A First Course on Kinetics and Reaction Engineering
Example 7.2

Problem Purpose

This problem illustrates the use of the Bodenstein steady state approximation to eliminate the concentration of reactive intermediates from a mechanistic rate expression. It also presents some additional information about 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." According to transition state theory, the rate expression for the rate of reaction (1) with respect to B would be given by equation (2).

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

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

Lindemann [1] suggested that the mechanism for reaction (1) is given by reactions (3) through (5), where an asterisk denotes 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 and product each have sufficient energy to react). Treating the collision-activated molecules as reactive intermediates, 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).

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

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

$$B^* + M \rightleftarrows B + M \tag{5}$$

Problem Solution

The rate of reaction (1) with respect to B is equal to the sum of the rates of the mechanistic steps with respect to B. In this particular case, B is only produced in reaction (5), so the rate of reaction (1) with respect to B is just equal to the rate of step (5), as shown in equation (7).

$$r_{B,1} = \sum_{\substack{s=\text{ all} \\ \text{steps}}} \nu_{B,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{\nu_{n,s}} \right) \tag{6}$$

$$r_{B,1} = k_{5,f}[B^*][M] - k_{5,r}[B][M] \tag{7}$$

The concentration of B* appears in equation (7), making it unsuitable as a rate expression. The Bodenstein steady state approximation can be used to eliminate the concentration of B* from equation (7). The Bodenstein steady state approximation can be applied to both reactive intermediates, A* and B*, by setting their net rate of formation equal to zero as expressed in equations (9) and (11), respectively.

$$0 = \sum_{\substack{s=\text{ all} \\ \text{steps}}} v_{A*,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-v_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} \left[n \right]^{v_{n,s}} \right) \tag{8}$$

$$0 = \left(k_{3,f} \left[A \right]\left[M \right] - k_{3,r} \left[A* \right]\left[M \right] \right) - \left(k_{4,f} \left[A* \right] - k_{4,r} \left[B* \right] \right) \tag{9}$$

$$0 = \sum_{\substack{s=\text{ all} \\ \text{steps}}} v_{B*,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} \left[m \right]^{-v_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} \left[n \right]^{v_{n,s}} \right) \tag{10}$$

$$0 = \left(k_{4,f} \left[A* \right] - k_{4,r} \left[B* \right] \right) - \left(k_{5,f} \left[B* \right]\left[M \right] - k_{5,r} \left[B \right]\left[M \right] \right) \tag{11}$$

Equations (9) and (11) can be solved to obtain expressions for the concentrations of A* and B*, equations (12) and (13). This can be done by hand or using symbolic algebra software; only the result is shown here.

$$\left[A* \right] = \frac{k_{3,f} k_{5,f} \left[A \right]\left[M \right] + k_{3,f} k_{4,r} \left[A \right] + k_{4,r} k_{5,r} \left[B \right]}{k_{3,r} k_{5,f} \left[M \right] + k_{3,r} k_{4,r} + k_{4,f} k_{5,f}} \tag{12}$$

$$\left[B* \right] = \frac{k_{3,r} k_{5,r} \left[B \right]\left[M \right] + k_{3,f} k_{4,f} \left[A \right] + k_{4,f} k_{5,r} \left[B \right]}{k_{3,r} k_{5,f} \left[M \right] + k_{3,r} k_{4,r} + k_{4,f} k_{5,f}} \tag{13}$$

Equation (13) can then be substituted into equation (7); after simplification, the rate of reaction (1) with respect to B is obtained, equation (14).

$$r_{B,1} = \frac{k_{3,f} k_{4,f} k_{5,f} \left[A \right]\left[M \right] - k_{3,r} k_{4,r} k_{5,r} \left[B \right]\left[M \right]}{k_{3,r} k_{5,f} \left[M \right] + k_{3,r} k_{4,r} + k_{4,f} k_{5,f}} \tag{14}$$

Notice that [M] is proportional to the total pressure since M can represent any molecule in the system. If the numerator and denominator of equation (14) are both divided by [M], equation (15) results. At sufficiently large values of [M], the second term in the denominator of equation (15) will become negligible compared to the first term in the denominator, as shown in equation (16).

$$r_{B,1} = \frac{k_{3,f} k_{4,f} k_{5,f} \left[A \right] - k_{3,r} k_{4,r} k_{5,r} \left[B \right]}{k_{3,r} k_{5,f} + \left(\dfrac{k_{3,r} k_{4,r} + k_{4,f} k_{5,f}}{\left[M \right]} \right)} \tag{15}$$

$$r_{B,1} = \frac{k_{3,f}k_{4,f}k_{5,f}[A] - k_{3,r}k_{4,r}k_{5,r}[B]}{k_{3,r}k_{5,f}} = \frac{k_{3,f}k_{4,f}k_{5,f}}{k_{3,r}k_{5,f}}[A] - \frac{k_{3,r}k_{4,r}k_{5,r}}{k_{3,r}k_{5,f}}[B] \tag{16}$$

If $k_{1,f}$ and $k_{1,r}$ are defined according to equations (17) and (18), the second form of the rate expression in equation (16) becomes equal to the transition state rate expression given in the problem statement as equation (2), and reproduced here as equation (19).

$$k_{1,f} = \frac{k_{3,f}k_{4,f}k_{5,f}}{k_{3,r}k_{5,f}} \tag{17}$$

$$k_{1,r} = \frac{k_{3,r}k_{4,r}k_{5,r}}{k_{3,r}k_{5,f}} \tag{18}$$

$$r_{B,1} = k_{1,f}[A] - k_{1,r}[B] \tag{19}$$

It is interesting to note that the limiting form of the mechanistic rate expression of equation (14) at very low pressures is given by equation (20). Thus, the warning given in Example 6.2 is valid. When we allow unimolecular reactions as mechanistic steps and use a transition state theory expression to represent their rates, we are limiting the applicability of the resulting mechanistic rate expression to high pressure regimes.

$$\begin{aligned}
r_{B,1} &= \frac{k_{3,f}k_{4,f}k_{5,f}[A][M] - k_{3,r}k_{4,r}k_{5,r}[B][M]}{k_{3,r}k_{5,f}[M] + k_{3,r}k_{4,r} + k_{4,f}k_{5,f}} \\
&= \frac{k_{3,f}k_{4,f}k_{5,f}}{k_{3,r}k_{4,r} + k_{4,f}k_{5,f}}[A][M] - \frac{k_{3,r}k_{4,r}k_{5,r}}{k_{3,r}k_{4,r} + k_{4,f}k_{5,f}}[B][M] \\
&= k'_{1,f}[A][M] - k'_{1,r}[B][M]
\end{aligned} \tag{20}$$

References Cited

1.   Lindemann, F.A., *Discussion on the Radiation Theory of Chemical Action.* Trans. Faraday Soc., 1922. **17**: p. 598.