Chapter 14
Chemical Kinetics

Review

- **Chemical kinetics:** the area of chemistry concerned with the speeds or rates of reactions.
- **Reaction rate:** the speed at which a chemical reaction occurs / the change in the concentration of reactants or products per unit of time.
- **The collision model:** molecules must collide to react, the greater the number of collisions per second, the greater the reaction rate.
- **Factors that affect reaction rate:** the greater the frequency of collisions, the higher the reaction rate.
  1) Physical state of the reactant;
  2) Reactant concentration;
  3) Reaction temperature;
  4) The presence of a catalyst;
- **Instantaneous rate:** the rate at a particular instant during the reaction, it is determined from the slope of the curve at a particular point in time.
- **Reaction rates and stoichiometry:**

$$aA + bB \rightarrow cC + Dd$$

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

- **Rate law:** the equation shows how the rate depends on reactant concentrations.

$$aA + bB \rightarrow cC + Dd$$

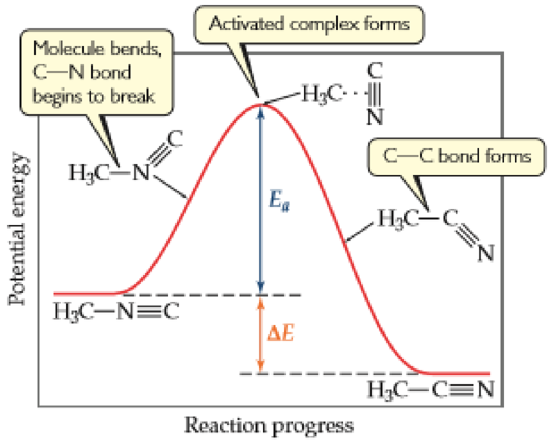
$$\text{rate} = k[A]^m[B]^n$$

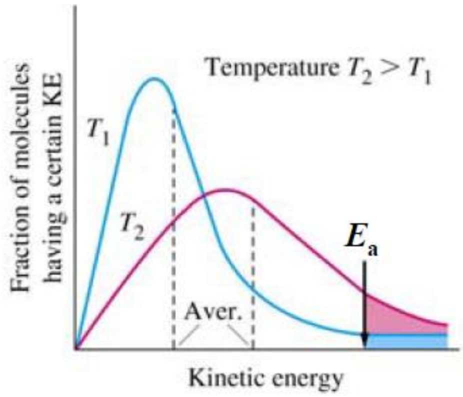
  1) k is the rate constant, the magnitude of k is affected by *temperature* and by the *presence of a catalyst*, the unit of rate constant depend on the overall reaction order of the rate law.
  2) m and n is the reaction order.
  3) For any reaction, the rate law must be determined experimentally.
  4) A large value of k ($\sim 10^9$ or higher) means a fast reaction and a small value of k (10 or lower) means a slow reaction.

- **Overall reaction order:** the sum of the orders with respect to each reactant represented in the rate law.
- **First-order reaction:** rate depends on the concentration of a single reactant raised to the first power.
- **Second-order reaction:** rate depends either on a reactant concentration raised to the second power or on the concentrations of two reactants each raised to the first power.
- **Zero-order reaction:** rate of disappearance of A is independent of [A].
- **Half-life ($t_{1/2}$):** the time required for the concentration of a reactant to reach half its initial value.
- **Summary:**

Reaction order	Differential rate law	Integrated rate law	Half-life ($t_{1/2}$)
0	$-\frac{d[A]}{dt} = k$	$[A] = [A]_0 - kt$	$\frac{[A]_0}{2k}$
1	$-\frac{d[A]}{dt} = k[A]$	$\ln[A] = \ln[A]_0 - kt$	$\frac{\ln 2}{k}$
2	$-\frac{d[A]}{dt} = k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{k[A]_0}$
3	$-\frac{d[A]}{dt} = k[A]^3$	$\frac{1}{[A]^2} = \frac{1}{[A]_0^2} + 2kt$	$\frac{3}{2k[A]_0^2}$

- **Activation energy (E_a)**
  1) The minimum energy required to initiate a chemical reaction.
  2) The difference between the energy of the starting molecule and the highest energy along the reaction pathway.
  3) The rate depends on the magnitude of E_a, generally, the speed of reaction would increase with the decrease of the value of E_a.
- **Activated complex (transition state)**: the molecule having the arrangement of atoms shown at the top of the barrier.





- **The Arrhenius equation:**

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$\ln k_2 - \ln k_1 = \left(-\frac{E_a}{RT_2} + \ln A\right) - \left(-\frac{E_a}{RT_1} + \ln A\right)$$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 \cdot T_2}\right)$$

k: rate constant;
E_a: activation energy;
R: gas constant;
T: absolute temperature;
A: frequency factor, related to the frequency of effective collision;

- **Reaction mechanism:** the steps by which a reaction occurs.
  1) **Elementary reaction:** a chemical reaction in which one or more chemical species react directly to form products in a single reaction step and with a single transition state.
     $CO+NO_2=CO_2+NO$
     rate=k[CO][NO_2]
  2) Multistep mechanism: the reaction appears to proceed in a sequence of elementary reactions.
     $H_2+Br_2=2HBr$
     rate=k[H_2][Br_2]$^{1/2}$
     ① $Br_2 \rightleftharpoons 2Br$ (fast)
     ② $Br+H_2 \rightarrow HBr+H$ (slow)
     ③ $H+Br_2 \rightarrow HBr+Br$ (fast)
- **Molecularity:** the number of molecules that participate as reactants in an elementary reaction.

- **Intermediate:** the substance that formed in one elementary reaction and consumed in the next.
- **Rate Laws:**

  1） The rate law for *elementary reaction* is based directly on its molecularity.

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	A $\longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	A + A $\longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	A + B $\longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	A + A + A $\longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	A + A + B $\longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	A + B + C $\longrightarrow$ products	Rate $= k[A][B][C]$

  2） The slowest step (rate-determining step/rate-limiting step) in a *multistep reaction* determines the overall rate.

- **Catalyst**: a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself, it lowers the overall activation energy for a chemical reaction.
  1) **Homogeneous catalyst**: a catalyst that is present in the same phase as the reactants in a reaction mixture;
  2) **Heterogeneous catalyst**: a catalyst that exists in a phase different from the phase of the reactant molecules, usually as a solid in contact with either gaseous reactants or reactants in a liquid solution.
  3) **Enzyme:** a large number of marvelously efficient biological catalysts.
- **Active site:** the reaction any given enzyme catalyzes takes place at a specific location in the enzyme.
- **Substrate:** the substances that react at this site.
- **Lock-and-key model:** the substrate is pictured as fitting neatly into the active site, much like a key fits into a lock.
- **Enzyme–substrate complex:** the combination of enzyme and substrate.
- **Enzyme inhibitor**: the activity of an enzyme is destroyed if some molecule other than the substrate specific to that enzyme binds to the active site and blocks entry of the substrate.