20 Chemical kinetics

Physical constants: $R = 8.3145$ J K^{-1} mol^{-1}, $k_B = 1.381 \times 10^{-23}$ J K^{-1}, $h = 6.626 \times 10^{-34}$ J s, $N_A = 6.022 \times 10^{23}$ mol^{-1}, $F = 96,485$ C mol^{-1}, mass unit (u) = 1.6605×10^{-27} kg, 1 τ = 133.3 N m^{-2}, 0 °C = 273.15 K.

Many of these questions involve manipulating tables of data and plotting graphs; you will find it convenient to do this using a spreadsheet package, such as EXCEL.

20.1 The alkaline hydrolysis of ethyl ethanoate in aqueous solution is first order in ester and OH^-, and so second order overall

$$\frac{d[OH^-]}{dt} = -k_{2nd}[\text{ester}][OH^-].$$

In an experiment to verify this rate law, a reaction mixture was prepared in which the initial concentration of ester and OH^- were both 0.025 mol dm^{-3}. At intervals after the reaction was initiated, a 10 cm^3 aliquot of the reaction mixture was withdrawn and mixed with 10 cm^3 of 0.05 mol dm^{-3} HCl(aq). This amount of acid is sufficient to neutralize any unreacted OH^-, thus quenching the reaction. The remaining acid was then titrated with 0.02 mol dm^{-3} NaOH(aq) to the end point in the usual way. This method gave the following data at 0 °C

t / s	vol. of titre / cm^3	n_{titre} / mol	n_{aliquot} / mol	$[OH^-]$ / mol dm^{-3}
120	13.4	2.68×10^{-4}	2.32×10^{-4}	0.0232
300	14.3			
600	15.6			
900	16.4			
1200	17.4			
1500	18.1			
1800	18.5			

Complete the table in the following way (to help you, the first line has been completed).

(a) Work out the amount in moles of OH^- in the volume of NaOH solution added in the titration. Enter this in the column headed n_{titre}.

(b) Work out the amount in moles of H^+ in the acid used to quench the reaction mixture, and hence the amount in moles of *unreacted* OH^- in the aliquot: this is n_{aliquot}.

(c) Finally, work out the concentration of OH^- in the aliquot, and enter this into the final column.

Since the initial concentrations of OH^- and ester are equal, the rate law can be simplified to $d[OH^-]/dt = -k_{2nd}[OH^-]^2$. It therefore follows that a plot of $1/[OH^-]$ against t should be a straight line.

Make such a plot and use it to estimate a value for the second-order rate constant, stating the units of your result. (These are real data, and so some scatter is to be expected).

Test the data to see if they fit a first-order rate law (i.e. plot $\ln[OH^-]$ against t).

20.2 The same reaction as in 20.1 can be studied by measuring the conductance as a function of time. Although the number of ions do not change in the course of the reaction, the identity of the ions does, with OH^- ions being gradually replaced by ethanoate ions. The latter are less effective at passing a current, so the conductance *decreases* as the reaction proceeds.

If the conductance at time t is $G(t)$, and at long times (when the reaction has gone to completion) the conductance is G_∞, then it can be shown that the concentration of OH^- is proportional to the difference $(G(t) - G_\infty)$.

A reaction mixture was prepared in which the initial concentration of ethyl ethanoate was 0.25 mol dm^{-3}, and that of NaOH was 0.0025 mol dm^{-3}. The ester is thus in excess so the rate law becomes

$$\frac{d[OH^-]}{dt} = -k_{1st}[OH^-],$$

where the pseudo first-order rate constant k_{1st} is given by k_{2nd}[ester]. For a first-order process we expect a plot of $\ln[\mathrm{OH}^-]$ against t to be a straight line with slope $-k_{1st}$. As was explained in section 20.2.1 on page 770, for such a first-order process we can also plot the log of any quantity which is *proportional* to concentration. In this case we can therefore plot $\ln(G(t) - G_\infty)$ against time.

The following data were obtained at 0 °C

t / s	60	120	180	240	300	360	420	480
G / arb. units	85.5	75.0	65.9	60.3	56.6	52.7	51.0	48.9

At long times the conductance was measured as 45.0 . Use these data to plot a suitable graph from which you can determine the pseudo first-order rate constant, and hence determine the second-order rate constant.

20.3 The reaction between propanone and bromine in aqueous acid conditions was studied by measuring the absorbance at 400 nm due to Br_2. The initial concentrations of propanone and acid were both 0.50 mol dm^{-3}, with both reagents being in excess compared to the bromine.

The following data of absorbance at 400 nm as a function of time were obtained at 298 K

t / s	0	60	120	180	240	300	360	420
abs.	0.995	0.964	0.903	0.830	0.772	0.739	0.679	0.605

The path length provided by the cuvette was 1 cm, and the extinction coefficient of Br_2 at 400 nm is 168 mol^{-1} dm^3 cm^{-1}.

(a) Convert the absorbance data to concentrations, and then plot concentration as a function of time. You should find that the graph is a straight line, implying that the reaction is zero-order in bromine.

(b) Determine a value for the (pseudo) zero-order rate constant, stating its units.

(c) Assuming that the reaction is first order in both propanone and acid, determine the second-order rate constant for the overall reaction, stating its units.

20.4 The gas-phase reaction between NO and O_2

$$2\mathrm{NO} + \mathrm{O_2} \longrightarrow 2\mathrm{NO_2}$$

is thought to have the following rate law, which is overall third order

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = -k_{3rd}[\mathrm{O_2}][\mathrm{NO}]^2.$$

If the initial concentration of NO is twice the initial concentration of O_2, then this ratio will persist as the reaction proceeds, in which case the rate law simplifies to

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = -k'_{3rd}[\mathrm{O_2}]^3,$$

where $k'_{3rd} = 4k_{3rd}$.

(a) Integrate this rate law to show that the concentration of O_2 varies with time in the following way

$$\frac{1}{[\mathrm{O_2}]^2} = \frac{1}{[\mathrm{O_2}]_0^2} + 2k'_{3rd}t,$$

where $[\mathrm{O_2}]_0$ is the concentration of O_2 at time zero.

For a gas phase reaction, the partial pressure can be used as a measure of the concentration. As was shown in section 20.1.4 on page 765, for this reaction under the initial conditions described above, the partial pressure of O_2 is given by $p_{tot} - \frac{2}{3}p_{tot,init}$, where p_{tot} is the total pressure, and $p_{tot,init}$ is its initial value.

The following data were obtained at 298 K for a mixture of NO and O_2 in the ratio 2:1

t / s	60	120	180	240	300	360	420	480
p_{tot} / τ	84.0	79.6	77.5	76.2	75.3	74.6	74.0	73.7

The pressure is given in units of Torr (τ), where 1 τ = 133.3 N m^{-2}. The initial pressure was 100.1 τ.

(b) By plotting a suitable graph, show that these data are consistent with the overall third-order rate law given above, and obtain a value of the rate constant, stating its units. [You can either use the pressure directly as a unit of concentration or convert the pressures to concentrations in mol dm^{-3} using the ideal gas law.]

20.5 The oxidation of methanoic acid by bromine

$$\text{HCOOH} + \text{Br}_2 + 2\text{H}_2\text{O} \longrightarrow \text{CO}_2 + 2\text{Br}^- + 2\text{H}_3\text{O}^+,$$

can be studied by setting up the reaction in an electrochemical cell, as illustrated in Fig. 20.3 on page 767. If it is arranged that in the reaction mixture the bromide ion is in excess, the potential (voltage) E generated by the cell is given by

$$E = C - \frac{RT}{2F}\ln[\text{Br}_2],$$

where F is the Faraday constant (96,485 C mol^{-1}) and C is a constant. The consumption of bromine can therefore be followed by measuring the potential as a function of time.

The rate law of this reaction is thought to be first order in bromine. An experiment was designed to investigate the order with respect to methanoic acid (a) and acid (b)

$$\text{rate} = k[\text{Br}_2][\text{HCOOH}]^a[\text{H}_3\text{O}^+]^b.$$

The reaction mixture is set up so that HCOOH and H_3O^+ are in excess, making the rate law pseudo first order

$$\text{rate} = k_{1\text{st}}[\text{Br}_2] \qquad k_{1\text{st}} = k[\text{HCOOH}]^a[\text{H}_3\text{O}^+]^b.$$

The above expression for the cell potential can be rearranged to

$$\ln[\text{Br}_2] = \frac{2FC}{RT} - \frac{2FE}{RT}.$$

(a) For a first-order process a plot of $\ln[\text{Br}_2]$ against time will have slope $-k_{1\text{st}}$. Show that it therefore follows that a plot of E against time will have slope $(k_{1\text{st}}RT)/(2F)$.

The following data were obtained at 25 °C for a reaction mixture with the following initial concentrations: $[\text{Br}_2] = 3.0 \times 10^{-3}$ mol dm^{-3}, [HCOOH] = 0.10 mol dm^{-3}, $[\text{H}_3\text{O}^+]$ = 0.05 mol dm^{-3}

time / s	0	60	120	180	240	300	360
E / V	−0.772	−0.766	−0.761	−0.757	−0.752	−0.745	−0.741

(b) Plot these data as described above, and hence obtain a value of the first-order rate constant.

Similar experiments, with different initial (excess) concentrations of methanoic acid and acid gave the following data (the value indicated by the * is obtained from the graph above)

run	1	2	3	4	5	6
[HCOOH] / mol dm^{-3}	0.10	0.10	0.10	0.12	0.16	0.22
$[\text{H}_3\text{O}^+]$ / mol dm^{-3}	0.05	0.12	0.25	0.15	0.15	0.15
$10^3 \times k_{1\text{st}}$ / s^{-1}	*	2.77	1.33	2.66	3.55	4.88

Runs 1, 2 and 3 have the same (excess) concentration of methanoic acid, but different (excess) concentrations of acid. Runs 4, 5 and 6 have the same (excess) concentration of acid, but different (excess) concentrations of methanoic acid.

Taking logarithms of the expression for $k_{1\text{st}}$ gives

Note that $10^3 \times k_{1\text{st}} = 2.77$ means $k_{1\text{st}} = 2.77 \times 10^{-3}$.

$$\ln k_{1\text{st}} = \ln k + a\ln[\text{HCOOH}] + b\ln[\text{H}_3\text{O}^+].$$

(c) For runs 1, 2 and 3 plot $\ln k_{1st}$ against $\ln[H_3O^+]$ and hence obtain a value for the order b from the slope of the graph.

(d) Similarly, use the data from runs 4, 5 and 6 to obtain a value for the order a. Comment on what your values for these orders imply about the mechanism for this reaction.

20.6 Aqueous Fe^{3+} reacts with thiocyanate (SCN^-) to give a complex which absorbs strongly at 460 nm

$$Fe(H_2O)_6^{3+} + SCN^- \longrightarrow Fe(H_2O)_5(SCN)^{2+} + H_2O.$$

The reaction is thought to be first order in each reactant

$$\text{rate} = k_{2nd}[Fe(H_2O)_6^{3+}][SCN^-].$$

The reaction was followed using a flow system in which a solution containing Fe^{3+} (concentration 2.0×10^{-4} mol dm^{-3}) was flowed together with a solution of SCN^- (concentration 0.2 or 0.3 mol dm^{-3}, in excess over the Fe^{3+}). The concentration of the complex was monitored at various distances down the flow tube by measuring the absorbance at 460 nm, giving the following data (at 298 K) for two different concentrations of SCN^-. The flow rate was 10 m s^{-1}.

distance / cm	10	20	30	40	50
absorbance ($[SCN^-]$ = 0.2 mol dm^{-3})	0.253	0.438	0.576	0.667	0.750
absorbance ($[SCN^-]$ = 0.3 mol dm^{-3})	0.344	0.569	0.708	0.802	0.842

Since the thiocyanate is in excess, the reaction is pseudo first order in Fe^{3+} and so, as shown on page 772, the time dependence of the concentration of the *product* (i.e. the complex, denoted B) is given by

$$\ln([B]_\infty - [B](t)) - \ln([B]_\infty) = -k_{1st}t,$$

where $[B]_\infty$ is the concentration of B at long time i.e. when the reaction has gone to completion.

(a) Assuming that the absorbance at time t, $A(t)$, is proportional to the concentration of B, show that

$$\ln\left(\frac{A_\infty - A(t)}{A_\infty}\right) = -k_{1st}t,$$

where A_∞ is the absorbance when the reaction has gone to completion.

(b) In this experiment the absorbance at long reaction times was 0.94. Determine the value of the pseudo first-order rate constant (by plotting a suitable graph) for the two different excess concentrations of thiocyanate.

(c) Hence, determine the value of the second-order rate constant.

[Note that you will have to convert the distances to times, using velocity = distance / time.]

20.7 The rate of the gas phase reaction between the hydroxyl radical and HCl gas

$$OH + HCl \longrightarrow H_2O + Cl$$

has been studied by a combination of flash photolysis and laser induced fluorescence. In this technique, the OH radicals were generated by applying a pulse of UV light from a laser to a small amount of water vapour. Subsequently, the concentration of the OH radicals was monitored by using a laser to promote them to an excited electronic state, and then measuring the intensity of the fluorescence (i.e. the light emitted) from these excited molecules. The intensity of the fluorescence, I_F, is proportional to the concentration of OH radicals.

The following data were obtained at 300 K and at 220 K for the indicated concentrations of HCl; the fluorescence intensity I_F is given in arbitrary units.

t / μs	0	100	200	300
I_F ([HCl] = 5×10^{15} molec. cm^{-3}, T = 300 K)	100	69.5	48.3	33.6
I_F ([HCl] = 1×10^{16} molec. cm^{-3}, T = 300 K)	100	48.3	23.3	11.3
I_F ([HCl] = 1×10^{16} molec. cm^{-3}, T = 220 K)	100	64.7	41.9	27.1

(a) By plotting a graph, show that in each case the decay of OH follows a first-order process, and hence determine the first-order rate constant.

(b) By comparing the two data sets at 300 K, show that the rate law is first order in HCl, and hence determine the overall second-order rate constant at this temperature. Also determine the second-order rate constant at 220 K. Be sure to state the units of each rate constant.

(c) Using the values of the rate constant at these different temperatures, determine the activation energy and pre-exponential factor for the reaction.

[Data kindly provided by Dr David Husain, Dept. of Chemistry, Cambridge.]

20.8 The gas phase decomposition of ethanal

$$CH_3CHO \longrightarrow CH_4 + CO$$

has the rate law

$$\frac{d[CH_3CHO]}{dt} = -k\,[CH_3CHO]^{\frac{3}{2}}.$$

(a) Integrate this rate law and hence obtain an expression for how the concentration of ethanal varies with time (assume that the concentration of ethanal at time zero is $[CH_3CHO]_0$).

(b) Determine the form a plot which would be expected to give a straight line for data which follows this rate law. How is the rate constant related to the slope of this plot?

(c) Find an expression for the half life of the reaction.

20.9 (a) Using the data in Table 20.1 on page 781, determine the collision cross section for an encounter between NO and Cl_2. Take the masses of N, O and Cl as 14, 16 and 35.5 mass units, respectively.

(b) Following the approach used in Example 20.3 on page 781, use simple collision theory to determine the value of the pre-exponential factor for the reaction between NO and Cl_2 at 298 K.

20.10 Rate constants for the following reaction (in solution)

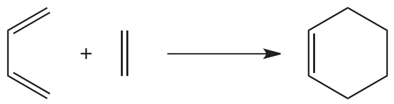
$$RBr + Cl^- \longrightarrow RCl + Br^- \qquad (R = n\text{Bu})$$

as a function of temperature are given in the following table. Use a graphical method to determine the enthalpy and entropy of activation.

T / °C	25.0	34.6	44.5	55.2	64.8
$10^5 \times k_{2nd}$ /mol^{-1} dm^3 s^{-1}	6.45	16.4	41.0	106	215

Is your value of $\Delta_r S^{\circ,\ddagger}$ consistent with the reaction proceeding via a mechanism in which RBr and Cl^- come together in the rate-limiting step?

20.11 Explain why it is that whereas the bimolecular gas phase Diels–Alder reaction



has $\Delta_r S^{\circ,\ddagger} = -150\ \mathrm{J\ K^{-1}\ mol^{-1}}$, the solution phase bimolecular reaction

$$\mathrm{Cr(H_2O)_6^{3+} + CNS^- \longrightarrow Cr(H_2O)_5(CNS)^{2+} + H_2O}$$

has $\Delta_r S^{\circ,\ddagger} = +125\ \mathrm{J\ K^{-1}\ mol^{-1}}$.