University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 22: Transition State Theory.
Atkins & DePaula: 7.6-7.7

A. Activated Kinetics

- Kinetic rate equations are governed by several principles. The first is the **Law of Mass Action.** It state that for a chemical reaction

$$\nu_A A + \nu_B B \xrightarrow{k_f} P \qquad (22.1)$$

the rate of formation of product i.e. d[P]/dt is dependent of the reaction concentrations:

$$\frac{d[P]}{dt} = k_f [A]^{\nu_A} [B]^{\nu_B} \qquad (22.2)$$

- However, the explicit dependence of stoichiometric coefficients is not general and rigorously only applies to elementary reactions. Deviations may occur for multiple steps involving reaction intermediates.
- **The Principle of Detailed Balance** states the relationship of kinetic constants at equilibrium. For a reversible reaction: $A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$ at equilibrium the forward and reverse reactions are equal:

$$\begin{aligned} rate_{forward} &= rate_{reverse} \\ k_f [A]_{eq} &= k_r [B]_{eq} \qquad (22.3) \\ \therefore K = \frac{k_f}{k_r} &= \frac{[B]_{eq}}{[A]_{eq}} \end{aligned}$$

- Equation 22.3 means the kinetic constants k_f and k_r are not independent. Their ratio is the equilibrium constant.
- In equilibrium thermodynamics the van't Hoff equation gives the temperature dependence of the enthalpy:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (22.4)$$

- Arrhenius proposed an analogous relationship for the temperature dependence of the kinetic constant

$$\frac{d \ln k_f}{dT} = \frac{E_a}{RT^2} \qquad (22.5)$$

- The assumption of the **Arrhenius equation** 22.5 is that the reaction rate is determined by the activation barrier E_a at which point on the reaction coordinate molecules are in a high energy 'activated state" or "transition-state". The diagram below schematizes the activation barrier E_a. A chemical or physical process whose rate follows equation 22.5 is called an activated process.

B. Transition State Theory

- Transition State Theory (TST) or Activated Complex Theory (ACT) is a reaction mechanism originally developed to describe gas phase collision reactions. It has the general reaction scheme:

$$A + B \overset{K^\dagger}{\rightleftharpoons} (AB)^\dagger \xrightarrow{k^\dagger} AB \tag{22.6}$$

where the reactants A and B collide to first form a transition state or activated complex which is designated $(AB)^\dagger$. The idea behind TST is that the transition state is an unstable, short-lived complex. In the case of a simple diatomic collision the transition state $(AB)^\dagger$ consists of the AB pair joined by a very weak bond. The colliding molecules A and B are assumed in "equilibrium" with the transition state where

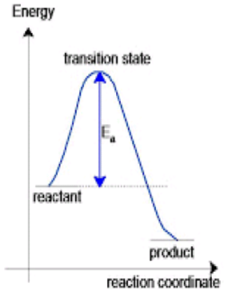

Figure 22.1: Barrier of Activation of Height E_a. The Transition State Complex formed between reactants is at the top of the Barrier

$$K^\dagger = \frac{[AB]^\dagger}{[A][B]} \tag{22.7}$$

- This equilibrium notation however involves the transition state which actually exists at a energy maximum and is thus transitory in nature, as its name implies.
- For the diatomic reaction mechanism the rate is given by

$$rate = k^\dagger\left[AB^\dagger\right] = k^\dagger K^\dagger[A][B] = k_2[A][B] \tag{22.8}$$

  - To evaluate the rate constant k_2, we can apply statistical methods to $K^\dagger$

$$K^\dagger \approx \frac{\frac{q_{AB}^\dagger}{N}}{\frac{q_A}{N}\frac{q_B}{N}} = \frac{q_{AB}^\dagger N}{q_A q_B} \tag{22.9}$$

where the partition functions of A, B, and $AB^\dagger$ are q_A, q_B, $q^\dagger_{AB}$, respectively .

  - The treatment of $q_{AB}^\dagger$ requires some explanation about the properties of the transition complex. It is assumed that when A and B form the transition complex the complex acquires translation, rotational, vibrational and electronic motions, which all must be reflected in the partition function, i.e.

$$q_{AB}^{\dagger} = q_{trans}^{\dagger} q_{rot}^{\dagger} q_{vib}^{\dagger} q_{elec}^{\dagger}$$

$$\frac{\left(2\pi m^{\dagger} k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 I^{\dagger} k_B T}{\sigma h^2} \frac{e^{-h\nu^{\dagger}/2k_B T}}{1-e^{-h\nu^{\dagger}/k_B T}} g_1^{\dagger} e^{D_e^{\dagger}/k_B T}$$

$$= \frac{\left(2\pi m^{\dagger} k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 I^{\dagger} k_B T}{\sigma h^2} \frac{1}{1-e^{-h\nu^{\dagger}/k_B T}} g_1^{\dagger} e^{D_0^{\dagger}/k_B T}$$

where in 22.5 we have used the relationship $D_e^{\dagger} = D_0^{\dagger} + \frac{h\nu^{\dagger}}{2}$ (22.10)

- In 22.5 the mass of the transition state in the translational partition function is just $m^{\dagger} = m_A + m_B$. In the rotational partition function where the reduced mass $\mu = \frac{m_A m_B}{m_A + m_B}$, $I^{\dagger} = \mu\left(R^{\dagger}\right)^2$ is the moment of inertia of the transition complex and $R^{\dagger}$ is the length of the bond that is in the process of forming between A and B. The term $g_1^{\dagger}$ is the degeneracy of the ground electronic state of the transition complex.
- The vibrational motion is treated in the following way. We assume as A and B come together to form the transition complex that translational motion along the reaction coordinate is eventually converted in part to a vibrational motion of the bond also directed along the reaction coordinate. We use the notation

$$K^{\dagger} = \frac{q_{AB,trans}^{\dagger} q_{AB,rot}^{\dagger} q_{AB,vib}^{\dagger}}{q_A q_B} N g_1 e^{D_0^{\dagger}/k_B T} \qquad (22.11)$$

where $q_{AB,vib}^{\dagger} = \frac{1}{1-e^{-h\nu^{\dagger}/k_B T}}$ is a reduced vibrational partition function.

- Now the vibrational of the bond in the transition complex is assumed to occur at a very low frequency such that

$$q_{AB,vib}^{\dagger} = \frac{1}{1-e^{-h\nu^{\dagger}/k_B T}} \approx \frac{1}{1-\left(1-h\nu^{\dagger}/k_B T\right)} = \frac{k_B T}{h\nu^{\dagger}} \qquad (22.12)$$

- In other words the bond vibration is calculated in the high temperature limit where $k_B T \gg h\nu^{\dagger}$. Now we also assume that the transition complex is converted to product AB within a vibrational period so that $k^{\dagger} \approx \nu^{\dagger}$. Using this expression and equation 22.7 we obtain

$$k_2 = k^{\dagger} K^{\dagger} \approx \nu^{\dagger} \frac{q_{AB,trans}^{\dagger} q_{AB,rot}^{\dagger}}{q_A q_B} \frac{k_B T}{h\nu^{\dagger}} N g_1^{\dagger} e^{D_0^{\dagger}/k_B T}$$

$$= \frac{q_{AB,trans}^{\dagger} q_{AB,rot}^{\dagger}}{q_A q_B} \frac{k_B T}{h} N g_1^{\dagger} e^{D_0^{\dagger}/k_B T} \qquad (22.13)$$

- This is called the Eyring equation. To equation 22.13 is added ad hoc a constant $\kappa < 1$. This is called the transmission coefficient and expresses the fact that not all collisions result in the formation of the transition complex. Normally $0.5 < \kappa < 1$, but κ can be quite small for atomic collisions. The final form for the Eyring equation is

$$k_2 \approx \kappa \frac{k_B T}{h} \bar{K}^\dagger N \tag{22.14}$$

where $\bar{K}^\dagger = \frac{q^\dagger_{AB,trans} q^\dagger_{AB,rot}}{q_A q_B} g_1^\dagger e^{D_0^\dagger / k_B T}$ is absent the degree of vibrational freedom treated in the high temperature limit and giving rise to the factor of $\frac{k_B T}{h}$.

- Reaction rates are normally measured as per mole quantities so in equation 22.9 N=N$_A$:

$$k_{2,m} = N_A \kappa \frac{k_B T}{h} \bar{K}^\dagger = \kappa \frac{RT}{h} \bar{K}^\dagger \tag{22.15}$$

B. Examples of Diatomic Transition State Calculations

- For the collision of two atoms we have

$$\begin{aligned}
q^\dagger_{AB,trans} q^\dagger_{AB,rot} g_1^\dagger &= \frac{V\left(2\pi\left(m_A + m_B\right) k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 \mu \left(R^\dagger\right)^2 k_B T}{h^2} g_1^\dagger \\
q_A &= \frac{V\left(2\pi\left(m_A\right) k_B T\right)^{3/2}}{h^3} g_1^A \\
q_B &= \frac{V\left(2\pi\left(m_B\right) k_B T\right)^{3/2}}{h^3} g_1^B
\end{aligned} \tag{22.16}$$

- Then we obtain for the rate constant

$$\begin{aligned}
k_2 = N_A \frac{\kappa k_B T}{h} e^{D_0^\dagger / k_B T} \frac{\left(2\pi\left(m_A + m_B\right) k_B T\right)^{3/2}}{h^3} \frac{8\pi^2 \mu \left(R^\dagger\right)^2 k_B T}{h^2} \times \\
\frac{h^3}{\left(2\pi\left(m_A\right) k_B T\right)^{3/2}} \frac{h^3}{\left(2\pi\left(m_B\right) k_B T\right)^{3/2}} \frac{g_1^\dagger}{g_1^A g_1^B} = N_A \sqrt{\frac{8\pi k_B T}{\mu}} \kappa \left(R^\dagger\right)^2 \frac{g_1^\dagger}{g_1^A g_1^B} e^{D_0^\dagger / k_B T}
\end{aligned} \tag{22.17}$$

- If $D_0^\dagger$ is reported in units of Joules per mole we must write:

$$k_2 = N_A \sqrt{\frac{8\pi k_B T}{\mu}} \kappa \left(R^\dagger\right)^2 \frac{g_1^\dagger}{g_1^A g_1^B} e^{D_0^\dagger / RT} \tag{22.18}$$

C. More Complicated Reactions: Ternary Complexes

- The simplest example of a ternary transition complex is the isotope exchange

$$H_2 + D \rightarrow HD + H \tag{22.19}$$

- The transition complex has linear form $H \cdots H \cdots D$ where the bonds lie along the reaction coordinate. The rate constant has the form:

$$k_2 \approx \kappa \frac{\overline{q}^{\dagger}_{HHD}}{q_D q_{H_2}} \frac{k_B T}{h} e^{\Delta D_0^{\dagger}/k_B T} = \kappa \frac{k_B T}{h} \overline{K}^{\dagger} \tag{22.20}$$

where $\Delta D_0^{\dagger} = D_0^{\dagger} - D_0^{H_2}$. The partition functions for q_D and q_{H2} are obtained as usual for atomic and diatomic species. The transition complex partition function $\overline{q}^{\dagger}_{HHD}$ is treated as follows. The transition complex is linear so it has a single moment of inertia and rotations are calculated by the same procedure used for a linear triatomic like CO_2 except that σ=1 for HHD.

- The vibrational partition function is treated as follows. Note for a linear triatomic there are four vibrational modes in the partition function corresponding to symmetric and asymmetric stretches and two equivalent bending modes

$$\begin{array}{ccc} \underset{\leftarrow}{H}\cdots\underset{\rightarrow}{H}\cdots\underset{\leftarrow}{D} & \underset{\leftarrow}{H}\cdots H\cdots\underset{\rightarrow}{D} & \underset{\downarrow}{H}\cdots\overset{\uparrow}{H}\cdots\underset{\downarrow}{D} \\ asymmetric & symmetric & Doubly\ \deg enerate \\ stretch & stretch & bend \end{array}$$

- The asymmetric stretch contributes to the reaction coordinate, is therefore treated in the high temperature limit and yields the k_BT/h term in the Eyring equation. The other three vibrational modes remain in the transition complex partition function

$$\overline{q}^{\dagger}_{HHD} = \frac{\left(2\pi\left(2m_H + m_D\right)k_B T\right)^{3/2}}{h^3} \frac{2I_{HHD}k_B T}{\hbar^2} g_1^{\dagger} \prod_{j=1}^{3} \frac{1}{1-e^{-h\nu_j/k_B T}} \tag{22.21}$$

.C. Gibbs Energy of Activation

- Returning to the general expression for the molar reaction rate $k_{2,m} = N_A k_2 = \kappa \frac{RT}{h} \overline{K}^{\dagger}$, we define formally the Gibbs energy of activation

$$\Delta G^{\dagger} = -RT \ln \overline{K}^{\dagger} \tag{22.22}$$

- Using equation 28.15 we now define the kinetic constant as:

$$k_{2,m} = \kappa \frac{RT}{h} e^{-\Delta G^{\dagger}/RT} \tag{22.23}$$

- Using the corresponding relationship between the Gibbs energy, enthalpy and entropy... $\Delta G^{\dagger} = \Delta H^{\dagger} - T\Delta S^{\dagger}$ we further obtain:

$$k_{2,m} = \kappa \frac{RT}{h} e^{-\Delta G^{\dagger}/RT} = \kappa \frac{RT}{h} e^{\Delta S^{\dagger}/R} e^{-\Delta H^{\dagger}/RT} \tag{22.24}$$

- Note equation 22.24 sets an upper limit for the activated reaction rate . For $\Delta G^{\dagger} = 0$ and $\kappa = 1$ at T=300K:

$$k_2^{\max} \approx \frac{k_B T}{h} = \frac{\left(1.38\times10^{-23} JK^{-1}\right)\left(300K\right)}{6.62\times10^{-34} Js} = 6.25\times10^{12} s^{-1} \tag{22.25}$$