

## Chap 12. Chemical kinetics (化學动力学)

Thermodynamics (熱力学):

反應是否會發生 Spontaneous  
or not spontaneous

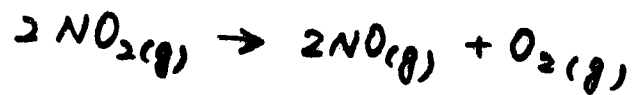
Chemical kinetics (动力学):

反應發生的快慢, 速率

1. Reaction Rates
2. Rate laws
3. Reaction mechanisms

# § 12.1 Reaction Rates

12-2

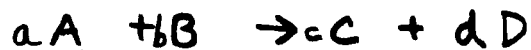


Reaction Rate of a chemical reaction:  
change in concentration of a reactant  
or product per unit time.

$$\text{Rate} = \frac{\text{concentration of A at time } t_2 - \dots t_1}{t_2 - t_1}$$

$$= \frac{\Delta [\text{A}]}{\Delta t}$$

Ex:



$$\text{Rate} = -\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{c} \frac{d[\text{C}]}{dt} = \frac{1}{d} \frac{d[\text{D}]}{dt}$$

Ex: Table 12.1  $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$   
& Fig 12.1

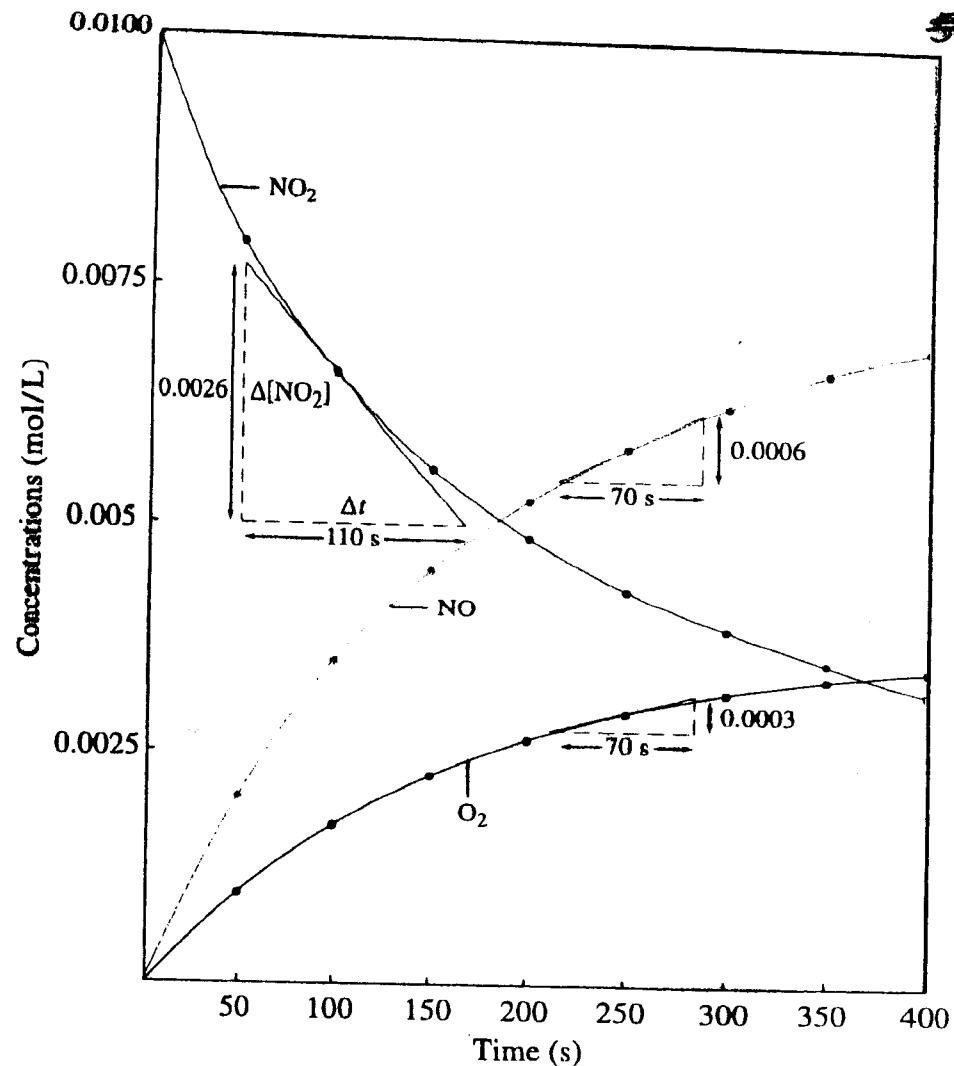


Figure 12.1  
The definition of rate



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$$\text{Rate} = - \frac{\text{change in } [\text{NO}_2]}{\text{time elapsed}} = - \frac{\Delta [\text{NO}_2]}{\Delta t} \quad 12-4$$

$$= - \frac{[\text{NO}_2]_{t=50} - [\text{NO}_2]_{t=0}}{50.5 - 0.5}$$

$$= - \frac{0.0079 - 0.0100 \text{ mol/L}}{50.5}$$

$$= +4.2 \times 10^{-5} \text{ mol/L}\cdot\text{sec}$$

(Average rates over 50-sec time interval)

see Table 12.2

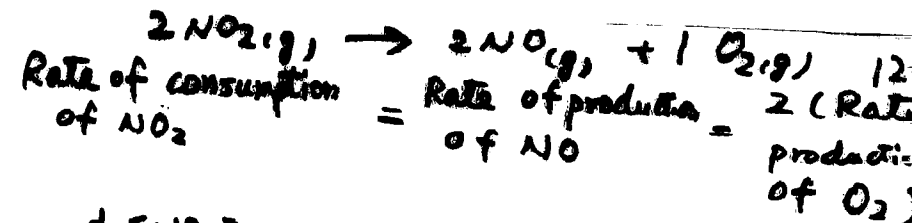
But, what about the instantaneous rate (the value of the rate at a particular time)?

↓

slope of the tangent line

$$= \lim_{\Delta t \rightarrow 0} \frac{\text{change in concentration } (\Delta [\text{NO}_2])}{\text{change in time } (\Delta t)}$$

$$= \frac{d[\text{NO}_2]}{dt}$$



$$- \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{NO}]}{dt} = 2 \left( \frac{d[\text{O}_2]}{dt} \right)$$

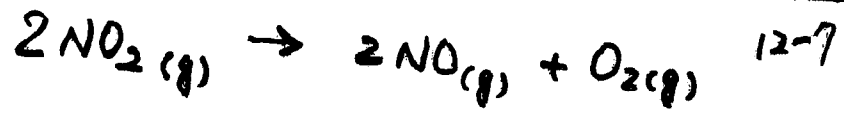
$$\text{or } -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{1}{1} \frac{d[\text{O}_2]}{dt}$$

## § 12.2 Rate Laws: An Introduction

$$\text{Rate} = -\frac{1}{2} \frac{\Delta [\text{NO}_2]}{\Delta t} = k [\text{NO}_2]^n$$

$$= \frac{\Delta [\text{O}_2]}{\Delta t} //$$

Reaction Rate will depend only on the concentrations of the reactants, if we choose conditions where the reverse reaction can be neglected.  
(例如反應剛開始時)



(1) at time = 0,  $\frac{\Delta[\text{NO}_2]}{\Delta t}$  only depends on concentrations of reactants

$$R = k[\text{NO}_2]^n \quad (\text{只考慮正反應})$$

(2) 平衡到達時 (at equilibrium)  
正反應速率 = 逆反應速率

此時  $\frac{\Delta[\text{NO}_2]}{\Delta t} = 0 \quad t = \infty$

$$\text{Rate} = k[\text{NO}_2]^n \rightarrow \begin{matrix} \text{order of the} \\ \text{reaction} \end{matrix}$$

↑  
rate const

1. n 只能由實驗求得, 不能由平衡式子直接寫出
2. 此式子只適用於 reverse reaction does not contribute 時

### Types of Rate Laws

(1) differential rate law (or rate law)  
expresses how the rate depends on concentration  
Rate =  $k[A]^n$

(2) integrated rate law:  
expresses how two concentrations depend on time

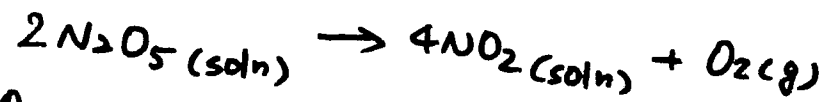
$$[A] = [A]_0 + \dots$$

see page 567

### Rate laws: A summary

Knowing the rate law for a reaction is important mainly because we can usually infer the individual steps involved in the reaction from the specific form of the rate law.

### § 12.3 Determining the form of the rate law



∴  $\text{O}_2(\text{g})$  evaporate, ∴ 逆反應可忽略

12-9<sup>144</sup>

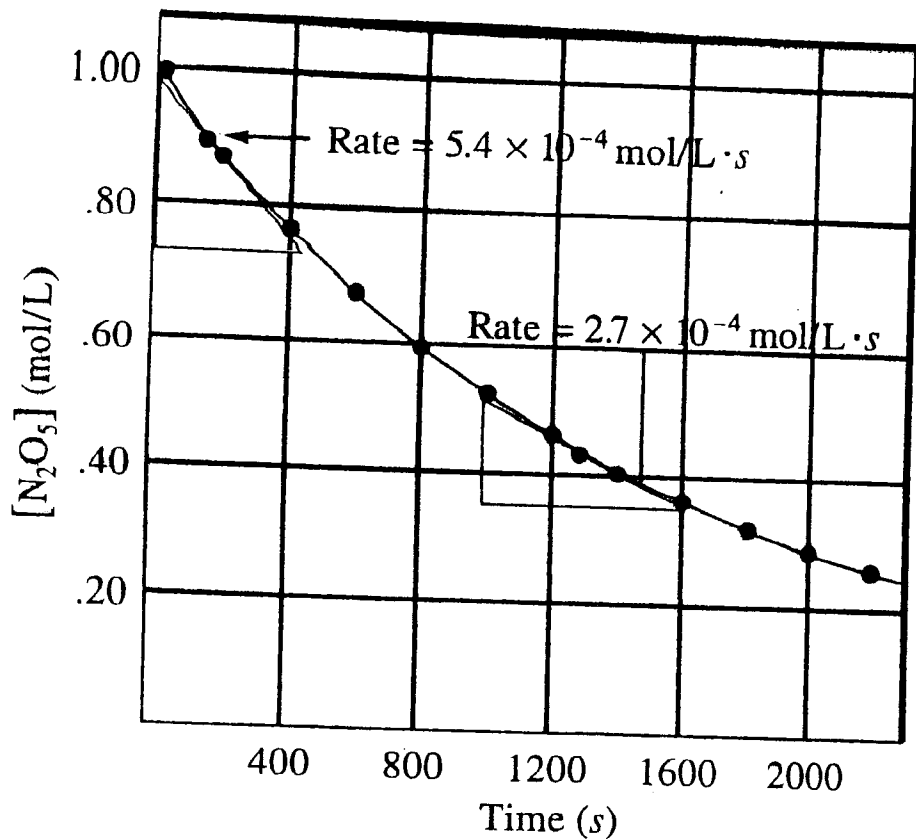


Figure 12.3  
Rate varies with concentration for N<sub>2</sub>O<sub>5</sub>

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See Fig 12.3 & Table 12.3

12-1

Rate =  $\frac{d[N_2O_5]}{dt}$  求切線斜率

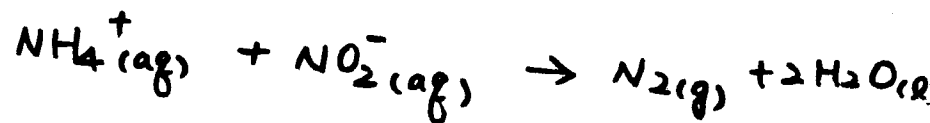
[N <sub>2</sub> O <sub>5</sub> ]	Rate (mol/L·sec)
0.90M	5.4 × 10 <sup>-4</sup>
0.45M	2.7 × 10 <sup>-4</sup>

Rate =  $k [N_2O_5]^n$  求 n

Rate 與 [N<sub>2</sub>O<sub>5</sub>] 成正比變化

n = 1 ⇒ first order reaction

Method of initial rates



$$Rate = -\frac{d[NH_4^+]}{dt} = k [NH_4^+]^m [NO_2^-]^n$$

Table 12.4. initial rate v.s. initial concentrations of reactants

↓  
求 m & n

Experiment 1:

$$\text{Rate 1} = 1.35 \times 10^{-7} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.100)^n (0.0050)^m$$

Experiment 2:

$$\text{Rate 2} = 2.70 \times 10^{-7} \frac{\text{mol}}{\text{L}\cdot\text{s}} = k (0.100)^n (0.01)^m$$

$$\text{相除} \frac{1}{2} = \frac{1.35 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{(0.0050)^m}{(0.01)^m} = \left(\frac{1}{2}\right)^m$$

$$\therefore m = 1$$

同理,

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{5.40 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{(0.200)^n}{(0.100)^n}$$

$$\frac{2}{1} = \left(\frac{2}{1}\right)^n$$

$$\therefore n = 1$$

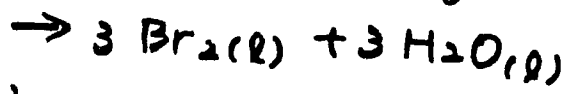
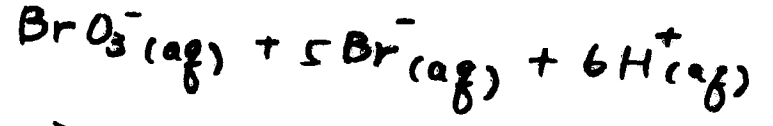
$$\therefore \text{Rate} = k [\text{NH}_4^+] [\text{NO}_2^-]$$

overall reaction order =  $m+n = 2$

$$k = \frac{\text{Rate}}{[\text{NH}_4^+][\text{NO}_2^-]} = \frac{1.35 \times 10^{-7} \frac{\text{mol}}{\text{L}\cdot\text{s}}}{(0.100) \frac{\text{mol}}{\text{L}} (0.0050) \frac{\text{mol}}{\text{L}}}$$

$$k = 2.7 \times 10^{-4} \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

Ex. 12.1 on page 570



\* overall rx order, orders for all three reactants, and the value of the rate constant

$$\text{Sol: Rate} = k [\text{BrO}_3^-]^n [\text{Br}^-]^m [\text{H}^+]^p$$

找只变动其中一个 reactant = 浓度的两个实验 (如 Exp 1 & Exp 2)

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.6 \times 10^{-3}}{8.0 \times 10^{-4}} = \frac{(0.20)^n}{(0.10)^n}$$

$$2 = \left(\frac{2}{1}\right)^n \therefore n = 1$$

相同方法

$$\frac{\text{Rate 3}}{\text{Rate 2}} = 2 = \frac{(0.20)^m}{(0.10)^m} = \left(\frac{2}{1}\right)^m \therefore m = 1$$

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{3.2 \times 10^{-3}}{8.0 \times 10^{-4}} = \left(\frac{0.20}{0.10}\right)^p$$

$$4 = \left(\frac{2}{1}\right)^p \therefore p = 2$$

$$\therefore \text{Rate} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2 \quad 12-13$$

$$k = \frac{\text{Rate}}{[\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2} \quad \text{用 experiment 1 data 代入}$$

$$k = 8.0 \frac{\text{L}^3}{\text{mol}^3 \cdot \text{s}}$$

### § 12.4 The Integrated Rate Law

(how concentrations of reactants change with time)

Recall first order reaction  $aA \rightarrow \text{product}$

$$\begin{aligned} \text{Rate} &= k [\text{reactant}]^1 \\ &= k [A]^1 \end{aligned}$$

$$\text{Rate} = -\frac{d[A]}{dt} = k [A]^1$$

$$\therefore \frac{d[A]}{[A]} = -k dt$$

$$\text{积分} \int_{[A]=[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -k dt$$

$$\ln [A] \Big|_{[A]_0}^{[A]} = -k t \Big|_{t=0}^{t=t}$$

$$\ln [A] - \ln [A]_0 = -k t \quad 12-14$$

or

$$\ln \left( \frac{[A]}{[A]_0} \right) = -k t$$

integrated first-order law #

如以  $\ln [A]$  对 time 作图  
会得到斜率  $-k$  的直线

Ex. 12.2



verify that the rate law is first order in  $[\text{N}_2\text{O}_5] \rightarrow$  calculate rate constant

sol:

$\ln [\text{N}_2\text{O}_5]$  对 time 作图

$$\text{斜率} = -k = -6.93 \times 10^{-3} \text{ s}^{-1}$$

$$\therefore k = 6.93 \times 10^{-3} \text{ s}^{-1}$$

Ex 12.3 利用 Ex 12.2 data  
calculate  $[N_2O_5]$  at 150 sec

12-15

Sol:

$$\ln[A] - \ln[A]_0 = -kt$$

$$\therefore \ln[A] = \ln[A]_0 - kt$$

$$\ln[N_2O_5] = \ln[N_2O_5]_0 - kt$$

$$[N_2O_5]_0 = 0.1000 \frac{\text{mol}}{\text{L}}$$

$$t = 150 \text{ sec}$$

$$k = 6.93 \times 10^{-3} \text{ sec}^{-1}$$

代入  $\ln[N_2O_5] = \ln[0.1000] - 6.93 \times 10^{-3} \cdot 150$

$$\therefore \ln[N_2O_5] = -3.343$$

$$[N_2O_5]_{t=150} = e^{-3.343} = 0.0353 \frac{\text{mol}}{\text{L}}$$

#

## Half-Life of a first-order Reaction <sup>12</sup>

Half-life of a reaction: the time required for a reactant to reach half its original concentration ~~is~~

~~called~~ 濃度降到初始濃度的一半所需的時間

Ex. 將 Ex. 12.2 data 作圖 as fig. 12.5

$$t_{1/2} = 100 \text{ s} \quad (\text{由圖看出})$$

$$\ln[A] - \ln[A]_0 = -kt \quad \text{for first order rx}$$

when  $[A] = \frac{1}{2}[A]_0$

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$\ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right) = kt_{1/2}$$

$$\ln 2 = kt_{1/2} \Rightarrow t_{1/2} = \frac{\ln 2}{k}$$

general equation for the half-life of a first-order reaction



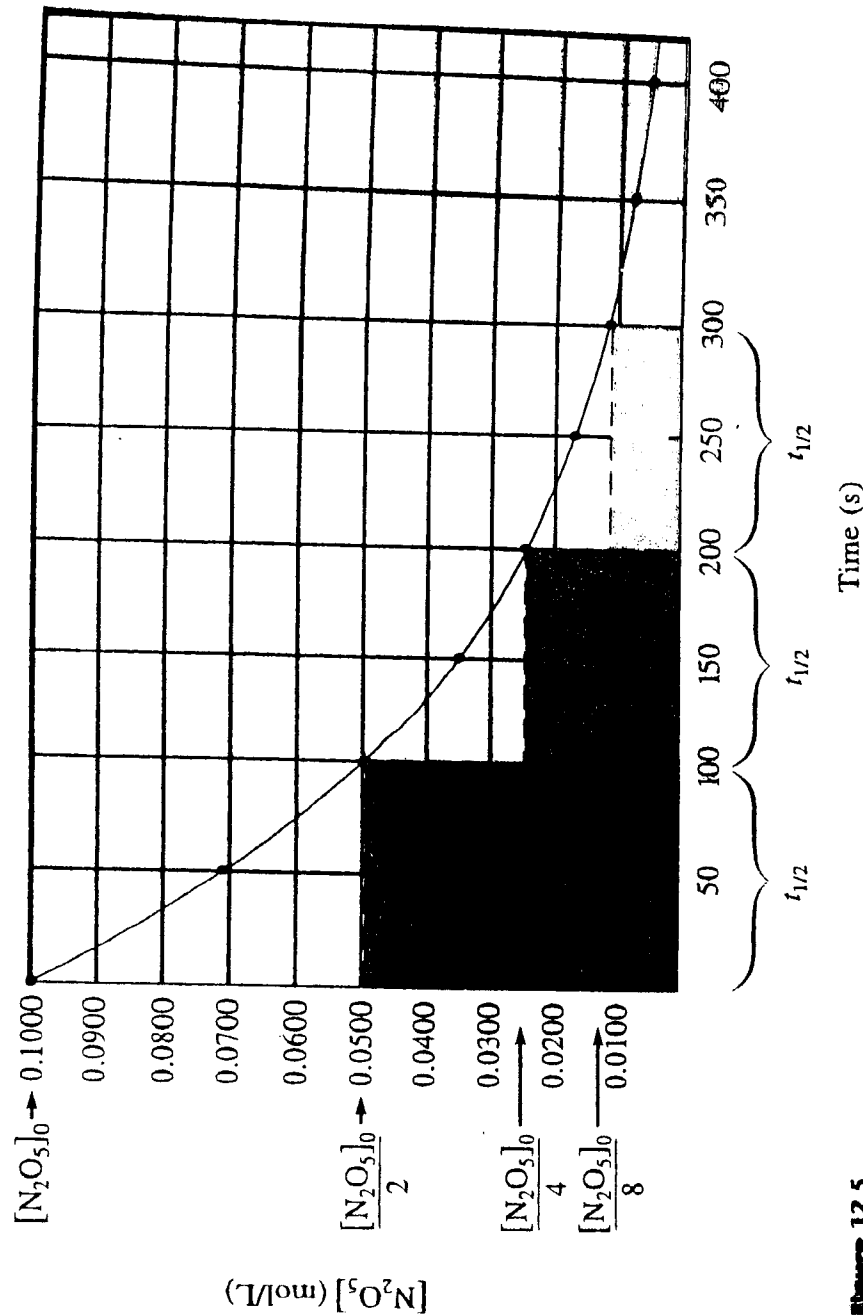


Figure 12.5

**Constant half life for first-order process**

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145  
12-17

Second-order rate law

12-18



$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

$$= -\frac{d[A]}{dt}$$

(second-order reaction)

$$\therefore -\frac{d[A]}{dt} = k[A]^2$$

$$+\frac{d[A]}{[A]^2} = -k dt$$

積分

$$\int \frac{d[A]}{[A]^2} = \int -k dt$$

$$-\frac{1}{[A]} \Big|_{[A]_0}^{[A]} = -k t \Big|_{0}^t$$

$$\Rightarrow \frac{1}{[A]} - \frac{1}{[A]_0} = +k t$$

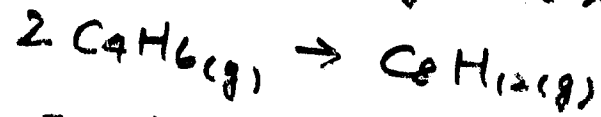
half life =?  $[A] = \frac{1}{2} [A]_0$

代入上式

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

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

Ex. 12.5 Determining rate laws 12-19



first order or second order?

Sol: Recall (1) first order rx:

$$\ln[A] = \ln[A]_0 - kt$$

∴ 以  $\ln[A]$  对 time 作图

⇒ 直线, 斜率 =  $-k$

(2) for second order rx:

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

以  $\frac{1}{[A]}$  对  $t$  作图

⇒ 直线, 斜率 =  $k$

see Fig 12.6

∴ 为 second order rx.

斜率 =  $+k$

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

zero-order rate laws 12-20

$$\text{Rate} = k[A]^0 = k(1) = k$$

$$-\frac{d[A]}{dt} = k$$

积分

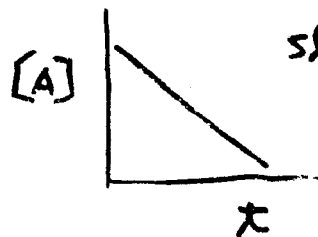
$$\int d[A] = -k \int dt$$

$$[A] \Big|_{[A]_0}^{[A]} = -kt \Big|_0^t$$

$$\boxed{[A] = [A]_0 - kt} \quad \#$$

see Fig 12.7

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

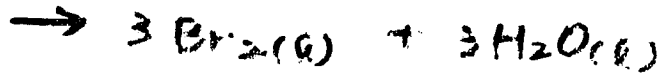
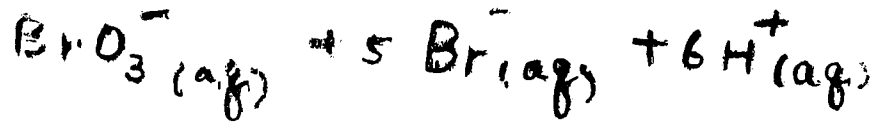


slope =  $-k$

代入  $\frac{1}{2}[A]_0 = [A]_0 - kt_{1/2}$

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

Integrated rate laws for reactants w/ more than one reactant



$$\text{Rate} = k [\text{BrO}_3^-]^m [\text{Br}^-]^n [\text{H}^+]^p$$

已知 (由实验求得)

$$\text{Rate} = - \frac{\Delta [\text{BrO}_3^-]}{\Delta t} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]$$

如果 experiment 在

$$[\text{BrO}_3^-]_0 = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{Br}^-]_0 = 1.0 \text{ M}$$

$$[\text{H}^+]_0 = 1.0 \text{ M}$$

且  $[\text{Br}^-] \gg [\text{BrO}_3^-]$

$$\begin{aligned} \text{Rate} &= k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2 \\ &= k [\text{BrO}_3^-] [\text{Br}^-]_0 [\text{H}^+]_0^2 \end{aligned}$$

$$\therefore [\text{Br}^-] \& [\text{H}^+] \gg [\text{BrO}_3^-] \Rightarrow \frac{[\text{Br}^-]}{[\text{Br}^-]_0} \approx \frac{[\text{H}^+]}{[\text{H}^+]_0}$$

$$\therefore \left. \begin{aligned} [\text{Br}^-] &\approx [\text{Br}^-]_0 \\ [\text{H}^+] &\approx [\text{H}^+]_0 \end{aligned} \right\} \text{at any time}$$

$$= (k [\text{Br}^-]_0 [\text{H}^+]_0^2) [\text{BrO}_3^-]$$

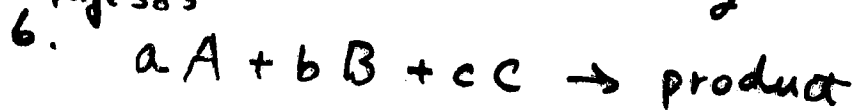
### §12.5 Rate Laws: A summary

Order	Zero	First	Second
	Rate = k	Rate = k[A]	Rate = k[A] <sup>2</sup>
	[A] = -kt + [A] <sub>0</sub>	ln[A] = -kt + ln[A] <sub>0</sub>	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
	Slope = -k	Slope = -k	Slope = k
	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

§ 12.5 Rate Law: A summary

12-23

page 583



$$\text{Rate} = k[A]^n[B]^m[C]^p$$

Let  $[B]_0$  &  $[C]_0 \gg [A]_0$

∴ at any time

$$[B]_t \approx [B]_0$$

$$[C]_t \approx [C]_0$$

$$\therefore \text{Rate} = \underbrace{k[B]_0^m[C]_0^p}_{k'} [A]^n$$

$$= k' [A]^n$$

求 n :

$[A]$  v.s. time

$\ln[A]$  v.s. time

$\frac{1}{[A]}$  v.s. time

page 583 #6.

12-2

$$\text{Rate} = k[A]^n[B]^m[C]^p$$

選擇適當條件

↓ 簡化成

$$\text{Rate} = k' [A]^n$$

when  $[B]_0 \gg [A]_0$

$[C]_0 \gg [A]_0$

$$k' = k[B]_0^m[C]_0^p$$

↓

how to calculate n ?

$[A]$  v.s.  $t$ , if linear.  $n=0$

$\ln[A]$  v.s.  $t$ , if linear  $n=1$

$\frac{1}{[A]}$  v.s.  $t$ , if linear  $n=2$

$k'$  can be calculated from the slope of the appropriate plot

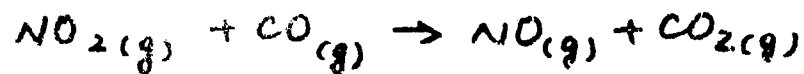
## § 12.6 Reaction mechanism.

12-25

A series of elementary steps that must satisfy two requirements.

1. The sum of the elementary steps must give the overall balanced equation for the reaction
2. The mechanism must agree with experimentally determined rate law

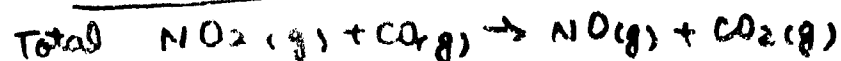
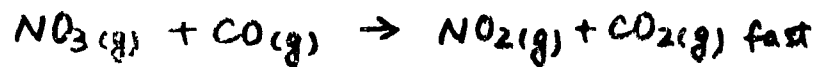
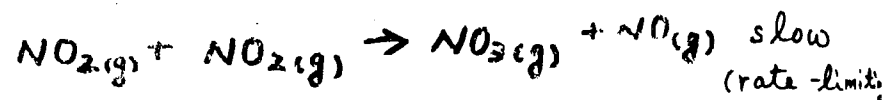
例題:



已知 rate law:

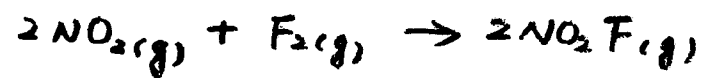
$$\frac{\Delta[\text{NO}_2]}{\Delta t} = k_1 [\text{NO}_2]^2$$

propose mechanism:



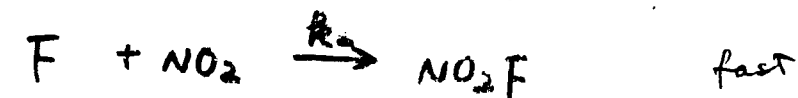
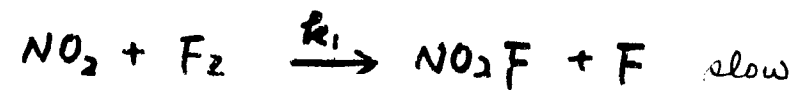
Sample Ex. 12.6.

12-26



$$\text{Rate} = k [\text{NO}_2][\text{F}_2] \quad (\text{experimental})$$

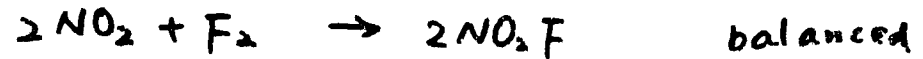
suggested mechanism:



right mechanism:

Sol:

overall rx:



$$\text{Rate law} = k [\text{NO}_2][\text{F}_2]$$

also satisfies experiment

acceptable mechanism

$$k = A e^{-E_a/RT}$$

↑  
rate constant

$$= z p e^{-E_a/RT}$$

↑            ↑  
collision    steric  
frequency   factor

## § 12.7 A model for chemical kinetics 12

chemical reactions speed up when the temperature is increased

Collision model: molecules must collide to react

Arrhenius (1880s proposed):

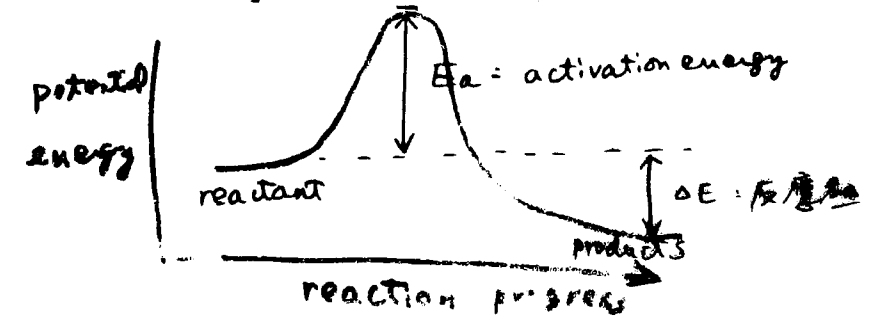
activation energy: threshold energy

~~a reaction~~ must be overcome to produce a chemical reaction

activated complex or transition state:

the arrangement of atoms found at the top of the potential energy 'hill'.

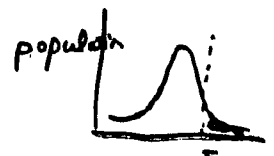
see Fig 12.10 transition state



Arrhenius equation!

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

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



a plot  $\ln k$  v.s  $(\frac{1}{T})$

→ slope  $(-\frac{E_a}{R})$

intercept  $\ln(A)$

Ex. 12.7

$k$  (rate const) v.s.  $T$ .

calculate  $E_a$ :

Sol.  $\ln k = f \left( \frac{1}{T} \right)$

slope =  $-\frac{E_a}{R}$

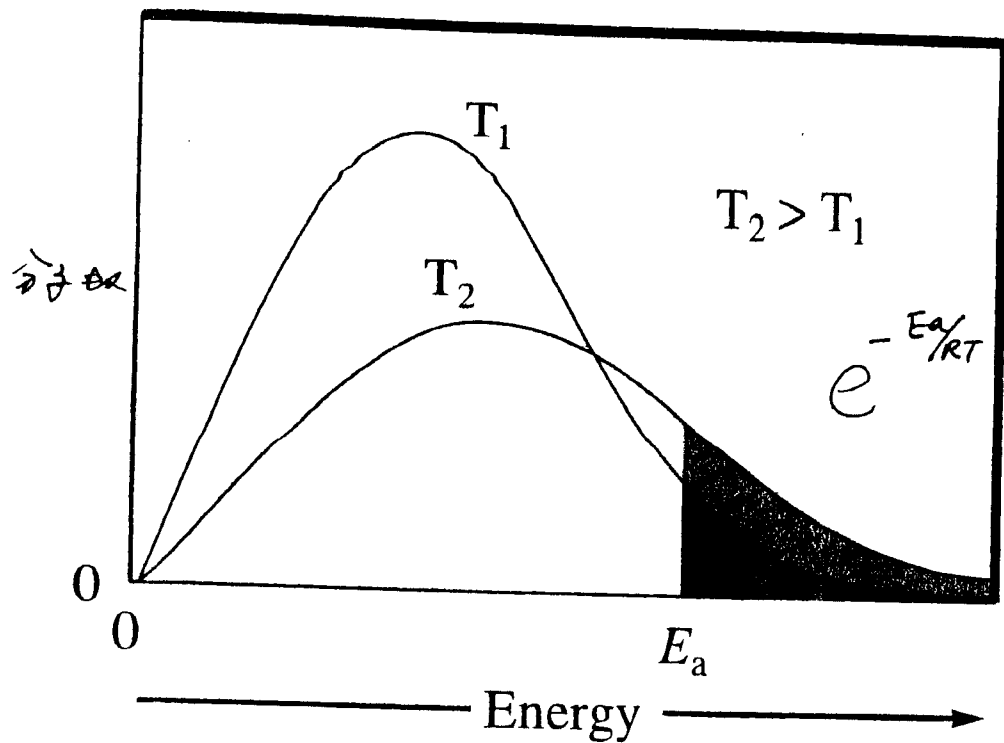


Figure 12.12  
Collision energy variation with temperature

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Rate depends on  $E_a$

not depends on  $\Delta E$  (反应热)

see Fig 12.12

$T \uparrow$ , # of molecules (w/ energy  $> E_a$ )  $\uparrow$

$\therefore$  Reaction rate  $\uparrow$

Number of collisions w/ the activation energy = (total number of collisions)  $\times e^{-E_a/RT}$

Molecular orientations also affect the reaction rate.

1. The collision must involve enough energy to produce the reaction:
2. The relative orientation of the reactants must allow formation of any new bonds necessary to produce products

### 3 12.8 Catalysis (催化)

12-32

see Fig. 12.15 & 12.16

catalysts "reduce" the activation energy of the reaction.

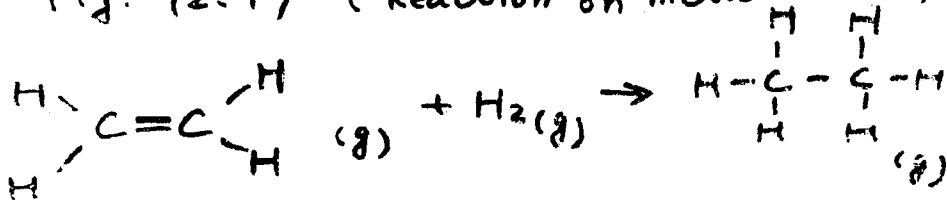
→ therefore, speed up the reaction

A catalyst is a substance that speeds up a reaction without being consumed itself.

homogeneous } catalyst 同相 催化剂  
 heterogeneous } 異相

heterogeneous catalysis:

see Fig. 12.17 (Reaction on metal surface)



At temperature  $T_1$ ,

$$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A)$$

At temperature  $T_2$ ,

$$\ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$$

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

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

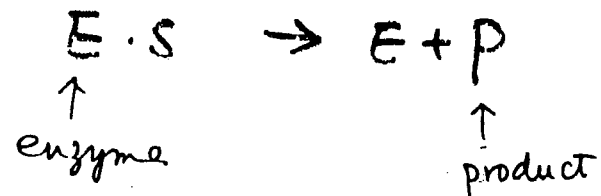
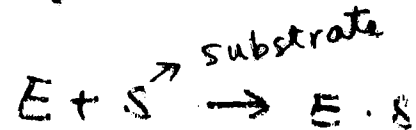
Ex. 12.8 page 591

12-31



Enzymes: Nature's catalysts

12-34



Heterogeneous catalysis involves

1. Adsorption and activation of the reactants

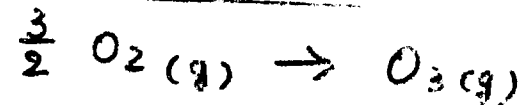
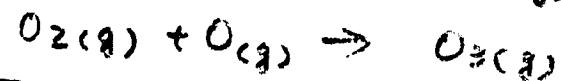
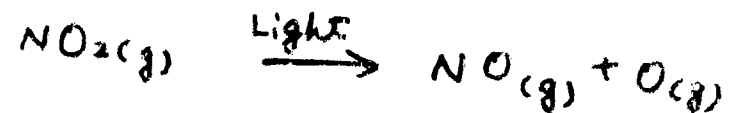
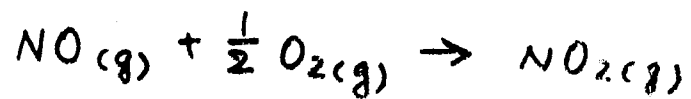
2. Migration of the adsorbed reactants on the surface

3. Reaction of the adsorbed substances

4. Escape, or desorption, of the products

---

Homogeneous catalysis



NO catalyzes the formation of ozone  
↑  
produced in any high-temp combustion