

Ch 11 Reaction Rate

Reaction rate and its influence factors.

11-1 Meaning of Reaction Rate; r

11-2 Reaction Rate and Concentration 濃度對 r 之影響

11-3 Reactant Concentration and Time 反應級數

11-4 Models for Reaction Rate 碰撞學說

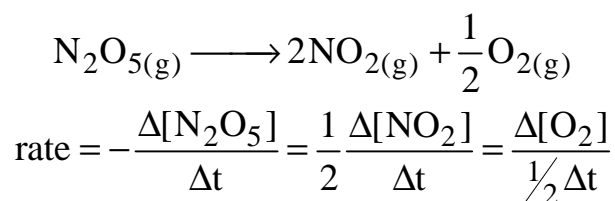
11-5 Reaction Rate and Temperature

11-6 Catalysis

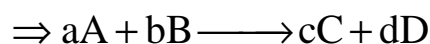
11-7 Reaction Mechanisms 反應機構

§ 11-1 Meaning of Reaction Rate

Reaction rate: the concentration of reactant or product changes with time.

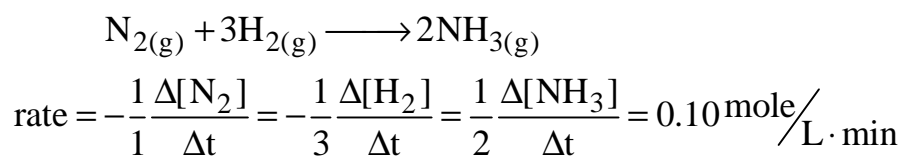


↳ 一定“+”值



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

例:



$$\frac{\Delta[\text{N}_2]}{\Delta t} = -0.10 \text{ mole/L} \cdot \text{min}$$

$$\frac{\Delta[\text{H}_2]}{\Delta t} = -0.30 \text{ mole/L} \cdot \text{min}$$

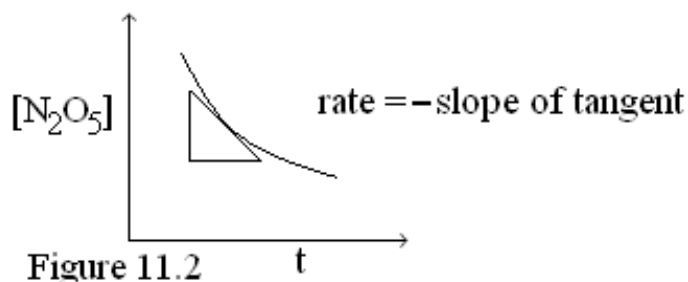
$$\frac{\Delta[\text{NH}_3]}{\Delta t} = 0.20 \text{ mole/L} \cdot \text{min}$$

r 單位: 固: $\Delta W_t / \Delta t$

液: $\Delta M / \Delta t$

氣: $\Delta P / \Delta t$

§ Measurement of Rate



§ 11-2 Reaction Rate and Reactant Concentration

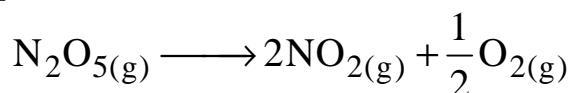
Reaction occurs as the result of collisions between reactant molecules.

↓

concentration ↑ ⇒ r ↑

$r \propto [\text{reactant}]$

§ Rate expression and rate constant

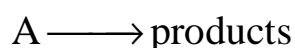


$r \propto [\text{N}_2\text{O}_5]$

rate expression: $r = k \cdot [\text{N}_2\text{O}_5]$

k: rate constant

§ Order of Reaction involving a single reactant



$r = k \cdot [\text{A}]^m$ m: order of the reaction

m = 0 零級反應

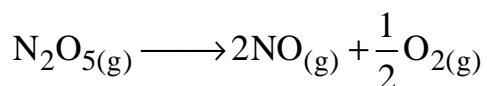
m = 1 一級反應

m = 2 二級反應

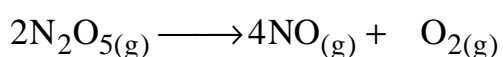
反應機構中之瓶頸反應 ←

The order of reaction, m, must be determined experimentally; it cannot be deduced from the coefficients in the balanced equation.

例:



$$r = k[\text{N}_2\text{O}_5]^1$$



$$r = k[\text{N}_2\text{O}_5]^1$$

與平衡係數無關

m 如何決定: ⇒ Ex 11-1 由實驗數據求 m

※

Ex 11-1 求 CH_3CHO 乙醛在 600°C 之 initial rate of decomposition

| | | | | |
|-----------------------|-----------------------------------------------------------------------------------|-------------------|-------------------|-------------------|
| | $\text{CH}_3\text{CHO}_{(g)} \longrightarrow \text{CH}_4_{(g)} + \text{CO}_{(g)}$ | | | |
| | [A ₁] | [A ₂] | [A ₃] | [A ₄] |
| [CH ₃ CHO] | 0.20M | 0.30M | 0.40M | 0.50M |
| rate, mole/s | 0.34 | 0.76 | 1.4 | 2.1 |
| | r ₁ | r ₂ | r ₃ | r ₄ |

Ans:

$$r = k \cdot [\text{CH}_3\text{CHO}]^m$$

$$\frac{r_2}{r_1} = \left(\frac{[A_2]}{[A_1]}\right)^m \qquad \frac{r_4}{r_3} = \left(\frac{[A_4]}{[A_3]}\right)^m$$

$$\frac{0.76}{0.34} = \left(\frac{0.30}{0.20}\right)^m \qquad \frac{2.1}{1.4} = \left(\frac{0.50}{0.40}\right)^m$$

$$2.2 = (1.5)^m \qquad 1.5 = (1.25)^m$$

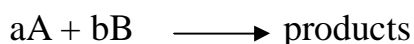
$$m \approx 2$$

$$m \approx 2$$

∴ 二級反應

$$\therefore r = k \cdot [\text{CH}_3\text{CHO}]^2$$

§ Order of reaction of more than one reactant



$$r = k \cdot [A]^m \cdot [B]^n$$

$$[B] = \text{constant}$$

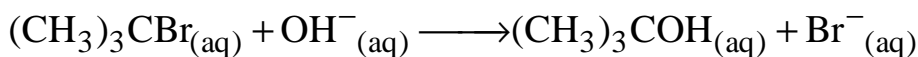
$$r_1 = k[A_1]^m[B]^n$$

$$r_2 = k[A_2]^m[B]^n$$

$$\frac{r_1}{r_2} = \frac{\cancel{k}[A_1]^m \cancel{[B]^n}}{\cancel{k}[A_2]^m \cancel{[B]^n}} = \left(\frac{[A_1]}{[A_2]}\right)^m \Rightarrow \text{求 } m$$

同理 $[A] = \text{constant} \Rightarrow \text{求 } n$

Ex 11-2: 55°C



第三丁基溴

第三丁醇

| | Expt 1 | Expt 2 | Expt 3 | Expt 4 | Expt 5 |
|-----------------------------------|--------|--------|--------|--------|--------|
| $[(\text{CH}_3)_3\text{Br}]$ | 0.50 | 1.0 | 1.5 | 1.0 | 1.0 |
| $[\text{OH}^-]$ | 0.050 | 0.050 | 0.050 | 0.10 | 0.20 |
| $r, \text{mole/L} \cdot \text{s}$ | 0.0050 | 0.010 | 0.015 | 0.010 | 0.010 |

Sol:

$$r = k[(\text{CH}_3)_3\text{Br}]^m[\text{OH}^-]^n$$

$$[\text{OH}^-] = C \quad \frac{r_2}{r_1} = \frac{0.010}{0.0050} = \left(\frac{[\text{A}_1]}{[\text{A}_2]}\right)^m = \left(\frac{1.0}{0.5}\right)^m$$

$$2.0 = (2.0)^m$$

$$m = 1$$

$$[(\text{CH}_3)_3\text{Br}] = C \quad \frac{r_2}{r_4} = \frac{0.010}{0.010} = \left(\frac{[\text{B}_4]}{[\text{B}_2]}\right)^n = \left(\frac{0.10}{0.050}\right)^n$$

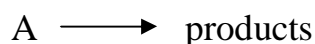
$$1 = (2)^n$$

$$n = 0$$

$$\therefore r = k[(\text{CH}_3)_3\text{Br}]^1$$

§ 11-3 Reactant Concentration and Time

§ first-order reactions



$$r = k[\text{A}]$$

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

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

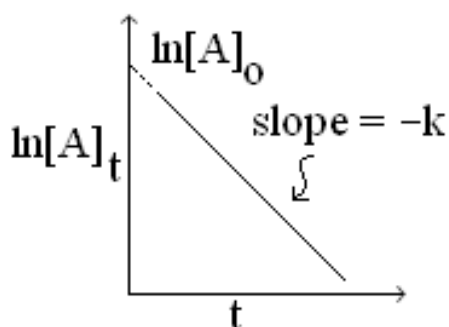
$$-\ln \frac{[\text{A}]_t}{[\text{A}]_0} = kt$$

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

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

一級反應 $\ln[\text{A}]_t = \ln[\text{A}]_0 - kt$

$$[\text{A}]_0 \text{ 已知 } \ln[\text{A}]_0 = \text{constant}$$



Ex 11-3: first-order decomposition of N_2O_5 at 67°C , $k = 0.35/\text{min}$

a) 6 minutes 之 concentration, $[\text{N}_2\text{O}_5]_0 = 0.200\text{M}$

b) $[\text{N}_2\text{O}_5]_t = 0.150\text{M}$; $t = ?$

c) $[\text{N}_2\text{O}_5]_t = \frac{1}{2} [\text{N}_2\text{O}_5]_0$, $t = ?$

Sol: 1st order reaction $\ln \frac{[A]_0}{[A]_t} = kt$

$$\text{a) } \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = 0.35 \cdot t \quad t = 6$$

$$\ln \frac{0.200}{[\text{N}_2\text{O}_5]_t} = 0.35 \cdot 6$$

$$\frac{0.200}{[\text{N}_2\text{O}_5]_t} = 8.2$$

$$[\text{N}_2\text{O}_5]_t = 0.024\text{M}$$

$$\text{b) } \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = k \cdot t$$

$$\ln \frac{0.200}{0.150} = 0.35 \cdot t$$

$$0.288 = 0.35 \cdot t$$

$$t = 0.82 \text{ min}$$

$$\text{c) } \ln 2 = kt$$

$$\ln 2 = 0.35 \cdot t$$

$$\ln 2 = t_{1/2} \cdot k$$

$$t = \frac{\ln 2 \rightarrow 0.693}{k} \quad \therefore t_{1/2} = \frac{\ln 2}{k}$$

$$= 2.0 \text{ min}$$

Q: 1 half life: 反應物之濃度(or 重量)減為原先之 $\frac{1}{2}$ 所需時間, $t_{1/2} \uparrow \Rightarrow r \downarrow$

$$\text{一級反應 } t_{1/2} = \frac{\ln 2}{k}$$

\downarrow
反應速率

Ex 11-4: ${}_{94}^{240}\text{Pu}$ 鈾 Plutonium; $t_{1/2} = 6.58 \times 10^3 \text{ years}$

a) the first-order rate constant for the decay of ${}_{240}\text{Pu}$?

b) 1000 year 後 the fraction of a sample left?

Sol: a) the first-order

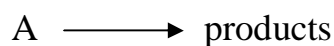
$$t_{1/2} = \frac{\ln 2}{k}$$

$$6.58 \times 10^3 = \frac{0.693}{k} \Rightarrow k = 1.05 \times 10^{-4} / \text{year}$$

$$\begin{aligned}
 \text{b)} \quad \ln \frac{x_0}{x} &= kt \\
 \ln \frac{x_0}{x} &= 1.05 \times 10^{-4} \cdot 10^3 \\
 &= 0.105 \\
 \frac{x_0}{x} &= 1.11 \\
 \therefore \frac{x_0}{x} &= 0.900 \\
 &= 90.0\%
 \end{aligned}$$

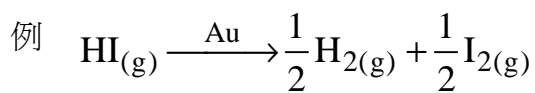
§ Zero- and Second-order reactions

§ Zero-order reaction:



$$-\frac{d[A]}{dt} = \text{rate} = k[A]^0 = k$$

反應速率為常數與反應物濃度無關

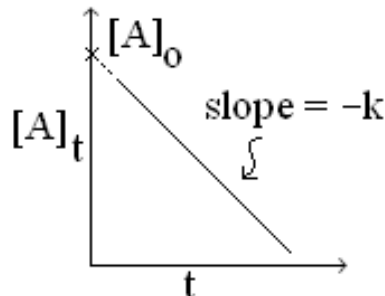


$$-\frac{d[A]}{dt} = k$$

$$\int_{[A]_0}^{[A]_t} -dA = \int_0^t k dt$$

$$[A]_0 - [A]_t = kt$$

零級反應 $\Rightarrow [A]_t = [A]_0 - kt$



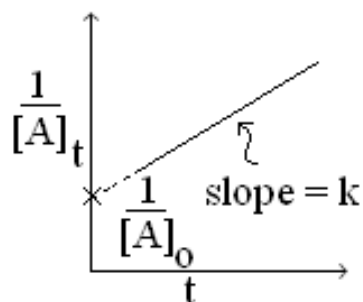
§ Second-order reaction

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

$$\int_{[A]_0}^{[A]_t} -\frac{d[A]}{[A]^2} = \int_0^t kt$$

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

二級反應 $\Rightarrow \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$



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

Table 11.2 half-life

| 反應級數 | 濃度-time relation | $t_{1/2}$ | linear plot | Equation |
|------|------------------------------------------|--------------------|----------------------------|------------------------------------------|
| 0 | $[A]_0 - [A]_t = kt$ | $[A]_0/2k$ | $[A]_t$ V.S. t | $[A]_t = [A]_0 - kt$ |
| 1 | $\ln \frac{[A]_0}{[A]_t} = kt$ | $0.693/k$ | $\ln[A]_t$ V.S. t | $\ln[A] = \ln[A]_0 - kt$ |
| 2 | $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$ | $\frac{1}{k[A]_0}$ | $\frac{1}{[A]_t}$ V.S. t | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ |

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

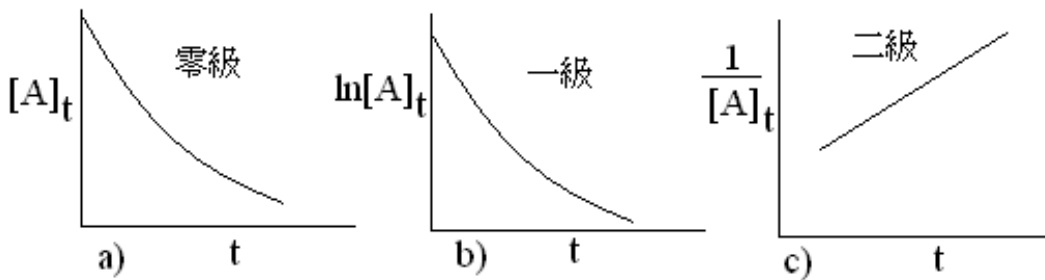
Ex 11-5: HI_(g) 之 decomposition 數據如下

| | | | | |
|------|------|------|------|------|
| t(h) | 0 | 2 | 4 | 6 |
| [HI] | 1.00 | 0.50 | 0.33 | 0.25 |

判定 the order of the reaction?

Sol:

| t(h) | [HI] _t | ln[HI] _t | $\frac{1}{[HI]_t}$ |
|------|-------------------|---------------------|--------------------|
| 0 | 1.00 | 0.00 | 1.00 |
| 2 | 0.50 | -0.69 | 2.00 |
| 4 | 0.33 | -1.10 | 3.03 |
| 6 | 0.25 | -1.39 | 4.00 |



呈現 linear 是(c)
 $\therefore 2^{\text{nd}}$ -order reaction

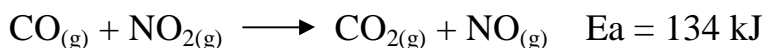
Ex 11-6: $r = k[A]^1[B]^2$

Sol:

| | |
|-----------------------------------------------|-----------------------|
| 1) $r_1 = k(1A)^1 \cdot (2B)^2 = 4kAB^2 = 4r$ | $\therefore 3$ 與 1 相同 |
| 2) $r_2 = k(2A)^1 \cdot (B)^2 = 2kAB^2 = 2r$ | |
| 3) $r_3 = k(4A)^1 \cdot (B)^2 = 4kAB^2 = 4r$ | |
| 4) $r_4 = k(2A)^1 \cdot (2B)^2 = 8kAB^2 = 8r$ | |

§ 11-4 Models for reaction rate

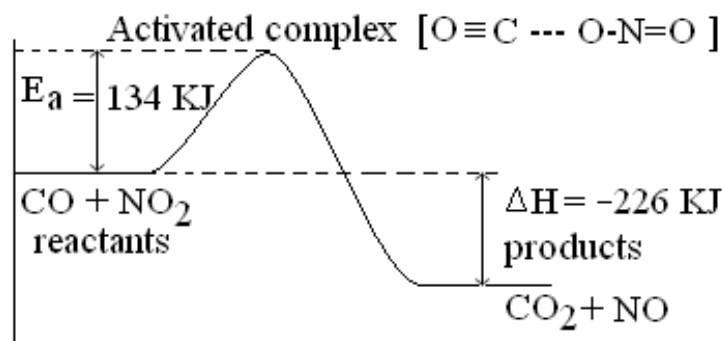
§ Collision model: Activation energy E_a



對任一反應都須一最小能量，使分子能做一有效碰撞

↓

CO 與 NO_2 碰撞其 $E > E_a(134 \text{ KJ})$ 才能使反應發生



- E_a : 1.活化錯合體與反應物間之能量差
2.使反應發生所需之最小能量

一般化學反應進行時，須先吸收能量(活化能)以破壞現有之化學鍵結，先生成活化複合體之後再生成新的鍵結(放出能量)，形成新的產物。

Collision model: \rightarrow rate constant

$$k = p \cdot z \cdot f$$

有效碰撞 p : steric factor; 碰撞時之“orientation 正確”才為有效碰撞

1. $E > E_a$ $p < 1$ p 為方位正確之碰撞機率

2. orientation 正確 z : collision frequency; the number of molecular collisions occurring in unit time at unit concentrations of reactants.

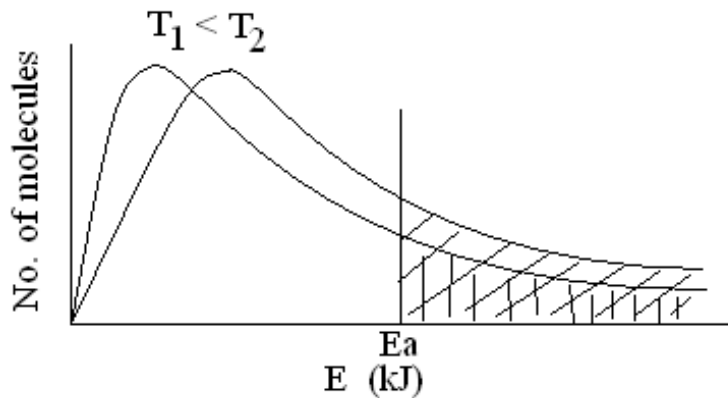
f : the fraction of collision with $E > E_a$

\rightarrow 即有效碰撞分率

$$f = e^{-E_a/RT} \quad E_a \uparrow \Rightarrow f \downarrow \Rightarrow k \downarrow$$

活化能越大，反應越不易發生

§ 11-5 Reaction rate and temperature



$T \uparrow$ $E > E_a$ 之分子數目 $\uparrow \Rightarrow f \uparrow \Rightarrow k \uparrow \Rightarrow r \uparrow$

$$\frac{r_2}{r_1} = 2^{\left(\frac{T_2 - T_1}{10}\right)}$$

反應溫度每上升 10°C 反應速率上升 1 倍

§ The Arrhenius equation: 阿瑞尼士方程式

$$k = p \cdot z \cdot f$$

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

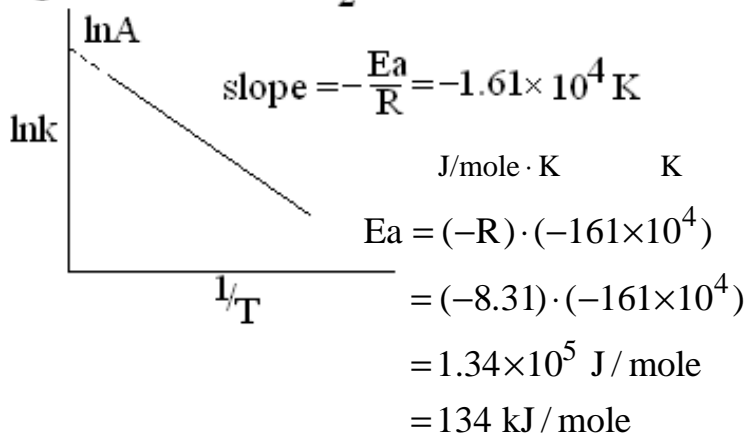
Arrhenius equation: **P**

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

$$\ln k = \ln A - E_a/RT \quad R: 8.31 \text{ J/mole} \cdot \text{K}$$

$$\ln k \text{ V.S. } \frac{1}{T} \text{ 作圖} \quad \text{slope} = -\frac{E_a}{R}$$

Figure 11-10 $\text{CO}-\text{NO}_2$ 反應



T 對平衡 k (rate constant) 之影響

§ Two-point equation relating k and T

Ch 9. Clausis-Clapeyron equation

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\left(\begin{array}{l} \ln k_1 = \ln A - \frac{E_a}{RT_1} \\ \ln k_2 = \ln A - \frac{E_a}{RT_2} \end{array} \right)$$

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

Ex 11-7: $T = 15^\circ\text{C} \rightarrow 25^\circ\text{C}$ $k_2 = 2k_1$

a) 求 E_a

b) rate constant at 100°C ? k at 25°C : $1.2 \times 10^{-2} \text{ L/mole} \cdot \text{s}$

c) $25^\circ\text{C} \rightarrow 35^\circ\text{C}$ k 增加若干%

Sol:

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

$$\ln 2 = \frac{E_a}{8.31} \left(\frac{1}{273+15} - \frac{1}{273+25} \right)$$

$$0.693 \cdot 8.31 = E_a(3.47 \times 10^{-3} - 3.36 \times 10^{-3})$$

$$E_a = 4.9 \times 10^4 \text{ J/mole}$$

$$= 49 \text{ kJ/mole}$$

$$\text{b) } \ln \frac{k_2}{1.2 \times 10^{-2}} = \frac{49000}{8.31} \cdot \left[\frac{1}{298} - \frac{1}{373} \right] = 3.98$$

$$\frac{k_2}{1.2 \times 10^{-2}} = 53$$

$$k_2 = 0.64 \text{ L/mole} \cdot \text{s}$$

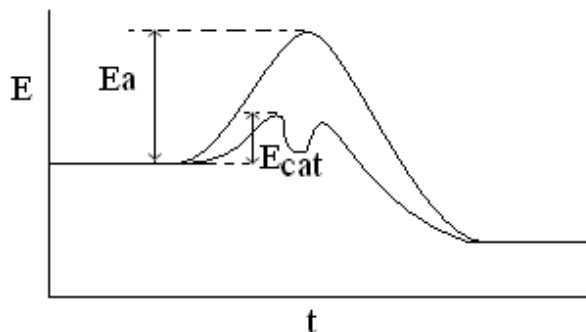
$$\text{c) } \ln \frac{k_2}{k_1} = \frac{49000}{8.31} \cdot \left[\frac{1}{298} - \frac{1}{308} \right]$$

$$= 0.642$$

$$\frac{k_2}{k_1} = e^{0.642} = 1.90$$

$\therefore k_2$ 較 k_1 大 90%

§ 11-6 Catalysis 催化

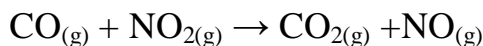


催化劑 catalyst:

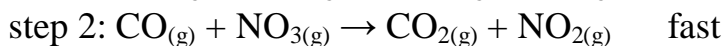
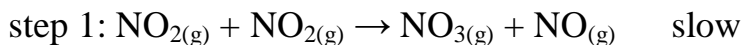
- 1.改善反應途徑
- 2.活化能較低
- 3.反應速率較高
- 4.反應前後 catalyst 之狀態及重量不變
- 5.不影響平衡(平衡常數)

§ 11-7 Reaction mechanisms 反應機構

1. Find the slowest step and equate the rate of the overall reaction to the rate of that step. 瓶頸反應 → 反應速率定步驟
2. Find the rate expression for the slowest step.



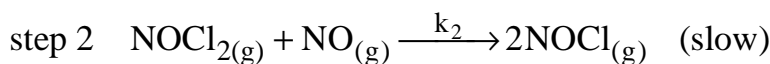
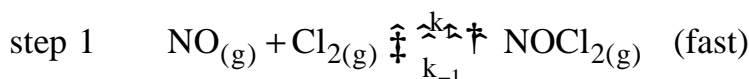
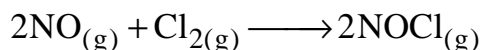
反應機構:



∴

$$\begin{aligned} r &= k \cdot [\text{NO}_2] \cdot [\text{NO}_2] \\ &= k \cdot [\text{NO}_2]^2 \end{aligned}$$

§ elimination of intermediate 中間產物之濃度不會出現在 r 中,設法消去



Sol:

$$r = k_2[\text{NOCl}_2][\text{NO}]$$

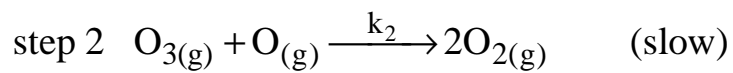
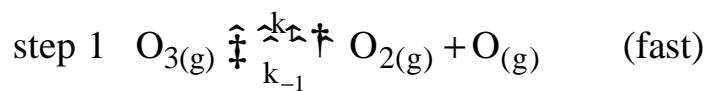
$$k_1[\text{NO}][\text{Cl}_2] = k_{-1}[\text{NOCl}_2]$$

$$= k_2 \cdot \frac{k_1}{k_{-1}} [\text{NO}][\text{Cl}_2][\text{NO}]$$

$$[\text{NOCl}_2] = \frac{k_1}{k_{-1}} [\text{NO}][\text{Cl}_2] \quad \text{代入}$$

$$= k'[\text{NO}]^2[\text{Cl}_2]$$

Ex 11-7: 求 $2\text{O}_{3(g)} \rightarrow 3\text{O}_{2(g)}$ 之 r



Sol:

$$r = k_2[\text{O}_3][\text{O}] \quad \begin{array}{l} \nearrow \text{中間產物，需消掉} \end{array}$$

$$\text{由 step 1: } k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]$$

$$[\text{O}] = \frac{k_1}{k_{-1}} \frac{[\text{O}_3]}{[\text{O}_2]} \quad \text{代入}$$

$$r = k_2 \cdot [\text{O}_3] \cdot \frac{k_1}{k_{-1}} \frac{[\text{O}_3]}{[\text{O}_2]}$$

$$= k' \frac{[\text{O}_3]^2}{[\text{O}_2]}$$