第三章　化学动力学基础

Chapter 3　The Basis of Chemical Dynamics

化学热力学成功预测了化学反应自发进行的方向，如：

$$2K(s) + 2H_2O(l) = 2K^+(aq) + 2OH^-(aq) + H_2(g) \qquad \Delta_r G^\ominus_{m,\,298K} = -404.82\ kJ\cdot mol^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g) \qquad \Delta_r G^\ominus_{m,\,298K} = -228.59\ kJ\cdot mol^{-1}$$

这两个反应的$\Delta G^\ominus_{298}<0$，所以此两个反应在 298K 时向正反应方向进行有利，但它们的化学反应速率却相差十万八千里：钾在水中的反应十分迅速剧烈，以至于燃烧；而把 H_2 和 O_2 的混合物于常温、常压下放置若干年，也观测不出反应的进行。前一类化学反应属于热力学控制的反应；后一类化学反应属于动力学控制的反应。

研究化学反应速率有着十分重要的实际意义。若炸药爆炸的速率不快，水泥硬化的速率很慢，那么它们就不会有现在这样大的用途；相反，如果橡胶迅速老化变脆，钢铁很快被腐蚀，那么它们就没有了应用价值。研究反应速率对生产和人类生活都是十分重要的。

在中学，我们已学过影响化学反应速率的因素：

1．The concentrations of the reactants：

Steel wool burns with difficulty in air, which contains 20 percents O_2 , but burst into a brilliant white flame in pure oxygen.

2．The temperature at which the reaction occur：

The rates of chemical reactions increase as temperature is increased. It’s for this reason that we refrigerate perishable food such as milk.

3．The presence of a catalyst：

The rates of many reactions can be increased by adding a substance known as a catalyst. The physiology of most living species depends crucially on enzymes, protein molecules that act as catalysts, which increase the rates of selected biochemical reactions.

4．The surface area of solid or liquid reactants or catalysts：

Reactions that involve solids often proceed faster as the surface area of the solid is increased. For example, a medicine in the form of a tablet will dissolve in the stomach and enter the bloodstream more slowly than the same medicine in the form of a fine powder.

§3-1　化学反应速率

The Rates of Chemical Reactions

一、化学反应速率表示法

1．Definition：通常以单位时间内反应物浓度的减少或生成物浓度的增加来表示。根据时间的长短，单位时间可用 s、min、hr、day、year 等不同单位表示，它由反应的快慢而

定。以反应 $2N_2O_5 \xrightarrow[CCl_4]{} 4NO_2 + O_2$ 为例：

化学反应速率可以表示成：$-d[N_2O_5]/dt$ 或者 $d[NO_2]/dt$

2．Units：$mol \cdot dm^{-3} \cdot s^{-1}$、$mol \cdot dm^{-3} \cdot min^{-1}$ 或者 $mol \cdot dm^{-3} \cdot hr^{-1}$

3．Average rate（平均速率） $\bar{v} = -\Delta[\text{反应物}]/\Delta t$

4．Instantaneous rate（瞬时速率）：$\lim\limits_{\Delta t \to 0}\{-\Delta[\text{反应物}]/\Delta t\} = -d[\text{反应物}]/dt$

对一般反应而言，$aA + bB \longrightarrow gG + hH$

用 $-d[A]/dt$、$-d[B]/dt$、$d[G]/dt$ 和 $d[H]/dt$ 中任何一种表示均可。实际上采用其中较易观察或测定者，如放出气体、自身颜色的变化、使指示剂变色等物质的浓度变化，来表示该反应的速率。

在一般情况下，上面各种速率不尽相同。但在等容条件下，

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

证明：由反应方程式得：$(-dn_A):(-dn_B):dn_G:dn_H = a:b:g:h$，

在等容条件下，浓度之比就等于物质的量之比：

即 $(-d[A]):(-d[B]):d[G]:d[H]=(-dn_A):(-dn_B):dn_G:dn_H=a:b:g:h$

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

Sample Exercise：The decomposition of N_2O_5 proceeds according to the equation：

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is 4.2×10^{-7} $mol \cdot dm^{-3} \cdot s^{-1}$，what is the rate of appearance of (a) NO_2； (b) O_2?

Solution：$\because -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

$$\therefore \frac{d[NO_2]}{dt} = -\frac{2d[N_2O_5]}{dt} = 2\times4.2\times10^{-7} = 8.4\times10^{-7}\ mol \cdot dm^{-3} \cdot s^{-1}$$

$$\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\times4.2\times10^{-7} = 2.1\times10^{-7}\ mol \cdot dm^{-3} \cdot s^{-1}$$

When we speak of the rate of a reaction without specifying a particular reactant or product, we will mean it in this sense.

二、反应活化能（Activation Energy）

In 1888 the Swedish chemist Svante Arrhenius suggested that molecules must possess a certain minimum amount of energy in order to react. According to the collision model, this energy comes from the kinetic energies of the colliding molecules.

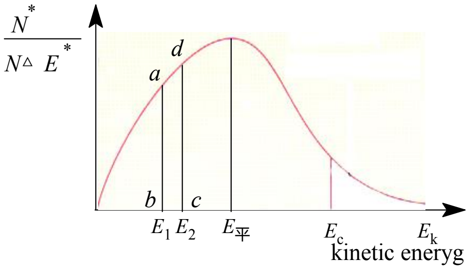


Fig. 3.1 Distribution of kinetic energies in gas molecules

1．分子运动速率分布（Maxwell-Boltzmann distribution）

(1) 图 3.1 中横坐标为动能(kinetic energy)，纵坐标为 ΔE^* 之间（即 $E_1 \rightarrow E_2$ 之间）所具有的分子分数，所以整条曲线与横坐标所围成的面积应为

$\dfrac{N}{N\cdot E}\cdot E = 1$，即 $S_t = 1$。图 3.1 中阴影部分面积为 $S_{abcd} = N^*/N$，即在温度 T 时，具有 E_1～E_2 能量的分子分数。E_c 表示发生反应所需要的临界能量（critical energy）。$E_{\text{平}}$表示 T 温度时的平均能量。

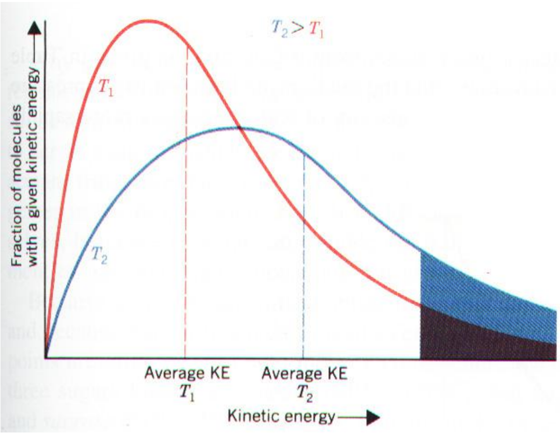


Fig. 3.2 Distribution of kinetic energies in a sample of gas molecules at two different temperatures

在大多数碰撞中，一个分子由于另一个分子消耗能量而获得能量，因此就有可能经过几次碰撞之后，一些分子就能获得比平均值高的能量，而另一些分子则具有比平均值低的能量。

(2) 升高温度（如图 3.2），大动能的分子分数增加，小动能的分子分数减少，所以分子的平均动能变大。

2．活化能（Activation energy） E_a

通常把化学反应所需要的临界能量(E_c)与一般分子的平均能量($E_{\text{平}}$)之差称为活化能。即 $E_a = E_c - E_{\text{平}}$

活化能的定义到目前为止有两种：

Lewis 定义：能够进行化学反应的活化反应物所具有的最低能量称为“临界能量”，所以他把“具有完成化学反应最小的、必须的能量，称为活化能”。

Tolman（托尔曼）定义：活化能是活化分子的平均能量与全部反应物分子平均能量之差。

我们是否可以这样认为：The minimum energy required to initiate a chemical reaction is called the activation energy, E_a . The value of E_a varies from reaction to reaction.

3．活化分子（Activated molecule）

凡能量高于临界能量的反应物分子，称为活化分子。从图 3.2 中可以看出：随着温度的升高，活化分子分数增加；对于不同的反应，临界能量(E_c)不同，含有的活化分子分数也不同。

4．有效碰撞（Effective collision）

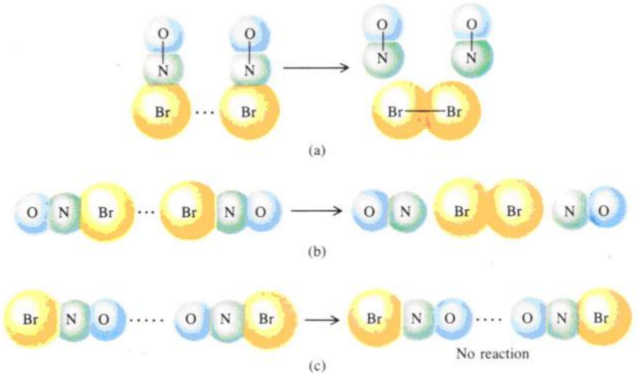


Figure 3.3
Several possible orientations for a collision between two BrNO molecules. Orientations (a) and (b) can lead to a reaction, but orientation (c) cannot.

粒子之间碰撞数目的计算表明：粒子之间碰撞频率是格外地高，在 STP 下，含 1mol A 和 1 mol B 的气态混合物中，A 和 B 之间分子的碰撞数目达 10^{30} 次 / 秒。如果

A 与 B 之间的每一次碰撞都能导致化学反应的话，那么，反应会在极短的时间内完成。正因为许多碰撞不是活化分子之间的碰撞，是属于无效的碰撞，即使活化分子之间的碰撞，也有“无效”碰撞（如图 3.3c 所示），所以在不同温度下，同一个化学反应也会有不同的反应速率。我们把能发生化学反应的碰撞，称为有效碰撞。

5．从定性角度来看，影响化学反应速率的因素

(1) 内因：a．取决于反应剂的性质，b．取决于反应剂参与的反应类型。

(2) 外因：a．浓度（或压力，对气体反应物而言）：虽然未改变活化分子的分数，但浓度增加，意味着增加了单位体积的活化分子总数，所以也增加了单位体积的活化分子数，导致有效碰撞次数增加，反应速率加快。

b．温度：升高温度，活化分子分数增加，有效碰撞次数增加，反应速率加快。

c．加入催化剂：使化学反应所需的临界能量变小（或变大 —— 指负催化剂），增加了活化分子分数，有效碰撞次数增加，反应速率增大。这些都可从图 3.1 的动能(E_k) —— $N^* / (N\Delta E^*)$图得到解释。

三、化学反应速率与浓度的关系（The Relationship of Chemical Reaction Rates and Concentrations）

1．反应速率与浓度的关系（The relationship of rate and concentration）

(1) 对于异相反应（heterogeneous reactions）：反应速率取决于相界面的接触面积。

(2) 对于均相反应 (homogeneous reactions）：反应速率取决于该相中反应物的浓度（或压强）。

(3) 反应速率与浓度的关系只有通过实验来测定。实验证明，反应物浓度与反应速率呈如下函数关系：$aA + bB \longrightarrow eE + fF$

rate = $k\,[A]^x\,[B]^y$，该式称为反应速率方程或质量作用定律（mass action law）。

式中 k：速率常数（rate constant），x：反应物 A 的级数(order)，y：反应物 B 的级数，$x + y$：反应的（总）级数，x、y 可以是正整数、负整数或分数。

For example：$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

Rate Data of the Reaction of Ammonium and Nitrites Ions in Water at 25℃

Exp. No.	Initial NH_4^+ Conce.（$mol\cdot dm^{-3}$）	Initial NO_2^- Conce.（$mol\cdot dm^{-3}$）	Observed Initial Rate（$mol\cdot dm^{-3}\cdot s^{-1}$）
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	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

The reaction order in NH_4^+ is 1; the reaction is first order in NH_4^+. It is also first order in NO_2^-. The overall reaction order is 1 + 1 = 2, we say the reaction is second order overall.

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

The following are some further examples of rate law：

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$　　　　rate = $k[N_2O_5]$

$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g)$　　　rate = $k[CHCl_3][Cl_2]^{1/2}$

$H_2(g) + I_2(g) \longrightarrow 2HI(g)$　　　rate = $k[H_2][I_2]$

$N_2O(g) \xrightarrow{Au} N_2(g) + 1/2O_2(g)$　　　rate = $k[N_2O]^0 = k$

The values of these exponents are determined experimentally. However, we also occasionally encounter rate laws in which the reaction order is fractional or even negative , although reaction orders are 0、1 or 2 in most rate laws.

(4) 速率常数的单位（units of rate constants）

a．因为 k 可看作反应物浓度为 1mol·dm^{-3} 时的反应速率，所以它只与温度和催化剂有关，而与反应物浓度无关；

b．速率常数的单位：$(\text{mol}\cdot\text{dm}^{-3})^{1-(x+y)}$ · 时间$^{-1}$；

c．通过 k 的单位可以判断反应级数：

(i) 若 k 的单位为时间$^{-1}$，则 $x + y = 1$，该反应为 first-order reactions；

(ii) 若 k 的单位为 mol·dm^{-3} · 时间$^{-1}$，该反应为 zero-order reactions。

(5) 只有一步完成的反应，即基元反应(elementary reactions)，其反应级数才等于此步骤中该反应物的系数的代数和。例如，某基元反应：$mA + nB \longrightarrow$ 产物，则 rate = $k[A]^m[B]^n$。

(6) 对于多步才能完成的反应，反应速率只取决于所有步骤中最慢的一步。

例如：反应 $C_2H_4Br_2 + 3KI \longrightarrow C_2H_4 + 2KBr + KI_3$ 的实际的反应步骤如下：

$C_2H_4Br_2 + KI \longrightarrow C_2H_4 + KBr + I + Br$　　　(slow)

$KI + I + Br \longrightarrow 2I + KBr$　　　(fast)

$KI + 2I \longrightarrow KI_3$　　　(fast)

rate = $k[C_2H_4Br_2][KI]$

所以一个反应的反应级数必须通过实验来确定。

(7) 在异相反应中，对纯固体或纯液体来说，其密度是一定的，因此在质量作用定律表达式中，通常不包括纯固体或纯液体物质的浓度，或者说这些物质的浓度为常数，可以并入反应速率常数内。在气相反应中，质量作用定律可以用分压代替浓度。

2．浓度与时间的关系（The relationship of concentration and time）

(1) 零级反应（zero-order reactions）

所谓零级反应是指反应速率与反应物浓度的零次方（即与反应物的浓度无关）成正比。零级反应较少，一些发生在固体表面上的反应属于零级反应。如氨在钨、铁等催化剂表面上的分解反应，就是零级反应。

$$NH_3(g) \xrightarrow[\text{catalysis}]{W} 1/2N_2(g) + 3/2H_2(g)$$

a．The zero-order rate equation：

若对任何一个零级反应：$A(g) \longrightarrow$ 产物，则$-d[A] / dt = k_0[A]^0 = k_0$，即 $d[A] = -k_0 d\,t$

当 $t = 0$ 时，$[A] = [A]_0$，当时间为 t 时，$[A] = [A]_t$，两边积分 $\int_{[A]_0}^{[A]_t} d[A] = \int_0^t (-k_0)dt$

$[A]_t - [A]_0 = -k_0(t - 0)$，整理得，$[A]_t = [A]_0 - k_0 t$

b．以零级反应的反应物浓度对时间 t 作图，呈直线关系，其斜率为$(-k_0)$；

c．当剩余反应物的浓度为起始浓度的一半时，即$[A]_t = [A]_0/2$，反应的时间 $t_{1/2}$ 称

为半衰期(half-life)。$t_{1/2}=\frac{1}{k_0}([A]_0-\frac{1}{2}[A]_0)=\frac{[A]_0}{2k_0}$，所以零级反应的半衰期与反应物的初始浓度成正比。

(2) 一级反应（first – order reactions）

一级反应就是反应速率与反应物浓度的一次方成正比。一级反应比较普遍，常见的一级反应有：大多数的放射性衰变，一般的热分解反应及分子重排反应等。

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ rate = $k_1[N_2O_5]$

$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$ rate = $k_1[H_2O_2]$

$SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$ rate = $k_1[SO_2Cl_2]$

a．The first-order rate equation：

对任何一个“一级反应”：$B(g) \longrightarrow$ 产物而言， $-d[B] / dt = k_1[B]^1$

$\therefore -\frac{d[B]}{[B]}=k_1dt$， 两边积分 $\int_{[B]_0}^{[B]_t}-\frac{d[B]}{[B]}=\int_0^t k_1dt$ 得

$\ln\frac{[B]_0}{[B]_t}=k_1t$， 或者 $\lg\frac{[B]_0}{[B]_t}=\frac{k_1t}{2.303}$， 或者 $\ln[B]_t = \ln[B]_0 - k_1t$

b．在一级反应中，以反应物浓度的对数对时间 t 作图，呈一条直线。其斜率为 $(-k_1)$（用自然对数表达式）或（$-k_1 / 2.303$）（用常用对数）。

c．一级反应的半衰期($t_{1/2}$)：$\ln[B]_0 - \ln([B]_0 / 2) = k_1\cdot t_{1/2}$ $\therefore t_{1/2} = \ln2 / k_1 = 0.693 / k_1$

即一级反应的半衰期 $t_{1/2}$ 是一个常数，它与反应物的初始浓度无关。

Sample Exercise 1：The first-order rate constant for the decomposition of a certain insecticide in water at 12℃ is 1.45 yr^{-1}, A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} $g\cdot cm^{-3}$ of water. Assume that the effective temperature of the lake is 12℃. (a) What is the concentration of the insecticide on June 1 of the following year? (b) How long will it take for the concentration of the insecticide to drop to 3.0×10^{-7} $g\cdot cm^{-3}$?

Solution：(a) Substituting $k = 1.45$ yr^{-1}，$t = 1.00$ yr and $[\text{insecticide}]_0 = 5.0\times10^{-7}$ $g\cdot cm^{-3}$ into equation $\ln[\text{insecticide}]_{t=1\,yr} = \ln(5.0\times10^{-7}) - 1.45\times1.00 = -15.96$

$\therefore [\text{insecticide}]_{t=1\,yr} = 1.2\times10^{-7}$ $g\cdot cm^{-3}$ （即$[A]_t$，$[A]_0$单位必须相同）

(b) Again substitution into equation with $[\text{insecticide}]_t = 3.0\times10^{-7}$ $g\cdot cm^{-3}$，

$\ln(3.0\times10^{-7}) = -1.45t + \ln(5.0\times10^{-7})$

$t = \{-\ln(3.0\times10^{-7}) + \ln(5.0\times10^{-7})\} / 1.45 = 0.35$ (yr)

Sample Exercise 2：已知过氧化氢分解成水和氧气的反应是一级反应：$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$，反应速率常数为 0.0410min，求：(a) 若$[H_2O_2]_0 = 0.500$ $mol\cdot dm^{-3}$，10.0 min 后，$[H_2O_2]_{t=10\,min}$是多少？(b) H_2O_2分解一半所需时间是多少？

Solution：(a) $\ln\frac{[H_2O_2]_{t=10\,min}}{[H_2O_2]_0}=-k_1t$， $\therefore \ln[H_2O_2]_{t=10\,min}=\ln[H_2O_2]_0-k_1t=0.332$ $(mol\cdot dm^{-3})$

(b) $t_{1/2} = \ln2 / k_1 = 0.693 / 0.0410 = 16.9$ (min)

(3) 二级反应（second -order reaction）

a．The second - order rate equation：$1 / [A]_t = 1 / [A]_0 + k_2t$

若任何一个“二级反应”：$A + B \longrightarrow$ 产物 或者 $2A \longrightarrow$ 产物而言，

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t=k_2[\mathrm{A}][\mathrm{B}] \xRightarrow{[\mathrm{A}]=[\mathrm{B}]} k_2[\mathrm{A}]^2$$，或者 $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t=k_2[\mathrm{A}]^2$

$\mathrm{d}[\mathrm{A}]/[\mathrm{A}]^2=-k_2\mathrm{d}t$，两边积分得：

b．在二级反应中，以反应物浓度的倒数对时间 t 作图，呈一条直线，其斜率为 k_2

c．二级反应的半衰期：$\dfrac{1}{[\mathrm{A}]_0/2}=\dfrac{1}{[\mathrm{A}]_0}+k_2t_{1/2}$　　$\therefore t_{1/2}=\dfrac{1}{k_2[\mathrm{A}]_0}$

可见，二级反应半衰期与起始浓度的一次方呈反比，即反应物起始浓度越大，$t_{1/2}$越小。下列反应均是二级反应：

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$　　rate = $k_2[NO_2][CO]$

$CH_3COOC_2H_5(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$

rate = $k_2[CH_3COOC_2H_5][OH^-]$

$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$　　rate = $k_2[NO_2]^2$

四、反应速率与温度的关系（The Relationship of Rates and Temperature）

1．根据许多实验事实，总结出一条近似的经验规则，温度每升高 10℃，反应速率大约增大 2～4 倍，即 $k_{t+10}/k_t = 2～4$。这是 Van’t Hoff 归纳出来的一个近似的经验规律。有时又称为 Van’t Hoff’s rule.

2．1889 年瑞典科学家 S. Arrhenius 总结了大量的实验数据，得出了如下结论：

化学反应的速率常数（k）与温度之间呈指数关系。

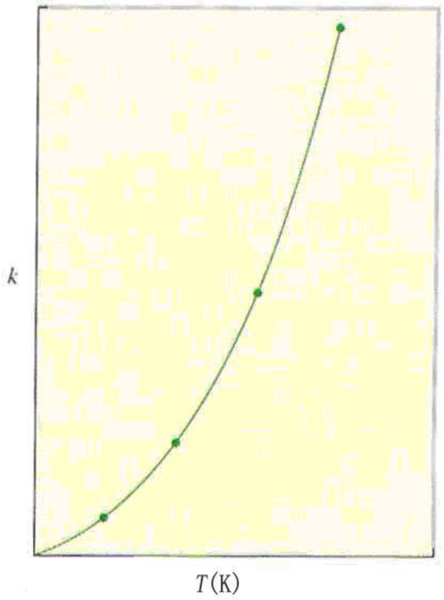


Fig. 3.4　A plot showing the exponential dependence of the rate constant on absolute temperature. The exact temperature dependence of k is different for each reaction. This polt represents the behavior of a rate constant that doubles for every increase in temperaute of 10 K.

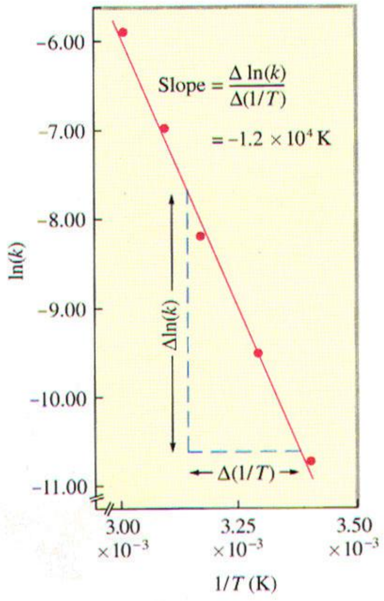


Fig. 3.5 Plot of ln(k) versus 1/T for the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. The value of the activation energy for this reaction can be obtained from the slope of the line, which equals $-E_a/R$.

3．公式：$k = A\cdot e^{-E_a/RT}$——The Arrhenius equation

式中 E_a— the activation energy　　A— the frequency factor, it is related to the frequency of collisions and the probability that the collisions are favorably oriented for reaction.

公式也可以表示成 $k = A\cdot\exp(-E_a/RT)$ （exp.：exponent）

一般化学反应的活化能在 40～400 kJ · mol^{-1} 范围之内

Reactions	Solvent	E_a / kJ · mol^{-1}
$CH_3COOC_2H_5 + NaOH$	水	47.3
$n - C_5H_{11}Cl + KI$	丙酮	77.0
$C_2H_5ONa + CH_3I$	乙醇	81.6
$C_2H_5Br + NaOH$	乙醇	89.5
$2HI \longrightarrow I_2 + H_2$	气相	184.1
$H_2 + I_2 \longrightarrow 2HI$	气相	165.3
$N_2O_5 \longrightarrow N_2O_4 + 1/2O_2$	气相	103.4
$(CH_2)_3 \longrightarrow CH_3CH{=}CH_2$	气相	272.0

对 Arrhenius 公式两边取自然对数，得：$\ln k = \ln A - \frac{E_a}{R}(\frac{1}{T})$，以 $\ln k$ 对 $1/T$ 作图，是一条直线，其斜率为 $-E_a/R$，截距为 $\ln A$。因此活化能可以通过实验来测定：用在不同温度下观察到的 k 值的自然对数对 $1/T$ 作图，斜率为 $-E_a/R$，从而求得 E_a（见图 3.5）。

4．不同温度下，速率常数之间的关系

已知温度为 T_1 时，速率常数为 k_1；温度为 T_2 时，速率常数为 k_2。由 Arrhenius equation 得：$\ln k_1 = \ln A - E_a/RT_1$ ①，$\ln k_2 = \ln A - E_a/RT_2$ ②

① − ② 得：

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

Sample Exercise 1：The following table shows the rate constants for the rearrangement of methyl isonitrile H_3C-NC at various temperature at various temperatures (these are the data that are graphed in right figure：

Temperature (℃)	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 ?

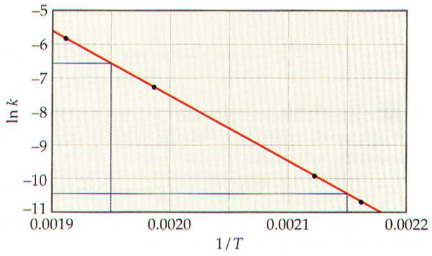


Fig 3.6 The natural logarithm of the rate constant for the rearrangement of methyl isonitrile as a function of 1/*T*.

Solution：(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 following table：

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

The slope of the line is obtained by choosing two well-separated points：

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

Slope = $-E_a/R$　　∴ $E_a = 1.9\times10^{4}\times 8.314 = 158\ \text{kJ·mol}^{-1}$

(b) To determine the rate constant, k_1, at 430.0 K, we can use above equation with E_a, $k_2 = 2.52\times10^{-5}\ \text{s}^{-1}$, $T_2 = 462.9\text{K}$, and $T_1 = 430\text{K}$.

$$\ln\frac{k_1}{2.52\times10^{-5}} = \frac{1.58\times10^{5}}{8.314}\left(\frac{1}{462.9}-\frac{1}{430.0}\right) = -3.14 \qquad \therefore k_1 = 1.09\times10^{-6}\ (\text{s}^{-1})$$

Sample Exercise 2：五氧化二氮晶体具有很高的蒸气压，在气相或惰性溶剂中都能全部分解，其分解反应为 $N_2O_5(s) \rightleftharpoons 1/2O_2(g) + N_2O_4(g) \rightleftharpoons 2NO_2(g)$。此反应为一级反应。由于分解产物 N_2O_4 和 NO_2 均溶于 CCl_4 中，只能有 O_2 放出，故 N_2O_5 在 CCl_4 中的分解可用气量管测定分解产物逸出 O_2 的体积来量度。下表是 0.7372 克 $N_2O_5(s)$在 30℃和 $p^\ominus$ 下的数据：

时间 t (s)	0	2400	9600	16800
体积 V_{O_2} (ml)	0	15.65	45.85	63.00

(a) 求算此反应的速率常数 k 及半衰期 $t_{1/2}$。

(b) 30℃时，分解 90.0% N_2O_5 所需时间为多少秒？

(c) 已知该反应活化能为 $1.03\times10^{5}\ \text{J·mol}^{-1}$，若要求 2400 秒内收集 60.00ml O_2（30℃时的体积），问需在什么条件下进行实验？（气体按理想气体处理）

Solution：(a) 由于 N_2O_5 的分解反应为一级反应，∴ $\ln c_0 - \ln c = kt$

若以体积表示，则 $\ln V_\infty - \ln(V_\infty - V_t) = kt$，$V_\infty$应为 0.7372g $N_2O_5(s)$完全分解所产生 O_2 的体积，相当于 $N_2O_5(s)$在 CCl_4 中的起始浓度，而$(V_\infty - V_t)$相当于时间 t 时 CCl_4 中剩下的 $N_2O_5(s)$的浓度。

$$V_\infty = \frac{1}{2}\times\frac{0.7372}{108}\times\frac{RT}{p} = \frac{1}{2}\times\frac{0.7372\times8.314\times303}{108\times101325} = 8.49\times10^{-5}\text{m}^3$$

$$\therefore k_1 = \frac{1}{2400}\ln\frac{84.9}{84.9-15.65} = 8.49\times10^{-5}(\text{s}^{-1})\ ,\quad k_2 = \frac{1}{9600}\ln\frac{84.9}{84.9-45.85} = 8.09\times10^{-5}(\text{s}^{-1})$$

$$k_3 = \frac{1}{16800}\ln\frac{84.9}{84.9-63.00} = 8.07\times10^{-5}(\text{s}^{-1})\ ,$$

$$\therefore \bar{k} = \frac{k_1+k_2+k_3}{3} = 8.22\times10^{-5}(\text{s}^{-1})\ ,\qquad t_{1/2} = \frac{\ln2}{k} = \frac{0.693}{8.22\times10^{-5}} = 8.43\times10^{3}(\text{s})$$

(b) 设 30℃时，分解 90.0% $N_2O_5(s)$所需时间为 t

$$\text{则}\ t = \frac{1}{k}\ln\frac{c_0}{c_0-0.9c_0} = \frac{1}{8.22\times10^{-5}}\ln10 = 2.80\times10^{4}(\text{s})$$

(c) 当 30℃时，2400 秒内只能收集到 15.65ml O_2，现要在此时间内收集到 60.00ml O_2，则需调节反应温度。在调节温度(T_2)下，速率常数为：

$$k_{(T_2)} = \frac{1}{2400}\ln\frac{84.9}{84.9-60.00} = 5.11\times10^{-4}(\text{s}^{-1})$$

根据 Arrhenius equation：$\ln[k_{(T_2)}/k_{(T_1)}] = \dfrac{E_a}{R}\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)$

代入数据，得 $\ln\dfrac{5.11\times10^{-4}}{8.22\times10^{-5}}=\dfrac{[T_2-(273+30)]\times1.03\times10^{5}}{8.314\times(273+30)T_2}$　　解得 $T_2=317\text{K}$

五、催化剂对反应速率的影响（The Affect of Catalyst on Chemical Rate）

升高温度虽然能加快反应速率，但高温有时会给反应带来不利的影响。例如有的反应在高温下会发生副反应，有的反应产物在高温下会分解等等。人们通过使用催化剂选择新的反应途径，以达到降低反应的活化能，进而加快反应速率。可见催化剂在现代化工业中具有何等重要的地位和作用。

考察化学反应动力学的另一种有效的方法是考察反应物变成生成物的位能变化。此理论称为过渡态理论（transition state theory）

1．过渡态理论：

化学反应进行时，反应物分子首先形成一种中间过渡状态的物质——活化络合物（activated complex），在该活化络合物中，反应物分子中的旧键已经松弛，而产物分子中的新键只初步形成，因此活化络合物分子是不稳定的，该活化络合物分子的位能比反应物分子及产物分子的位能高，其值由活化络合物分子结构来决定。

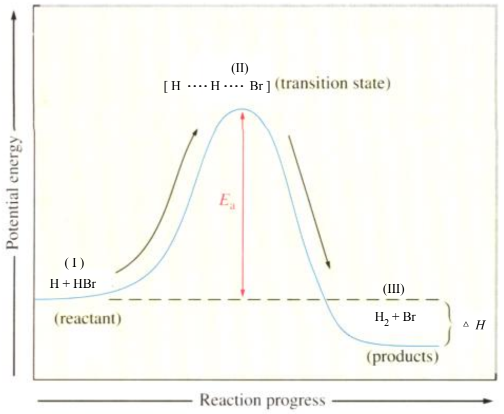


Fig. 3.7 Energy profile for the H + HBr ⟶ H_2 + Br

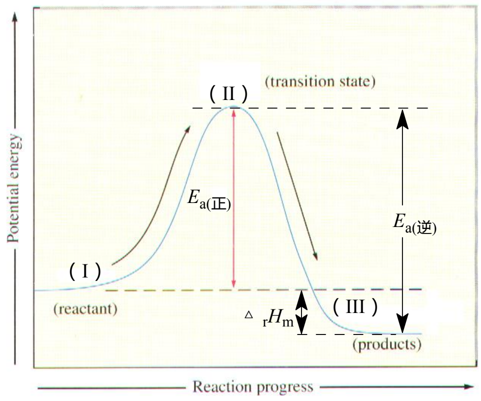


Fig. 3.8 Energy profile for the transition state theory

2．化学反应的位能图：

以一个最简单的直线型反应为例（图 3.7）：

$a + b - c \longrightarrow [a\cdots b\cdots c] \longrightarrow a - b + c$，例如：$H + H\text{–}Br \longrightarrow H\cdots H\cdots Br \longrightarrow H - H + Br$。为简便起见，假设碰撞沿着所有核，通过一条直线上发生的。

(1) 始态：H 和 H – Br 粒子离得相当远，相互不发生影响，其位能恰好等于 H 本身和 HBr 本身的位能总和；

(2) 过渡状态：当 H 和 HBr 靠近时，电子云的排斥力变得相当大，那就必须对体系作功，迫使粒子挤在一起，这意味着整个位能要增加，一直增加到相应的活化络合物的位能；

(3) 终态：随着活化络合物分裂，H – H 和 Br 的分离，位能下降。

3．过渡状态理论中的活化能（图 3.8）（Activation energy in the transition state theory）

(1) 正反应活化能：$E_{a(正)} = N_A(\varepsilon_{活化络合物} - \varepsilon_{反应物}) = E_{(II)} - E_{(I)}$

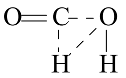
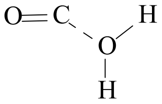
(2) 逆反应活化能：$E_{a(逆)} = N_A(\varepsilon_{活化络合物} - \varepsilon_{产物}) = E_{(II)} - E_{(III)}$

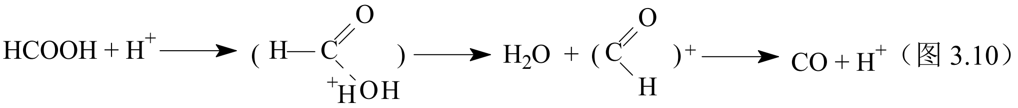
(3) 化学反应热：$\Delta_r H_m = E_{a(正)} - E_{a(逆)}$

4．催化剂（Catalyst）

(1) 催化剂的第一个基本性质 —— 改变反应速率。这是由于改变了反应途径，生成

了中间过渡产物，降低了活化络合物的能量。例如：HCOOH $\xrightarrow{\triangle}$ CO + H₂O。

在无催化剂时，HCOOH首先形成  （活化络合物），再转变成  ，然后分解成CO和H₂O（图3.9）。在H⁺离子催化下



$$HCOOH + H^+ \longrightarrow (H-C(=O)-\overset{+}{H}OH) \longrightarrow H_2O + (O=C-H)^+ \longrightarrow CO + H^+$$（图3.10）

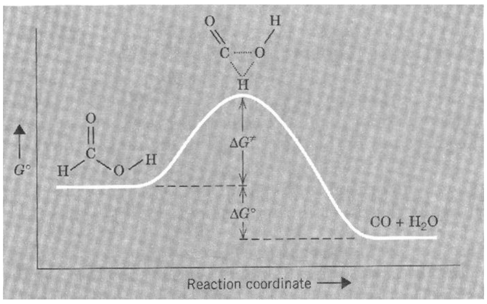


Fig. 3.9 The free energy profile for the decomposition of formic acid

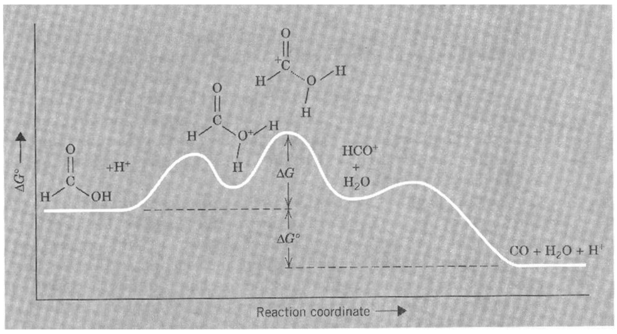


Fig. 3.10 The free energy profile for the acid catalyzed decomposition of formic acid

(2) 催化剂的第二个基本性质 —— 专一性。催化分为均相催化(homogeneous catalysis)和异相催化(heterogeneous catalysis)。例如：

$$H_2O_2(aq) \xrightarrow{Mn^{2+}} H_2O(l) + 1/2O_2(g) \quad , \quad N_2O(g) \xrightarrow{Au} N_2(g) + 1/2O_2(g)$$

$$Na_2SO_3 + 1/2O_2 \xrightarrow{Cu^{2+}(10^{-8}g)} Na_2SO_4 \quad , \quad CO + 2H_2 \xrightarrow{CuO+ZnO} H_3COH$$

在生物学中，有一类很重要的催化剂称为酶（enzymes）。在人体中，各种酶的催化非常专一：唾液酶（saliva）使淀粉转化为糖，酵母酶（zymase）使糖转化为醇和CO₂。人体中还有脂酶、麦芽糖酶、胃朊酶、胰朊酶、蛋白酶、乳糖酶……一大串催化剂。没有催化剂，就没有生命和近代文明。

1969年科学家第一次在实验室合成了一种酶 —— 核糖核酸酶。由于此工作，Stein、Moore和Anfinson获得了1972年Nobel化学奖。

(3) 自催化（autocatalysis, selfcatalysis）

例如，$IO_3^- + 3H_2SO_3 \longrightarrow I^- + 3SO_4^{2-} + 6H^+$ 的反应，生成的I⁻离子按照下列方程式催化：$IO_3^- + I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$，

$$3I_2 + 3HSO_3 + 3H_2O \longrightarrow 6I^- + 3SO_4^{2-} + 12H^+$$

这是因为I₂与H₂SO₃的反应要比IO_3^-与H₂SO₃的反应快得多。

§3-2　化学反应机理

Reaction Mechanisms

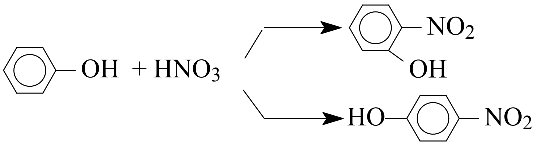
一、复杂反应（Complex Reactions）：

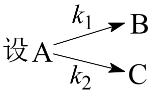
1．包含有两个或两个以上基元反应（elementary reactions）组合成的总反应，称为复杂反应。

2．典型的复杂反应有四类：对行反应（即对峙反应）、平行反应、连串反应及链反应。

(1) 对行反应　正向和逆向同时进行的反应，称为对行反应，即可逆反应。实际上，绝大多数反应都是可逆反应。因此，既要考虑正反应速率，也要考虑逆反应速率。对于正、逆反应都为一级反应的对行反应：A $\underset{k_r}{\overset{k_f}{\rightleftharpoons}}$ B，净反应速率(net rate) = k_f[A] − k_r[B]。

(2) 平行反应　相同反应条件下，反应物能同时进行几种不同的反应。

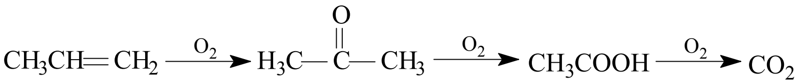
例如：

，设 

都为一级反应，

则−d[A] / d t = k_1[A] + k_2[A] = (k_1 + k_2)[A]，ln[A]$_0$ − ln[A]$_t$ = (k_1 + k_2) t

(3) 连串反应　凡反应所产生的物质能再起反应而产生其它物质的反应。



$$CH_3CH{=}CH_2 \xrightarrow{O_2} H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{O_2} CH_3COOH \xrightarrow{O_2} CO_2$$

设连串反应 A $\xrightarrow{k_1}$ B $\xrightarrow{k_2}$ C 都为一级反应，

则−d[A] / d t = k_1[A]，d[B] / d t = k_1[A] − k_2[B]

(4) 链反应　用某种方法（光、热、电等）使反应引发，产生自由基，发生一连串反应，反应自动进行下去，好像一条链一样，一环扣一环，直至反应停止，这类反应称为链反应。例如：$H_2 + Cl_2 \xrightarrow{hv} 2HCl$，其历程为：

$Cl_2 \xrightarrow{hv} 2Cl\cdot$（链的引发）

$$\left.\begin{array}{l} Cl\cdot + H_2 \longrightarrow HCl + \cdot H \\ H\cdot + Cl_2 \longrightarrow HCl + \cdot Cl \\ Cl\cdot + H_2 \longrightarrow HCl + \cdot H \end{array}\right\}\text{链的传递}$$

……………………………

$2Cl^-\cdot + M \longrightarrow Cl_2 + M$（链的终止）

二、复杂反应的近似处理方法

1．稳态近似法（steady state approximation）：

(1) 基本思想：在连串反应中，若中间产物 B 很活跃，极易继续反应，则 $k_2 >> k_1$，所以 B 在反应过程中的浓度很小，可视反应过程中 B 的浓度基本不变，那么 d[B] / dt = 0，称 B 的浓度处于稳态。

(2) 所谓稳态就是指某中间物的生成速率与消耗速率相等，导致其浓度不随时间而变化的状态。例如自由基就可以作稳态处理。

(3) 处理方法：以 $H_2 + Cl_2 \longrightarrow 2HCl$ 的历程为例：

$$Cl_2 \xrightarrow[k_1]{h\nu} 2Cl\cdot \ ,\qquad Cl\cdot + H_2 \xrightarrow{k_2} HCl + H\cdot$$

$$H\cdot + Cl_2 \xrightarrow{k_3} HCl + Cl\cdot \ ,\qquad 2Cl\cdot \xrightarrow{k_4} Cl_2$$

写出此反应的速率方程式及反应级数。

解答：H · 与 Cl · 都是自由基，它们都处于稳态

∴ $d[H\cdot] / dt = k_2[Cl\cdot][H_2] - k_3[H\cdot][Cl_2] = 0$

则 $k_2[Cl\cdot][H_2] = k_3[H\cdot][Cl_2]$ ①

$d[Cl\cdot] / dt = 2k_1[Cl_2] + k_3[H\cdot][Cl_2] - k_2[Cl\cdot][H_2] - 2k_4[Cl\cdot]^2 = 0$ ②

（∵ $-\dfrac{d[Cl_2]}{dt} = \dfrac{1}{2}\dfrac{d[Cl\cdot]}{dt}$ ∴ $-\dfrac{2d[Cl_2]}{dt} = \dfrac{d[Cl\cdot]}{dt}$ ）

①式代入②式得：$2k_1[Cl_2] - 2k_4[Cl\cdot]^2 = 0$ ∴ $[Cl\cdot] = \{(k_1/k_4)[Cl_2]\}^{1/2}$

∴ $d[HCl]/dt = k_2[Cl\cdot][H_2] + k_3[H\cdot][Cl_2] = 2k_2[Cl\cdot][H_2] = k'[Cl_2]^{1/2}[H_2]$

其中 $k' = k_2 \cdot (2k_1/k_4)^{1/2}$，∴ 此反应的级数为 1.5 级

2．平衡态近似法（pre – equilibria）

对于机理 $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow[slow]{k_2} D$， $d[D] / dt = k_2[C]$ ，

由于第一个反应很快达到平衡，则 $k_1[A][B] = k_{-1}[C]$

∴ $d[D] / dt = (k_1 k_2 / k_{-1})[A][B]$

三、已知反应速率方程，推测反应机理

Sample Example：Burns and Dainton have investigated the kinetics of the oxidation of CO by Cl_2 to yield phosgene as in $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ and found their experimental results to be represented by the rate equation : $d[COCl_2] / dt = k_r[Cl_2]^{3/2}[CO]$. Postulate a mechanism that is consistent with this rate equation.

推测活化络合物的方法：The atoms involved in the slow step of a reaction can be evaluated as the sum of those represented in the numerator of the rate equation minus those represented in the denominator of the rate equation.

Solution：按照上面规则，该反应的活化络合物应为 Cl_3CO。因此最慢的步骤可以假设为 $COCl(g) + Cl_2(g) \longrightarrow COCl_2(g) + Cl(g)$。但单独一个方程不能组成反应机理，我们必须假设合理的快反应步骤：

$Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g)$ rapid equilibrium ①

$Cl(g) + CO(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COCl(g)$ rapid equilibrium ②

$COCl(g) + Cl_2(g) \xrightarrow{k_3} COCl_2(g) + Cl(g)$ rate determining ③

由③得 $\dfrac{d[COCl_2]}{dt} = k_3[COCl][Cl_2]$，由②得 $[COCl] = \dfrac{k_2[Cl][CO]}{k_{-2}}$

由①得 $[Cl] = \{\dfrac{k_1[Cl_2]}{k_{-1}}\}^{1/2}$ ∴ $\dfrac{d[COCl_2]}{dt} = (\dfrac{k_1}{k_{-1}})^{1/2}\dfrac{k_2}{k_{-2}}k_3[Cl_2]^{3/2}[CO]$

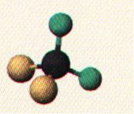
Practice Exercise：Propose a mechanism for the reaction

$$I^-(aq) + OCl^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$$

That is consistent with the experimental rate equation $\mathrm{d}[\mathrm{IO}^-]/\mathrm{d}t = k_\mathrm{r}[\mathrm{I}^-][\mathrm{OCl}^-]/[\mathrm{OH}^-]$

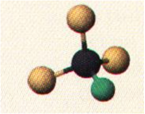
Depletion of Stratospheric Ozone

Much of our life in the United States today depends on refrigeration. We cool our homes, cars, offices, and shopping centers with air conditioners. We preserve our food and medicines with refrigerators. Until very recently all of these refrigeration units used *chlorofluorocarbons*, or CFCs, as the heat−exchanging fluid. That situation has now changed dramatically, in part because of laboratory studies of the kinetics of the reactions that CFCs might undergo in the stratosphere.



freon−12

dichlorodifluoromethane



freon−11t

richlorofluoromethane

Nonflammable, nontoxic CFCs such as CCl_2F_2 were discovered by scientists at the Frigidaire Division of General Motors in 1928. By 1988, the total worldwide consumption of CFCs was over 1×10^9 kilograms annually. In the United States thousands of businesses produced CFC−related goods and services worth more than ＄28 billion a year, and there were more than 700,000 CFC−related jobs. CFCs were used in the United States mostly as refrigerants, foam−blowing agents for polystyrene and polyurethane, aerosol propellants, and industrial solvents.

It is ironic that the very properties that led to the first use of CFCs are now causing worldwide concern. Once gaseous CFCs are released into the troposphere, that part of the earth's atmosphere ranging from the surface to an altitude of about 10 km, they persist for a long time because there is no mechanism for their destruction. Through atmospheric mixing they riseto the stratosphere where they are eventually destroyed by solar radiation — but with significant consequences to our environment, as first recognized by M. J. Molina and F. S. Rowland in 1974 (Figure A). From laboratory experiments, they predicted that continued use of CFCs would lead eventually to a significant depletion of the ozone layer around the earth. This is a serious concern because, for every 1% loss of ozone from the stratosphere, an additional 2% of the sun's high−energy ultraviolet radiation can reach earth's surface, resulting in increases in skin cancer, damage to plants, and possbibly other effects that we do not even suspect at this time.

Ozone is produced in the stratosphere when high−energy ultraviolet radiation causes the photodissociation of oxygen to give O atms, which react with O_2 molecules:

$O_2\,(g) + \text{radiation}\ (\lambda < 280\ \text{nm}) \longrightarrow 2O\,(g)$ $\qquad$ $O\,(g) + O_2\,(g) \longrightarrow O_3\,(g)$

The ozone produced by this mechanism in the stratosphere is quite abundant (10 ppm), which is fortunate because O_3 is also photodissociated by sunlight, $O_3\,(g) \longrightarrow O\,(g) + O_2\,(g)$, And the O atoms produced react with more O_2 to regenerate O_3. The process keeps 95% to 99% of the sun's ultraviolet radiation from reaching earth's surface.

The problem with CFCs is that they disrupt the protective ozone layer by a "chlorine catalytic cycle." The CFCs rise to the stratosphere where C−Cl bonds are broken by high−energy photons. The Cl atoms attack ozone to give ClO, chlorine oxide, and oxygen: $Cl\,(g) + O_3\,(g) \longrightarrow ClO\,(g) + O_2\,(g)$

This would not necessarily be a problem, except that ClO can react with an O atom to give O_2 and regenerates a Cl atome: $ClO\,(g) + O\,(g) \longrightarrow Cl\,(g) + O_2\,(g)$

The Cl atom can then destroy still another O_3, and so on and on in a "catalytic cycle." The net reaction is the destruction of a significant quantity of ozone. It is estimated that each Cl atom can destroy as many as 100,000 ozone molecules before the Cl atom is inactivated or returned to the troposphere (probably as HCl).

At least two other major kinds of reactions are believed to *interfere* with ozone loss. In one case ClO reacts with nitrogen monoxide, NO, to release a Cl atom and form NO_2. The NO_2 goes on to regenerate a molecule of ozone. In another reaction, ClO forms chlorine nitrate ($ClONO_2$), a compound that at least temporarily acts as a "chlorine reservoir." Eventually, though, this compound also breaks apart and frees Cl atoms to resume their ozone destruction.

If these interference reactions are important, CFCs might have only a minimal effect on earth's ozone layer. In the early spring in the southern hemisphere, however, the ozone layer over the Antarctic is significantly depleted, a fact clearly illustrated in satellite images of ozone concentration done in the early 1990s (Figure B). One theory used to explain this observation involves the high–altitude clouds that are common over the Antarctic continent in the winter. Chlorine nitrate could condense in these extremely cold clouds, and chlorine atoms could also be trapped as HCl. Rowland and Molina estimate that one out of every three or four collisions of $ClONO_2$ with HCl–containing ice crystals leads to reactions such as $ClONO_2 + HCl \longrightarrow HNO_3 + Cl_2$

The first sunlight of spring that warms the clouds can trigger the release of atomic chlorine by photodissociating chlorine molecues. Because nitrogen oxides are trapped in the clouds as nitric acid, the "chlorine catalytic cycle" can run unchecked for 5 or 6 weeks in the spring.

Whatever the theories for the springtime Antarctic ozone loss, the problem is real, and people around the world have taken steps to halt any further deterioration. Chemical companies in the United States have halted CFC production and are actively searching for substitutes. In January, 1989, 24 nations signed the *Montreal Protocal*, which calls for reductions in production and use of certain CFCs. Another meeting in Denmark in 1992 led to a complete ban on CFC production.

But there will be trade–offs. For example, CFC substitutes now available are less efficient as refrigerants, so it is estimated that appliances will use 3% more electricity in the United States, and this will increase consumer costs. Furthermore, because electricity is mostly generated by burning fossil fuels, the amount of CO_2 evolved will increase, which in turn will contribute to the "greenhouse" effect.

CFCs and their relation to ozone depletion is just one more example of the risks–and–benefits problem. In this case scientists and citizens have concluded that the risks of CFCs outweigh the benefits.

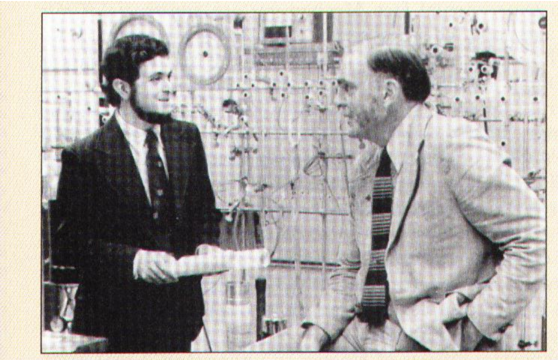


Figure A Mario J. Molina (*left*) and F. Sherwood Rowland (*right*). These scientists first recognized the potential for the depletion of the earth's atmosphere by CFCs. Rowland is Professor of Chemistry at the University of California, Irvine, and Molina is Professor of Environmental Sciences at the Massachusetts Institute of Technology. Molina and Rowland shared the 1995 Nobel Prize in Chemistry with Paul Crutzen of Germany for their studies of the earth's ozone layer and the effect of pollutants on it. (*The Bettmann Archive*)

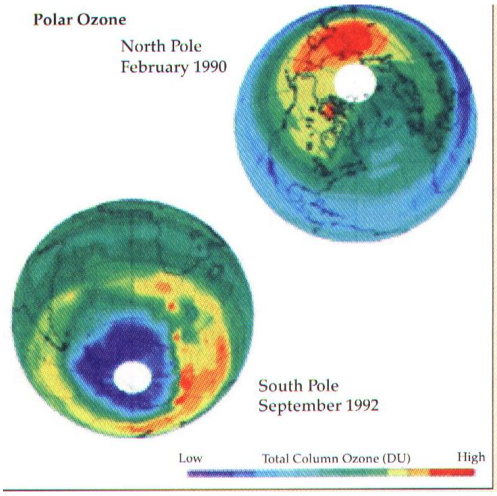


Figure B This satellite image, acquired in September 1992, shows that the stratospheric ozone concentration is depleted near the South Pole. The image is color–coded to indicate relative concentrations, blue being low and red being high. For more images and information on ozone in the atmosphere go to Web site http://daac.gsfc.nasa.gov. (*NASA*)