Problem 7.2

Problem Purpose

This problem will help you determine whether you have mastered the learning objectives for this unit. It also highlights another aspect of unimolecular reactions.

Problem Statement

The solution to Example 6.1 claimed that even though unimolecular reactions cannot be elementary, "[in most cases] a unimolecular reaction will obey the rate expression predicted by transition state theory, except at very low pressures." Example 7.2 validated this statement for a reaction that was unimolecular in both the forward and reverse directions. This problem considers reaction (1), which is unimolecular in the forward direction, but bimolecular in the reverse direction. According to transition state theory, the rate expression for the rate of reaction (1) with respect to B would be given by equation (2).

$$A \rightleftarrows B + C \tag{1}$$

$$r_{B,1} = k_{1,f}[A] - k_{1,r}[B][C] \tag{2}$$

Suppose that the mechanism for reaction (1) is given by reactions (3) and (4), where an A* represents a collision-activated molecule and M represents a molecule of any type. Note that reaction (4) is an elementary reaction because it can occur just as written (the reactant has sufficient energy to react). Treating the collision-activated molecule as a reactive intermediate, use the Bodenstein steady state approximation to derive a rate expression for reaction (1) and show that at high pressures it is equivalent to the transition state rate expression given in equation (2).

$$A + M \rightleftarrows A^* + M \tag{3}$$

$$A^* \rightleftarrows B + C \tag{4}$$