12 The rates of reactions

12.1 The thermal decomposition of N_2O_5 in the gas phase has the overall reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2.$$

Using the approach described in section 12.1.1 on page 409, write down the value of the stoichiometric coefficients of the reactant and each product. Then, write down the expression for the rate of reaction in terms of the slope of a plot of $[N_2O_5]$ against time, $[NO_2]$ against time, and $[O_2]$ against time.

12.2 By writing the units of concentration as 'conc' and the units of time as 'time', determine the units of the rate constants in the following rate laws

$$\text{rate} = k_1\,[N_2O_5] \qquad \text{rate} = k_2\,[PhCH_2Br]\,[DABCO]$$
$$\text{rate} = k_3\,[RH]\,[Cl_2]^{\frac{1}{2}} \qquad \text{rate} = k_4\,[CH_3CHO]^{\frac{3}{2}}$$
$$\text{rate} = k_5\,\frac{[O_3]^2}{[O_2]} \qquad \text{rate} = k_6.$$

12.3 The thermal decomposition of N_2O_5 in the gas phase is found to be first order in $[N_2O_5]$. The first order rate constant, k_{1st}, has been measured as a function of temperature as follows

T / K	349	368	378	396
k_{1st} / s^{-1}	0.0068	0.041	0.13	0.50

Make an Arrhenius plot of these data, and hence determine a value for the activation energy and the pre-exponential factor; state the units of each quantity.

12.4 Methanoic acid is oxidized in acid solution by Br_2 according to the following stoichiometric equation

$$HCOOH + Br_2 + 2H_2O \longrightarrow CO_2 + 2Br^- + 2H_3O^+.$$

It is found that the rate of reaction depends on the concentration of HCOOH and Br_2, and is also influenced by the concentration of added H_3O^+. If H_3O^+ and HCOOH are in excess, then it is found that the reaction is first order in $[Br_2]$. The following rate law was therefore proposed

$$\text{rate} = k_{obs}[Br_2][HCOOH]^a[H_3O^+]^b,$$

where a and b are the orders with respect to HCOOH and H_3O^+, respectively.

If H_3O^+ and HCOOH are in excess the rate law can be written

$$\text{rate} = k_{1st}[Br_2],$$

where k_{1st} is a pseudo first-order rate constant.

(a) Write down an expression for k_{1st}.

(b) The following values of k_{1st} were measured for different excess concentrations of HCOOH and H_3O^+:

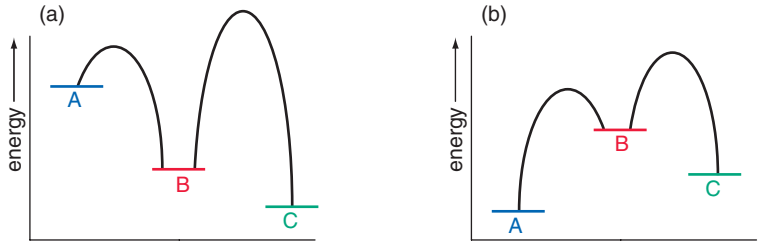
[HCOOH] / mol dm^{-3}	0.10	0.10	0.12	0.22
[H_3O^+] / mol dm^{-3}	0.05	0.12	0.15	0.15
k_{1st} / s^{-1}	7.00×10^{-3}	2.92×10^{-3}	2.80×10^{-3}	5.13×10^{-3}

By comparing the data in the first two columns, determined the value of b. Similarly, determine the value of a by comparing the data in the third and fourth columns.

(c) Use all of the data in the table to determine an average value of k_{obs}; state the units of this rate constant.

12.5 Consider the following two energy profiles for the reaction scheme (all reactions are first order)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C.$$



In each case, discuss whether or not the pre-equilibrium and/or the steady-state approaches can be used to analyse the overall kinetics. Using the appropriate approximation(s) in each case, obtain expressions for the rate of formation of C , identify the rate-limiting step, and mark the apparent activation energy on the energy profiles.

12.6 Consider the following reaction scheme, in which all of the reactions are first order and reversible.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C.$$

By equating the rates of formation and loss of B, show that the steady-state concentration of B is given by

$$[B]_{SS} = \frac{k_1[A] + k_{-2}[C]}{k_2 + k_{-1}}.$$

Hence show that the overall rate of change of the concentration of C is given by

$$\text{rate of change of [C]} = \frac{k_1k_2[A] - k_{-1}k_{-2}[C]}{k_2 + k_{-1}}.$$

Under what conditions will this steady-state analysis be valid? Draw an energy profile for such a situation, marking on it all of the activation energies.

12.7 The reaction (in solution) between Br_2 and dicyanomethane, $CH_2(CN)_2$, has the overall stoichiometry.

$$CH_2(CN)_2 + Br_2 \longrightarrow CHBr(CN)_2 + Br^- + H^+.$$

The following mechanism, involving the intermediate $CH(CN)_2^-$, is proposed

$$\begin{aligned} CH_2(CN)_2 &\xrightarrow{k_1} CH(CN)_2^- + H^+ \\ CH(CN)_2^- + H^+ &\xrightarrow{k_{-1}} CH_2(CN)_2 \\ CH(CN)_2^- + Br_2 &\xrightarrow{k_2} CH(CN)_2Br + Br^-. \end{aligned}$$

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By putting the intermediate in the steady state, show that

$$\text{rate of formation of } CH(CN)_2Br = \frac{k_1 k_2 [CH_2(CN)_2][Br_2]}{k_{-1}[H^+] + k_2[Br_2]}.$$

Under what conditions will this analysis be valid?

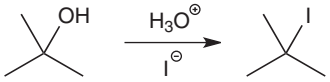
What simplification of the expression for the rate law occurs if: (a) the rate of reaction 2 is much greater than that of reaction −1; (b) the rate of reaction −1 is much greater than that of reaction 2? In each case, identify the rate-limiting step and the apparent activation energy.

12.8 In aqueous solution the oxidation of Fe^{II} by Pb^{IV} is though to proceed via the intermediate species Pb^{III} according to the following mechanism

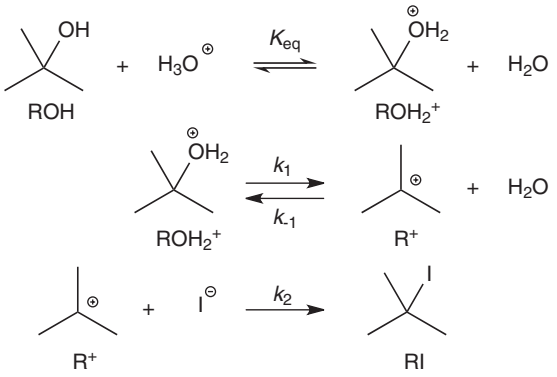
$$\begin{aligned} Fe^{II} + Pb^{IV} &\xrightarrow{k_1} Fe^{III} + Pb^{III} \\ Fe^{III} + Pb^{III} &\xrightarrow{k_{-1}} Fe^{II} + Pb^{IV} \\ Fe^{II} + Pb^{III} &\xrightarrow{k_2} Fe^{III} + Pb^{II}. \end{aligned}$$

Assuming that Pb^{III} can be placed in the steady state, determine the overall rate law for the rate of change of the concentration of Fe^{III}.

12.9 Under acid conditions and in aqueous solution, *t*-butanol undergoes a substitution reaction with iodide to give *t*-butyl iodide



Experimentally the rate law for this reaction is found to be first order in the concentration of the *t*-butanol and also first order in H_3O^+, but not to have a dependence on the concentration of the iodide. The fact that the rate depends on the concentration of the acid is a clue that protonation is involved at some stage. A possible mechanism is



The reason for proposing the initial protonation as the first step is that the dissociation of ROH_2^+ to give R^+ and H_2O is thought to be considerably faster than the dissociation of ROH to give R^+ and OH^-.

(a) Assuming that ROH and ROH_2^+ are in equilibrium, show that

$$[ROH_2^+] = K_{eq}[ROH][H_3O^+]. \qquad (12.1)$$

(b) Apply the steady-state approximation to R^+ and hence shown that

$$[R^+]_{SS} = \frac{k_1 K_{eq}[ROH][H_3O^+]}{k_{-1} + k_2[I^-]}.$$

You will need to use the expression for $[ROH_2^+]$ from Eq. 12.1 on page 41.

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(c) The rate of formation of the alkyl iodide is simply $k_2[R^+][I^-]$. Using you expression for $[R^+]$, show that

$$\text{rate of formation of RI} = \frac{k_1 k_2 K_{eq}[ROH][H_3O^+][I^-]}{k_{-1} + k_2[I^-]}.$$

If it can be assumed that the rate at which R^+ reacts with iodide is much faster than the rate at which the carbenium ion reacts with H_2O, show that the rate of formation of RI can be approximated by

$$\text{rate of formation of RI} = k_1 K_{eq}[ROH][H_3O^+].$$

(d) Give an interpretation of this rate law, identifying the rate-limiting step.

12.10 The destruction of ozone by Cl atoms in the stratosphere can be modelled using the following four reactions

$$\begin{aligned} \text{initiation} \quad & Cl_2 \xrightarrow{k_1} 2Cl \\ \text{propagation} \quad & Cl + O_3 \xrightarrow{k_2} ClO + O_2 \\ & ClO + O_3 \xrightarrow{k_3} Cl + 2O_2 \\ \text{termination} \quad & Cl + Cl \xrightarrow{k_4} Cl_2. \end{aligned}$$

(a) Write down an expression equating the rate of formation and loss of Cl; do the same for ClO.

(b) Compare these two equations carefully, and hence deduce that, in the steady state,

$$[Cl] = \sqrt{\frac{k_1[Cl_2]}{k_4}}.$$

(c) Using your equation equating the rate of formation and loss of ClO, together with the above expression for [Cl], to show that

$$[ClO] = \frac{k_2}{k_3}\sqrt{\frac{k_1[Cl_2]}{k_4}}.$$

(d) Hence show that the rate of loss of ozone is given by

$$\text{rate of loss of ozone} = 2k_2[O_3]\sqrt{\frac{k_1[Cl_2]}{k_4}}.$$

(e) Explain why this final expression does not include the rate constant k_3. Also, discuss the origin of the term in the square root.

12.11 This question concerned the mechanism of the $H_2 + Br_2$ reaction discussed in section 12.9.1 on page 432. In that section it was assumed that the concentration of HBr was low, so that the inhibition step (step 4) could be omitted. This question explores the effect of including this step.

Taking into account *all five* steps in the mechanism, show that equating the rate of formation and loss of Br gives

$$2k_1[Br_2] + k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] + 2k_5[Br]^2.$$

Further, by equating the rate of formation and loss of H show that

$$k_2[Br][H_2] = k_3[H][Br_2] + k_4[H][HBr]. \qquad (12.2)$$

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By adding together these two equations show that

$$[\mathrm{Br}] = \left(\frac{k_1}{k_5}\right)^{\frac{1}{2}} [\mathrm{Br_2}]^{\frac{1}{2}}.$$

Substitute this expression for [Br] into Eq. 12.2 and rearrange the result to obtain an expression for [H].

The rate of formation of HBr is

$$\text{rate of formation of HBr} = k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}].$$

Use Eq. 12.2 to show that this can be rewritten

$$\text{rate of formation of HBr} = 2k_3[\mathrm{H}][\mathrm{Br_2}],$$

and then substitute your expression for [H] into this to obtain, after some rearrangement

$$\text{rate of formation of HBr} = \frac{2k_2\left(\frac{k_1}{k_5}\right)^{\frac{1}{2}} [\mathrm{H_2}][\mathrm{Br_2}]^{\frac{3}{2}}}{[\mathrm{Br_2}] + \left(\frac{k_4}{k_3}\right)[\mathrm{HBr}]}.$$

Compare this rate law with the experimentally determined form.

12.12 It is possible that the gas phase reaction between NO and O_2 to give NO_2

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

proceeds via the following mechanism involving the intermediate N_2O_2

$$\begin{aligned} 2\mathrm{NO} &\xrightarrow{k_1} \mathrm{N_2O_2} \\ \mathrm{N_2O_2} &\xrightarrow{k_{-1}} 2\mathrm{NO} \\ \mathrm{N_2O_2} + \mathrm{O_2} &\xrightarrow{k_2} 2\mathrm{NO_2}. \end{aligned}$$

Show how this mechanism can be consistent with the experimentally observed rate law

$$\text{rate of formation of } \mathrm{NO_2} = k_{\mathrm{obs}}[\mathrm{O_2}][\mathrm{NO}]^2,$$

and give an expression for k_{obs}.

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