A First Course on Kinetics and Reaction Engineering

Example 25.1

Problem Purpose

This example illustrates the qualitative analysis of a PFR.

Problem Statement

Reactions (1) and (2) are typical, irreversible, liquid-phase reactions. Reaction (1) is first order and reaction (2) is second order. Suppose each reaction was run separately in an isothermal, steady state plug flow reactor using the same feed mixture, which was chosen so that the initial rates of the two reactions would be equal. Without performing any calculations, sketch the conversion versus space time for the two systems on the same set of axes.

$$A \rightarrow Y \tag{1}$$

$$2\,A \rightarrow Z \tag{2}$$

Problem Solution

These are typical reactions, so the rate will decrease as the reactant concentration decreases (we don't need to consider temperature effects since the reactors are isothermal). They are also irreversible, so we don't expect the product concentration to affect the rate significantly, and we expect the conversion to eventually reach 100% at sufficiently large space times.

Both curves should start at zero conversion at time zero for obvious reasons. If the space time is increased slightly from zero, we expect some reaction to occur in both cases, and as a consequence, the conversion will increase. Thus, both plots should initially have a positive slope. If the space time is increased a little more, we again expect additional conversion. However, the rate during the added space time (i.e. at the end of the PFR) will not be as large as it was during the first increment of space time. The reason for this is that the concentration of the reactant will be lower during the added space time (since some already reacted), and this will cause the rate to be lower. Accordingly, the conversion will increase during the added space time, but not as much as it did initially. Thus, the slope of the conversion versus time plot should decrease as the space time increases. This behavior will continue for all space times, so that by the time the space time is very large, the conversion will have asymptotically approached 100% at which point the slope will be zero. At this point all the reactant will have been consumed, since this is an irreversible reaction. To summarize, both curves start at zero conversion, they increase monotonically with the steepest slope at time zero, the slope steadily decreases and eventually reaches zero at the same time the conversion reaches one.

The only remaining questions are whether the two curves should cross or not, and which curve should be higher initially. We are told that initially the rates are equal, in which case we expect the rate of the second order reaction to decrease more rapidly than the rate of the first order reaction. This is easily predicted by considering the relative rates when the concentration has fallen by 1%. At this point, the first order rate will be 0.99 of the original value, but the second order rate will be (0.99)2, or 0.98 of its original value. Thus, if the rate for the second order system is becoming smaller, relative to the first order system, then the concentration of A will remain higher and the conversion will be lower. Thus, the second order plot should lie below the first order plot, and they should not cross. They should look like the curves below: