In Class Exercise for Chapter 14 – Chemical Kinetics

1. Initial rate data at 25°C are listed in the table for the reaction:

$$NH^+_{4(aq)} + NO^-_{2(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)}$$

Experiment	$\left[NH^+_{4(aq)}\right]_0$	$\left[NO^-_{2(aq)}\right]_0$	Initial rate (mol/L·s)
1	0.24	0.10	7.2 x 10^{-6}
2	0.12	0.10	3.6 x 10^{-6}
3	0.12	0.15	5.4 x 10^{-6}

(a) What is the rate law?

$$rate = k\left[NH_4^+\right]^m\left[NO_2^-\right]^n$$

$$\frac{rate_1}{rate_2} = \frac{7.2\times10^{-6}\,\frac{mol}{L\bullet s}}{3.6\times10^{-6}\,\frac{mol}{L\bullet s}} = \frac{2}{1} = \frac{k\left(0.24\,\frac{mol}{L}\right)^m\left(0.10\,\frac{mol}{L}\right)^n}{k\left(0.12\,\frac{mol}{L}\right)^m\left(0.10\,\frac{mol}{L}\right)^n} = \left(\frac{2}{1}\right)^m \rightarrow m = 1$$

$$\frac{rate_3}{rate_2} = \frac{3.6\times10^{-6}\,\frac{mol}{L\bullet s}}{5.4\times10^{-6}\,\frac{mol}{L\bullet s}} = \frac{2}{3} = \frac{k\left(0.12\,\frac{mol}{L}\right)^m\left(0.10\,\frac{mol}{L}\right)^n}{k\left(0.12\,\frac{mol}{L}\right)^m\left(0.15\,\frac{mol}{L}\right)^n} = \left(\frac{2}{3}\right)^m \rightarrow m = 1$$

$$rate = k\left[NH_4^+\right]\left[NO_2^-\right]$$

(b) What is the value of the rate constant?

$$7.2\times10^{-6}\,\frac{mol}{L\bullet s} = k\left(0.24\,\frac{mol}{L}\right)\left(0.10\,\frac{mol}{L}\right) \rightarrow k = 3.0\times10^{-4}\,\frac{L}{mol\bullet s}$$

(c) What is the reaction rate when the concentrations are

$$\left[NH_4^+\right] = 0.39M \;\;\&\;\; \left[NO_2^-\right] = 0.052M$$

$$rate = 3.0\times10^{-4}\,\frac{L}{mol\bullet s}\left(0.39\,\frac{mol}{L}\right)\left(0.052\,\frac{mol}{L}\right) = 6.1\times10^{-6}\,\frac{mol}{L\bullet s}$$

2. The rearrangement of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) is a first-order reaction and has a rate constant of 5.11 x 10^{-5} s^{-1} at 472 K.

$$CH_3 - N \equiv C \rightarrow CH_3 - C \equiv N$$

If the initial concentration of CH_3NC is 0.0340 M:

(a) What is the molarity of CH_3NC after 2 hours?

$$rate = k\left[CH_3NC\right] = 5.11\times10^{-5}s^{-1}\left[CH_3NC\right] \quad t = 2hr\times\frac{3600\,s}{1\,hr} = 7200\,s$$

$$\ln\left[CH_3NC\right] = -kt + \ln\left[CH_3NC\right]_0 \rightarrow \left[CH_3NC\right] = e^{-kt+\ln\left[CH_3NC\right]_0} = e^{-kt}\left[CH_3NC\right]_0$$

$$\left[CH_3NC\right] = e^{-7200\,s\times5.11\times10^{-5}s^{-1}}\left(0.0340\,\frac{mol}{L}\right) = 0.0235\,\frac{mol}{L}$$

(b) How many minutes does it take for the CH_3NC concentration to drop to 0.0300 M?

$$\ln\left[CH_3NC\right] = -kt + \ln\left[CH_3NC\right]_0 \rightarrow t = -\ln\left(\frac{\left[CH_3NC\right]}{\left[CH_3NC\right]_0}\right)/k$$

$$t = -\ln\left(\frac{0.0300\,\frac{mol}{L}}{0.0340\,\frac{mol}{L}}\right)/5.11\times10^{-5}s^{-1}\times\frac{1\min}{60\,s} = 40.8\min$$

(c) How many minutes does it take for 20% of the CH_3NC to react?

$$t = -\ln\left(\frac{0.8*0.0340\,\frac{mol}{L}}{0.0340\,\frac{mol}{L}}\right)/5.11\times10^{-5}\,s^{-1}\times\frac{1\text{ min}}{60\ s} = 72.8\text{ min}$$

(d) What is the half life (in minutes) of the reaction?

$$t_{1/2} = 0.693/k = 0.693/5.11\times10^{-5}\,s^{-1}\times\frac{1\text{ min}}{60\ s} = 226\text{ min}$$

3. Hydrogen iodide decomposes slowly to H_2 and I_2 at 600 K. The reaction is second in HI and the rate constant is 9.7 x 10^{-6} M^{-1} s^{-1}. If the initial concentration of HI is 0.100 M:

(a) What is its molarity after a reaction time of 6.00 days?

$$\frac{1}{[HI]} = kt + \frac{1}{[HI]_0} \rightarrow [HI] = \left(kt + \frac{1}{[HI]_0}\right)^{-1}$$

$$[HI] = \left(9.7\times10^{-6}\,\frac{L}{mol\bullet s}\times\frac{60\ s}{1\text{ min}}\times\frac{60\text{ min}}{\text{hr}}\times\frac{24\text{ hr}}{1\text{ day}}\times 6\text{ days} + \frac{1}{0.100\,\frac{mol}{L}}\right)^{-1} = 0.0665\,\frac{mol}{L}$$

(b) What is the time (in days) when the HI concentration reaches a value of 0.020 M?

$$\frac{1}{[HI]} = kt + \frac{1}{[HI]_0} \rightarrow t = \frac{1}{k}\left(\frac{1}{[HI]} - \frac{1}{[HI]_0}\right)$$

$$t = \frac{1}{9.7\times10^{-6}\,\frac{L}{mol\bullet s}}\times\frac{1\text{ min}}{60\ s}\times\frac{\text{hr}}{60\text{ min}}\times\frac{1\text{ day}}{24\text{ hr}}\left(\frac{1}{0.020\,\frac{mol}{L}} - \frac{1}{0.100\,\frac{mol}{L}}\right) = 47.7\text{ days}$$

(c) What is the half-life of the reaction?

$$t_{1/2} = \frac{1}{k[HI]_0} = \frac{1}{9.7\times10^{-6}\,\frac{L}{mol\bullet s}\left(0.100\,\frac{mol}{L}\right)}\times\frac{1\text{ min}}{60\ s}\times\frac{\text{hr}}{60\text{ min}}\times\frac{1\text{ day}}{24\text{ hr}} = 11.9\text{ days}$$

(d) How many days does it take for the concentration of HI to drop from 0.0250 M to 0.0125 M?

$$t = \frac{1}{9.7\times10^{-6}\,\frac{L}{mol\bullet s}}\times\frac{1\text{ min}}{60\ s}\times\frac{\text{hr}}{60\text{ min}}\times\frac{1\text{ day}}{24\text{ hr}}\left(\frac{1}{0.0125\,\frac{mol}{L}} - \frac{1}{0.0250\,\frac{mol}{L}}\right) = 47.7\text{ days}$$

$$t_{1/2} = \frac{1}{k[HI]_0} = \frac{1}{9.7\times10^{-6}\,\frac{L}{mol\bullet s}\left(0.0250\,\frac{mol}{L}\right)}\times\frac{1\text{ min}}{60\ s}\times\frac{\text{hr}}{60\text{ min}}\times\frac{1\text{ day}}{24\text{ hr}} = 47.7\text{ days}$$

4. The following mechanism has been proposed for the reaction of nitric oxide & chlorine:

$$step\ 1: \quad NO_{(g)} + Cl_{2(g)} \rightarrow NOCl_{2(g)}$$

$$step\ 2: \quad NOCl_{2(g)} + NO_{(g)} \rightarrow 2NOCl_{(g)}$$

(a) What is the overall reaction?

$$step\ 1: \quad NO_{(g)} + Cl_{2(g)} \rightarrow NOCl_{2(g)}$$

$$\underline{step\ 2: \quad NOCl_{2(g)} + NO_{(g)} \rightarrow 2NOCl_{(g)}}$$

$$2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$$

(b) Identify any reaction intermediates.

$NOCl_{2(g)}$

(c) What is the molecularity of each elementary step?

Both are bimolecular

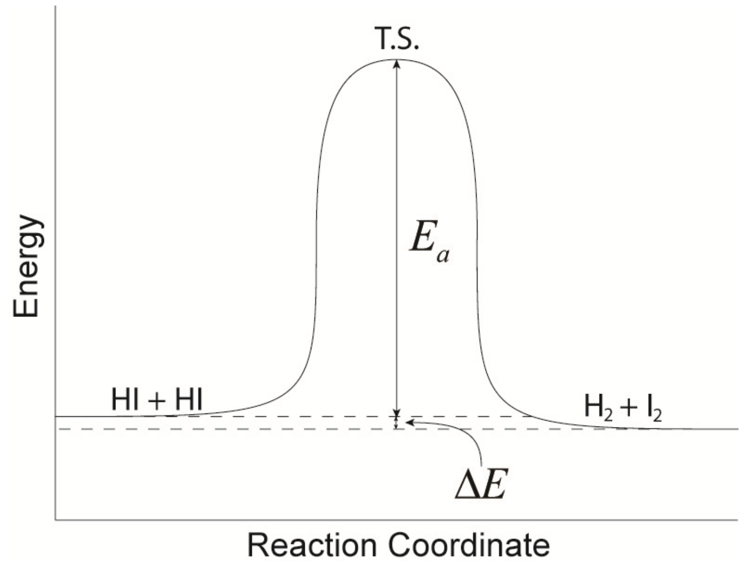
(d) What is the rate law if the first step is slow and the second is fast?

$rate = k[NO][Cl_2]$

5. Values of $E_a = 183\, kJ/mol$ and $\Delta E = -9\, kJ/mol$ have been measured for the reaction:

$$2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$$

Sketch a potential energy profile for this reaction that shows the potential energy of the reactants, products, the transition state, E_a and ΔE. What is the E_a for the reverse reaction?



$$E_{a,reverse} = (183 + 9)\, kJ = 192 kJ$$

6. The following mechanism has been proposed for the decomposition of dinitrogen pentaoxide, which has an experimental rate law and mechanism as shown below.

$$rate = -\frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5]$$

$N_2O_{5(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_{2(g)} + NO_{3(g)}$	*fast*
$NO_{2(g)} + NO_{3(g)} \xrightarrow{k_2} NO_{(g)} + NO_{2(g)} + O_{2(g)}$	*slow*
$NO_{(g)} + NO_{3(g)} \xrightarrow{k_3} 2NO_{2(g)}$	*fast*

(a.) Write a balanced equation for the overall reaction.

$$N_2O_{5(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_{2(g)} + NO_{3(g)} \qquad \textit{fast}$$

$$NO_{2(g)} + NO_{3(g)} \xrightarrow{k_2} NO_{(g)} + NO_{2(g)} + O_{2(g)} \qquad \textit{slow}$$

$$NO_{(g)} + NO_{3(g)} \xrightarrow{k_3} 2NO_{2(g)} \qquad \textit{fast}$$

$$2N_2O_{5(g)} + NO_{2(g)} + NO_{3(g)} + NO_{(g)} + NO_{3(g)} \rightarrow 2NO_{2(g)} + 2NO_{3(g)} + NO_{(g)} + NO_{2(g)} + O_{2(g)} + 2NO_{2(g)}$$

$$2N_2O_{5(g)} + NO_{2(g)} + 2NO_{3(g)} + NO_{(g)} \rightarrow 5NO_{2(g)} + 2NO_{3(g)} + NO_{(g)} + O_{2(g)}$$

$$2N_2O_{5(g)} + \cancel{NO_{2(g)}} + \cancel{2NO_{3(g)}} + \cancel{NO_{(g)}} \rightarrow 4\cancel{5}NO_{2(g)} + \cancel{2NO_{3(g)}} + \cancel{NO_{(g)}} + O_{2(g)}$$

$$\boxed{2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}}$$

(b.) Are there any intermediates and if so what are they?

NO_3 and NO

(c.) Verify the rate law given above.

$$k_1[N_2O_5] = k_{-1}[NO_2][NO_3]$$

$$rate = k_2[NO_2][NO_3] = k_2\frac{k_1}{k_{-1}}[N_2O_5] = K[N_2O_5]$$