Ch12

#32

a. 設 $R = k[ClO_2]^x[OH^-]^y$

由前二組實驗數據..

$2.3\times10^{-1} = k[0.100]^x[0.100]^y$

$5.75\times10^{-2} = k[0.0500]^x[0.100]^y$

$\Rightarrow 4.00 = \frac{(0.100)^x}{(0.0500)^x} = (2.00)^x \Rightarrow x = 2$

由第二與三組數據..

$2.3\times10^{-1} = k(0.1)^2(0.1)^y$

$1.15\times10^{-1} = k(0.1)^2(0.05)^y$

$\Rightarrow 2.00 = \frac{(0.1)^y}{(0.05)^y} = (2.0)^y \Rightarrow y = 1$

所以.. Rate law 為 $\boxed{R = k[ClO_2]^2[OH^-]^1}$

代入第二組數據於 rate law 中..

$2.30\times10^{-1}\ \frac{mol}{L\cdot s} = k\left(0.1\ \frac{mol}{L}\right)^2\left(0.1\ \frac{mol}{L}\right)^1$

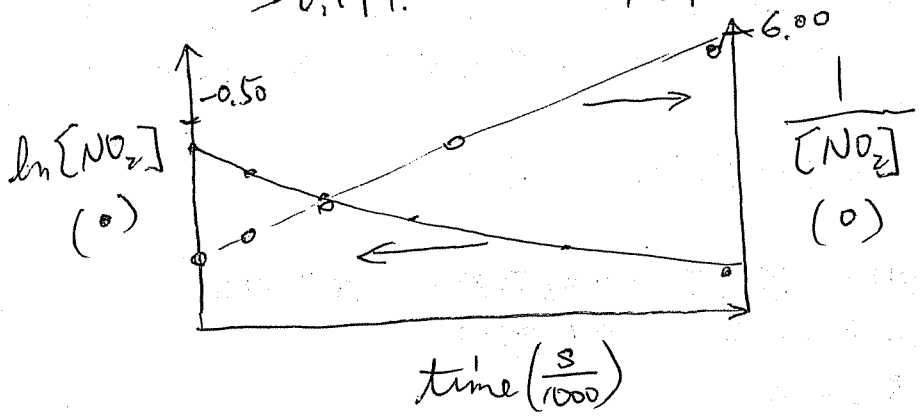
$\Rightarrow \boxed{k = 2.30\times10^2\ \frac{L^2}{mol^2\cdot s}}$

b. $R = 2.3\times10^2\ \frac{L^2}{mol^2\cdot s}\times\left(0.175\ \frac{mol}{L}\right)^2\left(0.0844\ \frac{mol}{L}\right)$

$\boxed{R = 0.594\ \frac{mol}{L\cdot s}}$

#35 將 $[NO_2]$ 求 $\ln[NO_2]$ 與 $\frac{1}{[NO_2]}$，再繪相對於時間的線是否為直線。

Time	$[NO_2]$ mol/L	$\ln[NO_2]$	$\frac{1}{[NO_2]}$
0	0.500	~~0.00~~	2.00
1.20×10^3	0.444	−0.693	2.25
3.00×10^3	0.381	−0.812	2.62
4.50×10^3	0.340	−0.965	2.94
9.00×10^3	0.250	−1.079	4.00
1.80×10^4	0.174	−1.386	5.75
		−1.749	



由上圖，

$\frac{1}{[NO_2]}$ vs. time 是線性 (linear)，故此為 2nd order RXN

- Rate law.. $R = k[NO_2]^2$
  integrated rate law.. $\frac{1}{[NO_2]} = kt + \frac{1}{[NO_2]_0}$

- 直線斜率 $= k$

$$= \frac{\Delta y}{\Delta x} = \frac{5.75 - 2.00}{1.80\times10^4 - 0} = 2.08\times10^{-4}\ \frac{L}{mol\cdot s}$$

- 利用積分 rate law 求 $[NO_2]$..

$$\frac{1}{[NO_2]} = 2.08\times10^{-4}\ \left(\frac{L}{mol\cdot s}\right) \times 2.70\times10^4\ (s) + \frac{1}{(0.500)\ M} = 7.62$$

$$\Rightarrow [NO_2] = 0.131\ M$$

#46 1st order rate law: $\ln\left(\frac{[A]}{[A]_0}\right) = -kt$

$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{14.3\,d} = \boxed{4.85\times10^{-2}\,d^{-1}}$

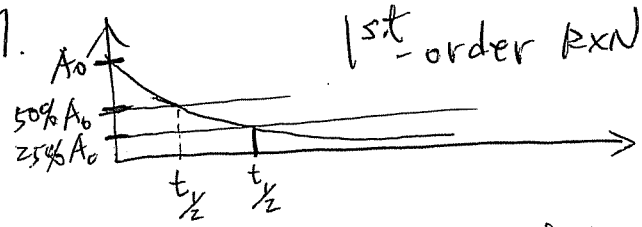
若 $[A]_0 = 100$

則當95%消耗之後 $\Rightarrow [A] = 5.0$

$\Rightarrow \ln\left(\frac{5}{100}\right) = -4.85\times10^{-2}(d^{-1}) \times t$

$\Rightarrow \boxed{t = 62\ days}$

#47. a. 1st order RxN ⇒ 每個 $t_{1/2}$ 等長.



反應 75% completed 表示反應物已剩下 $\sqrt{A_0\text{的}25\%}$

因為 $t_{1/2}$ 表示消耗 $\frac{1}{2}A_0$ 的時間.

表示此反應經過 2個 $t_{1/2}$

$t_{1/2} = 320/2 = 160\ s.$

⇒ 第一個 $t_{1/2} = 160$ sec
第二個 $t_{1/2} = 160$ sec

b. $0.693 = k \cdot t_{1/2} \Rightarrow k = \frac{0.693}{160} = 4.33\times10^{-3}\ s^{-1}$

設 $[A]_0 = 100 \Rightarrow [A]_{(at\ 90\%\ complete)} = 10$

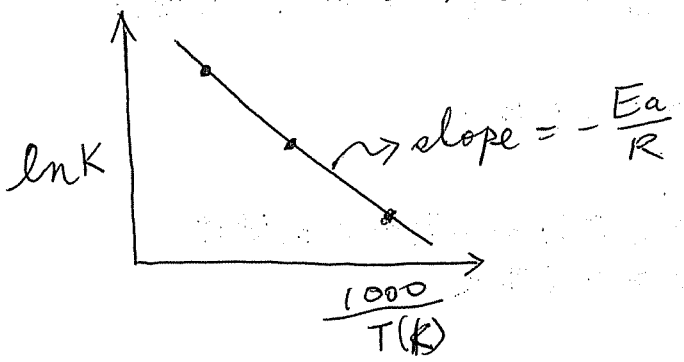
$\Rightarrow \ln\left(\frac{10}{100}\right) = -kt \Rightarrow t = \frac{\ln(0.1)}{-4.33\times10^{-3}\ s^{-1}} = \boxed{532\ sec}$

#61

$K = A\,e^{\left(\frac{-Ea}{RT}\right)}$ 取对数 $\ln K = -\frac{Ea}{RT} + \ln A$

$\ln K$ vs. $\frac{1}{T}$ 是一条直线

$T(K)$	$k(s^{-1})$	$\frac{1}{T}(K^{-1})$	$\ln K$
338	4.9×10^{-3}	2.96×10^{-3}	-5.32
318	5.0×10^{-4}	3.14×10^{-3}	-7.60
298	3.5×10^{-5}	3.36×10^{-3}	-10.26



$$\text{slope} = \frac{-10.76-(-5.85)}{(3.4\times10^{-3}-3.00\times10^{-3})K^{-1}} = -1.2\times10^{4}K = -\frac{Ea}{R}$$

$$Ea = 1.2\times10^{4}K \times 8.3145\ J/K\cdot mol$$

$$= 1.0\times10^{5}\ J/mol = \boxed{1.0\times10^{2}\ KJ/mol}$$

#62.

公式 $\ln K = -\frac{E_a}{RT} + \ln A$

a. $\text{slope} = -\frac{E_a}{R} = -1.10 \times 10^4 K$

$E_a = 1.10 \times 10^4 K \times 8.3145 \frac{J}{K \cdot mol} = 91.5 \frac{KJ}{mol}$

b. $y\ \text{intercept} = \ln A$

$A = e^{33.5} = 3.54 \times 10^{14} s^{-1}$

c. $\ln K = -\frac{E_a}{RT} + \ln A$

$K = A \exp(-E_a/RT)$

$= 3.54 \times 10^{14} \times \exp\left[\frac{-9.15 \times 10^{-4} J/mol}{8.3145 J/K \cdot mol \times 298 K}\right]$

$= 3.24 \times 10^{-2} s^{-1}$