8

Reaction kinetics

Answers to worked examples

WE 8.1 The rate of a reaction

For the reaction between nitrogen and hydrogen

$$N_2\text{ (g)} + 3\ H_2\text{ (g)} \rightarrow 2\ NH_3\text{ (g)}$$

the rate of formation of ammonia was measured as 10 mmol dm^{-3} s^{-1}. What was the rate of consumption of hydrogen?

Strategy

Use the stoichiometry of the reaction to determine the rate at which hydrogen is consumed relative to that at which the ammonia is produced.

Solution

For every 2 mol of NH_3 (g) produced, 1 mol of N_2 (g) and 3 mol of H_2 (g) are consumed. Thus

$$\begin{aligned}\text{Rate of consumption of hydrogen} &= 3/2 \times \text{ rate of formation of ammonia}\\ &= 1.5 \times 10\ \text{mmol dm}^{-3}\text{s}^{-1}\\ &= 15\ \text{mmol dm}^{-3}\text{s}^{-1}\end{aligned}$$

WE 8.3 Integrated rate equations

Write an integrated rate equation for reaction of two methyl radicals to form ethane in Equation 8.3 (p.346). Explain how a value of the rate constant *k* can be found from experimental measurements of concentration of the methyl radical at different times during the course of the reaction: $2\ CH_3^{\bullet} \rightarrow C_2H_6$ (8.3)

Strategy

Use Equation 8.4 to express the rate of reaction in terms of the rate of change of methyl radicals. Consider how the integrated rate equation, Equation 8.7b, may be tested graphically.

Solution

The reaction is a second order elementary reaction. Using Equation 8.4,

$$\text{rate of reaction} = \frac{1}{\nu_{\mathrm{J}}}\frac{\mathrm{d[J]}}{\mathrm{d}t}$$

where ν_J is the stoichiometric number for J, and is positive for products and negative for reactants, then

$$\text{rate of reaction} = -\frac{1}{2}\frac{\mathrm{d[CH_3\cdot]}}{\mathrm{d}t}$$

The differential rate equation is thus

$$-\frac{1}{2}\frac{\mathrm{d[CH_3]}}{\mathrm{d}t} = k[\mathrm{CH_3\cdot}]^2$$

which is equivalent to

$$\frac{\mathrm{d[CH_3]}}{\mathrm{d}t} = -2k[\mathrm{CH_3\cdot}]^2$$

The integrated rate equation is given by Equation 8.7b

$$\frac{1}{[\mathrm{CH_3\cdot}]_t} = \frac{1}{[\mathrm{CH_3\cdot}]_0} + 2kt$$

This has the same form as a straight-line graph

$$y = mx + c$$

Thus a plot of

$$y = \frac{1}{[\mathrm{CH_3\cdot}]_t}$$

against

$$x = t$$

should be a straight line with a gradient of

$$m = 2k$$

and an intercept

$$c = \frac{1}{[CH_3\cdot]_0}$$

WE 8.5 Using the initial rate method to investigate the reaction between bromate ions and bromide ions

The acid-catalysed bromination of propanone was investigated using the initial rate method at 298 K

$$CH_3COCH_3\ (aq) + Br_2\ (aq) \rightarrow CH_3COCH_2Br\ (aq) + Br^-\ (aq) + H^+\ (aq)$$

The concentration of Br_2 was monitored in five separate experiments. By inspection of the following data, determine the order of the reaction with respect to each of the substances in the table.

	Initial Concentration / mol dm^{-3}			Initial Rate
Experiment	[CH_3COCH_3 (aq)]	[Br_2 (aq)]	[H^+ (aq)]	/ 10^{-6} mol dm^{-3} s^{-1}
1	0.30	0.05	0.05	5.60
2	0.30	0.10	0.05	5.60
3	0.30	0.05	0.10	11.1
4	0.40	0.05	0.20	30.5
5	0.40	0.05	0.05	7.55

Strategy

By inspecting the data, find out how the initial rate varies as the concentration of each reactant is changed. To isolate the effect of each individual reactant, compare experiments that differ in the concentration of only one substance at a time.

Solution

Order with respect to Br_2: Comparing experiments 1 and 2, $[Br_2]$ doubles, but the rate stays the same, so the reaction is zero order with respect to Br_2.

Order with respect to H^+: Comparing experiments 1 and 3, $[H^+]$ doubles and the rate doubles; comparing experiments 4 and 5, $[H^+]$ decreases by a factor of 4 and the rate decreases by a factor of 4, so the reaction is first order with respect to H^+.

Order with respect to CH_3COCH_3: Comparing experiments 1 and 5, $[CH_3COCH_3]$ increases by a third and the rate increases by a third, so the reaction is first order with respect to CH_3COCH_3.

WE 8.7 The steady state approximation: deriving a rate equation to test a proposed mechanism

(a) Show that the proposed mechanism is consistent with the overall equation for the reaction.

(b) Give the molecularity of each of the three elementary reactions in the proposed mechanism.

(c) Suggest why the reaction: $2\,NO + O_2 \rightarrow 2\,NO_2$ is unlikely to be an elementary reaction.

(d) An alternative mechanism that has been considered is

$$NO + NO \rightarrow NO_2 + N \qquad \text{slow}$$

$$N + O_2 \rightarrow NO_2 \qquad \text{fast}$$

Explain why this mechanism can be discounted.

Strategy

(a) Check that the individual mechanistic steps combine to give the overall stoichiometric equation for the reaction. (b) Count the number of reactant species for each mechanistic step. (c) Consider the likelihood of a three-body collision in the gas phase. (d) Check whether the rate equation for the rate-determining step is consistent with the observed kinetics.

Solution

(a) For a reaction mechanism to be consistent with the overall reaction, the individual steps should sum to give the overall stoichiometric equation.

$$2\ NO \rightleftharpoons N_2O_2$$
$$N_2O_2 + O_2 \rightarrow 2\ NO_2 \qquad +$$
$$\overline{2\ NO + N_2O_2 + O_2 \rightarrow 2\ NO_2 + N_2O_2}$$

where the N_2O_2 appears as both a reactant and a product, so cancels to give

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

(b)
$$2\ NO \rightarrow N_2O_2$$

The step involves the collision of two molecules, so is bimolecular.

$$N_2O_2 \rightarrow 2NO$$

One molecule decomposes so the step is unimolecular.

$$N_2O_2 + O_2 \rightarrow 2\ NO_2$$

Two molecules react in a single step, which is therefore bimolecular.

(c) A simultaneous collision between three molecules in the gas phase is statistically very unlikely.

(d) The first step would be rate determining. The rate equation for this step would thus be the rate equation for the overall reaction:

$$\text{rate of reaction} = k[NO]^2$$

This does not match the observed kinetics, so the mechanism is not plausible.

WE 8.9 Comparing rate constants at different temperatures

Sucrose is hydrolysed in the digestive system to form glucose and fructose. The activation energy for the reaction is +108 kJ mol^{-1}. At 298 K, the rate constant is 1.85×10^{-4} dm^3 mol^{-1} s^{-1}. Calculate the rate constant for the reaction at body temperature, 37 °C (310 K).

Strategy

Use Equation 8.25, which relates the values of the rate constant for a reaction at two different temperatures to the activation energy.

Solution

Using Equation 8.25

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

then

$$\ln k_{310}/k_{298} = \frac{E_a}{R}\left(\frac{1}{298\ \text{K}} - \frac{1}{310\ \text{K}}\right)$$

$$= \frac{108 \times 10^3 \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{298\ \text{K}} - \frac{1}{310\ \text{K}}\right)$$

$$= 1.687$$

so that

$$k_{310}/k_{298} = e^{+1.687} = 5.405$$

and therefore

$$k_{310} = 5.405 \times k_{298}$$

$$= 5.405 \times 1.85 \times 10^{-4}\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$$

$$= 1.00 \times 10^{-3}\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$$

Answers to boxes

Box 8.3 Atmospheric lifetime of methane

Calculate a value for the half life (in years) of methane under the conditions in the troposphere.

Strategy

Use Equation 8.9 to determine the half life from the pseudo-first-order rate constant.

Solution

Using Equation 8.9

$$t_{½} = \ln 2\,/k' = \ln 2\,/k[\mathrm{OH}]_{\mathrm{constant}}$$
$$= 0.693/(3.9 \times 10^{6}\,\mathrm{mol^{-1}\,dm^{3}s^{-1}} \times 1 \times 10^{-15}\,\mathrm{mol\,dm^{-3}})$$
$$= 178 \times 10^{6}\,\mathrm{s} = 5.6\,\mathrm{a}$$

Box 8.7 Pharmacokinetics

The breakdown in the body of the chemotherapy drug, cisplatin, is found to follow first-order kinetics. The rate constant at body temperature is $1.87 \times 10^{-3}\,\mathrm{min^{-1}}$. The concentration of the drug in the body of a cancer patient is $5.16 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$. What will the concentration be after 24 hours?

Strategy

Write an integrated rate equation that shows how the concentration of cisplatin varies with time. By substituting the values for the rate constant and the initial concentration, determine the concentration of the drug after 24 hours.

Solution

Using Equation 8.6b for a first order reaction,

$$\ln\frac{[\mathrm{cisplatin}]_t}{[\mathrm{cisplatin}]_0} = -\,kt = -1.87 \times 10^{-3}\,\mathrm{min^{-1}} \times (24 \times 60)\,\mathrm{min} = -2.693$$

Thus,

$$[\mathrm{cisplatin}]_t = [\mathrm{cisplatin}]_0\mathrm{e}^{-2.693}$$

$$= 5.16 \times 10^{-4}\ \text{mol dm}^{-3} \times \text{e}^{-2.693}$$
$$= 3.49 \times 10^{-5}\ \text{mol dm}^{-3}$$

A quick check using Equation 8.9, shows that for this reaction, the half life is

$$t_{½} = \ln 2\,/k = 0.693/1.87 \times 10^{-3}\text{min}^{-1} = 371\ \text{min} = 6.2\ \text{hr}$$

so that 24 hr corresponds to about four half lifes. We might therefore expect the concentration to have dropped by a factor of $(0.5)^4 = 0.0625$, which is consistent with the concentration calculated using Equation 8.9b.

$$[\text{cisplatin}]_t \approx (½)^4 \times [\text{cisplatin}]_0$$
$$\approx 0.0625 \times 5.16 \times 10^{-4}\ \text{mol dm}^{-3}$$
$$\approx 3.23 \times 10^{-5}\ \text{mol dm}^{-3}$$

Answers to end of chapter questions

1. The energy profiles **A–D** represent four different reactions. All the diagrams are drawn to the same scale. Which of the energy profiles **A–D** represents:

(a) the most exothermic reaction;

(b) the most endothermic reaction;

(c) the reaction with the largest activation energy;

(d) the reaction with the smallest activation energy?

Strategy

(a) and (b) Consider the difference in the potential energy of the reactants and products. Assume that the difference in potential energy is indicative of the difference in enthalpy. (c) and (d) Consider the height of the potential-energy barrier, which represents the activation energy for the reaction.

Solution

(a) **C** is the most exothermic, because the potential energy of the products is so much lower than the potential energy of the reactants.

(b) **A** is the most endothermic, because the potential energy of the products is much higher than the potential energy of the reactants.

(c) **A** has the largest activation energy, because the barrier between the reactants and products is highest.

(d) **C** has the smallest activation energy, because there is only a very low barrier between the reactants and products.

3. Under certain experimental conditions, the rate of the following reaction is 5.86×10^{-6} mol dm^{-3} s^{-1}

$$N_2O\,(g) \rightarrow 2\,N_2\,(g) + O_2\,(g)$$

Calculate values for d[NO]\d$t$, d[N_2]\d$t$ and d[O_2]\d$t$.

Strategy

Define the rate of reaction for each species in same way as in Equation 8.4, noting the stoichiometric coefficients for the particular reaction. Rearrange the equation, using the value for the rate of reaction to determine the rate of change of concentration for the various species.

Solution

From Equation 8.4,

$$v = \text{Rate of reaction} = -\frac{1}{2}\frac{\text{d}[\text{N}_2\text{O}]}{\text{d}t} = \frac{1}{2}\frac{\text{d}[\text{N}_2]}{\text{d}t} = \frac{\text{d}[\text{O}_2]}{\text{d}t}$$

Thus,

$$\frac{\text{d}[\text{N}_2\text{O}]}{\text{d}t} = -2v = -2 \times 5.86 \times 10^{-6} \text{mol dm}^{-3}\text{s}^{-1} = -1.17 \times 10^{-5} \text{mol dm}^{-3}\text{s}^{-1}$$

$$\frac{\text{d}[\text{N}_2]}{\text{d}t} = 2v = 2 \times 5.86 \times 10^{-6} \text{mol dm}^{-3}\text{s}^{-1} = 1.17 \times 10^{-5} \text{mol dm}^{-3}\text{s}^{-1}$$

$$\frac{\text{d}[\text{O}_2]}{\text{d}t} = v = 5.86 \times 10^{-6} \text{mol dm}^{-3}\text{s}^{-1}$$

5. For the reaction of NO and H_2

$$2\text{ NO (g)} + 2\text{ H}_2\text{ (g)} \rightarrow \text{N}_2\text{ (g)} + 2\text{ H}_2\text{O (g)}$$

The rate equation is given by, rate of reaction = $k[\text{NO}]^2[\text{H}_2]$

(a) What are the orders of the reaction with respect to NO and H_2?

(b) What is the overall order of the reaction?

(c) What would happen to the rate of reaction if:

(i) $[\text{H}_2]$ were doubled;

(ii) $[\text{H}_2]$ were halved;

(iii) [NO] were doubled;

(iv) [NO] were increased by a factor of three?

Strategy

Use the rate law to determine how the rate of reaction changes when the concentration is varied.

Solution

(a) The rate equation is of the form

$$\text{rate of reaction} = k[\text{A}]^a[\text{B}]^b \ldots$$

where a is the order of the reaction with respect to A, b is the order with respect to B, and so on. Thus, examining the rate equation, the order with respect to NO is 2 and with respect to H_2 is 1.

(b) The overall order is the sum of the orders with respect to the individual components. Thus, the overall order is 1 + 2 = 3.

(c) (i) Rate would double; (ii) Rate would halve.; (iii) Rate would quadruple; (iv) Rate would increase by a factor of 9.

7. The data below were obtained for the decomposition of difluorine oxide (F_2O) at 298 K. Verify that this is a second order reaction and determine the rate constant at 298 K.

t / s	0	60	120	180	240	300	360	420
$[F_2O]$/ 10^{-3} mol dm^{-3}	7.2	5.5	4.6	3.8	3.3	2.9	2.6	2.4

Strategy

From Equation 8.7b, which is the integrated rate equation for a second-order reaction, plot a graph of $1/[F_2O]$ against t. A straight-line graph will indicate that the reaction is second order with respect to F_2O. The gradient of the graph will then be $2k$.

Solution

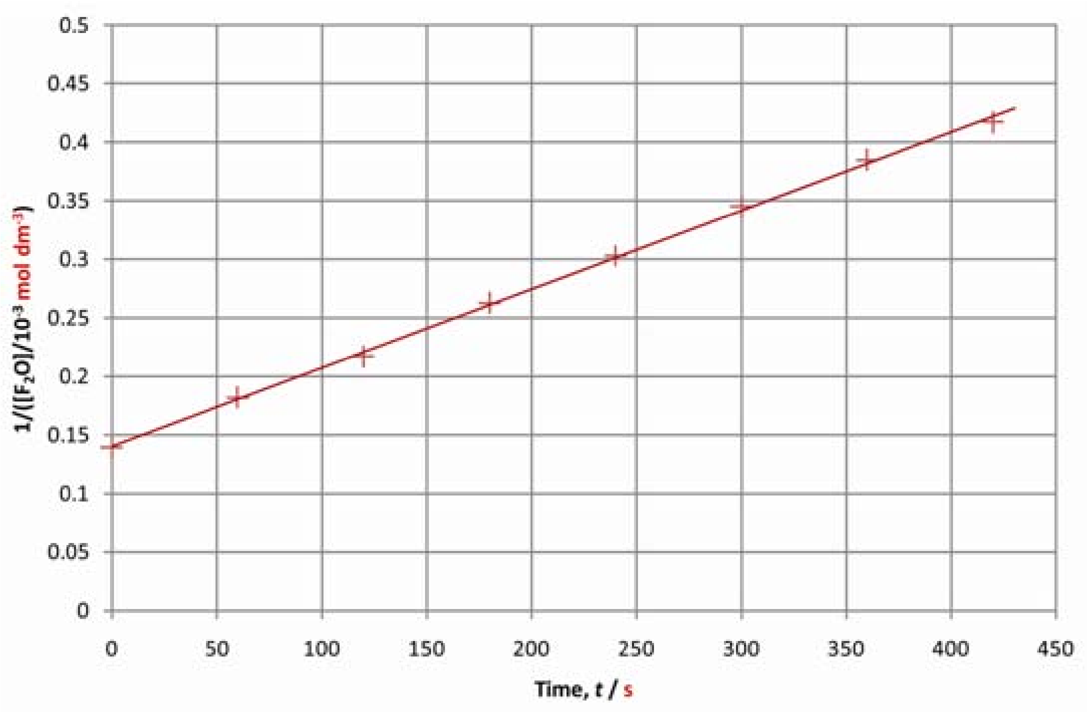
From Equation 8.7b

$$\frac{1}{[F_2O]_t} = \frac{1}{[F_2O]_0} + 2kt$$

Constructing a table

t / s	0	60	120	180	240	300	360	420
$[F_2O]$/ 10^{-3} mol dm^{-3}	7.2	5.5	4.6	3.8	3.3	2.9	2.6	2.4

$(1/[F_2O])$ / 10^3 dm^3 mol^{-1}	0.139	0.182	0.217	0.263	0.303	0.345	0.385	0.417



The plot is a straight line, showing that the reaction is second order with respect to F_2O. The gradient is

$$m = 2k = 6.71 \times 10^{-4} / 10^3 \mathrm{dm^3 mol^{-1} s^{-1}} = 0.671\ \mathrm{dm^3 mol^{-1}\ s^{-1}}$$

so that, at 298 K,

$$k = 0.336\ \mathrm{dm^3 mol^{-1}\ s^{-1}}$$

9. The addition of bromine to propene is an elementary reaction with a rate constant, k

$$CH_2{=}CHCH_3 + Br_2 \rightarrow CH_2BrCHBrCH_3$$

Kinetic studies were carried out at 298 K using excess Br_2. For $[Br_2]_0 = 0.20$ mol dm^{-3}, the pseudo-first order rate constant, k', for the reaction was found to be 900 s^{-1}. What is the value of k at 298 K?

Strategy

Noting that the reaction is an elementary reaction that is second order overall, write a differential rate law in terms of the concentration of propene and bromine. Re-write the expression as a pseudo-first-order rate law, for which the concentration of bromine is assumed to be constant because the reagent is present in excess. Hence derive an expression for the pseudo-first-order rate constant. Substitute the concentration of bromine and the measured value to determine the true second-order rate constant.

Solution

The reaction is elementary, so we may write

$$\text{rate of reaction} \;=\; k[\mathrm{Br_2}][\text{propene}]$$

Using excess Br_2, so that the concentration remains at its initial value

$$\text{rate of reaction} \;=\; k[\mathrm{Br_2}]_0[\text{propene}] = k'[\text{propene}]$$

Hence,

$$k' = k[\mathrm{Br_2}]_0$$

and therefore

$$k = k'/[\mathrm{Br_2}]_0 = 900\ \mathrm{s^{-1}}/0.20\ \mathrm{mol\ dm^{-3}} = 4500\ \mathrm{mol^{-1}dm^3s^{-1}}$$

11. The investigation described in Question 10 was repeated a number of times, each time using a different concentration of ethanal, $[CH_3CHO]_0$. A value for k' was found in each case. The following results were obtained.

$[CH_3CHO]_0$ / 10^{-7} mol dm^{-3}	1.2	2.4	4.0	5.1
k' / 10^3 s^{-1}	1.12	2.10	3.65	4.50

Confirm that the reaction is first order with respect to ethanal and determine the second order rate constant for the reaction. (Incorporate the value of k' determined in Question 10 into your analysis.)

Strategy

Plot k' against [ethanal]. The gradient of the graph will be the true second-order rate constant.

Solution

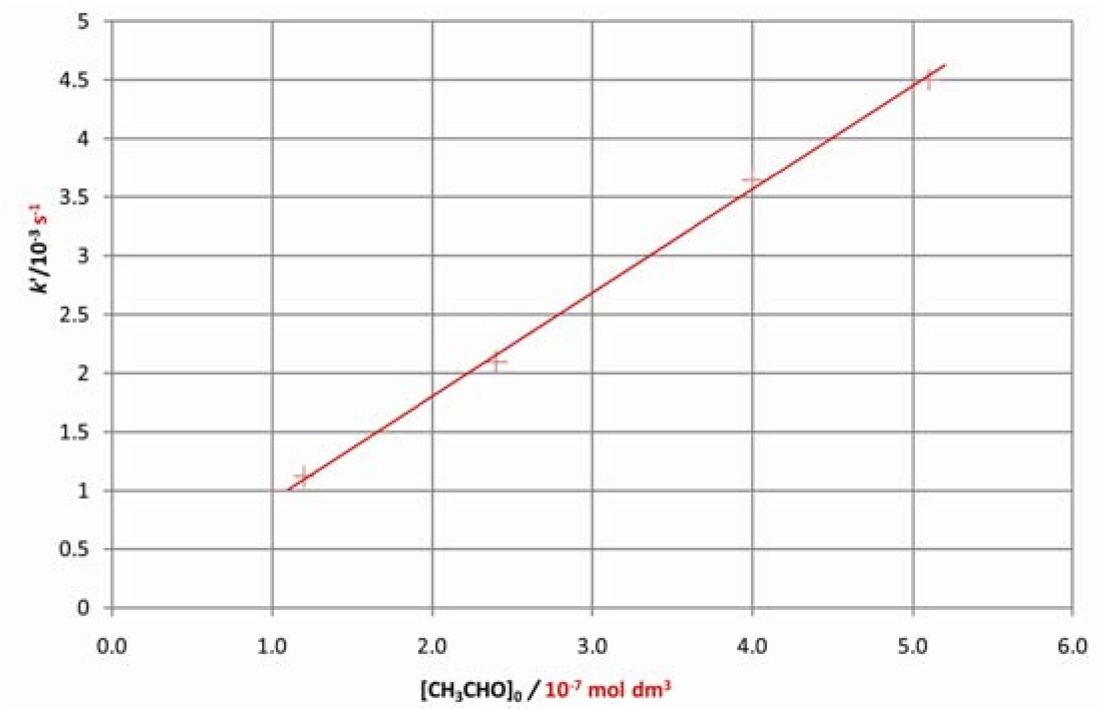
From Question 10, using excess CH_3CHO,

$$\textbf{Rate of reaction} = \boldsymbol{k}[\mathbf{CH_3CHO}]_\mathbf{0}[\cdot\,\mathbf{OH}] = \boldsymbol{k}'[\cdot\,\mathbf{OH}]$$

so that

$$k' = k[CH_3CHO]_0$$

Thus, plotting k' against $[CH_3CHO]$,



gives a straight-line graph with a gradient

$$k = 0.882 \times 10^{-10}\ \mathrm{dm^3\ mol^{-1} s^{-1}}.$$

13. Rate constants at a series of temperatures were obtained for the decomposition of azomethane:

$$CH_3N_2CH_3 \rightarrow 2\,CH_3^{\cdot} + N_2$$

Use the data in the table to find the activation energy, E_a, for the reaction.

T / K	523	541	560	576	593
k / 10^{-6} s^{-1}	1.8	15	60	160	950

Strategy

Use the Arrhenius equation, Equation 8.24, and plot a graph of ln k against 1 / T. Determine the activation energy from the gradient of the graph.

Solution

From the Arrhenius equation, Equation 8.24,

$$\ln k = \ln A - E_a/R\left(\frac{1}{T}\right)$$

a graph of ln k against $1/T$ should have a gradient

$$m = -E_a/R$$

Taking logs,

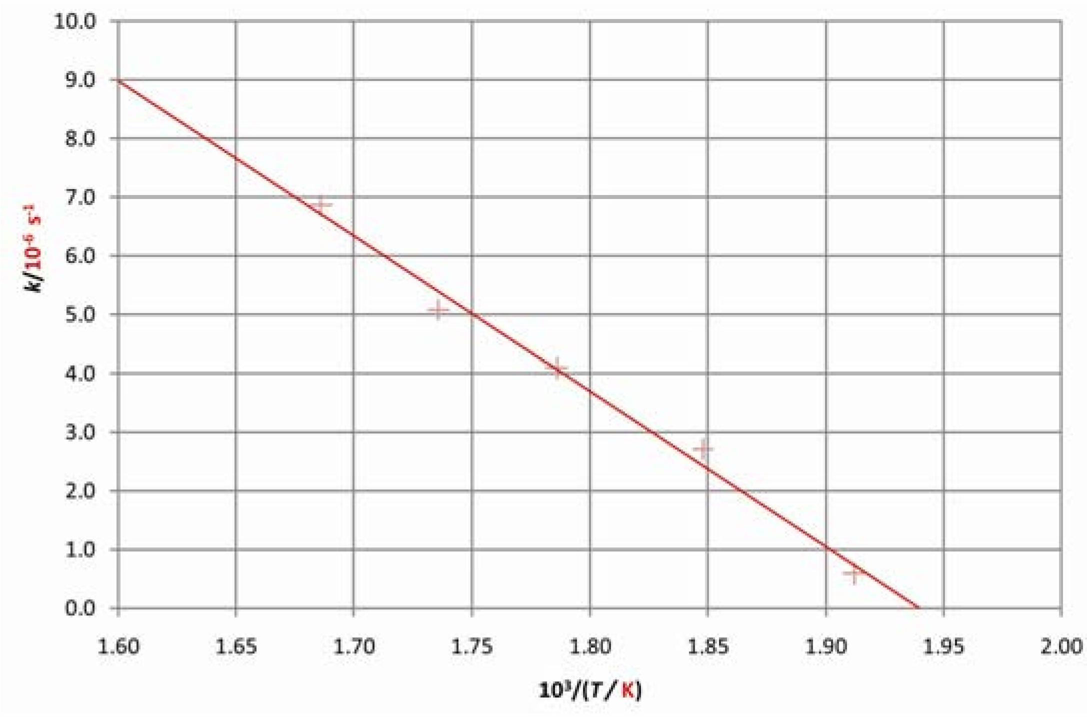
T / K	523	541	560	576	593
$(1/T)$ / 10^{-3} K^{-1}	1.912	1.848	1.786	1.736	1.686
k / 10^{-6} s^{-1}	1.8	15	60	160	950
ln (k / 10^{-6} s^{-1})	0.59	2.71	4.09	5.08	6.86

results in a graph with a gradient

$$m = -E_a/R = -26.45 \times 10^3\,\mathrm{K}$$

so that

$$E_a = -m \times R = 26.45 \times 10^3 \text{K} \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} = +220 \text{ kJ mol}^{-1}$$



15. Molecules move much more slowly in solution than in the gas phase. The progress of a molecule is frequently stopped, and the direction of motion changed, on collision with solvent molecules. A reaction in solution between two reactants, A and B, can be described by a model involving three processes. In the first, the reactants diffuse towards one another (rate constant, k_d). When they encounter one another they form AB, called an *encounter complex*, and stay together for $\sim 10^{-10}$ s, trapped in a *solvent cage*. The separation of the A and B by leaving the solvent cage is described by a rate constant k_{-d}. Alternatively, the encounter complex can react, to form the products, with a rate constant k_r. The overall mechanism is

$$\text{A} + \text{B} \rightleftharpoons \text{AB} \rightleftharpoons \text{products}$$

The individual steps can be treated as elementary reactions, and the steady state approximation can be applied to AB, since it is so short-lived.

(a) What is the order of each of the three steps in the mechanism and what are the units of the rate constants for each step?

(b) Show that the rate of forming the products is given by

$$\text{rate of reaction} = \frac{k_\text{d}k_\text{r}}{k_{-\text{d}} + k_\text{r}}[\text{A}][\text{B}]$$

and write down an expression for the overall rate constant, *k.*

(c) Simplify this expression for a case in which:

(i) reaction to form the products is much faster than diffusion of A and B from the solvent cage;

(ii) diffusion of A and B from the solvent cage is much faster than reaction to form the products.

In each case, state which is the rate-determining step.

Strategy

Apply the steady-state approximation, using Equation 8.15. Derive an expression for the rate constant in terms of the rate constants for the individual elementary steps. Consider how the expression for the rate constant may be simplified if the rate constant for either diffusion or reaction is negligibly small.

Solution

(a) The initial step is second order so that the units of k_d are $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. The other two steps are first order so that the units of $k_{-\text{d}}$ and k_r are s^{-1}.

(b) The encounter complex AB is very short lived, so we can use the steady state approximation, Equation 8.15,

$$\frac{\text{d[AB]}}{\text{d}t} = \text{rate of formation of AB} - \text{rate of consumption of AB} = 0$$

$$= k_\text{d}[\text{A}][\text{B}] - (k_{-\text{d}}[\text{AB}] + k_\text{r}[\text{AB}]) = 0$$

so,

$$k_\text{d}[\text{A}][\text{B}] = k_{-\text{d}}[\text{AB}] + k_\text{r}[\text{AB}] = (k_{-\text{d}} + k_\text{r})[\text{AB}]$$

and therefore

$$[\text{AB}] = \frac{k_\text{d}}{k_{-\text{d}} + k_\text{r}}[\text{A}][\text{B}]$$

Thus,

$$\text{rate of reaction} = k_\text{r}[\text{AB}] = \frac{k_\text{r}k_\text{d}}{k_{-\text{d}} + k_\text{r}}[\text{A}][\text{B}]$$

so that the apparent rate constant is

$$k = \frac{k_r k_d}{k_{-d} + k_r}$$

(c) (i) If k_r is much greater than k_{-d}, then

$$k_{-d} \ll k_r$$

and so

$$k = \frac{k_r k_d}{k_{-d} + k_r} \approx \frac{k_r k_d}{k_r}$$

The rate-determining step is the diffusion of A and B to form the complex. Once the encounter complex is formed, it reacts before separation can occur.

(ii) If, however,

$$k_{-d} \gg k_r$$

and so

$$k = \frac{k_r k_d}{k_{-d} + k_r} \approx \frac{k_r k_d}{k_{-d}} = K_d k_r$$

where K_d is the equilibrium constant for the formation of the encounter complex AB. In this case, the rate-determining step is the reaction of AB to form the products.

17. After intravenous injection of a drug to treat hypertension, the blood plasma of the patient was analysed for the remaining drug at various times after the injection.

t / min	50	100	150	200	250	300	400	500
[drug]/ 10^{-9} g cm^{-3}	650	445	304	208	142	97	45	21

(a) Is the removal of the drug in the body a first or second order process?

(b) Calculate the rate constant, k, and the half life, $t_{1/2}$, for the process.

(c) An essential part of drug development is achieving an optimum value of $t_{1/2}$ for effective operation and elimination of the drug from the bloodstream. What would be the possible problems if $t_{1/2}$ were too short or too long?

Strategy

(a) Test whether the data is consistent with either a first or second-order rate equation using the integrated rate equations, Equation 8.6a and 8.7b. For a first-order reaction, a plot of ln[drug] against *t* should be a straight line, whereas for a second-order reaction, a plot of 1/[drug] against *t* will be a straight line.

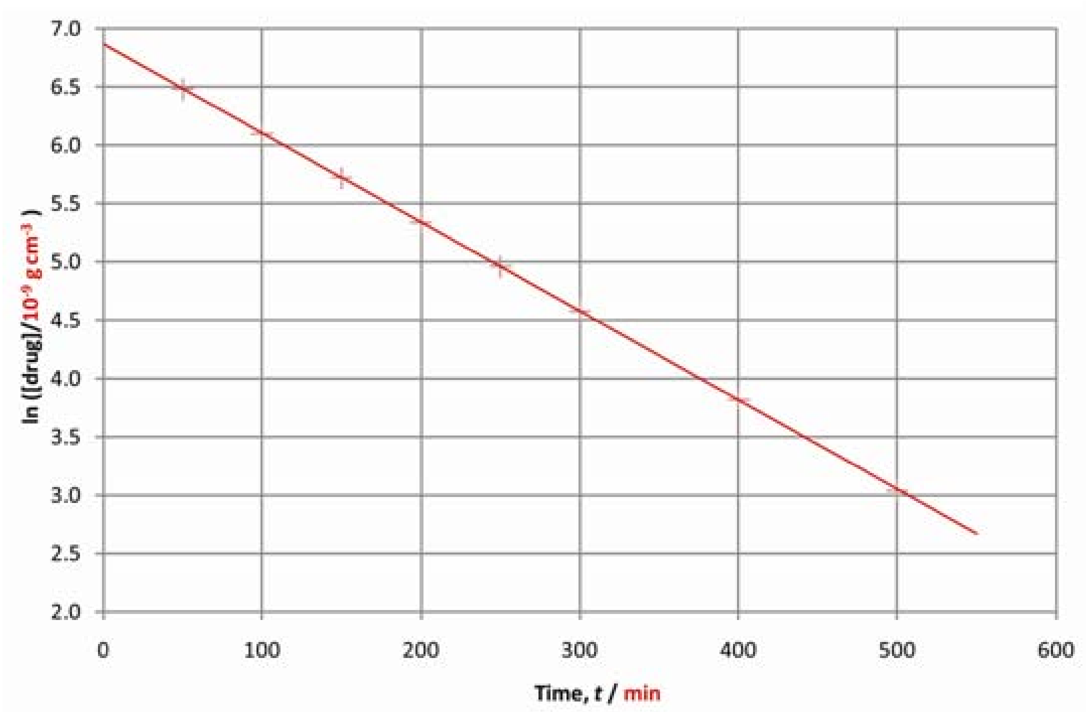
Solution

(a) Using Equation 8.6a, if the reaction is first order, then

$$\ln[\text{drug}]_t = \ln[\text{drug}]_0 - kt$$

Thus, taking logs, and plotting a graph,

t / min	50	100	150	200	250	300	400	500
[drug]/ 10^{-9} g cm^{-3}	650	445	304	208	142	97	45	21
ln ([drug]/ 10^{-9} g cm^{-3})	6.48	6.10	5.72	5.34	4.96	4.58	3.82	3.04



results in a plot with a gradient

$$m = -k = -0.0076 \text{ min}^{-1}$$

This is equivalent to a rate constant

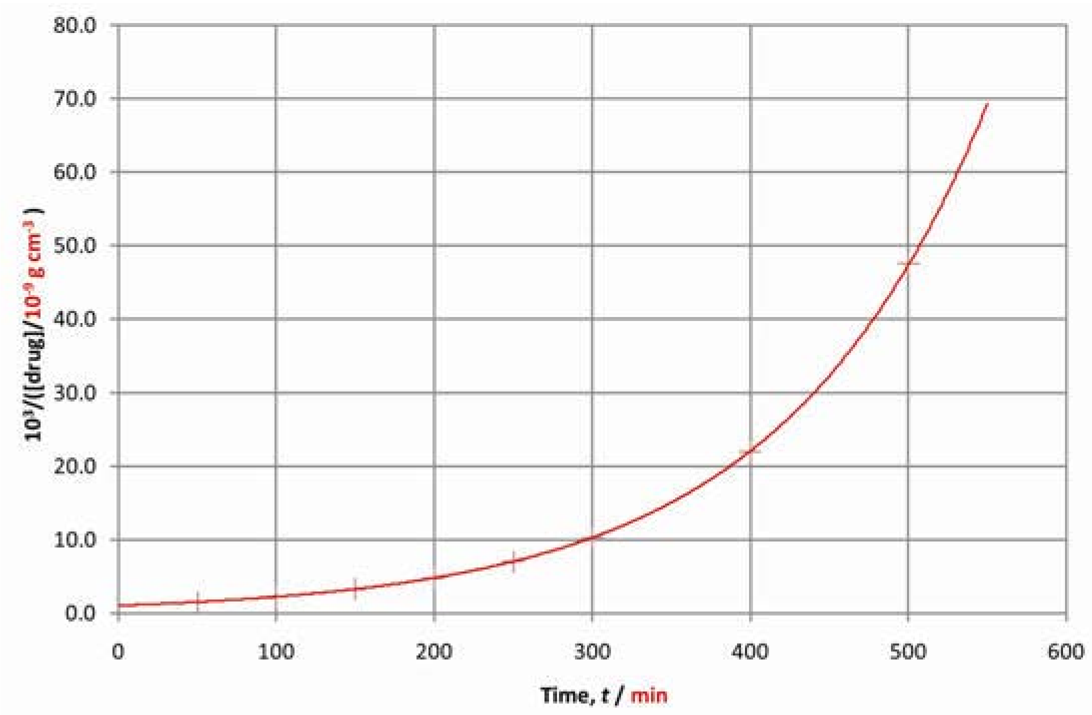
$$k = 1.27 \times 10^{-4} \text{s}^{-1}$$

The half life is thus, from Equation 8.9

$$t_{1/2} = \ln 2\,/k = 0.693/1.27 \times 10^{-4} \text{s}^{-1} = 5460 \text{ s} = 1.52 \text{ hr}$$

Using Equation 8.7b to confirm that the reaction is not second order, then a graph of 1/[drug] against *t* is clearly a curve, demonstrating that the process is not second order with respect to the drug.

t / min	50	100	150	200	250	300	400	500
[drug]/ 10^{-9} g cm^{-3}	650	445	304	208	142	97	45	21
*1000/([drug] / 10^{-9} g cm^{-3})	1.54	2.25	3.29	4.81	7.03	10.3	22.0	47.6



(c) If the half life is too short, the drug may not remain long enough in the body to reach its target and be effective. If, however, the half life is too long, there is increased risk of side effects. If the drug is taken in doses, it will accumulate in the body.