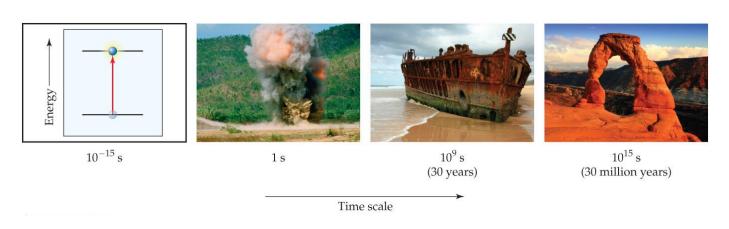# Chapter 14

Chemical Kinetics

By Zhen-Yu Wu

Chemical
Kinetics

Chemical Kinetics

- In chemical kinetics, we study **the rate** (or speed) at which a chemical process occurs.

- Besides information about the speed at which reactions occur, kinetics also sheds light on the **reaction mechanism**, a molecular-level view of the path from reactants to products.

10^{-15} s   1 s 10^9 s (30 years) 10^{15} s (30 million years)

Time scale

Chemical Kinetics

The research object of chemical kinetics

化学动力学研究化学反应的速率和反应的机理以及温度、压力、催化剂、溶剂和光照等外界因素对反应速率的影响，把热力学的反应可能性变为现实性。

例如：

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3(g)$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l)$$

动力学认为：

需一定的T（773k），
P（3×10^7Pa）和催化剂

点火（10^{-6}s）;加温1073K爆炸;
用钯为催化剂常温瞬时完成;
常温无催化剂需10^{25}年

Chemical
Kinetics

1. 化学动力学的任务和目的

Mission： 化学动力学是研究化学反应速率的科学。其基本任务是研究各种因素（如反应系统中各物质的浓度、温度、催化剂、光、介质……）对反应速率的影响，揭示化学反应如何进行的机理；研究物质的结构与反应系性能的关系。

Aim： 通过化学动力学的研究，可以知道如何控制反应条件以改变反应速率。**使反应按人们所希望的速率进行，并得到人们所希望得到的产物。**

如工业上的许多反应，我们可以通过控制反应条件以提高反应速率从而达到提高产率的目的；而对另一些反应，我们则希望降低其反应速率，如金属的腐蚀、食品变质、塑料老化、人体衰老等过程。

Chemical
Kinetics

The relationship between chemical kinetics and chemical thermodynamics

动力学和热力学的关系是相辅相成的。

经热力学研究认为是可能的，但实际进行时反应速率太小，则可以通过动力学研究，降低其反应阻力，缩短达到平衡的时间。

经热力学研究认为是不可能进行的反应，则没有必要再去研究如何提高反应速率的问题了。过程的可能性与条件有关，有时改变条件可使原条件下热力学上不可能的过程成为可能。

Chemical
Kinetics

Reaction Rate

- **Rate** is a change in concentration over a time period: $\Delta[\;]/\Delta t$.

- Δ means "change in."

- [ ] means molar concentration.

- t represents time.

- Types of rate measured:

➢average rate

➢instantaneous rate

➢initial rate

➢……

Chemical
Kinetics

Following Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Table 14.1 Rate Data for Reaction of C_4H_9Cl with Water

Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

➤ Rate of a reaction is measured using the change in concentration of a reactant or a product over time.

➤ In this example, $[C_4H_9Cl]$ is followed.

Chemical Kinetics

Following Reaction Rates

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Table 14.1 Rate Data for Reaction of C_4H_9Cl with Water

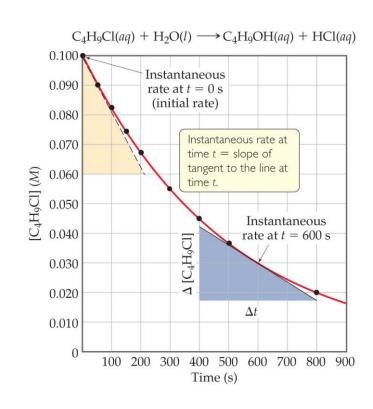| Time, t (s)	$[C_4H_9Cl]$ (M)		Average Rate (M/s)
0.0	0.1000		1.9×10^{-4}
50.0	0.0905		1.7×10^{-4}
100.0	0.0820		1.6×10^{-4}
150.0	0.0741		1.4×10^{-4}
200.0	0.0671		1.22×10^{-4}
300.0	0.0549		1.01×10^{-4}
400.0	0.0448		0.80×10^{-4}
500.0	0.0368		0.560×10^{-4}
800.0	0.0200		
10,000	0		

➤ The average rate is calculated by the –(change in $[C_4H_9Cl]$) ÷ (change in time).

➤ The table shows the average rate for a variety of time intervals.

Chemical Kinetics

Concentration Plot

- A plot of the data gives more information about rate.

- The slope of the curve at one point in time gives the **instantaneous rate**.

- The instantaneous rate at time zero is called the **initial rate**; this is often the rate of interest to chemists.

- This figure shows instantaneous and initial rate of the earlier example.

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Instantaneous rate at $t = 0$ s (initial rate)

Instantaneous rate at time t = slope of tangent to the line at time t.

Instantaneous rate at $t = 600$ s

$\Delta[C_4H_9Cl]$

Δt

[C₄H₉Cl] (M): 0.100, 0.090, 0.080, 0.070, 0.060, 0.050, 0.040, 0.030, 0.020, 0.010, 0

Time (s): 100 200 300 400 500 600 700 800 900

Note: Reactions typically slow down over time!

Chemical Kinetics

Relative Rates

- As was said, rates are followed using a reactant *or* a product. Does this give the same rate for each reactant and product?

- Rate is dependent on stoichiometry.

- If we followed *use* of C_4H_9Cl and compared it to *production* of C_4H_9OH, the values would be the same. Note that the *change* would have opposite signs—one goes down in value, the other goes up.

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Chemical
Kinetics

Relative Rates and Stoichiometry

- What if the equation is *not* 1:1?
- What will the relative rates be for:

$$2\ O_3\ (g)\ \rightarrow\ 3\ O_2\ (g)$$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

1. Expression of reaction rate
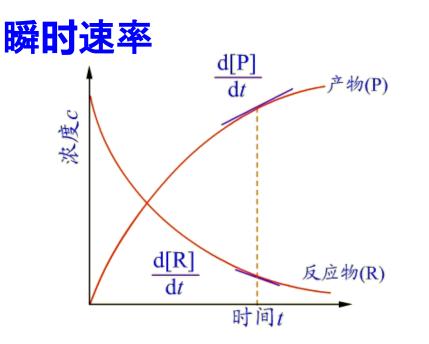
对于任意化学反应 $aA + bB \rightarrow gG + hH$

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{g}\frac{d[G]}{dt} = \frac{1}{h}\frac{d[H]}{dt}$$

例如，对于气相反应： $N_2O_5(g) = N_2O_4(g) + \frac{1}{2}O_2(g)$

在定温定容条件下： $r = -\frac{d[N_2O_5]}{dt} = \frac{d[N_2O_4]}{dt} = 2\frac{d[O_2]}{dt}$

Chemical
Kinetics

1. Expression of reaction rate

瞬时速率

$$\frac{d[P]}{dt}$$ 产物(P)

浓度 c

$$\frac{d[R]}{dt}$$ 反应物(R)

时间 t

反应物和产物的浓度随时间的变化

$$R \longrightarrow P$$

$$r_R = \frac{-d[R]}{dt}$$

$$r_p = \frac{d[P]}{dt}$$

在浓度随时间变化的图上，在时间 t 时，作交点的切线，就得到 t 时刻的瞬时速率。显然，反应刚开始，速率大，然后不断减小，体现了反应速率变化的实际情况。

Chemical
Kinetics

Factors that Affect Reaction Rates

1) Physical state of the reactants

2) Reactant concentrations

3) Reaction temperature

4) Presence of a catalyst

All through Collisions !!!

Chemical
Kinetics

Physical State of the Reactants

- The more readily the reactants collide, the more rapidly they react (Pressure).

- Homogeneous reactions are often faster.

- Heterogeneous reactions that involve solids are faster if the surface area is increased; i.e., a fine powder reacts faster than a pellet or tablet.

Chemical
Kinetics

Reactant Concentrations

- Increasing reactant concentration generally increases reaction rate.

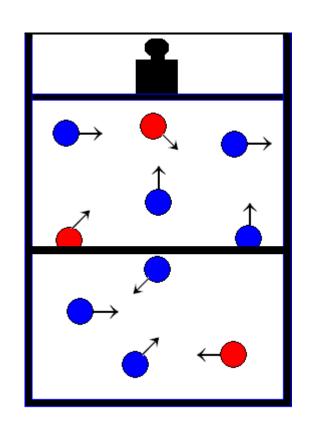- Since there are more molecules, more collisions occur.

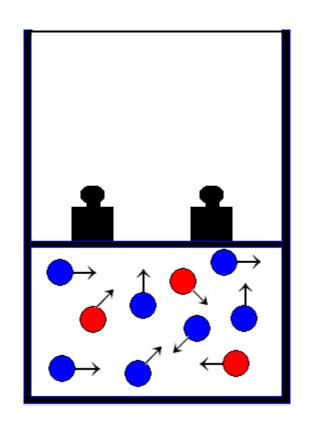Steel wool heated in air (about 20% O_2) glows red-hot but oxidizes to Fe_2O_3 slowly

Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly

Chemical Kinetics

压强对反应速率的影响

结论：**增大压强**，相当于**增大反应物浓度**，反应速率**加快**。

Chemical
Kinetics

注意：**a、压强影响，只适用于讨论有气体参加的反应。**

b、压强影响反应速率，必须伴随有压强改变时体积的改变现象。否则，压强的变化并没有作用到反应的体系上。即压强变则体积变，实际是浓度的变化。若容器的体积不变，因为各气体的浓度没有变，则速率不变。

Chemical
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Temperature

- Reaction rate generally increases with increased temperature.

- Kinetic energy of molecules is related to temperature.

- At higher temperatures, molecules move more quickly, increasing numbers of collisions and the energy the molecules possess during the collisions.

Chemical Kinetics

Presence of a Catalyst

- Catalysts affect rate without being in the overall balanced equation.

- Catalysts affect the kinds of collisions, changing the mechanism (individual reactions that are part of the pathway from reactants to products).

- Catalysts are critical in many biological reactions.

Chemical
Kinetics

Effect of the concentration on Rate

- How do we determine what effect the concentration of each reactant has on the rate of the reaction?

- We keep every concentration constant *except* for one reactant and see what happens to the rate. *Then*, we change a different reactant. We do this until we have seen how *each* reactant has affected the rate.

Chemical
Kinetics

An Example of How Concentration Affects Rate

- $NH_4^+ + NO_2^- = N_2 + H_2O$

- Experiments 1–3 show how $[NH_4^+]$ affects rate.

- Experiments 4–6 show how $[NO_2^-]$ affects rate.

Table 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

Chemical Kinetics

Concentration and Rate Law

- This means

$$\text{Rate} \propto [NH_4^+]$$

$$\text{Rate} \propto [NO_2^-]$$

Therefore,

$$\text{Rate} \propto [NH_4^+][NO_2^-]$$

which, when written as an equation, becomes

$$\text{Rate} = k\,[NH_4^+][NO_2^-]$$

- This equation is called the **rate law**, and k is the **rate constant**.

More about Rate Law - Reaction order

- The exponents tell the **order** of the reaction with respect to each reactant.

- In our example from the last slide:

$$\text{Rate} = k\,[\text{NH}_4^+]\,[\text{NO}_2^-]$$

- The order with respect to each reactant is 1. (It is *first order* in NH_4^+ and NO_2^-.)

- The *reaction* is *second order* (1 + 1 = 2; we just add up all of the reactants' orders to get the reaction's order).

- What is *k*? It is the **rate constant**. It is a temperature-dependent quantity.

Chemical
Kinetics

First Order Reactions

- Some rates depend *only* on one reactant to the first power.

- These are *first order* reactions.

- The rate law becomes:

    Rate = *k* [A]

Chemical Kinetics

Relating k to [A] in a First Order Reaction

$$\int 1/x\ dx = \ln|x| + C$$

- rate = $k\,[A]$

- rate = $-\Delta\,[A]\,/\,\Delta t$

- So: $k\,[A]\ =\ -\Delta\,[A]\,/\,\Delta t$

- Rearrange to: $\Delta\,[A]\,/\,[A]\ =\ -\,k\,\Delta t$

- Integrate: $\ln\,([A]\,/\,[A]_o)\ =\ -\,k\,t$

- Rearrange: $\ln\,[A]\ =\ -\,k\,t\ +\ \ln\,[A]_o$

- Note: this follows the equation of a line:
  $y\ =\ m\,x\ +\ b$

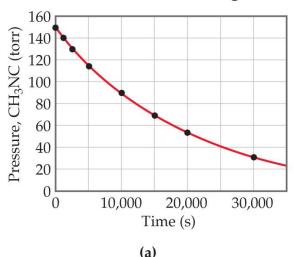- So, a plot of $\ln\,[A]$ vs. t is linear.

Chemical Kinetics

An Example: Conversion of Methyl Isonitrile to Acetonitrile
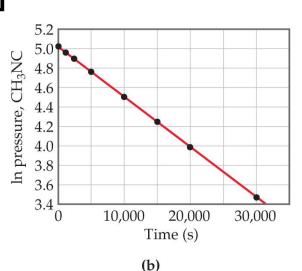
- The equation for the reaction:

$$CH_3NC \rightarrow CH_3CN$$

- It is first order.

$$\text{Rate} = k\,[CH_3NC]$$

(a)

(b)

Finding the Rate Constant, *k*

- Besides using the rate law, we can find the rate constant from the plot of ln [*A*] vs. *t*.
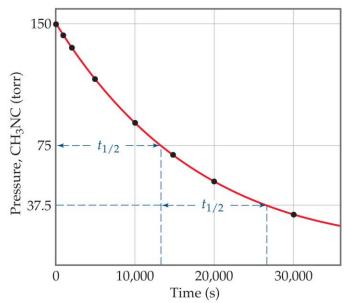
- Remember the integrated rate law:

$$\ln [A] \ = \ - \, k \, t \ + \ \ln [A]_{o}$$

- The plot will give a line. Its slope will equal −*k*.

Half-life

- Definition: The amount of time it takes for one-half of a reactant to be used up in a chemical reaction.

- First Order Reaction:
  - $\ln [A] = -kt + \ln [A]_o$
  - $\ln ([A]_o/2) = -k t_{1/2} + \ln [A]_o$
  - $-\ln ([A]_o/2) + \ln [A]_o = k t_{1/2}$
  - $\ln ([A]_o / [A]_o/2) = k t_{1/2}$
  - $\ln 2 = k t_{1/2}$ or $t_{1/2} = 0.693/k$

Chemical Kinetics

Second Order Reactions

- Some rates depend *only* on a reactant to the second power.

- These are *second order* reactions.

- The rate law becomes:

$$\text{Rate} = k\,[A]^2$$

Chemical
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Solving the Second Order Reaction for $A \rightarrow$ Products

1、 $\int x^{\alpha}dx = x^{(\alpha+1)}/(\alpha+1)+C$ $(\alpha \neq -1)$
2、 $\int 1/x \, dx = \ln|x|+C$

- rate $= k\,[A]^2$

- rate $= - \Delta\,[A]\,/\,\Delta\,t$
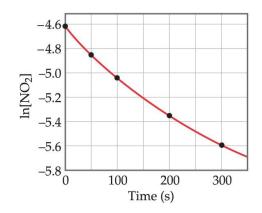
- So, $k\,[A]^2 = - \Delta\,[A]\,/\,\Delta\,t$

- Rearranging: $\Delta\,[A]\,/\,[A]^2 = - k\,\Delta\,t$

- Using calculus: $1/[A] = 1/[A]_o + k\,t$

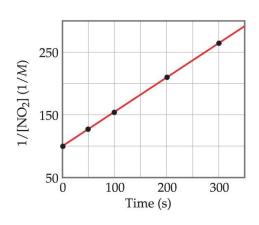- Notice: The linear relationships for first order and second order reactions differ!

Chemical
Kinetics

An Example of a Second Order Reaction: Decomposition of NO_2

➤ A plot following NO_2 decomposition shows that it must be second order because it is linear for $1/[NO_2]$, *not* linear for $\ln [NO_2]$.

➤ Equation:

$$NO_2 \rightarrow NO + \tfrac{1}{2} O_2$$

Half-Life and Second Order Reactions
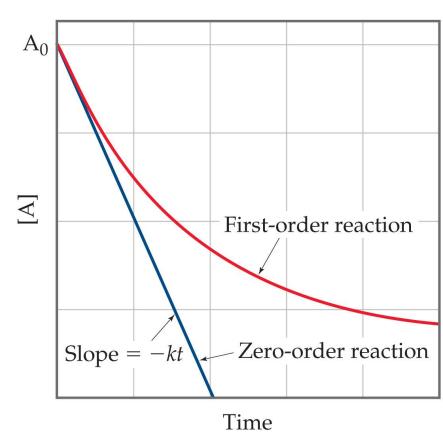
- Using the integrated rate law, we can see how half-life is derived:
  - $1/[A] = 1/[A]_o + k\,t$
  - $1/([A]_o/2) = 1/[A]_o + k\,t_{\frac{1}{2}}$
  - $2/[A]_o - 1/[A]_o = k\,t_{\frac{1}{2}}$
  - $t_{\frac{1}{2}} = 1/(k\,[A]_o)$

- So, half-life is a concentration dependent quantity for second order reactions!

Chemical
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Zero Order Reactions

- Occasionally, rate is *independent* of the concentration of the reactant:

- Rate = *k*

- These are *zero order* reactions.

- These reactions are linear in concentration.

A_0

[A]

First-order reaction

Slope = $-kt$

Zero-order reaction

Time

7. 反应的级数

速率方程中，各反应物浓度项上的指数称为该反应物的级数；

所有浓度项指数的代数和称为该反应的总级数，通常用 n 表示。

n 的大小表明浓度对反应速率影响的大小。

反应级数可以是正数、负数、整数、分数或零，有的反应无法用简单的数字来表示级数。

反应级数是由实验测定的。

Chemical
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例如：

$r = k_0$ 零级反应

$r = k[\text{A}]$ 一级反应

$r = k[\text{A}][\text{B}]$ 二级,对A和B各为一级

$r = k[\text{A}]^2[\text{B}]$ 三级,对A为二级,对B为一级

$r = k[\text{A}][\text{B}]^{-2}$ 负一级反应

$r = k[\text{A}][\text{B}]^{1/2}$ 1.5级反应

$r = k[\text{A}][\text{B}]/(1-[\text{B}]^{1/2})$ 无简单级数

Chemical
Kinetics

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.

- Molecules can only react if they collide with each other with **sufficient energy and proper geometry**.

- Attention: Although the number of collisions between reactants is large, chemical reaction is not necessary to take place in every collision.

- In chemistry, the collision that can produce chemical reaction is called **effective collision**; the more effective collisions, the faster the reaction rate.

Chemical
Kinetics

Factors That Affect Reaction Rate - A microscopic view

1. Frequency of collisions

2. Orientation of molecules

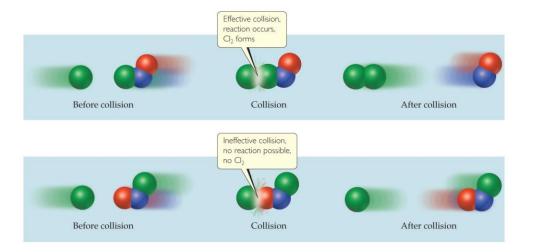3. Energy needed for the reaction to take place (activation energy)

Chemical Kinetics

The frequency of collision

- The **collision model** is based on the kinetic molecular theory.

- Molecules must collide to react.

- If there are more collisions, more reactions can occur.

- So, higher molecule density means more collisions, and the reaction rate is faster.

- Also, if the temperature is higher, molecules move faster, causing more collisions and a higher rate of reaction.

Chemical
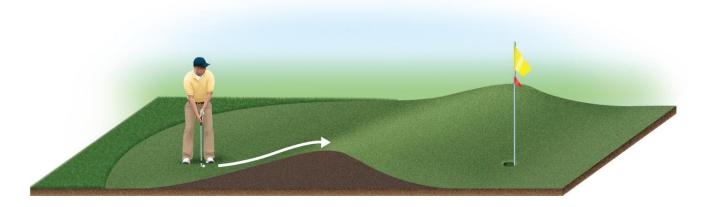Kinetics

Orientation of Molecules

- Molecules can often collide without forming products.

- Aligning molecules properly can lead to chemical reactions.

- Bonds must be broken and made, and atoms need to be in proper positions.
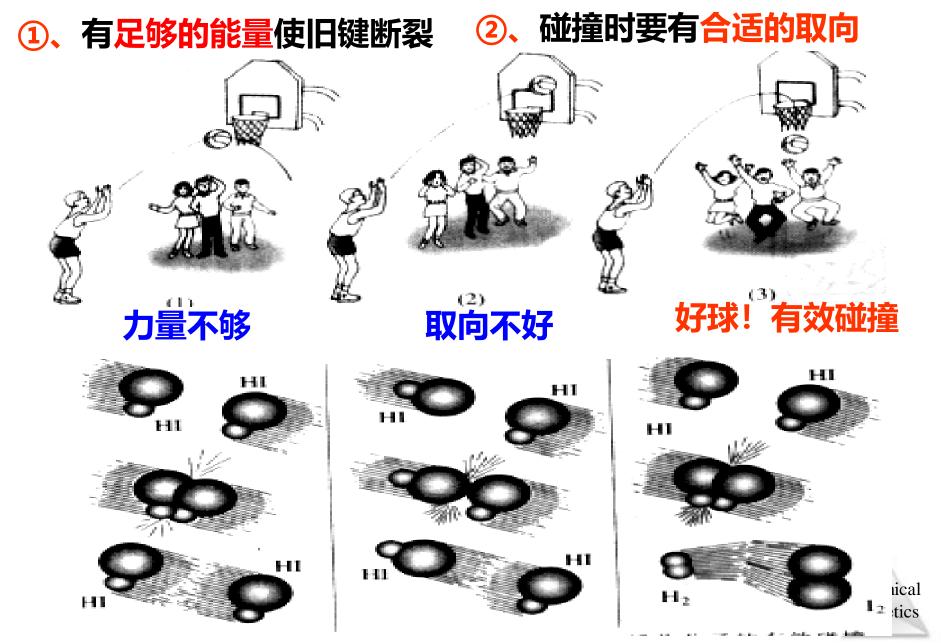

Effective collision, reaction occurs, Cl_2 forms

Before collision   Collision   After collision

Ineffective collision, no reaction possible, no Cl_2

Before collision   Collision   After collision

Chemical Kinetics

Energy Needed for a Reaction to Take Place (Activation Energy)

- The minimum energy needed for a reaction to take place is called **activation energy（活化能)**.

- An energy barrier must be overcome for a reaction to take place, much like the ball must be hit to overcome the barrier in the figure below.
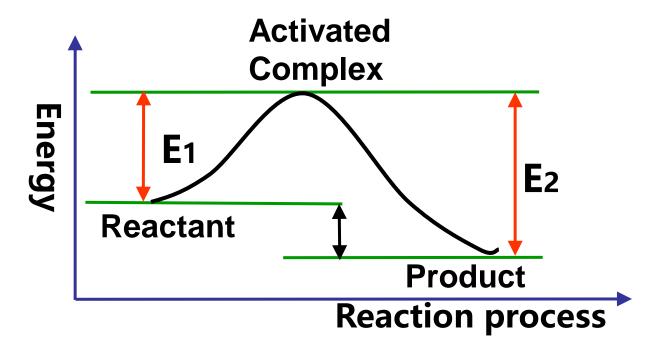

Chemical
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反应物分子要具有什么条件才能发生有效碰撞？

①、有足够的能量使旧键断裂　　**②、碰撞时要有合适的取向**

力量不够　　　　　　**取向不好**　　　　　　**好球！有效碰撞**
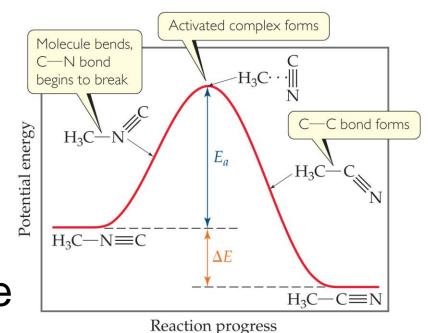
Transition State (Activated Complex)

- Energy rises as the reaction proceeds until the particles reach the state with **activation** energy .
- The organization of the atoms at this **activation** energy state is called the **transition state** (or activated complex).

Chemical
Kinetics

Reaction Progress

- Plots are made to show the energy possessed by the particles as the reaction proceeds.

- At the highest energy point, the transition state is formed. (only for the minimum energy path)

- Reactions can be endothermic or exothermic after this.

Chemical Kinetics

activated molecules

In chemistry, the molecules that can effectively collide to react are called activated molecules.

1. Activated molecules have high energy, and the molecules with insufficient energy can only become activated molecules after obtaining energy.

2. When the temperature is constant, the percentage of active molecules in the reactant is constant and is proportional to the temperature.
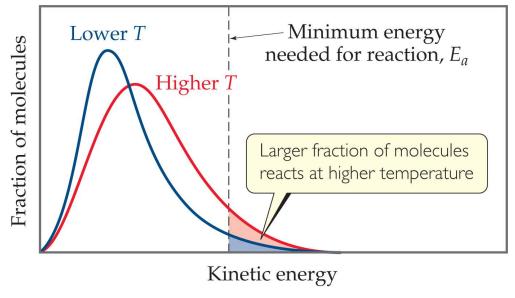
Percentage of active molecules:

（**Number of active molecules /Number of reactants**）**×100%**
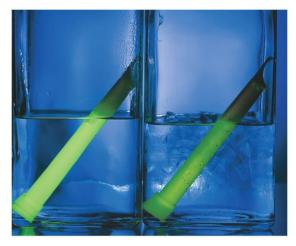
Distribution of the Energy of Molecules
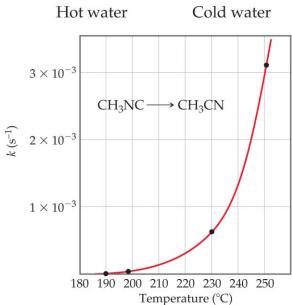
- Gases have an average temperature, but each individual molecule has its own energy.

- At higher temperatures, more molecules possess the energy needed for the reaction to occur.

Temperature and Rate: The Energy of Molecules
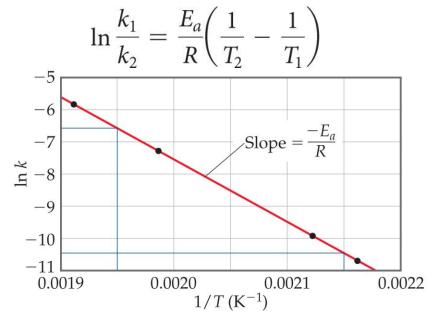
- Generally, as temperature increases, rate increases.

- The rate constant is temperature dependent: it increases as temperature increases.

- Rate constant doubles (approximately) with every 10 °C rise.

Hot water   Cold water

$CH_3NC \longrightarrow CH_3CN$

Chemical Kinetics
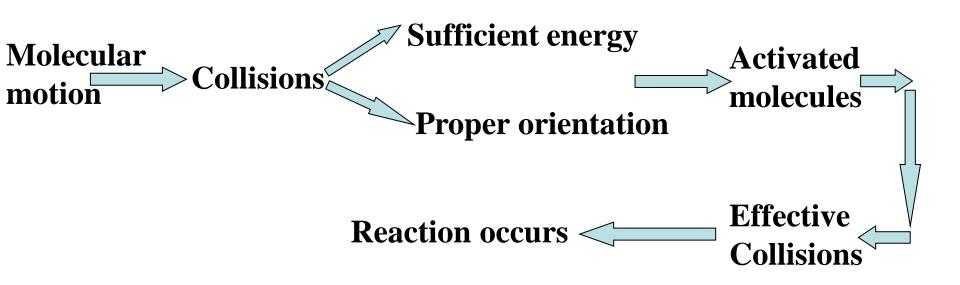
The Relationship Between Activation Energy & Temperature

- Arrhenius noted relationship between activation energy and temperature: $k = Ae^{-E_a/RT}$

- Activation energy can be determined graphically by reorganizing the equation: $\ln k = -E_a/RT + \ln A$

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

Chemical Kinetics

How a reaction occurs?

Molecular motion → **Collisions**

Collisions → **Sufficient energy**

Collisions → **Proper orientation**

→ **Activated molecules** →

→ **Effective Collisions** → **Reaction occurs**

- 化学反应速率与单位时间内分子间的有效碰撞次数（有效碰撞频率）有关。

Chemical Kinetics

Factors that Affect Reaction Rates

1) Physical state of the reactants

2) Reactant concentrations

3) Reaction temperature

4) Presence of a catalyst

1. Frequency of collisions

2. Orientation of molecules

3. Energy needed for the reaction to take place (activation energy)

4. Temperature affects 1 and 3; $k = Ae^{-Ea/RT}$

Chemical Kinetics

Law vs. Theory

- Kinetics gives *what* happens. We call the description the *rate law*.

- *Why* do we observe that rate law? We explain with a *theory* called a **mechanism**.

- A mechanism is a series of stepwise reactions that show how reactants become products.

Chemical Kinetics

Reaction Mechanisms

- Reactions may occur all at once or through several discrete steps that cannot be further divded.

- Each of these processes is known as an **elementary reaction** or **elementary process**.

Chemical
Kinetics

Molecularity (反应分子数)

Table 14.3 Elementary Reactions and Their Rate Laws

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 $= k[A][B][C]$

- The **molecularity** of an elementary reaction tells how many molecules are involved in that step of the mechanism.
- Elementary reaction's reaction order is related to molecularity

Chemical
Kinetics

4. Elementary reaction (基元反应)

基元反应简称元反应，如果一个化学反应，反应物分子（或离子、原子、自由基等）在碰撞中相互作用直接转化为生成物分子，这种反应称为基元反应。

例如：

$$Cl_2 + M = 2Cl + M$$
$$Cl + H_2 = HCl + H$$
$$H + Cl_2 = HCl + Cl$$
$$2Cl + M = Cl_2 + M$$

式中M是指反应器壁或其他第三分子体，是惰性物质，不参与反应，只具有传递能量的作用

注意：对于基元反应，其反应方程计量关系是不能随意按比例扩大缩小的。

Chemical
Kinetics

反应分子数

　　对于基元反应，直接作用所必需的反应物微观粒子（分子、原子、离子、自由基）数，称为反应分子数。反应分子数可区分为单分子反应、双分子反应和三分子反应，四分子反应目前尚未发现。反应分子数只可能是简单的正整数1，2或3。（注意：反应分子数的概念只适用于基元反应）

　　反应分子数属于微观范畴。

基元反应	反应分子数
$A \longrightarrow P$	单分子反应
$A + B \longrightarrow P$	双分子反应
$2A + B \longrightarrow P$	三分子反应

Chemical
Kinetics

5. 质量作用定律

　　对于基元反应，反应速率与反应物浓度的幂乘积成正比。幂指数就是基元反应方程中各反应物的系数。这就是质量作用定律，它只适用于基元反应（G. M. 古德贝格和 P.瓦格1867年提出，由分子碰撞理论推出）。

例如：　　　基元反应　　　　　　　　　反应速率r

(1)　$Cl_2 + M = 2Cl + M$　　　　　$k_1[Cl_2][M]$

(2)　$Cl + H_2 = HCl + H$　　　　　$k_2[Cl][H_2]$

(3)　$H + Cl_2 = HCl + Cl$　　　　　$k_3[H][Cl_2]$

(4)　$2Cl + M = Cl_2 + M$　　　　　$k_4[Cl]^2[M]$

Chemical
Kinetics

反应级数和反应分子数

应当指出：

1. 反应分子数和反应级数是两个不同的概念。反应分子数是理论上的概念，是对微观上的基元反应而言的。而反应级数是对宏观化学反应而言的，反应级数必须从实验上确定。

2. 反应分子数和反应级数所取的数值也不相同。反应级数的数值可以是有理数，而反应分子数却只能是正整数。基元反应必然是级数为正整数的反应，但级数为正整数的反应却不一定是基元反应。

Chemical
Kinetics

5. 总反应

我们通常所写的化学方程式只代表反应的化学计量式，反映了参与反应的物质之间量的关系，而并不代表反应的真正历程。

计量方程式仅表示反应的总效果，称为"总反应"。

由反应物分子（或离子、原子、自由基等）直接作用而生成新产物的反应，称为"基元反应"。

简单反应：仅由一种基元反应组成的总反应。

复合反应：由两种或两种以上的基元反应组成的总反应。 例如，下列反应为总反应：

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$$H_2 + I_2 \longrightarrow 2HI$$

$$H_2 + Br_2 \longrightarrow 2HBr$$

这三个化学反应的计量式相似，但反应历程却大不相同

Chemical Kinetics

6. 反应机理

所谓反应机理（或反应历程）一般是指该反应是由哪些基元反应组成的。在有些情况下，反应机理还要给出所经历的每一步的立体化学结构图。

同一反应在不同的条件下，可有不同的反应机理。了解反应机理可以掌握反应的内在规律，从而更好的驾驭反应。

化学反应方程，除非特别注明，一般都属于化学计量方程，而不代表基元反应。

例如：$H_2 + Cl_2 \longrightarrow 2HCl$

反应机理：

$$Cl_2 + M \rightarrow 2Cl\bullet + M$$

$$Cl\bullet + H_2 \rightarrow HCl + H\bullet$$

$$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$$

$$2Cl\bullet + M \rightarrow Cl_2 + M$$

Chemical
Kinetics

6. 反应机理

说明：

1）一般的化学反应方程式虽然都具有热力学含义，但却不一定具有动力学含义，只有基元反应才具有动力学含义。

2）质量作用定律反映的是基元反应的动力学规律。因此质量作用定律只能应用于简单反应或总反应中的每一个基元反应，而不能直接应用于总反应。即总反应不符合质量作用定律。
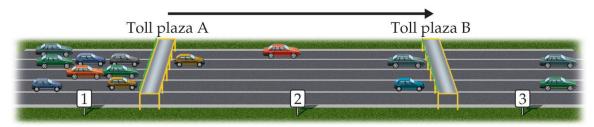
Chemical
Kinetics

Termolecular?

- Termolecular steps require three molecules to simultaneously collide with the proper orientation *and* the proper energy.

- These are rare, if they indeed do occur.

- These *must* be slower than unimolecular or bimolecular steps.

- Nearly *all* mechanisms use *only* unimolecular or bimolecular reactions.
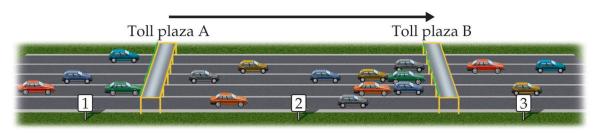
Chemical
Kinetics

Multistep reactions

- The overall reaction cannot occur faster than the slowest reaction in the mechanism.
- We call that the **rate-determining step**.

(a) Cars slowed at toll plaza A, rate-determining step is passage through A

(b) Cars slowed at toll plaza B, rate-determining step is passage through B

Chemical
Kinetics

What is required of a plausible mechanism——How to determine elementary steps?

- The *rate law* must be able to be devised from the rate-determining step.

- The *stoichiometry* must be obtained when all steps are added up.

- Each step must balance, like any equation.

- All intermediates are made and used up.

- Any catalyst is used and regenerated.

Chemical Kinetics

A Mechanism With a Slow Initial Step

$$NO_2 + CO \rightarrow NO + CO_2$$

Rate = k [NO_2][CO] ? But Rate = k [NO_2]^2

Step 1: $NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$ (slow)

Step 2: $NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$ (fast)

Overall: $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Step 2 is much faster than step 1; that is, $k_2 >> k_1$, telling us that the intermediate $NO_3(g)$ is slowly produced in step 1 and immediately consumed in step 2.

Chemical Kinetics

A Mechanism With a Slow Initial Step (continued)

- The easiest way to complete the first step is to make a product:

$$NO_2 + NO_2 \rightarrow NO + NO_3$$

- We do not see NO_3 in the stoichiometry, so it is an **intermediate**, which needs to be used in a faster next step.

$$NO_3 + CO \rightarrow NO_2 + CO_2$$

A Mechanism With a Slow Initial Step (completed)

- Since the first step is the slowest step, it gives the rate law.

- If you add up all of the individual steps (2 of them), you get the stoichiometry.

- Each step balances.

- This is a plausible mechanism.

$$\text{Rate} = k\,[NO_2]^2$$

A Mechanism With a Fast Initial Step

- Equation for the reaction:

  $$2\ NO + Br_2 \rightleftharpoons 2\ NOBr$$

- The rate law for this reaction is found to be

  $$Rate = k\,[NO]^2\,[Br_2]$$

- Because termolecular processes are rare, this rate law suggests a multistep mechanism.

A Mechanism With a Fast Initial Step (continued)

- The rate law indicates that a quickly established equilibrium is followed by a slow step.

- Step 1: $NO + Br_2 \rightleftharpoons NOBr_2$

- Step 2: $NOBr_2 + NO \rightarrow 2\ NOBr$

Chemical
Kinetics

What is the Rate Law?

- The rate of the overall reaction depends upon the rate of the slow step.

- The rate law for that step would be

$$\text{Rate} = k_2[\text{NOBr}_2]\,[\text{NO}]$$

- But how can we find $[\text{NOBr}_2]$?

Chemical
Kinetics

[NOBr$_2$] (An Intermediate)?

- NOBr$_2$ can react two ways:
  - With NO to form NOBr.
  - By decomposition to reform NO and Br$_2$.
- The reactants and products of the first step are in equilibrium with each other.
- For an equilibrium (as we will see in the next chapter):

$$\text{Rate}_f = \text{Rate}_r$$

The Rate Law (Finally!)

- Substituting for the forward and reverse rates:

$$k_1 \, [NO] \, [Br_2] \; = \; k_{-1} \, [NOBr_2]$$

- Solve for $[NOBr_2]$, then substitute into the rate law:

$$\text{Rate} = k_2 \, (k_1/k_{-1}) \, [NO] \, [Br_2] \, [NO]$$
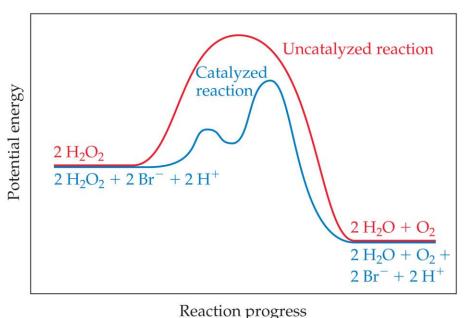
- This gives the observed rate law!

$$\text{Rate} = k \, [NO]^2 \, [Br_2]$$

Catalysts

- Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.

- Catalysts change the mechanism by which the process occurs.

Chemical Kinetics

Types of Catalysts

1) Homogeneous catalysts

2) Heterogeneous catalysts

3) Enzymes

Chemical
Kinetics

Homogeneous Catalysts
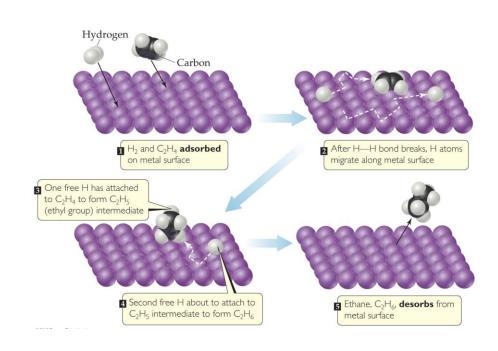
- The reactants and catalyst are in the same phase.

- Many times, reactants and catalyst are dissolved in the same solvent, as seen below.

NaBr catalyst about to be added to reaction mixture

$H_2O_2(aq)$ in acidic solution

$2\,Br^-(aq) + H_2O_2(aq) + 2\,H^+(aq)$
$\longrightarrow Br_2(aq) + 2\,H_2O(l)$
brown

$Br_2(aq) + H_2O_2(aq) \longrightarrow$
$2\,Br^-(aq) + 2\,H^+(aq) + O_2(g)$
colorless   bubbles

Chemical
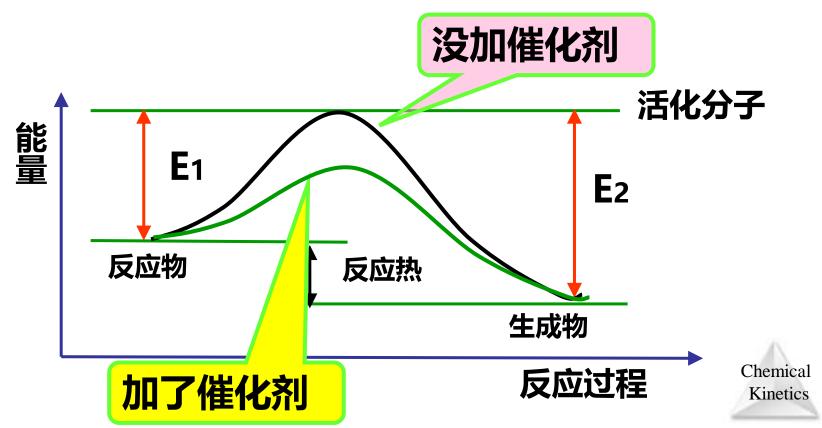Kinetics

Heterogeneous Catalysts

- The catalyst is in a different phase than the reactants.

- Often, gases are passed over a solid catalyst.

- The adsorption of the reactants is often the rate-determining step.

Hydrogen

Carbon

1 H$_2$ and C$_2$H$_4$ **adsorbed** on metal surface

2 After H—H bond breaks, H atoms migrate along metal surface

3 One free H has attached to C$_2$H$_4$ to form C$_2$H$_5$ (ethyl group) intermediate

4 Second free H about to attach to C$_2$H$_5$ intermediate to form C$_2$H$_6$

5 Ethane, C$_2$H$_6$, **desorbs** from metal surface

Chemical Kinetics

催化剂对化学反应速率的影响
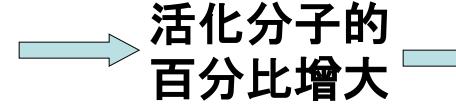
使用催化剂 ⟹ 降低活化能

催化剂对化学反应速率的影响

使用催化剂 ⟹ 降低活化能

⟹ 活化分子的
百分比增大 ⟹ 活化分子的
数目增多

⟹ 有效碰撞
次数增多 ⟹ 化学反应
速率加快

Chemical
Kinetics

4、催化剂对化学反应速率的影响。

　　原因：　在其他条件不变时，使用催化剂可以大大降低反应所需要的能量，会使更多的反应物分子成为活化分子，大大增加活化分子百分数，因而使反应速率加快。

　　规律：　催化剂可以改变化学反应的速率。

Chemical
Kinetics

小结：影响化学反应速率的外因
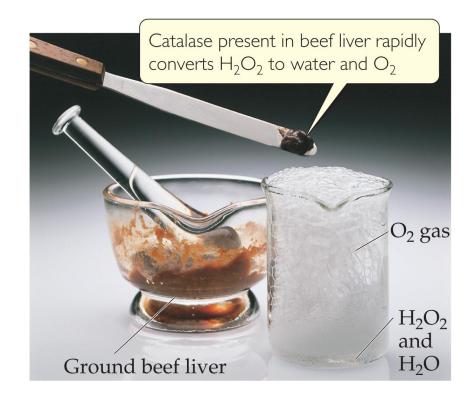
影响　　　外因	单位体积内			有效碰撞次数	化学反应速率
	分子总数	活化分子数	活化分子百分数		
增大反应物浓度	增加	增加	不变	增加	加快
增大压强	增加	增加	不变	增加	加快
升高温度	不变	增加	增加	增加	加快
使用催化剂	不变	增加	增加	增加	加快

Chemical Kinetics

Enzymes

- **Enzymes** are biological catalysts.

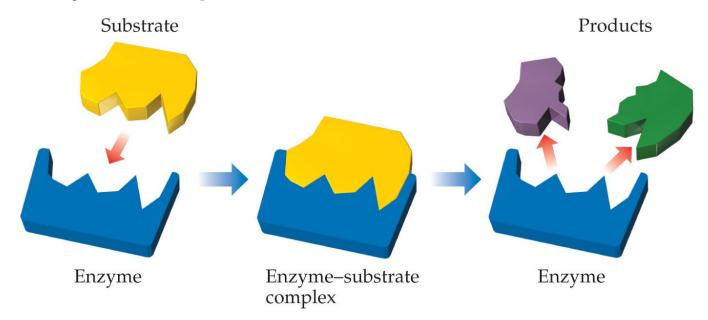- They have a region where the reactants attach. That region is called the **active site**. The reactants are referred to as **substrates**.

Catalase present in beef liver rapidly converts H_2O_2 to water and O_2

O_2 gas

H_2O_2 and H_2O

Ground beef liver

Chemical Kinetics

Lock-and-Key Model

- In the enzyme–substrate model, the substrate fits into the active site of an enzyme, much like a key fits into a lock.

- They are specific.

Substrate

Products

Enzyme

Enzyme–substrate complex

Enzyme

In a reaction involving reactants in the gas state, how does increasing the partial pressures of the gases affect the reaction rate?

A. The effect of increasing the partial pressures of the reactive components of a gaseous mixture depends on which side of the chemical equation has the most gas molecules.

B. Increasing the partial pressures of the reactive components of a gaseous mixture has no effect on the rate of reaction if each reactant pressure is increased by the same amount.

C. Increasing the partial pressures of the reactive components of a gaseous mixture increases the rate of reaction.

D. Increasing the partial pressures of the reactive components of a gaseous mixture decreases the rate of reaction.

What is the difference between average rate and instantaneous rate? In a given reaction, can these two rates ever have the same numeric value?

A. An instantaneous rate is measured at a particular point in time of a reaction, whereas average rate is measured over a time period; Yes.

B. An instantaneous rate is measured at a particular point in time of a reaction, whereas average rate is measured over a time period; No.

C. An instantaneous rate is measured over a short time period, whereas average rate is measured over a large time period; Yes.

D. An instantaneous rate is measured over a short time period, whereas average rate is measured over a large time period; No.

Does the rate constant have the same units as the rate? Explain your answer.

A. Yes, the rate is directly proportional to the rate constant in a rate law.

B. Yes, only if the order of each concentration is one in the rate law.

C. No, as the order of each concentration changes in a rate law, the units of the rate constant change, but those of the rate are always concentration/time.

D. No, as the order of each concentration changes in a rate law, there are changes in the units of both.

The experimentally determined rate law for the reaction $2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$ is rate $= k[NO]^2[H_2]$.

a. What are the reaction orders in this rate law?
b. Does doubling the concentration of NO have the same effect on rate as doubling the concentration of H_2?

(a)

A. 2nd order in NO, 1st order in H_2, 2nd order overall
B. 2nd order in NO, 1st order in H_2, 3rd order overall
C. 1st order in NO, 1st order in H_2, 2nd order overall
D. 1st order in NO, 2nd order in H_2, 3rd order overall

(b)

A. Yes
B. No

What does it mean if k is 0?

A. The rate of the reaction is very slow.
B. There is no reaction.
C. The rate constant can not be calculated.
D. All of the above

Is it reasonable to say that enzymes stabilize the transition state for a reaction? Explain your answer.

A. Yes, because an enzyme is a catalyst.

B. No, because enzymes are different in structure and their properties than typical catalysts in non-biochemical reactions.

C. Possibly, but the nature of the transition states in the catalyzed and uncatalyzed reaction can be significantly different.

D. Yes, because it should form a stable intermediate, transition state.

In a chemical reaction, why does not every collision between reactant molecules result in formation of a product molecule?

A. If colliding atoms are of dissimilar sizes, then products are not favored to form.

B. If collisions do not occur with sufficient energy or proper orientation of colliding molecules, then products may not form.

C. If reactants are gas molecules, the particles are too far apart to collide over a reasonable time period and thus do not form products.

D. If reactants are liquid molecules, the particles are moving too slowly to provide sufficient energy to form products.

Suppose we have two reactions, A ⟶ B and B ⟶ C. You can isolate B, and it is stable. Is B the transition state for the reaction A ⟶ C?

A. Yes, because B is an intermediate.

B. Yes, because B can be isolated.

C. No, because B is not stable.

D. No, because B can be isolated and transition states are by definition not stable.

What is the molecularity of the elementary reaction?

$$NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$$

A. Zero molecularity
B. Unimolecular
C. Bimolecular
D. Trimolecular

Exercise Determining Molecularity and Identifying Intermediates

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$$O_3(g) \rightarrow O_2(g) + O(g)$$
$$O_3(g) + O(g) \rightarrow 2\,O_2(g)$$

(a) Describe the molecularity of each elementary reaction in this mechanism. **(b)** Write the equation for the overall reaction. **(c)** Identify the intermediate(s).

Solution

(a) The first elementary reaction involves a single reactant and is consequently unimolecular. The second reaction, which involves two reactant molecules, is bimolecular.

(b) Adding the two elementary reactions gives

$$2\,O_3(g) + O(g) \rightarrow 3\,O_2(g) + O(g)$$

Because $O(g)$ appears in equal amounts on both sides of the equation, it can be eliminated to give the net equation for the chemical process:

$$2\,O_3(g) \rightarrow 3\,O_2(g)$$

(c) The intermediate is $O(g)$. It is neither an original reactant nor a final product but is formed in the first step of the mechanism and consumed in the second.

Exercise Predicting the Rate Law for an Elementary Reaction

If the following reaction occurs in a single elementary reaction, predict its rate law:

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

Solution

Plan Because we are assuming that the reaction occurs as a single elementary reaction, we are able to write the rate law using the coefficients for the reactants in the equation as the reaction orders.

Solve The reaction is bimolecular, involving one molecule of H_2 and one molecule of Br_2. Thus, the rate law is first order in each reactant and second order overall:

$$Rate = k[H_2][Br_2]$$

Comment Experimental studies of this reaction show that the reaction actually has a very different rate law:

$$Rate = k[H_2][Br_2]^{1/2}$$

Because the experimental rate law differs from the one obtained by assuming a single elementary reaction, we can conclude that the mechanism cannot occur by a single elementary step. It must, therefore, involve two or more elementary steps.

Why are termolecular elementary steps rare in gas-phase reactions?

A.   Gas reactions do not require three reactants.

B.   Unimolecular gas reactions are more likely.

C.   Odds of three particles simultaneously colliding together and properly oriented are very low.

D.   All of the above

Exercise Determining the Rate Law for a Multistep Mechanism

The decomposition of nitrous oxide, N2O, is believed to occur by a two-step mechanism:

$$N_2O(g) \rightarrow N_2(g) + O(g) \qquad \text{(slow)}$$

$$N_2O(g) + O(g) \rightarrow N_2(g) + O_2(g) \qquad \text{(fast)}$$

(a) Write the equation for the overall reaction. **(b)** Write the rate law for the overall reaction.

Solution

Solve (a) Adding the two elementary reactions gives

$$2\ N_2O(g) + O(g) \rightarrow 2\ N_2(g) + 2\ O_2(g) + O(g)$$

Omitting the intermediate, O(g), which occurs on both sides of the equation, gives the overall reaction:

$$2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$$

(b) The rate law for the overall reaction is just the rate law for the slow, rate-determining elementary reaction. Because that slow step is a unimolecular elementary reaction, the rate law is first order:

$$\text{Rate} = k[N_2O]$$

Why can't the rate law for a reaction generally be deduced from the balanced equation for the reaction?

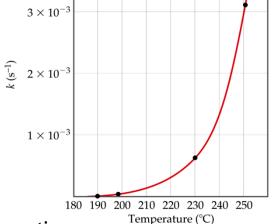A. All reactions are not elementary, single step, as in the balanced equation for the reaction.

B. The balanced equation gives no information about the rate constant, which is part of a rate law.

C. The extent of a reaction as shown by a balanced equation does not depend on concentrations.

D. The rate law depends not on the overall balanced reaction, but on the slowest step in the reaction mechanism.

How does a homogeneous catalyst compare with a heterogeneous one regarding the ease of recovery of the catalyst from the reaction mixture?

A. A heterogeneous catalyst is easier to remove from a reaction mixture because of phase differences.

B. A heterogeneous catalyst is easier to remove from a reaction mixture because it is present in the greatest quantity.

C. A homogeneous catalyst is easier to remove from a reaction mixture because of phase differences.

D. A homogenous catalyst is easier to remove from a reaction mixture because it is easier to identify in the reaction mixture.

Exercise Determining the Activation Energy

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures (these are the data points in Figure 14.14):

Temperature (°C)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

(a) From these data, calculate the activation energy for the reaction.
(b) What is the value of the rate constant at 430.0 K?

Solution

Plan We can obtain E_a from the slope of a graph of ln k versus 1/T. Once we know E_a, we can use Equation 14.21 together with the given rate data to calculate the rate constant at 430.0 K.
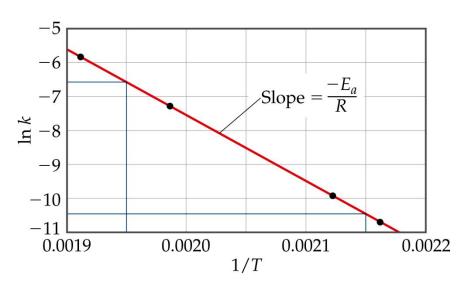
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad\qquad [14.21]$$

Exercise Determining the Activation Energy

Solve
(**a**) We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$, and the natural log of each rate constant, $\ln k$. This gives us the table shown at the right:

T (K)	$1/T$ (K^{-1})	$\ln k$
462.9	2.160×10^{-3}	-10.589
472.1	2.118×10^{-3}	-9.855
503.5	1.986×10^{-3}	-7.370
524.4	1.907×10^{-3}	-5.757

A graph of $\ln k$ versus $1/T$ is a straight line.

Exercise Determining the Activation Energy

The slope of the line is obtained by choosing any two well-separated points and using the coordinates of each:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

$$\text{Slope} = -\frac{E_a}{R}$$

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K^{-1}. Thus, the overall units for the slope are K. The slope equals $-E_a/R$. We use the value for the gas constant R in units of J/mol-K (Table 10.2).We thus obtain

$$E_a = -(\text{slope})(R) = -(-1.9 \times 10^4 \, \text{K})\left(8.314 \frac{\text{J}}{\text{mol-K}}\right)\left(\frac{1 \, \text{kJ}}{1000 \, \text{J}}\right)$$

$$= 1.6 \times 10^2 \, \text{kJ/mol} = 160 \, \text{kJ/mol}$$

We report the activation energy to only two significant figures because we are limited by the precision with which we can read the graph.

Exercise Determining the Activation Energy

(**b**) To determine the rate constant, k, at $T_1 = 430.0$ K, we can use Equation 14.21 with $Ea = 160$ kJ/mol and one of the rate constants and temperatures from the given data, such as $k_2 = 2.52$ x 10^{-5} s^{-1} and $T_2 = 462.9$ K:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad [14.21]$$

Thus,

$$\ln\left(\frac{k_1}{2.52 \times 10^{-5}\ s^{-1}}\right) = \left(\frac{160\ \text{kJ/mol}}{8.314\ \text{J/mol-K}}\right)\left(\frac{1}{462.9\ \text{K}} - \frac{1}{430.0\ \text{K}}\right)\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right) = -3.18$$

$$\frac{k_1}{2.52 \times 10^{-5}\ s^{-1}} = e^{-3.18} = 4.15 \times 10^{-2}$$

$$k_1 = (4.15 \times 10^{-2})(2.52 \times 10^{-5}\ s^{-1}) = 1.0 \times 10^{-6}\ s^{-1}$$

Note that the units of k_1 are the same as those of k_2.

How does the half-life of a second-order reaction change as the reaction proceeds?

A. The half-life does not change as the reaction proceeds.

B. The half-life increases as the reaction proceeds.

C. The half-life decreases as the reaction proceeds.

D. The half-life increases for some reactions and decreases for others (2nd order reactions) as the reaction proceeds.

$$\frac{1}{k[A]_0} = t_{1/2}$$

The rate of a reaction can be increased by

a. increasing reactant concentrations.

b. increasing the temperature.

c. adding a suitable catalyst.

d. All of the above

Over time, the rate of most chemical reactions tends to _____.

a. increase

b. decrease

c. remain constant

d. oscillate

If tripling the concentration of reactant A multiplies the rate by a factor of nine, the reaction is _____ order in A.

a. zeroth

b. first

c. second

d. third

Reaction: A + B → C + D
Rate = k[A][B]
The overall order of this reaction is

a. first.

b. second.

c. third.

d. fourth.

Reaction: W + X → Y + Z
Rate = k[W]
The order of this reaction with respect to X is

a. zeroth.

b. first.

c. second.

d. third.

The time required for the concentration of a reactant to be reduced to half of its initial value is called the

a. midpoint of the reaction.

b. equivalence point of the reaction.

c. half-rate of the reaction.

d. half-life of the reaction.

If k is the rate constant of a first-order reaction, the half-life of the reaction is:

$$\frac{0.693}{k} = t_{1/2}$$

a. 0.693/k

b. 0.693k

c. k/2

d. 2k

The value of the rate constant (k) for a first-order reaction is 0.010 sec^{-1}. What is the half-life of this reaction?

a. 10 seconds

b. 69 seconds $\dfrac{0.693}{k} = t_{1/2}$

c. 100 seconds

d. 690 seconds

A + B → products, Rate = k[A], k = 0.010 sec⁻¹, Initial [A] = 0.100 M, Final [A] = 0.00100 M How long will this take?

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

a. 69 seconds

b. 138 seconds

c. 460 seconds

d. 690 seconds

Rate = k[A]^2,   Initial [A] = 0.100 M,
k = 0.0214 M^{-1} sec^{-1}
What is the half-life of this second-order reaction?

$$\frac{1}{k[A]_0} = t_{1/2}$$

a. 69 seconds

b. 138 seconds

c. 467 seconds

d. 690 seconds

Rate = k[A]², Initial [A] = 0.100 M, k = 0.0214 M⁻¹ sec⁻¹

Rate = $k[A]^2$, Initial $[A] = 0.100$ M, $k = 0.0214$ M^{-1} sec^{-1}

After 1.00 hour, what is the concentration of reactant A?

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

a. 0.0500 M

b. 0.0250 M

c. 0.0189 M

d. 0.0115 M

The minimum energy that a collision between molecules must have for a reaction to occur is called the

a. initial energy.

b. internal energy.

c. external energy.

d. energy of activation.

At 298 K, k = 1.36 × 10^{-7} sec^{-1}.
At 323 K, k = 2.72 × 10^{-6} sec^{-1}.
The energy of activation for this reaction is

$$k = Ae^{-E_a/RT}$$

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

a. 100 kJ/mole.

b. 310 kJ/mole.

c. 690 kJ/mole.

d. 1000 kJ/mole.

The rate-determining step is the _____ step in a reaction mechanism.

a. first

b. last

c. fastest

d. slowest

Adding a catalyst increases the rate of a chemical reaction because the presence of the catalyst

a. increases molecular velocities.

b. increases molecular collisions.

c. decreases energy of activation.

d. All of the above

1. 对于在一个体积不变的密闭容器中进行的可逆反应：$C_{(s)} + O_2 = CO_{2\ (g)}$

- 下列说法中错误的是（ D ）

- A将碳块粉碎成粉末可以加快化学反应速率

- B增大氧气的量可以加快化学反应速率

- C增大压强可以加快化学反应速率

- D增加碳的量可以加快化学反应速率

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2.反应C(s)+H_2O(g)=CO(g)+H_2(g)在一可变容积的密闭容器中进行，下列条件的改变对其反应速率几乎无影响的是(*AC*)

A.增加C的量

B.将容器的体积缩小一半

C.保持体积不变，充入N_2使体系压强增大

D.保持压强不变，充入N_2使容器体积变大

E.保持压强不变，充入CO使容器体积变大

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3.对于反应：$N_2 + O_2 \rightleftharpoons 2NO$，在密闭容器中进行，下列条件能加快反应速率的是　　（　AB　）

- A、缩小体积使压强增大；

- B、体积不变充入氮气使压强增大；

- C、体积不变充入惰性气体；

- D、使总压强不变，充入惰性气体。

4. NO和 CO都是汽车尾气中的物质，它们能很缓慢地反应生成CO_2和 N_2 对此反应有关的叙述中不正确的是 (AD)

　　A、降低温度能加快化学反应速率；

　　B、使用适当催化剂可以加快化学反应速率；

　　C、增大一氧化氮的量可以加快化学反应速率；

　　D、改变压强对化学反应速率没有影响。

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5.用3克块状大理石与30毫升3摩/升盐酸反应制取CO_2气体，若要增大反应速率，可采取的措施是①再加入30毫升3摩/升盐酸 ②改用30毫升6摩/升盐酸 ③改用3克粉末状大理石 ④适当升高温度

A. ①②④　　B. ②③④

C. ①③④　D. ①②③

答案：B

6.对于反应：$2SO_2 + O_2 \rightleftharpoons 2SO_3$，当其他条件不变时，只改变一个反应条件，将生成$SO_3$的反应速率的变化填入空格里(填写"增大""减小""不变")

编　号	改变的条件	生成SO_3的速率
①	升高温度	**增大**
②	降低温度	**减小**
③	增大O_2的浓度	**增大**
④	V_2O_5作催化剂	**增大**
⑤	压缩体积	**增大**

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7.下列关于催化剂的说法，正确的是
 A．催化剂能使不起反应的物质发生反应
B．催化剂在化学反应前后，化学性质和质量都不变
 C．催化剂能改变化学反应速率
 D．任何化学反应，都需要催化剂

答案：BC

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8. 下列说法正确的是（ **D** ）

A、一定条件下，增大反应物的量会加快化学反应速率。

B、增大压强，肯定会加快化学反应速率。

C、活化分子间所发生的碰撞为有效碰撞。

D、能够发生有效碰撞的分子叫活化分子。

9. 在C(固)+CO$_2$(气)=2CO(气) 的反应中。现采取下列措施：

(1)增大压强 ;(2)增加碳的量

(3)通入CO$_2$;(4)恒容下充入N$_2$;

(5)恒压下充入N$_2$

哪些措施能够使反应速率增大？为什么？

答案：(1)(3)

10.对于在溶液间进行的反应，对反应速率影响最小的因素是（ C ）
A、温度 B、浓度 C、压强 D、催化剂

11.下列条件的变化，是因为降低反应所需的能量而增加单位体积内的反应物活化分子百分数致使反应速率加快的是（ D ）
A、增大浓度 B、增大压强
C、升高温度 D、使用催化剂

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12. 设$NO + CO_2 \rightleftharpoons NO_2 + CO$(正反应吸热)反应速率为$v_1$；$N_2 + 3H_2 \rightleftharpoons 2NH_3$（正反应放热)反应速率为$v_2$。对于前述反应，当温度升高时，$v_1$和$v_2$变化情况为（ A ）

A、 同时增大   **B、** 同时减小

C、 v_1减少，v_2增大

D、 v_1增大，v_2减小

The limitation of chemical thermodynamics

化学热力学研究化学变化的方向、能达到的最大限度以及外界条件对平衡的影响。化学热力学只能预测反应的可能性，但无法预料反应能否发生？反应的速率如何？反应的机理如何？例如：

$$\Delta_r G_m^{\ominus} / kJ \cdot mol^{-1}$$

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \longrightarrow NH_3(g) \qquad -16.63$$

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O(l) \qquad -237.19$$

热力学只能判断这两个反应在标准状态下都能发生，但如何使它发生，热力学无法回答。

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