Chemical Kinetics Tutorial

Hankertrix
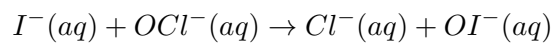
September 18, 2023

Contents

1 Question 1

1.1 (a)

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

1.2 (b)

For experiment 1:

$$\text{Rate of decrease of } [I^-] = \frac{2.40 \times 10^{-4} - 2.16 \times 10^{-4}}{10}$$
$$= 2.40 \times 10^{-6}$$

$$\text{Rate of decrease of } [OCl^-] = \frac{1.60 \times 10^{-4} - 1.36 \times 10^{-4}}{10}$$
$$= 2.40 \times 10^{-6}$$

For experiment 2:

$$\text{Rate of decrease of } [I^-] = \frac{1.20 \times 10^{-4} - 1.08 \times 10^{-4}}{10}$$
$$= 1.20 \times 10^{-6}$$

$$\text{Rate of decrease of } [OCl^-] = \frac{1.60 \times 10^{-4} - 1.48 \times 10^{-4}}{10}$$
$$= 1.20 \times 10^{-6}$$

For experiment 3:

$$\text{Rate of decrease of } [I^-] = \frac{2.40 \times 10^{-4} - 2.34 \times 10^{-4}}{10}$$
$$= 6.00 \times 10^{-7}$$

$$\text{Rate of decrease of } [OCl^-] = \frac{4.00 \times 10^{-5} - 3.40 \times 10^{-5}}{10}$$
$$= 6.00 \times 10^{-7}$$

For experiment 4:

$$\text{Rate of decrease of } [I^-] = \frac{1.20 \times 10^{-4} - 1.14 \times 10^{-4}}{10}$$
$$= 6.00 \times 10^{-7}$$

$$\text{Rate of decrease of } [OCl^-] = \frac{1.60 \times 10^{-4} - 1.54 \times 10^{-4}}{10}$$
$$= 6.00 \times 10^{-7}$$

Comparing experiment 1 and 2, the rate halves when $[I^-]$ halves, hence, the reaction is first-order with respect to I^-.

Comparing experiment 1 and 3, the rate decreases by 75% when $[OCl^-]$ decreases by 75%, hence, the reaction is first-order with respect to OCl^-.

Comparing experiments 2 and 4, the rate halves when $[OH^-]$ is doubled. This means that the reaction is negative first-order with respect to OH^-.

Thus, the rate law for the reaction is:

$$\text{Rate} = k[I^-][OCl^-][OH^-]^{-1}$$

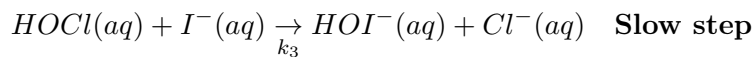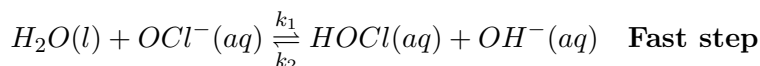Calculating the value of the rate constant using experiment 1:

$$2.40 \times 10^{-6} = k \times 2.40 \times 10^{-4} \times 1.60 \times 10^{-4} \times (1.00)^{-1}$$

$$k = 62.5 \, \text{s}^{-1}$$

1.3   (c)

The reaction is unlikely to occur through a single step reaction as the reaction is first order with respect to H^+, which is not found in the overall reaction and is a reaction intermediate, which suggests that the reaction occurs through a multistep mechanism.

1.4   (d)

$$H_2O(l) + OCl^-(aq) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HOCl(aq) + OH^-(aq) \quad \textbf{Fast step}$$

$$HOCl(aq) + I^-(aq) \underset{k_3}{\rightarrow} HOI^-(aq) + Cl^-(aq) \quad \textbf{Slow step}$$

$$HOI^-(aq) + OH^-(aq) \rightarrow OI^-(aq) + H_2O(l) \quad \textbf{Fast step}$$

Expressing the rate constant in terms of the rate constants for the elementary steps:

$$k = \frac{k_1 k_3}{k_2}$$

2 Question 2

At $25\,°C$, the k value is:
$$60 = \frac{\ln 2}{k}$$
$$k = \frac{\ln 2}{60}$$
$$k = 0.01155245301$$

At $32\,°C$, the k value is:
$$\ln 0.2 = -k(60) + \ln 0.5$$
$$k = -\frac{\ln 2 - \ln 5}{60}$$
$$k = 0.0152715122$$

Finding the required k value for X to decrease from $0.200\,\mathrm{mol}$ to $0.010\,\mathrm{mol}$:
$$\ln 0.01 = -k(60) + \ln 0.2$$
$$k = 0.0499288712$$

Finding $\frac{-E_a}{R}$ using the Arrhenius equation:
$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$\ln\left(\frac{0.01155245301}{0.0152715122}\right) = \frac{-E_a}{R}\left(\frac{1}{298.15} - \frac{1}{305.15}\right)$$
$$\frac{-E_a}{R} = -0.2790913488 \div 0.00007693958$$
$$\frac{-E_a}{R} = -3627.408969$$

Finding the required temperature:

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

$$\ln\left(\frac{0.0499288712}{0.0152715122}\right) = -3627.408969\left(\frac{1}{T_1} - \frac{1}{305.15}\right)$$

$$\ln\left(\frac{0.0499288712}{0.0152715122}\right) = \frac{-3627.408969}{T_1} - \frac{-3627.408969}{305.15}$$

$$-10.70268768 = \frac{-3627.408969}{T_1}$$

$$T_1 = \frac{-3627.408969}{-10.70268768}$$

$$T_1 = 338.925\,951\,2\,\text{K}$$

$$T_1 = 65.775\,051\,21\,^\circ\text{C}$$

$$T_1 \approx 65.8\,^\circ\text{C}$$

Hence, the minimum temperature required is $65.8\,^\circ$C.

3   Question 3

Getting the value of k for the reaction:

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

$$1.3 \times 10^{-5}k = \ln 2$$

$$k = \frac{\ln 2}{1.3 \times 10^{-5}}$$

$$k = 53319.01389$$

Using the integrated rate law for first-order reactions:

$$\ln(19.0 - \frac{1.3}{2}) = -53319.01389t + \ln 19.0$$

$$\ln 18.35 - \ln 19.0 = -53319.01389t$$

$$t = 6.528516213 \times 10^{-7}$$

$$t \approx 6.53 \times 10^{-7}$$

Thus, it will take 6.53×10^{-7} s for the pressure of NO_2 to reach $1.3\,\text{mm Hg}$.

4   Question 4

4.1   (a)

Using the integrated rate law for second-order reactions:

$$\frac{1}{\frac{0.001}{100} \times \frac{3.2}{2}} = 1.3 \times 10^{11}t + \frac{1}{\frac{3.2}{2}}$$

$$62500 - \frac{5}{8} = 1.3 \times 10^{11}t$$

$$62499.375 = 1.3 \times 10^{11}t$$

$$t = 4.807644231 \times 10^{-7}$$

$$t \approx 4.81 \times 10^{-7}$$

It will take 4.81×10^{-7} s to neutralise 99.999% of acid.

4.2   (b)

I would expect the rate of the acid-base neutralisation to be limited by the speed of mixing, since the reaction takes far less than even 1 microsecond to complete as stirring would take much longer than 1 microsecond to complete.

5 Question 5

Finding $[O_2]$:

$$\frac{1}{[O_2]^2} = 8kt + \frac{1}{([O_2]_0)^2}$$

$$\frac{1}{[O_2]^2} = 8(25)(120.0) + \frac{1}{(0.0100)^2}$$

$$\frac{1}{[O_2]^2} = 3.4 \times 10^4$$

$$[O_2]^2 = \frac{1}{3.4 \times 10^4}$$

$$[O_2] = \sqrt{\frac{1}{3.4 \times 10^4}}$$

$$[O_2] = 5.42326145 \times 10^{-3}$$

$$[O_2] \approx 5.42 \times 10^{-3} \text{ M}$$

The concentrations of NO would be double that of O_2 as its stoichiometric ratio to O_2 is $2:1$.

$$[NO] = 2 \times 5.42326145 \times 10^{-3}$$

$$[NO] = 1.08465229 \times 10^{-2}$$

$$[NO] \approx 1.08 \times 10^{-2} \text{ M}$$

The concentration of NO_2 will be double that of the reduction in $[O_2]$ as it is a product and its stoichiometric ratio to O_2 is $2:1$ as well.

$$[NO_2] = 2(0.0100 - 5.42326145 \times 10^{-3})$$

$$[NO_2] = 9.15347711 \times 10^{-3}$$

$$[NO_2] \approx 9.15 \times 10^{-3} \text{ M}$$

Hence, the concentration of NO is 1.08×10^{-2} M, the concentration of O_2 is 5.42×10^{-3} M, and the concentration of NO_2 is 9.15×10^{-3} M after 120.0 s.

6   Question 6

Finding the order of reaction with respect to NO_2 from the two experiments conducted at $600\,\text{K}$:

$$\frac{5.4 \times 10^{-7}}{2.2 \times 10^{-6}} = \frac{k(0.0010)^a}{k(0.0020)^a}$$

$$\frac{27}{110} = \frac{(0.0010)^a}{(0.0020)^a}$$

$$\ln\left(\frac{27}{110}\right) = \ln\left(\frac{(0.0010)^a}{(0.0020)^a}\right)$$

$$\ln\left(\frac{27}{110}\right) = \ln\left(\frac{0.0010}{0.0020}\right)^a$$

$$\ln\left(\frac{27}{110}\right) = a\ln\left(\frac{0.0010}{0.0020}\right)$$

$$a = 2.02647221$$

$$a \approx 2$$

Hence, the order of reaction with respect to NO_2 is second-order.

Finding the k value of the first experiment conducted at $600\,\text{K}$:

$$\text{Rate} = k[NO_2]^2$$

$$5.4 \times 10^{-7} = k(0.0010)^2$$

$$k = \frac{5.4 \times 10^{-7}}{(0.0010)^2}$$

$$k = 0.54$$

Finding the k value of the second experiment conducted at $600\,\text{K}$:

$$\text{Rate} = k[NO_2]^2$$

$$2.2 \times 10^{-6} = k(0.0020)^2$$

$$k = \frac{2.2 \times 10^{-6}}{(0.0020)^2}$$

$$k = 0.55$$

Getting the average value of k for the experiments conducted at $600\,\mathrm{K}$:

$$k_{600\,\mathrm{K}} = \frac{0.54 + 0.55}{2}$$

$$= 0.545$$

Finding the k value of the experiment conducted at $700\,\mathrm{K}$:

$$\text{Rate} = k[NO_2]^2$$

$$5.2 \times 10^{-5} = k(0.0020)^2$$

$$k = \frac{5.2 \times 10^{-5}}{(0.0020)^2}$$

$$k = 13$$

Using the Arrhenius equation to find $\frac{-E_a}{R}$ of the reaction:

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

$$\ln\left(\frac{0.545}{13}\right) = \frac{-E_a}{R}\left(\frac{1}{600} - \frac{1}{700}\right)$$

$$\ln\left(\frac{0.545}{13}\right) = \frac{-E_a}{R}\left(\frac{1}{4200}\right)$$

$$\ln\left(\frac{0.545}{13}\right) \div \frac{1}{4200} = \frac{-E_a}{R}$$

$$\frac{-E_a}{R} = -13322.05914$$

Finding the k at $660\,\text{K}$:

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

$$\ln\left(\frac{k_1}{13}\right) = -13322.05914\left(\frac{1}{660} - \frac{1}{700}\right)$$

$$\ln\left(\frac{k_1}{13}\right) = -13322.05914\left(\frac{1}{11550}\right)$$

$$\frac{k_1}{13} = e^{-13322.05914\left(\frac{1}{11550}\right)}$$

$$k_1 = 13e^{-13322.05914\left(\frac{1}{11550}\right)}$$

$$k_1 = 4.102203729$$

$$k_1 \approx 4.10$$

Using the integrated rate law for a second-order reaction:

$$\frac{1}{[NO_2]} = kt + \frac{1}{[NO_2]_0}$$

$$\frac{1}{0.0010} = 4.102203729t + \frac{1}{\frac{0.0055}{1}}$$

$$\frac{1}{0.0010} = 4.102203729t + \frac{1}{0.0055}$$

$$\frac{1}{0.0010} - \frac{1}{0.0055} = 4.102203729t$$

$$t = 199.449338$$

$$t \approx 199\,\text{s}$$

7 Question 7

Comparing experiment 1 and 2, the initial reaction rate approximately doubles when the initial concentration of A doubles. Hence, the reaction is first-order with respect to A.

Comparing experiment 2 and 3:

$$\frac{3.1 \times 10^{-5}}{3.1 \times 10^{-5}} = \frac{k(0.40)(0.10)^b}{k(0.10)(0.20)^b}$$

$$1 = \frac{4(0.10)^b}{(0.20)^b}$$

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

$$b = 2$$

Hence, the order of reaction is second-order with respect to B.

Finding the rate constant using experiment 1:

$$\text{Rate} = k[A][B]^2$$

$$1.5 \times 10^{-5} = k(0.20)(0.10)^2$$

$$k = 0.0075$$

Finding the rate constant using experiment 2:

$$\text{Rate} = k[A][B]^2$$

$$3.1 \times 10^{-5} = k(0.40)(0.10)^2$$

$$k = 0.00775$$

Finding the rate constant using experiment 3:

$$\text{Rate} = k[A][B]^2$$

$$3.1 \times 10^{-5} = k(0.10)(0.20)^2$$

$$k = 0.00775$$

Getting the average value of k at $700\,\text{K}$:

$$k = \frac{0.0075 + 0.00775 + 0.00775}{3}$$

$$= \frac{23}{3000}$$

Finding the rate constant at $600\,\text{K}$ using experiment 4:

$$\text{Rate} = k[A][B]^2$$

$$1.1 \times 10^{-5} = k(0.50)(0.50)^2$$

$$k = 0.000088$$

Using the Arrhenius equation to find the activation energy:

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

$$\ln\left(\frac{\frac{23}{3000}}{0.000088}\right) = \frac{-E_a}{R}\left(\frac{1}{700} - \frac{1}{600}\right)$$

$$\ln\left(\frac{\frac{23}{3000}}{0.000088}\right) \div -\frac{1}{4200} = \frac{-E_a}{R}$$

$$-\frac{E_a}{R} = -18762.66165$$

$$E_a = 18762.66165R$$

$$E_a = 18762.66165 \times 8.314$$

$$E_a = 155\,992.7689\,\text{J}\,\text{mol}^{-1}$$

$$E_a = 155.992\,768\,9\,\text{kJ}\,\text{mol}^{-1}$$

$$E_a \approx 156\,\text{kJ}\,\text{mol}^{-1}$$

8   Question 8

Using the integrated rate law for first-order reactions to get the value of k:

When $t = 10$, Absorbance$= 0.444$.

$$\ln(1.2 - 0.444) = -k(10) + \ln(1.2)$$

$$-10k = \ln(1.2 - 0.444) - \ln(1.2)$$

$$k = 0.04620354596$$

When $t = 20$, Absorbance$= 0.724$.

$$\ln(1.2 - 0.724) = -k(20) + \ln(1.2)$$

$$-20k = \ln(1.2 - 0.724) - \ln(1.2)$$

$$k = 0.04623294908$$

When $t = 100$, Absorbance$= 1.188$.

$$\ln(1.2 - 1.188) = -k(100) + \ln(1.2)$$

$$-100k = \ln(1.2 - 1.188) - \ln(1.2)$$

$$k = 0.04605170186$$

Finding the average value of k:

$$k = \frac{0.04620354596 + 0.04623294908 + 0.04605170186}{3}$$

$$= 0.0461627323$$

Getting the half-life of the reaction:

$$t_{\frac{1}{2}} = \frac{\ln 2}{0.0461627323}$$
$$= 15.01529797$$
$$\approx 15.0\,\text{s}$$

Hence, the half-life of the reaction is $15.0\,\text{s}$.

9 Question 9

Comparing experiment 1 and 2, when $[HI]$ tripled, the rate of reaction increased by 9 times. Hence, the order of reaction with respect to HI is second-order.

Getting the value of k from experiment 1:

$$\text{Rate} = k[HI]^2$$

$$1.8 \times 10^{-5} = k(0.10)^2$$

$$k = \frac{1.8 \times 10^{-5}}{(0.10)^2}$$

$$k = 0.0018$$

Getting the value of k from experiment 2:

$$\text{Rate} = k[HI]^2$$

$$1.6 \times 10^{-4} = k(0.30)^2$$

$$k = \frac{1.6 \times 10^{-4}}{(0.30)^2}$$

$$k = \frac{2}{1125}$$

Getting the average value of k:

$$k = \frac{0.0018 + \frac{2}{1125}}{2}$$

$$= \frac{161}{90000}$$

Getting the value of k from experiment 3:

$$\text{Rate} = k[HI]^2$$

$$3.9 \times 10^{-3} = k(0.20)^2$$

$$k = \frac{3.9 \times 10^{-3}}{(0.20)^2}$$

$$k = 0.0975$$

Using the Arrhenius equation to find the value of $\frac{-E_a}{R}$:

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

$$\ln\left(\frac{\frac{161}{90000}}{0.0975}\right) = \frac{-E_a}{R}\left(\frac{1}{700} - \frac{1}{800}\right)$$

$$\ln\left(\frac{\frac{161}{90000}}{0.0975}\right) = \frac{-E_a}{R}\left(\frac{1}{5600}\right)$$

$$\ln\left(\frac{\frac{161}{90000}}{0.0975}\right) \div \frac{1}{5600} = \frac{-E_a}{R}$$

$$\frac{-E_a}{R} = -22390.24303$$

Finding the rate constant k at $660\,\text{K}$:

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

$$\ln\left(\frac{k_1}{0.0975}\right) = -22390.24303\left(\frac{1}{660} - \frac{1}{800}\right)$$

$$\ln\left(\frac{k_1}{0.0975}\right) = -22390.24303\left(\frac{7}{26400}\right)$$

$$\frac{k_1}{0.0975} = e^{-5.936806864}$$

$$k_1 = e^{-5.936806864} \times 0.0975$$

$$k_1 = 0.00025744363$$

Finding the initial $[HI]$ to have a rate of 1.2×10^{-5} at $660\,\text{K}$:

$$\text{Rate} = k[HI]^2$$

$$1.2 \times 10^{-5} = 0.00025744363[HI]^2$$

$$[HI]^2 = 0.04661214525$$

$$[HI] = 0.2158984605$$

$$[HI] \approx 0.216\,\text{M}$$

Hence, the initial $[HI]$ that gives a rate of $1.2 \times 10^{-5}\,\text{M}\,\text{s}^{-1}$ at $660\,\text{K}$ is $0.216\,\text{M}$.

10 Question 10

10.1 (a)

Using the Arrhenius equation to find the activation energy:

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

$$\ln\left(\frac{2.60 \times 10^{-4}}{9.45 \times 10^{-3}}\right) = \frac{-E_a}{8.314}\left(\frac{1}{530 + 273.15} - \frac{1}{620 + 273.15}\right)$$

$$\ln\left(\frac{26}{945}\right) = \frac{-E_a}{8.314}(0.00012546466)$$

$$\ln\left(\frac{26}{945}\right) = -0.00001509077E_a$$

$$E_a = 238\,098.4005\,\text{J mol}^{-1}$$

$$E_a = 238.098\,400\,5\,\text{kJ mol}^{-1}$$

$$E_a \approx 238\,\text{kJ mol}^{-1}$$

10.2 (b)

Using the Arrhenius equation to find the rate constant at $580\,^{\circ}\text{C}$:

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

$$\ln\left(\frac{k_1}{9.45 \times 10^{-3}}\right) = \frac{-238.0984005 \times 10^3}{8.314}\left(\frac{1}{580 + 273.15} - \frac{1}{620 + 273.15}\right)$$

$$\ln\left(\frac{k_1}{9.45 \times 10^{-3}}\right) = -2.86382488 \times 10^4 \times (0.00005249406)$$

$$\ln\left(\frac{k_1}{9.45 \times 10^{-3}}\right) = -1.503338056$$

$$\frac{k_1}{9.45 \times 10^{-3}} = e^{-1.503338056}$$

$$k_1 = 2.10155319 \times 10^{-3}$$

Assuming that the order of reaction with respect to Teflon is first-order, the half-life of the reaction is:

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

$$= \frac{\ln 2}{2.10155319 \times 10^{-3}}$$

$$= 329.8261418$$

$$\approx 330\,\text{s}$$