

# A First Course on Kinetics and Reaction Engineering

## Example 5.5

### Problem Purpose

This problem illustrates the use of transition state theory. Upon solving it, one should gain some new insight into the equivalence of collision theory and transition state theory.

### Problem Statement

At first glance, it appears that simple collision theory and simple transition state theory yield very different expressions for the temperature dependence of the rate coefficient for an elementary reaction. Show that the reason for this is the simplified manner in which molecules are modeled in collision theory by applying transition state theory to the reaction between two point-mass molecules like those used in collision theory and showing that in that case, they predict the same temperature dependence.

### Problem Solution

According to transition state theory, the rate expression for an elementary reaction is given by equation (1). In this problem, we are told to assume the reactants, A and B, are point masses. In keeping with the assumptions of simple collision theory, we will assume that the activated complex is a single entity consisting of the two point masses separated by a small distance (approximately the sum of the collision radii of the reactants). Being point masses, the two reactants have only three degrees of freedom each, and these three degrees of freedom correspond to translational motion in the three coordinate directions. The partition coefficient for three dimensional translational motion is given by equation (2).

$$r_{j,f} = \frac{N_{Av} q_{AB^\ddagger}}{q_A q_B} \left\{ \frac{k_B T}{h} \right\} \exp\left(\frac{-\Delta E_0^0}{k_B T}\right) [A][B] \quad (1)$$

$$q_{trans} = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \quad (2)$$

Because the activated complex consists of two “connected” point masses, it will have six degrees of freedom. Three of the activated complex’s degrees of freedom correspond to translational motion, and the partition function for that three dimensional translational motion is again given by equation (2). For the activated complex, the mass appearing in equation (2) will equal the sum of the two point masses. Because the activated complex is linear (it consists of two separated points), two of its remaining degrees of freedom correspond to rotational motion about two axes that are perpendicular to each other and to the axis formed by the two point masses. The partition function for this two-dimensional rotational motion is given by equation (3), where  $I$  is the moment of inertia of the activated complex. The moment of inertia is a constant that can be calculated from the two point masses and the distance by which they are separated.

$$q_{rot} = \frac{8\pi^2 I k_B T}{h^2} \quad (3)$$

This leaves one degree of freedom that corresponds to vibrational motion. As discussed in the informational reading, one vibrational mode of the activated complex is taken to correspond to motion along the reaction coordinate. In this case, this vibration would involve the centers of mass moving closer and farther apart. The partition function for that degree of freedom is factored out of the total partition function for the activated complex,  $q_{AB^\ddagger}$ , that appears in equation (1). Thus, the three partition functions appearing in equation (1) are given by equations (4) through (6).

$$q_A = q_{trans,A} = \left( \frac{2\pi m_A k_B T}{h^2} \right)^{3/2} \quad (4)$$

$$q_B = q_{trans,B} = \left( \frac{2\pi m_B k_B T}{h^2} \right)^{3/2} \quad (5)$$

$$q_{AB^\ddagger} = q_{trans,AB^\ddagger} q_{rot,AB^\ddagger} = \left( \frac{2\pi (m_A + m_B) k_B T}{h^2} \right)^{3/2} \left( \frac{8\pi^2 I_{AB^\ddagger} k_B T}{h^2} \right) \quad (6)$$

Substitution of equations (4) through (6) into equation (1) and factoring out the temperature from each of the partition functions leads to equation (7) for the rate of an elementary reaction involving two point masses.

$$r_{j,f} = \frac{N_{Av} q_{AB^\ddagger}}{q_A q_B} \left\{ \frac{k_B T}{h} \right\} \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B]$$

$$r_{j,f} = \frac{N_{Av} \left( \frac{2\pi (m_A + m_B) k_B T}{h^2} \right)^{3/2} \left( \frac{8\pi^2 I_{AB^\ddagger} k_B T}{h^2} \right)}{\left( \frac{2\pi m_A k_B T}{h^2} \right)^{3/2} \left( \frac{2\pi m_B k_B T}{h^2} \right)^{3/2}} \left\{ \frac{k_B T}{h} \right\} \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B]$$

$$r_{j,f} = \frac{N_{Av} \left( \frac{2\pi (m_A + m_B) k_B}{h^2} \right)^{3/2} \left( \frac{8\pi^2 I_{AB^\ddagger} k_B}{h^2} \right)}{\left( \frac{2\pi m_A k_B}{h^2} \right)^{3/2} \left( \frac{2\pi m_B k_B}{h^2} \right)^{3/2}} \left\{ \frac{k_B}{h} \right\} \sqrt{T} \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B] \quad (7)$$

The activated complex is taken to be two point masses,  $m_A$  and  $m_B$ , separated by a distance equal to the collision radii of A and B,  $R_A$  and  $R_B$ . For the purpose of determining its moment of inertia, we can locate it on the  $x$ -axis with its center of mass at the origin. In this coordinate system, point mass A is

located as  $x = 0$ , and point mass B is located on the  $x$ -axis at  $x = R_A + R_B$ . In this orientation, the center of mass,  $x_{cm}$ , is found using equation (8). The moment of inertia is then found using equation (9).

Substitution of the  $x$ -coordinates of point mass A (0), point mass B ( $R_A + R_B$ ) and the center of mass (equation (8)) leads to equation (10) for the moment of inertia, where  $\mu$  is the reduced mass.

$$x_{cm} = \frac{m_B}{m_A + m_B} (R_A + R_B) \quad (8)$$

$$I = m_A (x_A - x_{cm})^2 + m_B (x_B - x_{cm})^2 \quad (9)$$

$$I = \frac{m_A m_B (R_A + R_B)^2}{(m_A + m_B)} = \mu (R_A + R_B)^2 \quad (10)$$

Returning to equation (7), substitution of equation (10) for the moment of inertia and collection of like terms leads to equation (11). Simple collision theory predicts the rate expression given in equation (12) (see equation (5.26) in the informational reading).

$$r_{j,f} = \frac{N_{Av} \left( \frac{2\pi(m_A + m_B)k_B}{h^2} \right)^{3/2} \left( \frac{8\pi^2 k_B \mu (R_A + R_B)^2}{h^2} \right)}{\left( \frac{2\pi m_A k_B}{h^2} \right)^{3/2} \left( \frac{2\pi m_B k_B}{h^2} \right)^{3/2}} \left\{ \frac{k_B}{h} \right\} \sqrt{T} \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B]$$

$$r_{j,f} = N_{Av} (2)^{3/2+3-3/2-3/2} \pi^{3/2+2-3/2-3/2} k_B^{3/2+1+1-3/2-3/2} h^{-3-2-1+3+3} \left( \frac{m_A + m_B}{m_A m_B} \right)^{3/2} \mu (R_A + R_B)^2 \sqrt{T} \times \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B]$$

$$r_{j,f} = N_{Av} (2)^{3/2} \pi^{1/2} k_B^{1/2} h^0 (\mu)^{3/2} \mu (R_A + R_B)^2 \sqrt{T} \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B]$$

$$r_{j,f} = N_{Av} \pi (R_A + R_B)^2 \sqrt{\frac{8k_B T}{\pi \mu}} \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B]$$

$$r_{j,f} = N_{Av} \sigma_{AB} \sqrt{\frac{8k_B T}{\pi \mu}} \exp\left( \frac{-\Delta E_0^0}{k_B T} \right) [A][B] \quad (11)$$

$$r_{AB,f} = N_{Av} \sigma_{AB} \sqrt{\frac{8k_B T}{\pi \mu}} \exp\left( \frac{-E_j}{RT} \right) C_A C_B \quad (12)$$

Comparing equations (11) and (12), shows that simple collision theory and transition state theory predict the exact same rate expression for an elementary reaction between two point-mass molecules.