum, the curve for the concentration of D remains concave down because the rate of reaction (1) is decreasing faster than the rate of reaction (2). This is evidenced in Figure 2 by the widening gap between the two rates just after the maximum. However as reactant A approaches complete conversion, the rate of reaction (1) decreases more slowly. At some point the two reaction rates decrease at equal rates, corresponding to the inflection point. This is the point in Figure 2 where the gap between the two rates is greatest. After that, the rate of reaction (2) decreases faster than the rate of reaction 1, and the curve becomes concave up.