XIII. Chemical Kinetics

\[ \text{ClNO}_2 (g) + \text{NO} (g) \rightarrow \text{NO}_2 (g) + \text{ClNO} (g) \quad \Delta H^\circ = -17.3 \text{ kJ}; \Delta G^\circ = -23.2 \text{ kJ} \]

How fast does the above reaction proceed spontaneously to the right? To answer this question the rate of the reaction (the change in concentration of a reactant or product per unit time) must be measured. The study of the rates and mechanisms of chemical reactions is called chemical kinetics.

In chemical kinetics reactions are classified into two groups.

- **Heterogeneous reactions** are reactions that occur at the interface (boundary) between two phases.
  
  **Example:** \( \text{C (s)} + \text{O}_2 (g) \rightarrow \text{CO}_2 (g) \)
  
  This reaction occurs at the surface of the carbon.

- **Homogeneous reactions** are reactions that occur in a single phase.
  
  **Example:** \( 2 \text{ NO} (g) + \text{O}_2 (g) \rightarrow 2 \text{ NO}_2 (g) \)
  
  This reaction occurs in the vapor phase.

A) Factors Affecting Reaction Rates at Constant Temperature

1) Concentration of the Reactants in Homogeneous Reactions

a) Rate Law

At constant temperature the rate of a homogeneous reaction is proportional to concentrations of the reactants raised to some power.

Consider the general reaction

\[ a \text{ A} + b \text{ B} \rightarrow c \text{ C} \]

rate \( \propto [\text{A}]^a[\text{B}]^b \)

Replace \( \propto \) with = and the proportionality constant \( k \).
There is no necessary relationship between the exponents \((x \text{ and } y)\) in the experimental rate law and the stoichiometric coefficients \((a \text{ and } b)\) in the balanced chemical equation for the overall reaction.

For the general reaction

\[
\text{a A} + \text{b B} \rightarrow \text{c C}
\]

The term rate is defined

\[
\text{rate of formation of C} = \frac{d[C]}{dt}
\]

\[
\text{rate of consumption of A} = -\frac{d[A]}{dt}
\]

The term rate is defined

\[
\text{rate} = \left(\frac{1}{b}\right) \frac{-d[B]}{dt} = \left(\frac{1}{a}\right) \frac{-d[A]}{dt} = \left(\frac{1}{c}\right) \frac{d[C]}{dt} = k[A]^x[B]^y
\]

\(\sim\) stoichiometric coefficients \(\sim\)

The rate of formation of C is related to the rate of consumption of A by the mole ratio.
\[
\frac{d[C]}{dt} = \left(\frac{c}{a}\right) \frac{-d[A]}{dt} = c\cdot k\cdot [A]^x\cdot [B]^y = k'\cdot [A]^x\cdot [B]^y
\]

where \( k' = ck \) and \( \frac{c}{a} \) is the mole ratio

**Example:** Calculate the rate of formation of HI

\[H_2 \ (g) + I_2 \ (g) \rightarrow 2 \ HI \ (g)\]

if the experimental rate law is

\[\text{rate} = \frac{-d[I_2]}{dt} = k[H_2][I_2]\]

\[\frac{d[HI]}{dt} = \left(\frac{2}{1}\right)\frac{-d[I_2]}{dt} = 2k[H_2][I_2]\]

b) **Order of the Reaction**

The order of a reaction is the sum of the exponents of the concentration terms in the rate law.

**Example:** Determine the order of the reaction

\[2 \ NO \ (g) + O_2 \ (g) \rightarrow 2 \ NO_2 \ (g)\]

if the experimental rate is

\[\frac{-d[NO]}{dt} = k[NO]^2[O_2]\]

The reaction is third order overall, second order in NO, and first order in O₂.

c) **Method of Initial Reaction Rates**

In this method the *initial rate* of the reaction is measured at or near time zero where the concentrations of all the reactants are known.

**Example:** Consider the following gaseous reaction
\[ \text{CINO}_2 (g) + \text{NO} (g) \rightarrow \text{NO}_2 (g) + \text{CINO} (g) \]

**Plot of Molarity of CINO\textsubscript{2} versus Time at 27°C**

Use the initial rate data in the following table to determine the rate law and rate constant for the reaction.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>[CINO\textsubscript{2}] (mo/L)</th>
<th>[NO] (mo/L)</th>
<th>(- \frac{d[CINO_2]}{dt}) (mo/L/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.3 \times 10^{-5}</td>
<td>5.3 \times 10^{-5}</td>
<td>2.2 \times 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>2.6 \times 10^{-5}</td>
<td>5.3 \times 10^{-5}</td>
<td>1.1 \times 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>5.3 \times 10^{-5}</td>
<td>1.1 \times 10^{-4}</td>
<td>4.4 \times 10^{-5}</td>
</tr>
</tbody>
</table>

\[
\text{rate} = -\frac{d[CINO_2]}{dt} = k[CINO_2]^x[NO]^y
\]

To determine the exponent \(x\) take the ratio of the rate data for experiment #2 to the data for experiment #1.
\[
\frac{rate_2}{rate_1} = \frac{k[ClNO_2]^x [NO]^y}{k[ClNO_2]^x_1 [NO]^y_1}
\]

\[
\frac{1.1 \times 10^{-5} \text{ M sec}}{2.2 \times 10^{-5} \text{ M sec}} = \frac{k(2.6 \times 10^{-5} M)^x (5.3 \times 10^{-5} M)^y}{k(5.3 \times 10^{-5} M)^x (5.3 \times 10^{-5} M)^y}
\]

Take the log of both sides of the equation.

\[
\log\left(\frac{1.1 \times 10^{-5} \text{ M sec}}{2.2 \times 10^{-5} \text{ M sec}}\right) = \log\left(\frac{k}{k}\right) + x\log\left(\frac{2.6 \times 10^{-5} M}{5.3 \times 10^{-5} M}\right) + y\log\left(\frac{5.3 \times 10^{-5} M}{5.3 \times 10^{-5} M}\right)
\]

\[
\log (0.50) = 0 + x\log (0.49) + 0
\]

\[
x = \frac{-0.30}{-0.31} = 0.97 = 1
\]

To determine the exponent \(y\) take the ratio of the rate data for experiment #3 to the data for experiment #1.

\[
\frac{4.4 \times 10^{-5} \text{ M sec}}{2.2 \times 10^{-5} \text{ M sec}} = \frac{k(5.3 \times 10^{-5} M)(1.1 \times 10^{-4} M)^y}{k(5.3 \times 10^{-5} M)(5.3 \times 10^{-5} M)^y}
\]

Take the log of both sides of the equation.

\[
\log\left(\frac{4.4 \times 10^{-5} \text{ M sec}}{2.2 \times 10^{-5} \text{ M sec}}\right) = \log\left(\frac{k}{k}\right) + \log\left(\frac{5.3 \times 10^{-5} M}{5.3 \times 10^{-5} M}\right) + y\log\left(\frac{1.1 \times 10^{-4} M}{5.3 \times 10^{-5} M}\right)
\]

\[
\log (2.0) = 0 + 0 + y\log (2.1)
\]

\[
y = \frac{0.30}{0.32} = 0.94 = 1
\]
Experimental rate law: \[ -\frac{d[ClNO_2]}{dt} = k[ClNO_2][NO] \]

Rearranging the rate law and substituting the data from experiment #1 into the resulting expression gives

\[ k = \frac{-\frac{d[ClNO_2]}{dt}}{[ClNO_2][NO]} = \frac{2.2 \cdot 10^{-5} \frac{M}{sec}}{(5.3 \cdot 10^{-5} M)(5.3 \cdot 10^{-5} M)} \]

\[ k = 7.8 \cdot 10^3 \frac{L}{mol \cdot sec} \]

2) Surface Area of the Interface in Heterogeneous Reactions

The rate of a heterogeneous reaction is proportional to area of the interface. The surface area of a solid increases as the particle size of the solid decreases. In reactions such as

\[ C(s) + O_2(g) \rightarrow CO_2(g) \]

the rate increases as the particle size of the solid, the carbon in the above example, decreases.

B) Theories of Reaction Rates and Temperature Dependency of k

1) Collision Theory

Consider the binuclear reaction

\[ A(g) + B(g) \rightarrow C(g) + D(g) \]

To form the products C and D, molecules A and B must come together, i.e. collide. The total number of collisions per liter per second between 1 mole of A molecules and 1 mole of B molecules at 25°C is

\[ \frac{Total \ Number \ of \ Collisions}{L \cdot sec} \approx 10^{34} (L \cdot sec)^{-1} \]

If a collision were the only requirement for the formation of products, then all gaseous reactions would proceed at the same explosive rate. Since all gaseous reactions do not occur at same rate at 25°C, other criteria in addition to the collision of the reacting molecules A and B must be satisfied in order to achieve product formation.
Many reactions involve the breaking of bonds or the alteration of molecular geometries. These changes require energy. Consequently if the collision is to result in products, the colliding molecules must achieve a critical energy called the energy of activation, $E_a$. Thus the rate of the reaction will depend on the total number of collision per liter per second and the fraction of those collision in which the combined energy of the colliding molecules is equal to or greater than $E_a$.

\[
\text{rate} = \frac{\text{Total number of collisions per liter -sec}}{\text{Fraction of collision with energy} \geq E_a}
\]

It is the kinetic energy of translation that molecules use to achieve the activation energy $E_a$.

**Distribution of Translational Energies of Gaseous Molecules**

Consider the following cases at 298 K. If $E_a$ for the reaction is 240 J, then collisions between A and B molecules with $KE_T$, kinetic energy of translation, equal to or greater than 120 J will result in products. Since the percentage of molecule with $KE_T \geq 120$ J is large (see the diagram above), the number of collisions per liter per second that will result
in products is large and the rate of the reaction will be very fast.

If $E_a$ for the reaction is 24 kJ, then collisions between A and B molecules with $KE_T$ equal to or greater than 12 kJ will result in products. Since the percentage of molecules with $KE_T \geq 12$ kJ is very small (see diagram above) at 25°C, the number of collisions per liter per second that will result in products is very small and the rate of the reaction will be very slow.

What effect will an increase in temperature have on the rate of the reaction? If $E_a$ for the reaction is 24 kJ and the temperature is increased from 298 to 600 K, then the percentage of molecules with $KE_T \geq 12$ kJ will increase, i.e. the percentage of molecules with $KE_T \geq 12$ kJ is larger at 600 K than at 298 K (see diagram above). An increase in the percentage of molecules with $KE_T \geq 12$ kJ will result in an increase in the reaction rate.

The following equation exhibits the dependency of the rate on $E_a$ and $T$ outlined above.

\[
\text{rate} = \frac{\text{Total number of collisions}}{\text{per sec}} \times \exp\left(-\frac{E_a}{RT}\right)
\]

The rate of the reaction increases as the temperature increases and/or the energy of activation decreases.

Not all collisions with energy $\geq E_a$ result in products. In addition to a combined energy $\geq E_a$ the colliding molecules must also approach in the correct spatial orientation for bond forming and breaking.

**Example:** $H_2 + I_2 \rightarrow 2 HI$

\[
H_2 + I_2 \quad \rightarrow \quad H \quad \rightarrow \quad H \quad \rightarrow \quad \text{no reaction}
\]

\[
H_2 + I_2 \quad \rightarrow \quad H \quad \rightarrow \quad I \quad \rightarrow \quad 2 HI
\]
If the rate is expressed as

\[ \text{rate} = k N^*_A N^*_B \]

where \( N^*_A \) and \( N^*_B \) are the number of molecules of A and B in 1 liter, then \( k \) is

\[ k = q \left[ \frac{\text{Total number of collisions}}{\text{liter-sec}} \right] \left[ \exp \left( -\frac{E_a}{RT} \right) \right] \]

The preexponential term is constant over a short temperature range and is represented by \( A \).

\[ k = A \left[ \exp \left( -\frac{E_a}{RT} \right) \right] \quad (1) \]

Eq 1 is called the \textit{Arrhenius equation}. If we take the natural logarithm of both sides of eq 1, then the Arrhenius equation has the form

\[ \ln(k) = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T} \right) + \ln(A) \]

The plot of \( \ln(k) \) versus \( 1/T \) will give a straight line with a slope of \(-E_a/R\).

\textbf{Example:} \( \text{ClNO}_2 \) (g) + NO (g) \( \rightarrow \) \( \text{NO}_2 \) (g) + ClNO (g)
Note: The rate constants at temperatures $T_1$ and $T_2$ are related by the equation

$$\ln(k_2) = \left( \frac{E_a}{R} \right) \frac{T_2 - T_1}{T_2 T_1} + \ln(k_1)$$

2) Activated Complex Theory  

Henry Eyring

The reacting molecules must achieve a specific configuration called the *activated complex* in order for products to form.

As an illustration of an activated complex consider the addition of dichlorocarbene to ethylene to form 1,1-dichlorocyclopropane.  (Moss, R. A. *Acc. Chem. Res.* 1980, 13, 58)

$$Cl_2C + H_2CCH_2 \rightarrow H_2CC(Cl_2)CH_2$$
The enthalpy diagram illustrates the relative enthalpies of the reactants, $H_r$; the activated complex, $H_a$; and the product, $H_p$. The bond lengths, angles, and enthalpies in the diagram are theoretical values that were obtain from molecular orbital calculations with the aid of the PC Spartan plus package.

As the dichlorocarbene approaches the ethylene molecule from above and forms the activated complex, the carbon-carbon bond in the ethylene lengthens and the carbon-carbon bonds between the dichlorocarbene and ethylene begin to develop.

The difference in the enthalpies of the reactants and activated complex is called the enthalpy of activation.
**Enthalpy of Activation:** $\Delta H^\ddagger = H_i - H_f$

For reactions in solution the enthalpy of activation is related to the activation energy by

$$E_a = \Delta H^\ddagger + RT$$

In this theory the rate constant depends on the free energy of activation.

$$k = (2.08 \times 10^{10} \text{ M}^{-1} \text{sec}^{-1})(T) \left[ \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \right]$$

where

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

K. Fukui: “A majority of chemical reactions should take place at the position and in the direction of maximum overlap of the highest occupied molecular orbital (HOMO) on one reacting species with the lowest unoccupied molecular orbital (LUMO) on the other reacting species.” (Fukui, K, Acc. Chem. Res. 1971, 4, 57)

Boundary Surfaces of the LUMO on the Dichlorocarbene, HOMO on the Ethylene, and the MO Resulting from the Overlap of the LUMO and HOMO in the Activated Complex

**LUMO (2p,) on the Dichlorocarbene**

**HOMO (π MO) on the Ethylene**

**Resulting MO on Activated Complex**
As the dichlorocarbene approaches the ethylene and forms the activated complex, the empty LUMO (mostly the 2p AO on the carbon) on the dichlorocarbene overlaps with the filled HOMO (π MO) on the ethylene molecule and electron density flows from the ethylene to the dichlorocarbene. The flow of electron density away from the ethylene weakens the ethylene π bond and initiates the development of C-C bonds between the dichlorocarbene and the ethylene.

C) Multistep Reactions

Many reactions occur in a sequence of elementary reactions or steps.

**Example:** \(2 \text{Br}^- \text{(aq)} + \text{H}_2\text{O}_2 \text{(aq)} + 2 \text{H}^+ \text{(aq)} \rightarrow \text{Br}_2 \text{(aq)} + 2 \text{H}_2\text{O} \text{(aq)}\)

\[
1^\text{st} \text{Step: } \text{H}^+ + \text{Br}^- + \text{H}_2\text{O}_2 \xrightarrow{k_1 \text{slow}} \text{HOBr} + \text{H}_2\text{O} \quad \text{elementary reaction, slow, rate - determining, trimolecular}
\]

\[
2^\text{nd} \text{Step: } \text{H}^+ + \text{Br}^- + \text{HOBr} \xrightarrow{k_2 \text{fast}} \text{Br}_2 + \text{H}_2\text{O} \quad \text{elementary reaction, fast, trimolecular}
\]

\[
\text{Overall: } 2 \text{H}^+ + 2 \text{Br}^- + \text{H}_2\text{O}_2 \rightarrow \text{Br}_2 + 2 \text{H}_2\text{O}
\]

One step in the sequence is the slower or slowest step (first step in the example above). This step determines the rate of the overall reaction and is called the *rate-determining* or rate-limiting step. The rate-determining step is the elementary reaction in the sequence of steps with the largest energy of activation, \(E_a\).

The HOBr in the sequence above is called an *intermediate*. An intermediate is a species that is formed in one step (elementary reaction) and consumed in another, i.e. it is neither a reactant nor a product.

The number of species that come together to form the activated complex in an elementary reaction is called the *molecularity* of the reaction. Both steps in the example above are *trimolecular*, i.e. three species come together to form the activated complex. Reactions in which two species combine to form the activated complex are said to be *bimolecular*. When the activated complex forms from one reactant, the elementary reaction is said to be *unimolecular*.

D) Reaction Mechanisms

A *reaction mechanism* is the sequence of steps that leads to the overall reaction. The two steps in the example above constitute the reaction mechanism for the formation of bromine.

The experimental rate law contains information concerning the nature of all the steps preceding and including the rate-determining step. If the exponents in the experimental rate law are NOT
equal to the stoichiometric coefficients in the balanced chemical equation for the OVERALL reaction, then the reaction will occur in a sequence of steps.

To obtain a possible mechanism for a chemical reaction

**Step #1:** Write a sequence of steps that add to give the overall reaction and identify the rate-determining step.

**Step #2:** Derive a rate law for the proposed mechanism. Write down the rate law for the rate-determining step. If the rate law contains concentration terms for intermediates, relate these concentrations terms to the concentrations of the reactants. Note: Exponents in the rate law for an ELEMENTARY reaction are equal to the stoichoimetric coefficients in the balanced chemical equation for the ELEMENTARY reaction.

**Step #3:** Compare the derived and experimental rate laws. If the two rate laws are identical, then the mechanism is possible provided that it is consistent with our knowledge of chemistry.

**Example:** For the chemical reaction

\[ 2 \text{N}_2\text{O}_5 \rightarrow 2 \text{N}_2\text{O}_4 + \text{O}_2 \]

the experimental rate law is

\[ \frac{d[\text{N}_2\text{O}_4]}{dt} = k_{\text{obs}}[\text{N}_2\text{O}_5] \]  

(1)

Is the following mechanism possible?

\[ \text{N}_2\text{O}_5 \overset{K}{\rightleftharpoons} \text{NO}_2 + \text{NO}_3 \quad \text{fast, equilibrium} \]

\[ \text{NO}_2 + \text{NO}_3 \rightarrow_{k_1} \text{NO} + 1/2 \text{O}_2 + \text{NO}_3 \quad \text{slow} \]

\[ \text{NO} + \text{NO}_3 \rightarrow_{k_2} \text{N}_2\text{O}_4 \quad \text{fast} \]

**Step #1:** Given above. The second step is the rate-determining step.

**Step #2:**

\[ \frac{d[\text{N}_2\text{O}_4]}{dt} = \text{rate of rate-determining step} = k_1[\text{NO}_2][\text{NO}_3] \]  

(2)

The concentrations [NO₂] and [NO₃] are related to the concentration of the reactant [N₂O₅] through the equilibrium in the first step.
Substituting eq 3 into eq 2 gives

\[
\frac{d[N_2O_4]}{dt} = k_1K[N_2O_5] \quad (4) \quad (\text{derived rate law})
\]

Step #3: A comparison of eqs 1 and 4 reveals that both the experimental and derived rate law are first order in \(N_2O_5\) and thus identical.

\[
k_{\text{obs}} = k_1K
\]

Thus, the proposed reaction mechanism is possible.