9

Reaction kinetics

Answers to worked examples

WE 9.1 The rate of a reaction

For the reaction between nitrogen and hydrogen

$$N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g)$$

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 9.2 Writing differential rate equations for elementary reactions

The alkaline hydrolysis of bromomethane is an elementary reaction

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

(a) Write a rate equation for the reaction in terms of the differential for consumption of CH_3Br.

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

Strategy

Use Equation 9.5 (p.986) to express the rate of reaction in terms of the reactants.

Solution

(a)

$$-\frac{\mathrm{d}[\mathrm{CH_3Br}]}{\mathrm{d}t} = k[\mathrm{CH_3OH}][\mathrm{Br^-}]$$

(b) The reaction is first order with respect to methanol, and first order with respect to bromide ions, and is therefore second order overall.

WE 9.3 Writing integrated rate equations

Write an integrated rate equation for reaction of two methyl radicals to form ethane in Equation 9.3 (p.386). 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:

$$2\ \mathrm{CH_3^{\bullet}} \rightarrow \mathrm{C_2H_6} \qquad (9.3)$$

Strategy

Use Equation 9.4 (p.386) to express the rate of reaction in terms of the rate of change of methyl radicals. Consider how the integrated rate equation, Equation 9.7b (p.389), may be tested graphically.

Solution

The reaction is a second order elementary reaction. Using Equation 9.4 for a reactant

$$\text{rate of reaction} = -\frac{1}{a}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}$$

then

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

The differential rate equation is thus

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

which is equivalent to

$$\frac{d[CH_3^\bullet]}{dt} = -2k[CH_3^\bullet]^2$$

The integrated rate equation is given by Equation 9.7b

$$\frac{1}{[CH_3^\bullet]_t} = \frac{1}{[CH_3^\bullet]_0} + 2kt$$

This has the same form as a straight-line graph

$$y = mx + c$$

Thus a plot of $y = 1/[CH_3^\bullet]_t$ against $x = t$ is a straight line with a gradient equal to

$$m = +2k$$

WE 9.4 Isomerization of cyclopropane

The reaction of methyl radicals to form ethane was investigated using the flash photolysis technique described on p.398. The following results were obtained at 295 K.

t / 10^{-4} s	0	3.00	6.00	10.0	15.0	20.0	25.0	30.0
$[CH_3^\bullet]$ / 10^{-8} mol dm^{-3}	1.50	1.10	0.93	0.74	0.55	0.45	0.41	0.35

Show that the reaction is second order and find a value for the rate constant at 295 K.

Strategy

For a second order reaction, the integrated rate equation is given by Equation 9.7b (p.389):

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

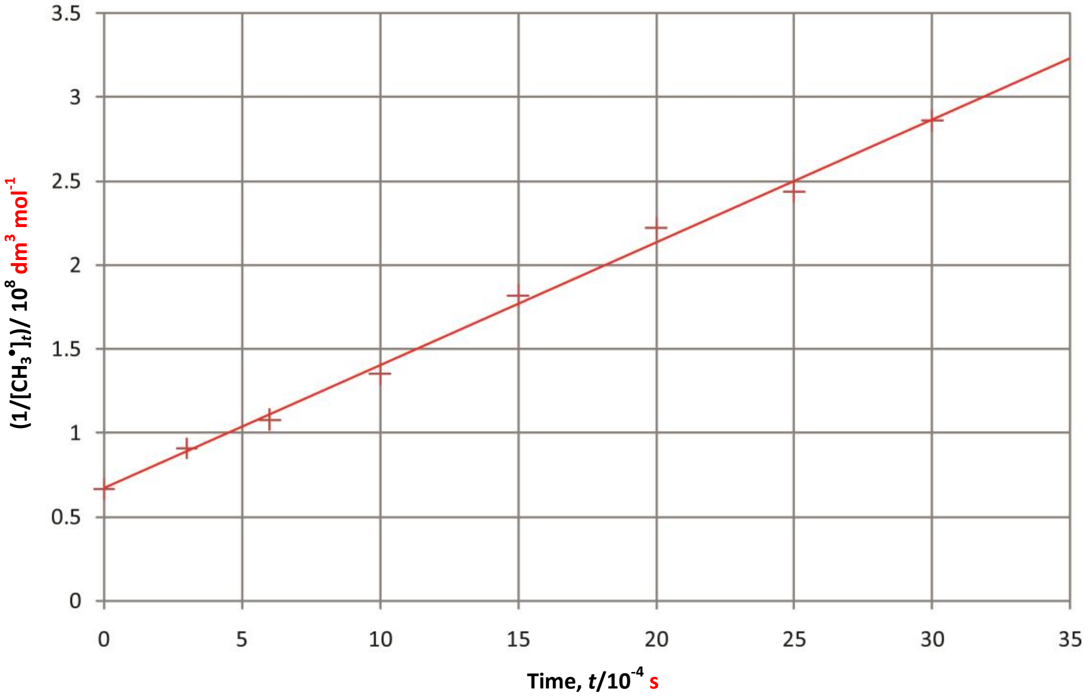
If the reaction is second order, a plot of $1/[CH_3^\bullet]_t$ against t will be a straight line with a gradient equal to $+2k$.

Solution

Calculating values of $1/[CH_3^\bullet]_t$

t / 10^{-4} s	0	3.00	6.00	10.0	15.0	20.0	25.0	30.0
$[CH_3^\bullet]_t$/ 10^{-8} mol dm^{-3}	1.50	1.10	0.93	0.74	0.55	0.45	0.41	0.35
$(1/[CH_3^\bullet]_t)$/ 10^8 dm^3 mol^{-1}	0.667	0.909	1.08	1.35	1.82	2.22	2.44	2.86

and plotting the values against t



The graph is a straight line.

$$\text{Gradient} = 2k = 7.43 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

so that $$k = 3.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad \text{(at 295 K)}$$

WE 9.5 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

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

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^{-5} 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 9.6 Using integrated rate equations to investigate the reaction of iodine with hex-1-ene

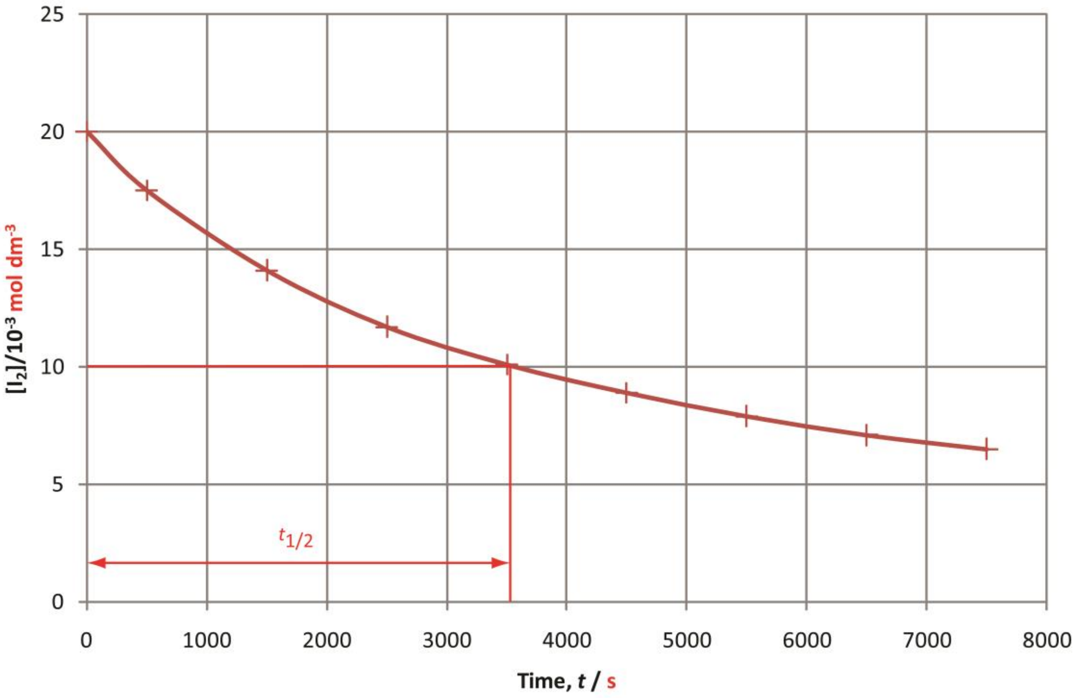
Suggest an alternative way of showing that the reaction is not first order with respect to I_2 that would have saved you plotting ln [I_2] against time.

Strategy

Use the first plot of $[I_2]$ against t to measure at least three half lives in different areas of the curve. If these are *not* constant, the reaction is *not* first order.

Solution

For a first-order reaction, the half life is constant and is independent of the concentration of the reactant. This is not true for other orders of reaction, where the half life varies with concentration. For this reaction, it is clear that the half life is not constant, but becomes longer as the concentration of iodine decreases. The time taken for the concentration to drop from 10×10^{-3} mol dm^{-3} to 5×10^{-3} mol dm^{-3} is, for example, much longer than that for 20×10^{-3} mol dm^{-3} to 10×10^{-3} mol dm^{-3}.



WE 9.7 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: $2NO + O_2 \rightarrow 2NO_2$ 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 molecules that come together to form the transition state 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 add up to give the overall stoichiometric equation.

$$2\,NO \rightleftharpoons N_2O_2$$

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

$$2\,NO + \cancel{N_2O_2} + O_2 \rightarrow 2\,NO_2 + \cancel{N_2O_2}$$

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) $2\,NO \rightarrow N_2O_2$ bimolecular (involves collision of two molecules)

$N_2O_2 \rightarrow 2NO$ unimolecular (one molecule decomposes)

$N_2O_2 + O_2 \rightarrow 2\,NO_2$ bimolecular (two molecules react in a single step)

(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:

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

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

WE 9.8 Finding an activation energy

The decomposition of a drug in humans was found to be a first-order process.

The activation energy for the decomposition is +95 kJ mol^{-1} and $A = 5 \times 10^{10}$ s^{-1}.

(a) What is the rate constant for the decomposition at 310 K?

(b) How long will it take the concentration of the drug in the blood to fall to half its initial value?

Strategy

(a) Substitute the values for the activation energy and the pre-exponential factor into the Arrhenius equation. You can use either Equation 9.24a or Equation 9.24b (p.421).

(b) Use Equation 9.9 (p.392), which expresses how the half life for a first order reaction depends upon the rate constant.

Solution

(a) Using the Arrhenius equation, Equation 9.24a

$$\begin{aligned} k &= A\mathrm{e}^{-(E_\mathrm{a}/RT)} \\ &= 5 \times 10^{10}\,\mathrm{s}^{-1} \times \mathrm{e}^{-(95\times10^3 \cancel{\mathrm{J}}\,\cancel{\mathrm{mol}^{-1}}/8.314 \cancel{\mathrm{J}}\,\cancel{\mathrm{K}^{-1}}\,\cancel{\mathrm{mol}^{-1}} \times 310\,\cancel{\mathrm{K}})} \\ &= 5 \times 10^{-6}\,\mathrm{s}^{-1} \end{aligned}$$

Using the Arrhenius equation, Equation 9.24b

$$\ln k = \ln A - \frac{E_\mathrm{a}}{R}\left(\frac{1}{T}\right)$$

$$\ln k = 24.635 - \frac{(+95\times10^3\,\cancel{\mathrm{J}}\,\cancel{\mathrm{mol}^{-1}})}{(8.314\,\cancel{\mathrm{J}}\,\cancel{\mathrm{K}^{-1}}\,\cancel{\mathrm{mol}^{-1}}) \times 310\,\cancel{\mathrm{K}}}$$

$$= 24.635 - 36.860 = -12.225$$

$$k = 5 \times 10^{-6}\,\mathrm{s}^{-1} \text{ (at 310 K)}$$

(Units of k for first order reaction are s^{-1}.)

(b) From Equation 9.9, for a first order reaction,

$$t_{½} = \ln 2\,/k = 0.693/5 \times 10^{-6}\ \mathrm{s^{-1}} \;=\; 141000\ \mathrm{s} \;=\; 40\ \mathrm{hr}$$

WE 9.9 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 9.25, which relates the values of the rate constant for a reaction at two different temperatures to the activation energy.

Solution

Using Equation 9.25

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

$$\ln\frac{k_{310}}{k_{298}} = \frac{(+108\times10^3\ \mathrm{J\ mol^{-1}})}{8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}} \times \left(\frac{1}{298\ \mathrm{K}} - \frac{1}{310\ \mathrm{K}}\right)$$

$$= \frac{(+108\times10^3\ \cancel{\mathrm{J}}\ \cancel{\mathrm{mol}}^{-1}}{8.314\ \cancel{\mathrm{J}}\ \cancel{\mathrm{K}}^{-1}\ \cancel{\mathrm{mol}}^{-1}} \times (1.299\times10^{-4}\ \cancel{\mathrm{K}}^{-1})$$

$$= 12990 \times (1.229 \times 10^{-4}) = 1.687$$

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

At 298 K, $k_{298} = 1.85 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, so
$k_{310} = 9.999 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} $= 1.00 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} (to 3 sig. fig.)

Answers to boxes

Box 9.3 Atmospheric lifetime of methane

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

Strategy

Use Equation 9.9 (p.392) to determine the half life from the pseudo-first order rate constant.

Solution

Using Equation 9.9, $$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

For methane, $$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\mathrm{OH}]_{\mathrm{constant}}}$$

$$k = 3.9 \times 10^6\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

So $$t_{\frac{1}{2}} = \frac{0.693}{(3.9\times10^6\ \cancel{\mathrm{dm}^3}\ \cancel{\mathrm{mol}^{-1}}\ \mathrm{s}^{-1}) \times (1\times10^{-15}\ \cancel{\mathrm{mol}}\ \cancel{\mathrm{dm}^{-3}})}$$

$$= 1.78 \times 10^8\ \mathrm{s}$$

$$= \left(\frac{1.777\times10^8}{60\times60\times24\times365}\right)\ \mathrm{a}$$

$$= 5.6\ \mathrm{a}\ \ (6\ \text{years to 1 sig. fig.})$$

Box 9.4 Using flash photolysis to monitor ClO$^\bullet$ radicals

Write a differential rate equation and an integrated rate equation for the formation of the ClO$^\bullet$ dimer from ClO$^\bullet$.

Strategy

Use Equation 9.4 (p.386) to define the rate of reaction in terms of the rate of change of the ClO$^\bullet$ radical concentration. The integrated rate equation is given by Equation 9.7b (p.389).

Solution

Differential rate equation

From Equation 9.4

$$\text{rate of reaction} = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{ClO}^\bullet]}{\mathrm{d}t} = k\,[\mathrm{ClO}^\bullet]^2$$

So $$\frac{\mathrm{d}[\mathrm{ClO}^\bullet]}{\mathrm{d}t} = -2\,k\,[\mathrm{ClO}^\bullet]^2$$

Integrated rate equation

From Equation 9.7b

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

So $$\frac{1}{[\mathrm{ClO}^\bullet]_\mathrm{t}} = \frac{1}{[\mathrm{ClO}^\bullet]_0} + 2kt$$

Box 9.7 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 1.87×10^{-3} min^{-1}. The concentration of the drug in the body of a cancer patient is 5.16×10^{-4} mol dm^{-3}. What will the concentration be after 24 hours?

Strategy

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

Solution

Use Equation 9.6a (p.388) for a first order reaction

$$\ln[\mathrm{A}]_t = \ln[\mathrm{A}]_0 - kt \qquad (9.6a)$$

and rearrange to give Equation 9.6b

$$\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt \qquad (9.6b)$$

For cisplatin, $[\mathrm{A}]_\mathrm{t}$ is the cisplatin concentration after 24 hr (1440 min)

$$\ln\frac{[\text{cisplatin}]_t}{[\text{cisplatin}]_0} = -kt = (-1.87\times10^{-3}\ \cancel{\text{min}^{-1}})\times 1440\ \cancel{\text{min}} = -2.693$$

$$\frac{[\text{cisplatin}]_t}{[\text{cisplatin}]_0} = 0.06769$$

$$\begin{aligned}[\text{cisplatin}]_t &= 0.06769\times(5.16\times10^{-4}\ \text{mol dm}^{-3})\\ &= 3.49\times10^{-5}\ \text{mol dm}^{-3}\quad(\text{where } t = 1440\ \text{min})\end{aligned}$$

(A quick check using Equation 9.9, shows that for this reaction, the half life is

$$t_{½} = \ln 2/k = 0.693/1.87\times10^{-3}\text{min}^{-1} = 371\ \text{min} = 6.2\ \text{hr}$$

so that 24 hr corresponds to about four half lives. You might therefore expect the concentration to have dropped by a factor of $(0.5)^4$ to 3.23×10^{-5} mol dm^{-3}, which is consistent with the concentration calculated using Equation 9.9b above.

$$\begin{aligned}[\text{cisplatin}]_t &\approx (½)^4\times[\text{cisplatin}]_0\\ &\approx 0.0625\times5.16\times10^{-4}\ \text{mol dm}^{-3}\\ &\approx 3.23\times10^{-5}\ \text{mol dm}^{-3})\end{aligned}$$

Box 9.8 The Michaelis-Menten mechanism

The following results were obtained for the enzyme-catalysed hydrolysis of ATP at 20 °C. The initial concentration of the enzyme, ATPase, was 1.5×10^{-8} mol dm^{-3}.

$[\text{ATP}]_0$ / μmol dm^{-3}	0.5	1.0	2.0	4.0
Initial rate / μmol dm^{-3} s^{-1}	0.54	0.82	1.11	1.36

Determine the maximum rate, (rate)$_{\text{max}}$, and the Michaelis constant, K_M, for the reaction.

Strategy

Use Equation 9.32 to draw a Lineweaver-Burk plot. This should be a straight line. Use values of the gradient and intercept of the line to determine (rate)$_{\text{max}}$ and the Michaelis constant, K_M.

Solution

Using Equation 9.32 (p.437)

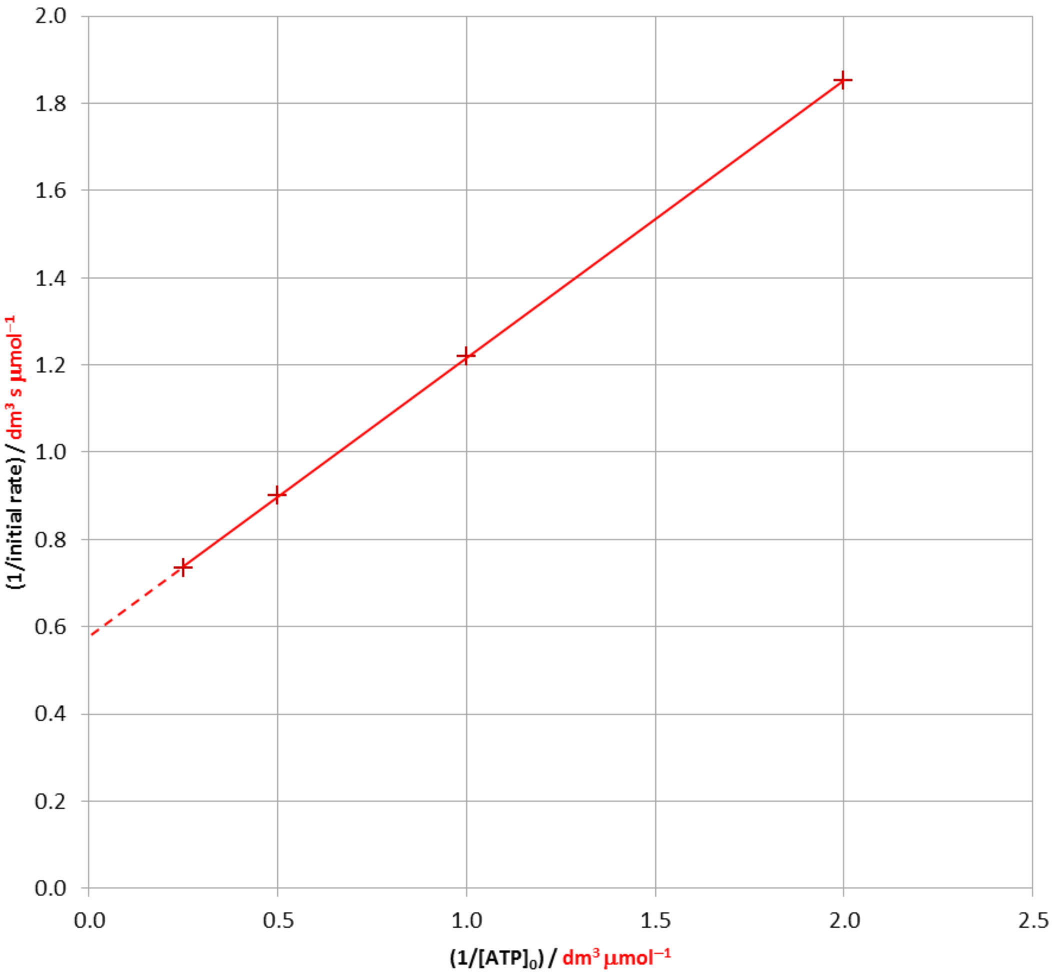
$$\frac{1}{\text{rate}} = \frac{1}{k_2[\text{E}]_0} + \frac{K_\text{M}}{k_2[\text{E}]_0[\text{S}]} \qquad (9.32)$$

$$= \frac{1}{(\text{rate})_\text{max}} + \frac{K_\text{M}}{(\text{rate})_\text{max}[\text{S}]}$$ where the maximum rate, $(\text{rate})_\text{max} = k_2[\text{E}]_0$

Tabulate values for 1/initial rate and $1/[\text{ATP}]_0$.

$1/[\text{ATP}]_0$ / dm^3 µmol^{-1}	2	1	0.5	0.25
1/initial rate / dm^3 s µmol^{-1}	1.85	1.22	0.90	0.74

A plot of 1/initial rate (y-axis) against $1/[\text{ATP}]_0$ (x-axis) (Lineweaver-Burk plot) is a straight line. The intercept on the y axis (where $1/[\text{ATP}]_0 = 0$) is $1/(\text{rate})_\text{max}$ and the gradient of the line is $K_\text{M}/(\text{rate})_\text{max}$.



Gradient = 0.637 s

Intercept on *y*-axis (when $1/[\mathrm{ATP}]_0 = 0$) is 0.580 $\mathrm{dm^3\ \mu mol^{-1}\ s}$

$$(\mathrm{rate})_{\mathrm{max}} = 1/\mathrm{intercept}$$

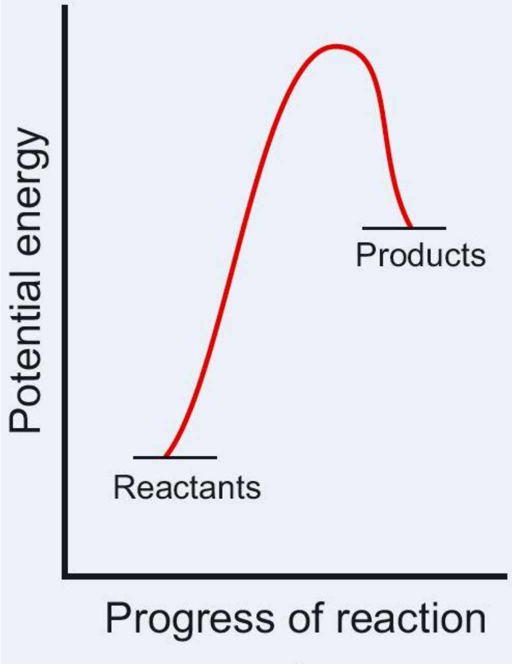
$$= 1.7\ \mathrm{\mu mol\ dm^{-3}\ s^{-1}}$$

$$K_\mathrm{M} = \mathrm{gradient} \times (\mathrm{rate})_{\mathrm{max}} = 0.637\ \cancel{\mathrm{s}} \times 1.72\ \mathrm{\mu mol\ dm^{-3}}\ \cancel{\mathrm{s^{-1}}}$$

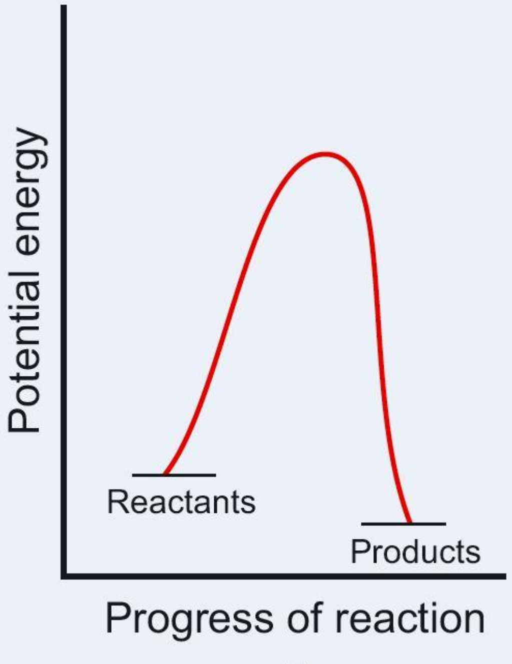
$$= 1.1\ \mathrm{\mu mol\ dm^{-3}}$$

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.



A



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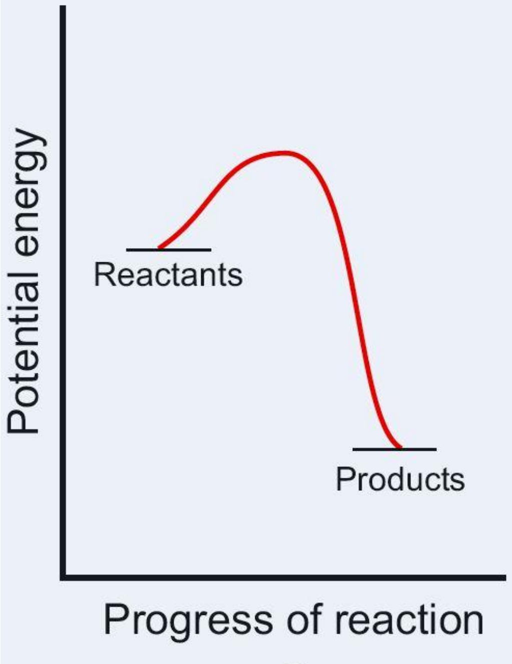

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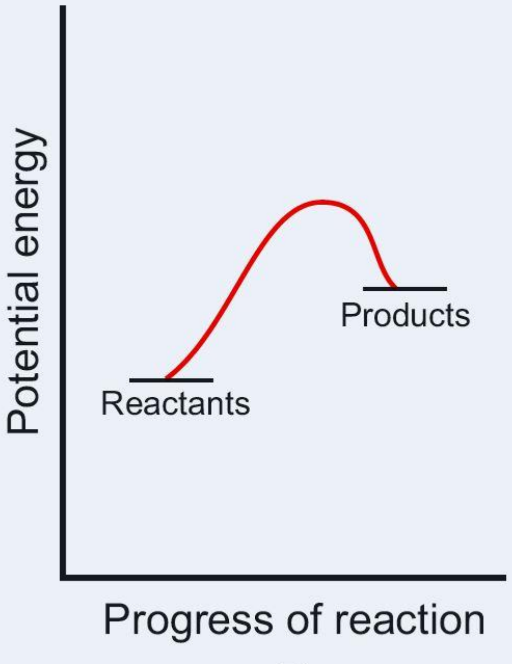


D

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.

2. The oxidation of ammonia in air is catalysed by platinum metal

$$4\,NH_3\,(g) + 5\,O_2\,(g) \rightarrow 4\,NO\,(g) + 6\,H_2O\,(g)$$

Write an expression for the rate of reaction in terms of differentials for the consumption of the reactants and formation of the products.

Strategy

Define the rate of reaction in terms of each reactant and product in same way as in Equation 9.4, noting the stoichiometric coefficients for the particular reaction.

Solution

From Equation 9.4,

$$\text{rate of reaction} = -\frac{1}{4}\frac{\mathrm{d}[\mathrm{NH_3}]}{\mathrm{d}t} = -\frac{1}{5}\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = \frac{1}{4}\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} = \frac{1}{6}\frac{\mathrm{d}[\mathrm{H_2O}]}{\mathrm{d}t}$$

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

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

Calculate values for $\frac{d[N_2O]}{dt}$, $\frac{d[N_2]}{dt}$ and $\frac{d[O_2]}{dt}$ under these conditions.

Strategy

Define the rate of reaction in terms of each reactant and product in same way as in Equation 9.4, 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 9.4,

$$\text{rate of reaction} = -\frac{1}{2}\frac{d[N_2O]}{dt} = \frac{1}{2}\frac{d[N_2]}{dt} = \frac{d[O_2]}{dt} = 5.86 \times 10^{-6}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Thus,

$$\frac{d[N_2O]}{dt} = -2 \times (5.86 \times 10^{-6}\ \text{mol dm}^{-3}\ \text{s}^{-1}) = -1.17 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

$$\frac{d[N_2]}{dt} = 2 \times (5.86 \times 10^{-6}\ \text{mol dm}^{-3}\ \text{s}^{-1}) = 1.17 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

$$\frac{d[O_2]}{dt} = 5.86 \times 10^{-6}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

4. Write the rate equation for the following elementary reactions and give the molecularity for each reaction.

(a) $Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$

(b) $CH_3N_2CH_3 \rightarrow 2\ CH_3^{\bullet} + N_2$

(c) $2\ Cl^{\bullet} \rightarrow Cl_2$

(d) $NO_2^{\bullet} + F_2 \rightarrow NO_2F + F^{\bullet}$

Strategy

Since these are elementary reactions, the rate equation for each reaction can be written from the stoichiometric equation. Consider the order of reaction with respect to each of the reactants.

Count the number of reactant molecules which come together to from the transition state for the reaction to determine the molecularity.

Solution

(a) Rate of reaction = $k[\text{Cl}^\bullet][\text{O}_3]$; bimolecular
(b) Rate of reaction = $k[\text{CH}_3\text{N}_2\text{CH}_3]$; unimolecular
(c) Rate of reaction = $k[\text{Cl}^\bullet]^2$; bimolecular
(d) Rate of reaction = $k[\text{NO}_2][\text{F}_2]$; bimolecular

5. For the complex 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

$$\text{rate of reaction} = k[\text{NO}]^2[\text{H}_2]$$

(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) $[H_2]$ is doubled;
- (ii) $[H_2]$ is halved;
- (iii) [NO] is doubled;
- (iv) [NO] is increased by a factor of three?

Strategy

Use the rate equation 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 for the given reaction, 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.

6. The gas phase decomposition of dinitrogen pentoxide (N_2O_5)

$$N_2O_5 \rightarrow NO_2^{\bullet} + NO_3^{\bullet}$$

was studied in a large stainless steel cell, at 294 K and a pressure of 1 bar. The concentration of N_2O_5 was monitored using infrared spectroscopy. The following results were obtained.

t / s	0	10	20	30	40	50	60	70	80	90	100
$[N_2O_5]$ /10^{-9} mol dm^{-3}	34.0	27.0	19.5	15.0	11.5	8.7	6.6	5.1	3.9	2.9	2.2

Show that the reaction is first order and find a value for the rate constant at 294 K.

Strategy

Use the integrated rate equation for a first order reaction (Equation 9.6a, p.388):

$$\ln[A]_t = \ln[A]_0 - kt \qquad (9.6a)$$

and plot $\ln[A]_t$ against t. If the plot is a straight line, the reaction is first order and the gradient is equal to $-k$.

Solution

From Equation 9.6a,

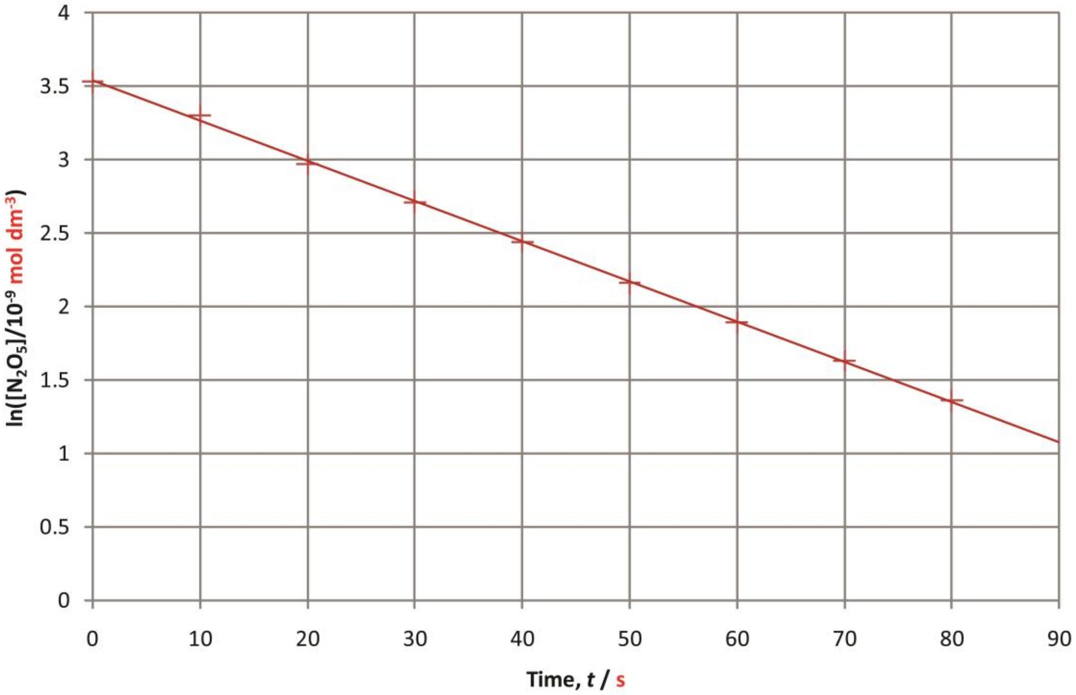
$$\ln[N_2O_5]_t = \ln[N_2O_5]_0 - kt$$

Draw up a table with values of $\ln[N_2O_5]$:

t / s	0	10	20	30	40	50	60	70	80	90	100

$[N_2O_5]$ / 10^{-9} mol dm^{-3}	34.0	27.0	19.5	15.0	11.5	8.7	6.6	5.1	3.9	2.9	2.2
ln ($[N_2O_5]$ / 10^{-9} mol dm^{-3})	3.53	3.30	2.97	2.71	2.44	2.16	1.89	1.63	1.36	1.06	0.79

and plot a graph of ln$[N_2O_5]$ against *t*.



The plot is a straight line, showing that the reaction is first order with respect to N_2O_5.

Gradient $= -k = -0.0274$ s^{-1}

So, $k = 2.74 \times 10^{-2}$ s^{-1} at 294 K.

7. The data below were obtained for the decomposition of difluorine oxide (F_2O) at 298 K.

$$2F_2O\,(g) \rightarrow 2F_2\,(g) + O_2\,(g)$$

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

Verify that this is a second order reaction and determine the rate constant at 298 K.

Strategy

Use the integrated rate equation for a second-order reaction (Equation 9.7b, p.389):

$$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + 2kt \qquad (9.7b)$$

and plot a graph of $1/[\mathrm{A}]_t$ against t. If the plot is a straight line, the reaction is second order and the gradient is equal to $2k$.

Solution

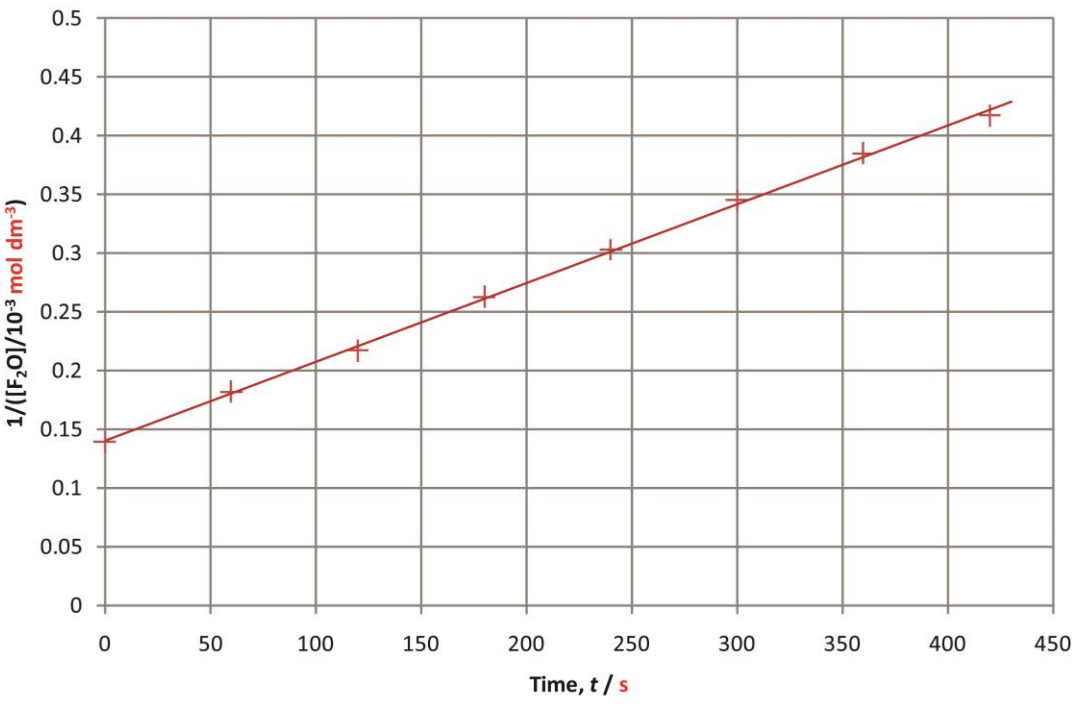
From Equation 9.7b

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

Draw up a table with values of $1/[\mathrm{F_2O}]$:

t / s	0	60	120	180	240	300	360	420
$[\mathrm{F_2O}]$/ 10^{-3} mol dm^{-3}	7.2	5.5	4.6	3.8	3.3	2.9	2.6	2.4
$(1/[\mathrm{F_2O}])$ / 10^3 dm^3 mol^{-1}	0.139	0.182	0.217	0.263	0.303	0.345	0.385	0.417

and plot a graph of $1/[\mathrm{F_2O}]$ against t.



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

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

so that, at 298 K,

$$k = 0.34 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

8. From the data provided in the table, deduce the rate law and the value of the rate constant for the following reaction

$CH_3COCH_3 + Br_2 + H^+ \rightarrow CH_3COCH_2Br + 2H^+ + Br^-$

	Initial concentration of CH_3COCH_3 / mol dm^{-3}	Initial concentration of Br_2 / mol dm^{-3}	Initial concentration of H^+ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	1.00	1.00	1.00	4.0×10^{-3}
2	2.00	1.00	1.00	8.0×10^{-3}
3	2.00	2.00	1.00	8.0×10^{-3}
4	1.00	1.00	2.00	8.0×10^{-3}

Strategy

You can write the general form of the rate equation for the reaction. By considering how the overall rate changes when the concentrations of each species change then the order with respect to each can be found.

Solution

The rate law has the form: Rate = $k\,[CH_3COCH_3]^a\,[Br_2]^b\,[H^+]^c$

From the data:

The rate doubles when $[CH_3COCH_3]$ doubles at constant $[Br_2]$ and $[H^+]$ (lines 1 and 2). Hence a = 1.

The rate stays constant when $[Br_2]$ doubles at constant $[H^+]$ and $[CH_3COCH_3]$ (lines 2 and 3). Hence b = 0

The rate doubles when $[H^+]$ doubles at constant $[CH_3COCH_3]$ and $[Br_2]$ (lines 1 and 4). Hence c = 1

Therefore, the rate equation is: Rate = $k\ [CH_3COCH_3]^1\ [Br_2]^0\ [H^+]^1$ or

Rate = $k\ [CH_3COCH_3]\ [H^+]$

From the data in line 1

4.0×10^{-3} mol dm^{-3} s^{-1} = k (1.00 mol dm^{-3}) (1.00 mol dm^{-3})

So $k = 4.0 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}

And the rate equation is

Rate = 4.0×10^{-3} dm^3 mol^{-1} s^{-1} $[CH_3COCH_3]\ [H^+]$

9. For a first order reaction, half of the reactant is used up after 15 s. What fraction of the reactant will remain after 1 min?

Strategy

You could use Equation 9.9 to determine the rate constant from the half life but in this case it is straightforward to find how many half-lives occur in 1 min and to calculate the fraction remaining since half the reactant will react in each 15 s period.

Solution

After 15 s, half the reactant will remain.

After 30 s half of the remaining reactant will remain i.e. one quarter of the original

After 45 s half of the remaining reactant will remain i.e. one eighth of the original

After 60 s (1 min) half of the remaining reactant will remain i.e. one sixteenth of the original

10. Cyclobutane decomposes to form ethane according to:

$C_4H_8\ (g) \rightarrow 2\ C_2H_4\ (g)$

A quantity of cyclobutane was sealed in a container and exerted a pressure of 53.30 kPa at 700 K. The pressure changed during the reaction as follows. At the end of the reaction, the pressure was 106.60 kPa.

Time / s	Total pressure / kPa
0	53.30
2000	64.53
4000	73.59
6000	80.53
8000	85.99
10000	90.39

Assuming the gases behave ideally, show graphically that the reaction is first order with respect to cyclobutane. Calculate the rate constant and the half life for the reaction

Strategy

You can use the stoichiometry to find out how the number of moles and hence (since the gases behave ideally) the pressure changes through the reaction. You can then find the pressure of CB and plot a graph of the data in a first order reaction form to find the rate constant. The half-life can be found from equation 9.9.

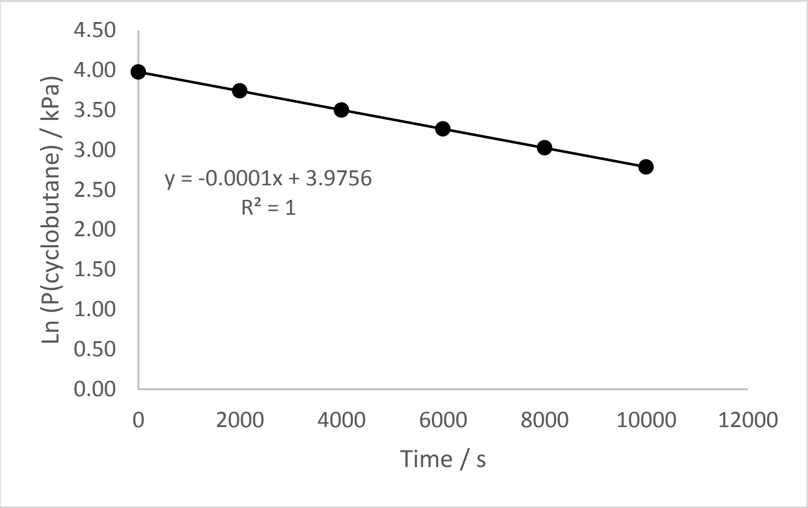
Solution

From the stoichiometry, for every CB molecule that decomposes, two molecules of ethane form. Hence, the increase in total pressure is equivalent to the pressure of CB that has reacted (for an ideal gas, pressure $\propto$ number of moles). The pressure of CB at each time can be found and, if the reaction is first order, a plot of ln $p_{\text{cyclobutane}}$ versus time should be linear with a slope equivalent to $-k$.

Time / s	Total pressure / kPa	Pressure increase / kPa	Pressure CB / kPa	Ln (P(CB))
0	53.3	0	53.3	3.98
2000	64.53	11.23	42.07	3.74
4000	73.59	20.29	33.01	3.50

6000	80.53	27.23	26.07	3.26
8000	85.99	32.69	20.61	3.03
10000	90.39	37.09	16.21	2.79

Which gives a graph



From linear regression, the slope is $-0.00012\ \mathrm{s}^{-1}$ so $k = 0.00012\ \mathrm{s}^{-1}$

For a first order reaction, $t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{0.693}{0.00012\ \mathrm{s}^{-1}} = 5775\ \mathrm{s}$

11. The rate constant for the decomposition of a compound in solution is 2.0×10^{-4} s^{-1}. If the initial concentration is 0.02 mol dm^{-3}, what will the concentration of the compound be after 10 min?

Strategy

From the units of the rate constant, you can tell that the reaction follows first order kinetics. The integrated form of the first order rate equation can therefore be used to directly find the concentration after a certain time.

Solution

The integrated form of a first order rate equation is:

$\ln [A]_t = \ln [A]_0 - kt$

Substituting the data.

$\ln [A]_{10\ min} = \ln [0.02 \text{ mol dm}^{-3}] - (2.0 \times 10^{-4} \text{ s}^{-1}) \times (10 \text{ min} \times 60 \text{ s min}^{-1})$

$[A]_{10\ min} = 0.018 \text{ mol dm}^{-3}$

12. The reaction of methyl radicals to form ethane was investigated in a laser flash photolysis experiment at 300 K.

$$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$$

The rate constant for this reaction at 300 K is 3.7×10^{10} dm^3 mol^{-1} s^{-1}. The concentration of methyl radicals, $[CH_3^{\bullet}]$, at time $t = 0$ was 1.70×10^{-8} mol dm^{-3}. Calculate a value for $[CH_3^{\bullet}]$ at $t = 1.00 \times 10^{-3}$ s.

Strategy

The reaction is a second order elementary process. Use the integrated rate equation, Equation 9.7b (p.389):

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt \qquad (9.7b)$$

and substitute the values for $[A]_0$, k and t given in the question.

Solution

From Equation 9.7b

$$\frac{1}{[CH_3^{\bullet}]_t} = \frac{1}{[CH_3^{\bullet}]_0} + 2kt$$

$$\frac{1}{[CH_3^{\bullet}]} = \frac{1}{1.70\times10^{-8}\ \text{mol dm}^{-3}} + (2 \times (3.7 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \cancel{\text{s}^{-1}}) \times (1.00 \times 10^{-3}\ \cancel{\text{s}}))$$

$$= (5.88 \times 10^{7}\ \text{dm}^3\ \text{mol}^{-1}) + (7.40 \times 10^{7}\ \text{dm}^3\ \text{mol}^{-1})$$

$$= 13.3 \times 10^{7}\ \text{dm}^3\ \text{mol}^{-1}$$

$$[CH_3^{\bullet}] = 7.5 \times 10^{-9}\ \text{mol dm}^{-3}$$

13. The acid-catalysed hydrolysis of sucrose shows first order kinetics. The half life of the reaction at room temperature was found to be 190 min. Calculate the rate constant for the reaction under these conditions.

Strategy

Use Equation 9.9 (p.392), which gives an expression for the half life of a first order reaction.

Solution

$$t_{½} = \frac{\ln 2}{k} \qquad (9.9.)$$

$$k = \frac{\ln 2}{t_{½}} = \frac{0.693}{190 \times 60\ \mathrm{s}} = 6.1 \times 10^{-5}\ \mathrm{s}^{-1}$$

14. The reaction between $H_2PO_4^-$ and OH^- was investigated at 298 K using the initial rate method.

$$H_2PO_4^-\ (aq) + OH^-\ (aq) \rightarrow HPO_4^{2-}\ (aq) + H_2O\ (aq)$$

The following results were obtained.

	Initial rate / 10^{-3} mol dm^{-3} min^{-1}	$[OH^-]_0$ / 10^{-3} mol dm^{-3}	$[H_2PO_4^-]_0$ / 10^{-3} mol dm^{-3}
Experiment 1	2.0	0.40	3.0
Experiment 2	3.7	0.55	3.0
Experiment 3	7.1	0.75	3.0

(a) Plot a log–log graph to determine the order of reaction with respect to OH^-(aq).

(b) What further experiments would you need to do to find the order with respect to $H_2PO_4^-$?

Strategy

Use Equation 9.12 (p.404) and plot the log of the rate against the log of the concentration of A.

$$\log\ (\text{rate}) = m \log\ [A] + \log\ k' \qquad (9.12)$$

The gradient of the graph gives *m*, the order of the reaction with respect to A.

Solution

(a) The initial concentration of $H_2PO_4^-$ is the same in each experiment, so the rate equation for the reaction can be written as

$$\text{initial rate of reaction} = k' [OH^-]_0{}^m$$

where k' is an effective rate constant for the reaction of OH^-.

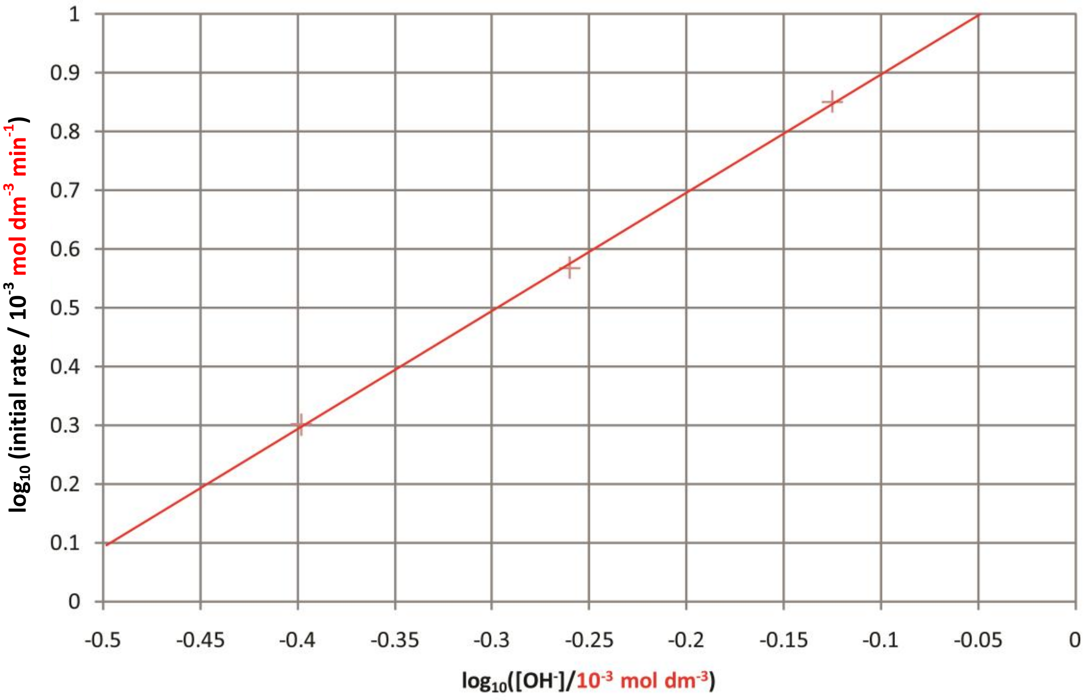
Taking logs of each side of the equation gives

$$\log(\text{initial rate})_0 = \log[OH^-]_0{}^m + \log k' = m \log[OH^-]_0 + \log k'$$

Draw up a table with values of $\log[OH^-]_0$ and $\log(\text{initial rate})_0$

$\log_{10}([OH^-]_0 / 10^{-3}\ \text{mol dm}^{-3})$	–0.398	–0.260	–0.125
$\log_{10}(\text{initial rate} / 10^{-3}\ \text{mol dm}^{-3}\ \text{min}^{-1})$	0.301	0.568	0.851

and plot a graph of $\log(\text{initial rate})_0$ against $\log[OH^-]_0$.



Gradient = 2. So the reaction is second order with respect to OH^-.

(b) Repeat the series of experiments for different initial concentrations of $[H_2PO_4^-]_0$, with constant values of $[OH^-]_0$, and use the same initial rate method to determine the order with respect to $H_2PO_4^-$. A plot of log (initial rate) against log $[H_2PO_4^-]_0$ will be a straight line with a gradient that is the order with respect to $H_2PO_4^-$.

15. 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

The reaction is an elementary process, so you can use the stoichiometric equation to write a rate equation in terms of the concentrations of propene and bromine. Re-write this as a pseudo-first order rate equation, 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, *k*′. Substitute the concentration of bromine and the measured value of *k*′ to determine the true second order rate constant, *k*.

Solution

The reaction is elementary, so you can write

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

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

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

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

So,

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

16*. The elementary reaction between ethanal (CH_3CHO) and $^\bullet OH$ radicals

$$CH_3CHO + {}^\bullet OH \rightarrow CH_3CO^\bullet + H_2O$$

was studied at 298 K, by laser flash photolysis, using laser-induced fluorescence to detect $^\bullet OH$ as a function of time. The ethanal concentration was 3.3×10^{-7} mol dm^{-3} and this concentration was much higher than the concentration of $^\bullet OH$ radicals. The following data for the concentration of $^\bullet OH$ radicals, relative to their concentration at zero time, were obtained.

t / 10^{-3} s	0	0.2	0.4	0.6	0.8	1.0	1.2	1.5
$[^\bullet OH]/[^\bullet OH]_0$	1	0.55	0.31	0.16	0.09	0.05	0.03	0.01

(a) Write a rate equation for the reaction.

(b) Show that, under the above conditions, the reaction follows pseudo-first order kinetics.

(c) Determine the pseudo-first order rate constant, k'.

Strategy

(a) The reaction is an elementary process, so you can use the stoichiometric equation to write a rate equation in terms of the concentrations of ethanol and $^\bullet OH$ radicals.

(b) and (c) The concentration of ethanal was much higher than the concentration of $^\bullet OH$ radicals, so you can rewrite the rate equation for a pseudo-first order process.

Use the integrated rate equation for a first order reaction (Equation 9.6a, p.388):

$$\ln[\mathrm{A}]_t = \ln[\mathrm{A}]_0 - kt \qquad (9.6a)$$

and plot the log of the relative concentration of $^\bullet OH$ radicals against time. If the plot is a straight line, the reaction is first order and the gradient is equal to $-k'$.

Solution

(a) Rate of reaction $= k\,[CH_3CHO]\,[^\bullet OH]$

(b) Using excess CH_3CHO,

rate of reaction $= k\,[CH_3CHO]_0\,[^\bullet OH] = k'\,[^\bullet OH]$

where $k' = k\,[CH_3CHO]_0$

Using Equation 9.6a for the pseudo-first order reaction

$$\ln [{}^\bullet OH]_t = \ln [{}^\bullet OH]_0 - k't$$

This may be rearranged as

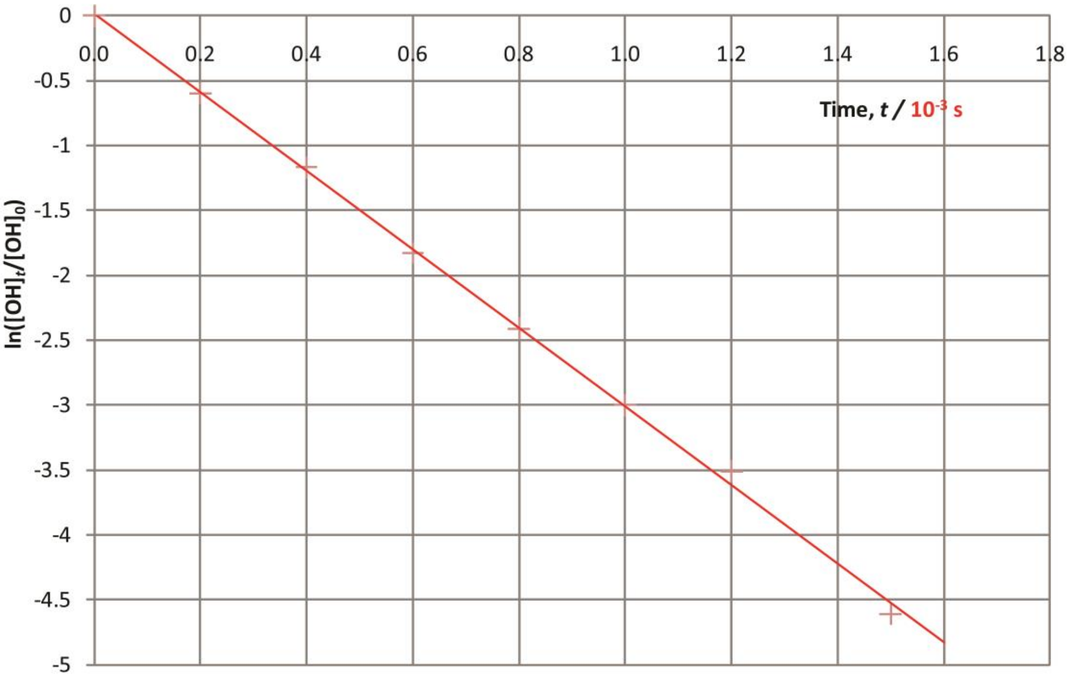
$$\ln ([{}^\bullet OH]_t / [{}^\bullet OH]_0) = -k't$$

so that a graph of $\ln ([{}^\bullet OH]_t / [{}^\bullet OH]_0)$ will be a straight line with a gradient of $-k$.

Draw up a table with values of $\ln ([{}^\bullet OH]_t / [{}^\bullet OH]_0)$

$t / 10^{-3}$ s	0	0.2	0.4	0.6	0.8	1.0	1.2	1.5
$[{}^\bullet OH]_t/[{}^\bullet OH]_0$	1	0.55	0.31	0.16	0.09	0.05	0.03	0.01
$\ln ([{}^\bullet OH]/[{}^\bullet OH]_0)$	0.00	−0.60	−1.17	−1.83	−2.41	−3.00	−3.51	−4.61

and plot $\ln ([{}^\bullet OH]_t / [{}^\bullet OH]_0)$ against time.



The plot is a straight line, showing that the reaction is pseudo-first order with respect to ${}^\bullet OH$.

(c) Gradient $= -k' = -3.02 \times 10^3\ s^{-1}$

so that $k' = 3.0 \times 10^3\ \text{s}^{-1}$ at 298 K.

17*. The investigation described in Question 16 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.

$[\text{ethanal}]_0$ / 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 Problem 12 into your analysis.)

Strategy

From Problem 12, using excess CH_3CHO,

$$\text{rate of reaction} = k\,[CH_3CHO]_0\,[{}^\bullet OH] = k'\,[{}^\bullet OH]$$

where $k' = k\,[CH_3CHO]_0$

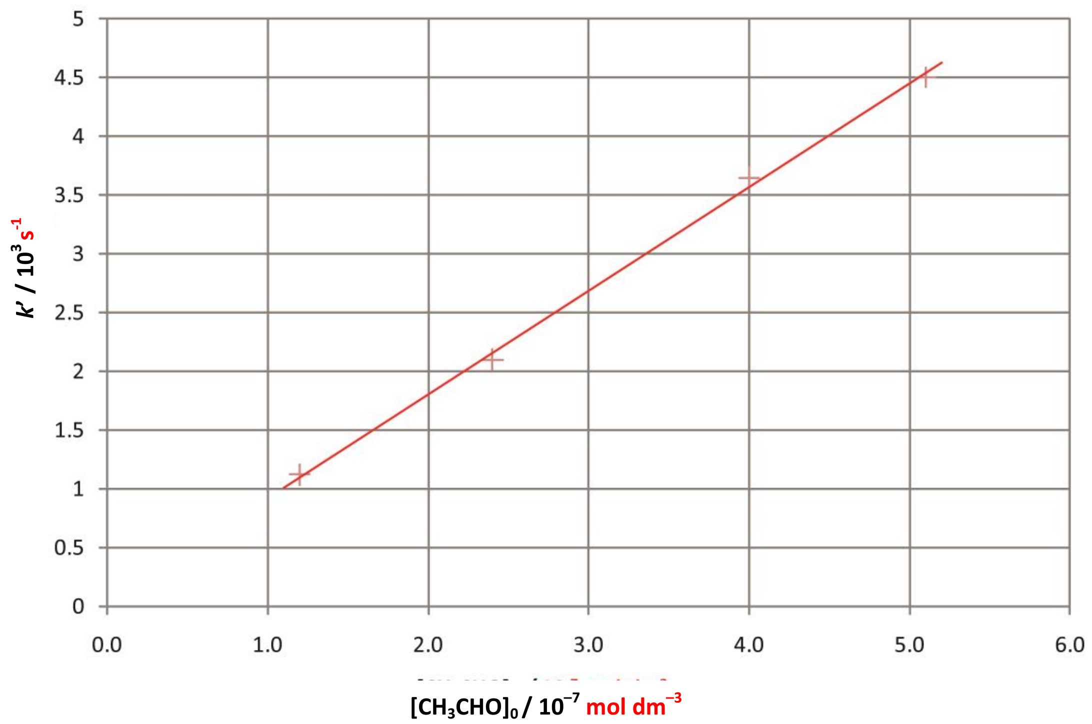
So, a plot of *k*′ against $[CH_3CHO]_0$ will be a straight line. The gradient of the line will be equal to *k*, the true second-order rate constant for the reaction.

Solution

In the presence of excess CH_3CHO,

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

Plot a graph of *k*′ against $[CH_3CHO]_0$ and measure the gradient.



The gradient of the line is 0.897×10^{10} $dm^3\ mol^{-1}\ s^{-1}$.

So, $k = 9.0 \times 10^9$ $dm^3\ mol^{-1}\ s^{-1}$.

18. The decomposition of ammonia on a platinum surface at 856°C

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

shows the following dependence of the concentration of ammonia gas on time.

t / s	0	200	400	600	800	1000	1200
[NH_3]/ 10^{-3} mol dm^{-3}	2.10	1.85	1.47	1.23	0.86	0.57	0.34

Find the order of the reaction and a value for the rate constant at 856°C. Suggest an explanation for the order you obtain.

Strategy

Test the data against the integrated rate equations expected for zero, first and second order reactions, Equations 9.13 (p.407), 9.6a (p.388) and 9.7b (p.389), respectively. By plotting appropriate graphs, determine which model the data fits and hence decide the order of the reaction.

Solution

For a zero order reaction, the rate equation has the form

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k$$

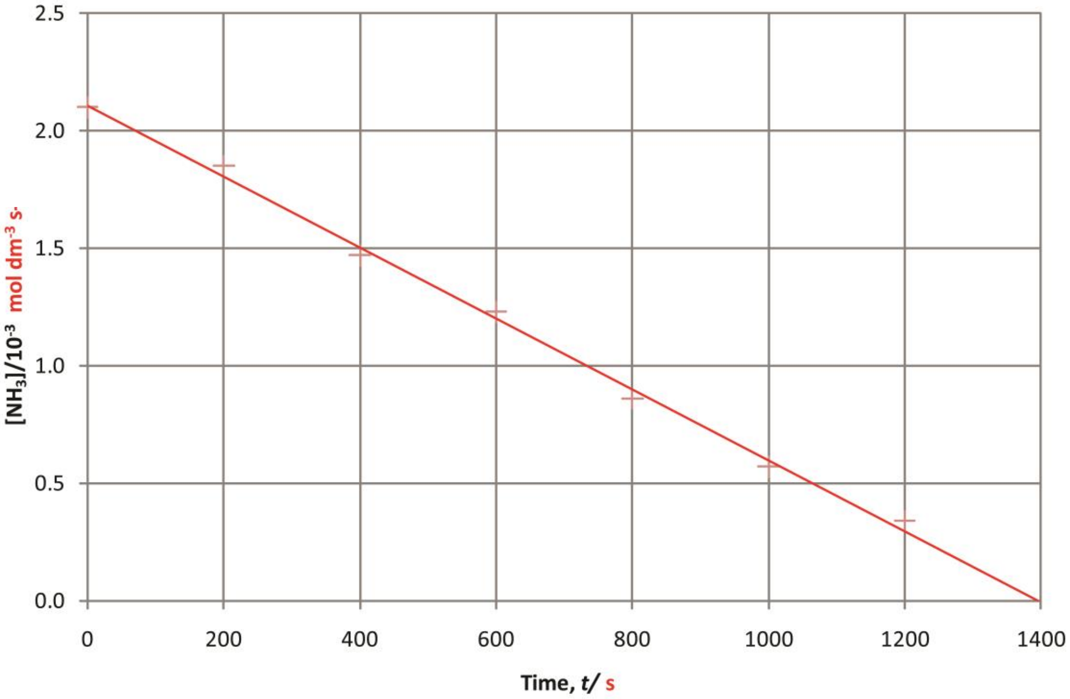
The integrated rate equation for a zero order reaction is given by Equation 9.13

$$[\mathrm{A}]_t \;=\; [\mathrm{A}]_0 - kt \qquad (9.13)$$

So, if the reaction has zero order with repect to ammonia

$$[\mathrm{NH_3}]_t \;=\; [\mathrm{NH_3}]_0 - kt$$

and a plot of $[\mathrm{NH_3}]$ against t will be a straight line with a gradient equal to $-k$.



The gradient of the line is -1.48×10^{-6} mol dm^{-3} s^{-1}, so that

$$k \;=\; 1.5 \times 10^{-6}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$$

Plots of ln[NH_3] against time and 1/[NH_3] against time are both curves, showing that the reaction is neither first order nor second order with respect to NH_3.

The decomposition takes place on the surface of the catalyst, so the rate of reaction depends on the concentration of ammonia adsorbed to the surface, rather than the concentration of gaseous ammonia. If the surface of the catalyst is saturated with ammonia, the concentration of adsorbed ammonia is constant. The rate of the reaction will then be constant and independent of the concentration of gaseous ammonia.

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

$$CH_3N_2CH_3 \rightarrow 2\ CH_3^{\bullet} + N_2$$

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 in the form of Equation 9.24b (p.421) and plot a graph of ln k against $1/T$. You can determine the activation energy from the gradient of the graph.

Solution

From the Arrhenius equation, Equation 9.24b

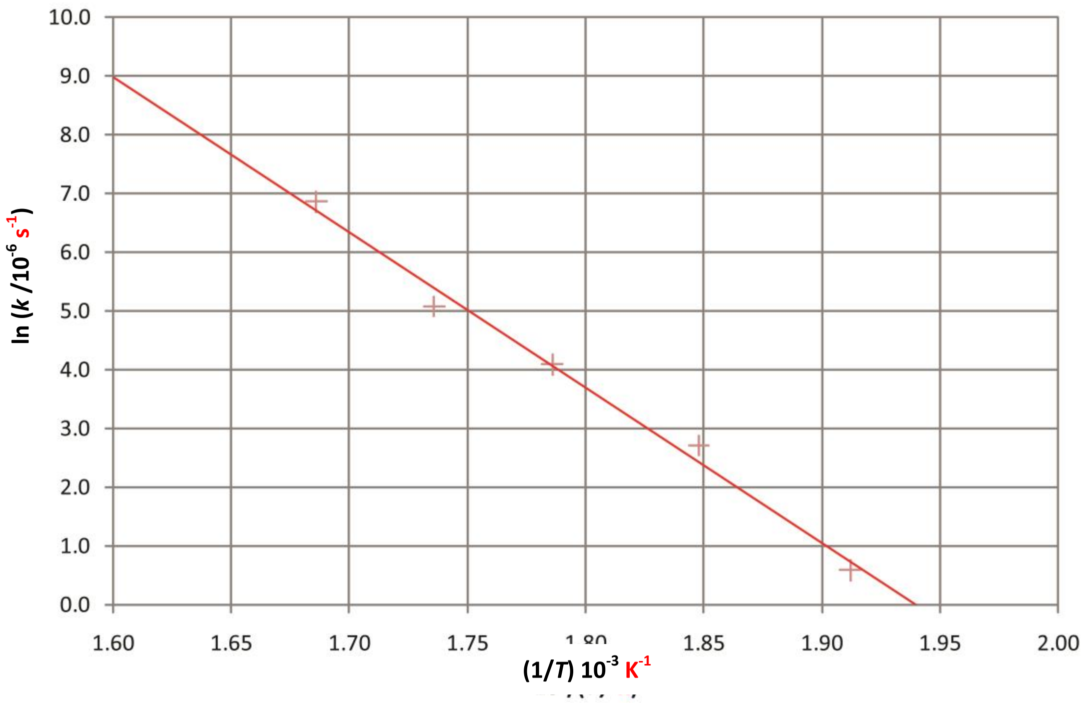
$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \qquad (9.24b)$$

A graph of ln k against $1/T$ will be a straight line with a gradient equal to $-E_a/R$. (The intercept (when $1/T = 0$) gives a value for ln A.)

Draw up a table with values for $1/T$ and ln k.

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

and plot a graph of ln k against $1/T$.



$$\text{Gradient} = -26.45 \times 10^3 \text{ K} = -\frac{E_a}{R}$$

$$\text{So, } E_a = (26.45 \times 10^3 \text{ K}) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = +220 \text{ kJ mol}^{-1}$$

20. The hydrolysis of hydrogencarbonate ions in water at a high pH:

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

follows the rate law: Rate = k [HCO_3^-] where k = 0.01 s^{-1} at 25 °C.

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

(b) What is the half-life of HCO_3^- if the initial concentration of HCO_3^-, $[HCO_3^-]_o$ = 0.001mol dm^{-3}?

(c) What is the rate constant of the above reaction at 350 K if the activation energy is 10.0 kJ mol^{-1}?

(d) The hydrolysis reaction is exothermic. Sketch a curve to show how the energy of the system changes in going from reactants to products. Indicate the activation energy for the forward and reverse reactions and the overall change in energy for the reaction.

Strategy

From the units of the rate constant, you can tell that the reaction follows first order kinetics and so you can find the half-life from the value of the rate constant. Finding the rate constant at a higher temperature involves using the Arrhenius equation.

Solution

(a) Rate = $k\,[\mathrm{HCO_3^-}]^1$ so FIRST order – also apparent from the units of $\mathrm{s^{-1}}$.

(b) For a first order reaction, $t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{0.693}{0.01\ \mathrm{s^{-1}}} = 69.3\ \mathrm{s}$

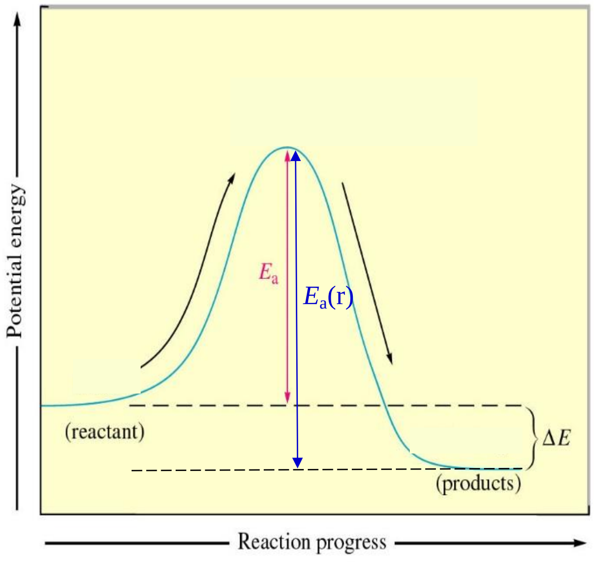
(c) Applying the Arrhenius equation at two temperatures,

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right); \quad \ln\frac{k_2}{0.01\ \mathrm{s^{-1}}} = \frac{+10.0\times10^3\ \mathrm{J\ mol^{-1}}}{8.314\ \mathrm{JK^{-1}mol^{-1}}}\left(\frac{1}{298\mathrm{K}} - \frac{1}{350\mathrm{K}}\right)$$

$$\ln\frac{k_2}{0.01\ \mathrm{s^{-1}}} = +0.5997$$

$$\frac{k_2}{0.01\ \mathrm{s^{-1}}} = e^{0.5997} = 1.822$$

$$k_2 = 1.822\times0.01\ \mathrm{s^{-1}} = 0.18\ \mathrm{s^{-1}}$$



E_a Activation energy for the forward reaction

E_a (r) Activation energy for the reverse reaction

ΔE Overall energy change for the reaction

21. Calculate the activation energy for a reaction where the rate constant is 5 times faster at 50 °C than at 20 °C?

Strategy

You have the ratio of two rate constants at two temperatures and so can use the Arrhenius equation.

Solution

From the Arrhenius equation,

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

$$\ln 5 = \frac{E_a}{8.314\ \mathrm{J\ mol^{-1}K^{-1}}}\left(\frac{1}{293\ \mathrm{K}} - \frac{1}{323\ \mathrm{K}}\right)$$

$$\ln 5 = E_a \times 3.813 \times 10^{-5}\ \mathrm{J\ mol^{-1}}$$

$$E_a = 42212\ \mathrm{J\ mol^{-1}} = 42.2\ \mathrm{kJ\ mol^{-1}}$$

E_a = 42212 J mol^{-1} = 42.2 kJ mol^{-1}

22. The A factor for the reaction of methane with hydroxyl radicals is

1.11×10^9 dm^3 mol^{-1} s^{-1}.

$$CH_4 + {}^{\bullet}OH \rightarrow CH_3{}^{\bullet} + H_2O$$

The activation energy for the reaction is +14.1 kJ mol^{-1}.

(a) Calculate the rate constant for the reaction at 220 K, which corresponds to a region close to the top of the troposphere.

(b) Compare the value you obtain in (a) with the value for the rate constant at 300 K, when $k = 3.9 \times 10^6$ dm^3 mol^{-1} s^{-1}. This corresponds to a region nearer the

Earth's surface, see Box 9.3 (p.396). Comment on the difference between the values for the rate constant at the two temperatures.

Strategy

(a) Use the Arrhenius equation, Equation 9.24a (p.421)

$$k = Ae^{-\frac{E_a}{RT}} \qquad (9.24a)$$

and substitute values for A, E_a, R and T, to find a value for the rate constant at 220 K.

(b) Think about the relative rates of removal of methane from the atmosphere at the two altitudes.

Solution

(a) Using Equation 9.24a for the reaction at 220 K

$$\begin{aligned} k &= 1.11 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \times e^{-\frac{+14.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 220 \text{ K}}} \\ &= 1.11 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \times e^{-7.709} \\ &= 1.11 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \times (4.489 \times 10^{-4}) \\ k &= 5.0 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (at 220 K)} \end{aligned}$$

(b) The rate constant is higher at the higher temperature, so that, for a given [$^\bullet$OH], the reaction of methane with hydroxyl radicals in faster nearer the surface of the Earth than at the top of the troposphere. The removal of methane from the atmosphere takes place more quickly at lower altitudes.

23. The following mechanism has been suggested for the gas phase oxidation of hydrogen bromide

$HBr + O_2 \rightarrow HOOBr$

$HOOBr + HBr \rightarrow 2HOBr$

$HOBr + HBr \rightarrow H_2O + Br_2$

No HOBr is found in the final products. Experimentally, the reaction is found to be first order in HBr and in O_2.

(a) Write a balanced stoichiometric equation for the reaction

(b) Why is the equation in (a) unlikely to represent the reaction mechanism?

(c) Show that the above mechanism is consistent with the observed orders of reaction

(d) Which step is likely to be the rate determining step?

Strategy

(a) Consider the reactants and products and write a balanced equation. (b) Think about what factors affect whether a reaction takes place and how they apply here (c) You can apply a steady state treatment since HOOBr and HOBr is a reactive intermediate (d) Consider which is likely to be the slowest step on the basis of the reactivity of the species involved.

Solution

(a) The reactants are HBr and O_2 while the products are H_2O and Br_2.

$4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$

(b) The equation in (a) requires five species to collide at the same time – which is so unlikely as to be practically impossible.

(c) Consider the consumption of HBr. From the above mechanism,

$HBr + O_2 \rightarrow HOOBr$ Rate constant = k_1

$HOOBr + HBr \rightarrow 2HOBr$ Rate constant = k_2

$HOBr + HBr \rightarrow H_2O + Br_2$ Rate constant = k_3

$$-\frac{d[HBr]}{dt} = k_1[HBr][O_2] + k_2[HOOBr][HBr] + k_3[HOBr][HBr]$$

But we do not know [HOOBr] and [HOBr]. Applying the steady state to these intermediate species,

$$\frac{\mathrm{d[Intermediate]}}{\mathrm{dt}} = 0$$

$$\frac{\mathrm{d[HOOBr]}}{\mathrm{d}t} = 0 = k_1\mathrm{[HBr][O_2]} - k_2\mathrm{[HOOBr][HBr]} \qquad (1)$$

$$\frac{\mathrm{d[HOBr]}}{\mathrm{d}t} = 0 = \ 2k_2\mathrm{[HOOBr][HBr]} - k_3\mathrm{[HOBr][HBr]} \qquad (2)$$

From (1),

$$\begin{aligned}
&0 = k_1\mathrm{[HBr][O_2]} - k_2\mathrm{[HOOBr][HBr]}\\
&k_1\mathrm{[HBr][O_2]} = k_2\mathrm{[HOOBr][HBr]}\\
&k_1\mathrm{[O_2]} = k_2\mathrm{[HOOBr]}\\
&\text{so} \qquad \mathrm{[HOOBr]} = \frac{k_1}{k_2}\mathrm{[O_2]} \qquad (3)
\end{aligned}$$

From (2)

$$\begin{aligned}
&0 = \ 2k_2\mathrm{[HOOBr][HBr]} - k_3\mathrm{[HOBr][HBr]}\\
&2k_2\mathrm{[HOOBr][HBr]} = k_3\mathrm{[HOBr][HBr]}\\
&2k_2\mathrm{[HOOBr]} = k_3\mathrm{[HOBr]}\\
&\text{so} \qquad \mathrm{[HOBr]} = \frac{2k_2}{k_3}\mathrm{[HOOBr]} \qquad (4)
\end{aligned}$$

Substituting (3) into (4)

$$\begin{aligned}
&\mathrm{[HOBr]} = \frac{2k_2}{k_3}\mathrm{[HOOBr]} \quad \text{but} \quad \mathrm{[HOOBr]} = \frac{k_1}{k_2}\mathrm{[O_2]}\\
&\text{so } \ \mathrm{[HOBr]} = \frac{2k_2}{k_3}\frac{k_1}{k_2}\mathrm{[O_2]} = \ \frac{2k_1}{k_3}\mathrm{[O_2]} \qquad (5)
\end{aligned}$$

Now, substitute (5) and (3) into the original rate equation for HBr,

$$-\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = k_1[\mathrm{HBr}][\mathrm{O_2}] + k_2[\mathrm{HOOBr}][\mathrm{HBr}] + k_3[\mathrm{HOBr}][\mathrm{HBr}]$$

$$-\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = k_1[\mathrm{HBr}][\mathrm{O_2}] + k_2\left(\frac{k_1}{k_2}[\mathrm{O_2}]\right)[\mathrm{HBr}] + k_3\left(\frac{2k_1}{k_3}[\mathrm{O_2}]\right)[\mathrm{HBr}]$$

$$-\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = k_1[\mathrm{HBr}][\mathrm{O_2}] + k_1[\mathrm{O_2}][\mathrm{HBr}] + 2k_1[\mathrm{O_2}][\mathrm{HBr}]$$

so $$-\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = 4k_1[\mathrm{HBr}][\mathrm{O_2}]$$

Hence the mechanism predicts that the decomposition of HBr is first order in both HBr and O_2

(d) The rate limiting step will be the slowest step. Since the second and third steps involve reactive intermediates, they will probably be fast. It is therefore likely that the reaction of HBr with O_2 will be rate limiting.

24. The mechanism for the formation of a DNA double helix from two strands A and B is as follows

strand A + strand B $\rightleftharpoons$ unstable helix fast

unstable helix → stable double helix slow

(a) Write the equation for the overall reaction.

(b) Experiments show that the overall reaction is first order with respect to strand A and first order with respect to strand B. Write the rate equation for the overall reaction using k for the overall rate constant.

(c) Assuming the processes involved are elementary reactions, derive an expression for the rate constant for the overall reaction in terms of the rate constants for the individual steps.

Strategy

(a) Add the two steps to give the overall equation for the reaction.

(c) Insert rate constants into the mechanism for the reaction.

$$\text{strand A} + \text{strand B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{unstable helix}$$

$$\text{unstable helix} \xrightarrow{k_2} \text{stable double helix}$$

The second step is slow, so you can assume that the first step comes to a rapid pre-equilibrium, which is undisturbed by the second step.

Write an expression for K_c for the pre-equilibrium in terms of the concentrations of the reactants and product. This is equal to the ratio of the rate constants for the forward and backward processes, as in Equation 9.14 (p.414).

Hence , find an expression for [unstable helix] in terms of the rate constants for the individual steps and the concentrations of strand A and strand B.

Rate of forming the stable double helix = k_2 [unstable helix], which equals the overall rate of reaction given in (b). Hence find an expression for k in terms of k_1, k_{-1} and k_2.

Solution

(a) The overall equation for the reaction is

$$\text{strand A} + \text{strand B} \rightarrow \text{stable double helix}$$

(b) The rate equation for the overall reaction is

$$\text{rate of reaction} = k\,[\text{strand A}]\,[\text{strand B}]$$

(c) Rate of forming the stable double helix = k_2 [unstable helix]

Using Equation 9.14 (p.414),

$$\frac{k_1}{k_{-1}} = K_c = \frac{[\text{unstable helix}]}{[\text{strand A}][\text{strand B}]}$$

Rearranging the equation to give an expression for [unstable helix]

$$[\text{unstable helix}] = K_c\,[\text{strand A}][\text{strand B}] = \frac{k_1}{k_{-1}}[\text{strand A}][\text{strand B}]$$

Rate of forming the stable double helix = k_2 [unstable helix]

$$= \frac{k_2 k_1}{k_{-1}}[\text{strand A}][\text{strand B}]$$

Rate of overall reaction = k[strand A][strand B]

so, $k = \dfrac{k_2 k_1}{k_{-1}}$

25. The reaction of methane with hydrogen atoms is an elementary process.

$$CH_4 + H^\bullet \rightleftharpoons CH_3^\bullet + H_2$$

The rate constant for the forward reaction at 1000 K is 1.6×10^8 dm^3 mol^{-1} s^{-1}.

The equilibrium constant, K_c, at the same temperature is 19.8. Calculate the rate constant for the reverse reaction at 1000 K.

Strategy

Use the expression for K_c in Equation 9.14 (p.414) and substitute data given in the problem.

Solution

Assume the rate constant for the forward reaction is k_1 and the rate constant for the reverse reaction is k_{-1}.

Using Equation 9.14

$$\frac{k_1}{k_{-1}} = K_c$$

So, $$k_{\text{reverse}} = \frac{1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{19.8} = 8.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

26*. 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 ~10^{-10} s, trapped in a *solvent cage*. The separation of 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

$$\mathrm{A} + \mathrm{B} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \underset{\text{encounter complex}}{\mathrm{AB}} \overset{k_r}{\rightleftharpoons} \text{products}$$

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

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

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

(b) and (c) Apply the steady-state approximation to the concentration of the encounter complex, AB, using Equation 9.15 (p.416). 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 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$. The other two steps are first order so that the units of k_{-d} and k_r are $\mathrm{s^{-1}}$.

(b) The encounter complex AB is very short lived, so you can use the steady state approximation, Equation 9.15 (p.416)

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

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

So,

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

Rearranging to give an expression for [AB]

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

Rate of forming products = k_r [AB] = $\dfrac{k_\mathrm{d}\ k_r}{(k_{\text{-d}} + k_r)}[\mathrm{A}][\mathrm{B}]$

Overall rate of reaction = k [A] [B]

so that the overall rate constant, k, is given by

$$k = \frac{k_\mathrm{d}k_\mathrm{r}}{(k_{-\mathrm{d}} + k_\mathrm{r})}$$

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

$$k_{-\mathrm{d}} \ll k_\mathrm{r}$$

and $k_{-\mathrm{d}}$ can be omitted from the bottom line of the equation for k, giving

$$k = \frac{k_\mathrm{d}k_\mathrm{r}}{(k_{-\mathrm{d}} + k_\mathrm{r})} \approx \frac{k_\mathrm{d}k_\mathrm{r}}{k_\mathrm{r}} = k_\mathrm{d}$$

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, $k_{-\mathrm{d}}$ is much greater than k_r

$$k_{-\mathrm{d}} \gg k_\mathrm{r}$$

then k_r can be omitted from the bottom line of the equation for k, giving

$$k = \frac{k_\mathrm{d}k_\mathrm{r}}{(k_{-\mathrm{d}} + k_\mathrm{r})} \approx \frac{k_\mathrm{d}k_\mathrm{r}}{k_{-\mathrm{d}}} = K_\mathrm{d}\,k_\mathrm{r}$$

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.

27. An exothermic reaction proceeds by the following three-step mechanism

$$A \rightleftharpoons B \rightarrow C \rightarrow D$$

The first step occurs rapidly and a pre-equilibrium is established. The second step is slow and is the rate-determining step.

(a) Draw the shape of the Gibbs energy profile for the reaction.

(b) How would the Gibbs energy profile differ if the third step were the rate-determining step of the reaction?

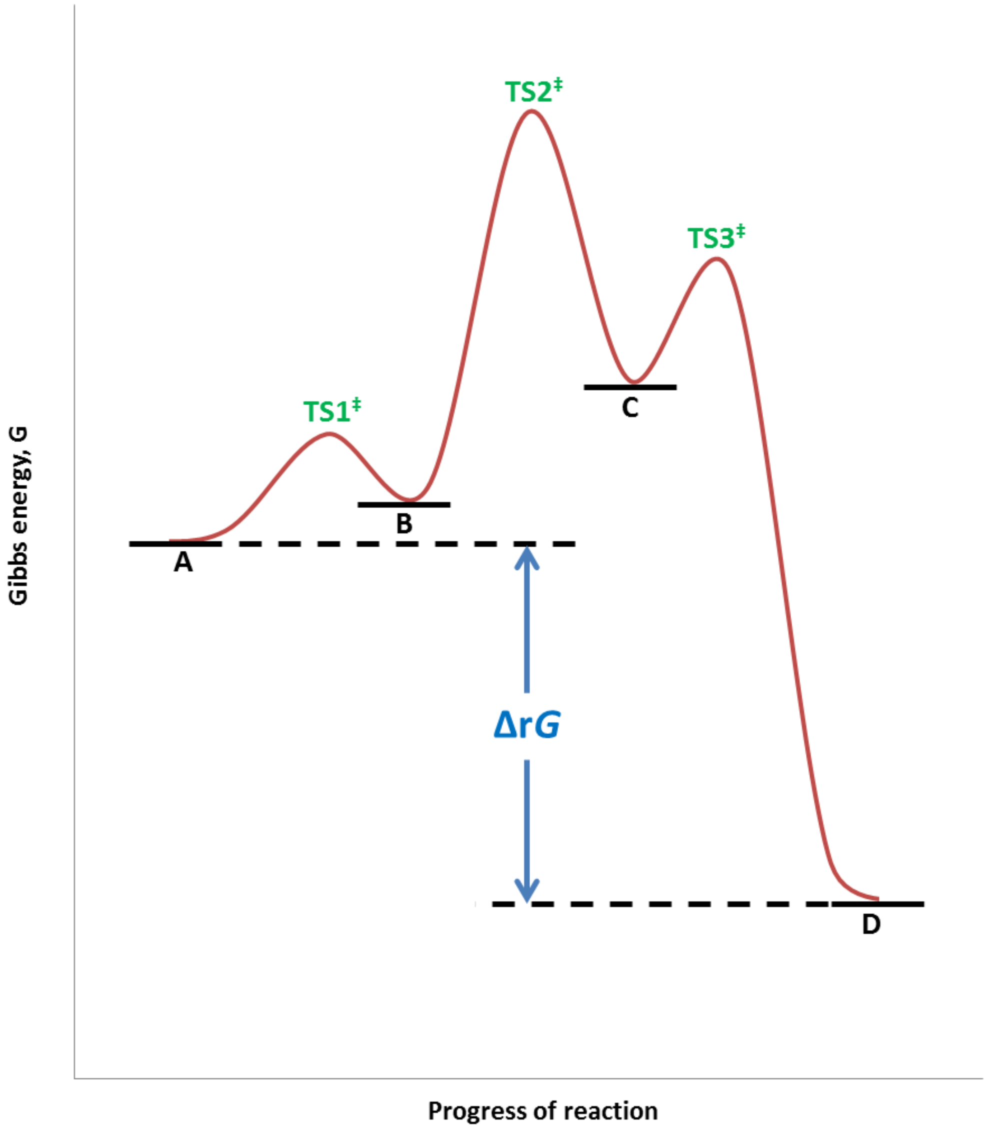
Strategy

Extend the arguments used to construct Figures 9.29 and 9.30 to a three-step reaction such as this. Remember that steps with a high Gibbs energy of activation are slow.

Solution

(a) The Gibbs energy profile shows three maxima corresponding to transition states for each of the three steps. There are two minima, corresponding to the intermediates, B and C. The second step (B → C) has the highest Gibbs energy of activation.

For example



(b) The third step would have the highest Gibbs energy of activation.

28. After intravenous injection of a drug to treat hypertension (high blood pressure), 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 order or second order rate equation using the integrated rate equations, Equation 9.6a (p.388) and 9.7b (p.389). 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

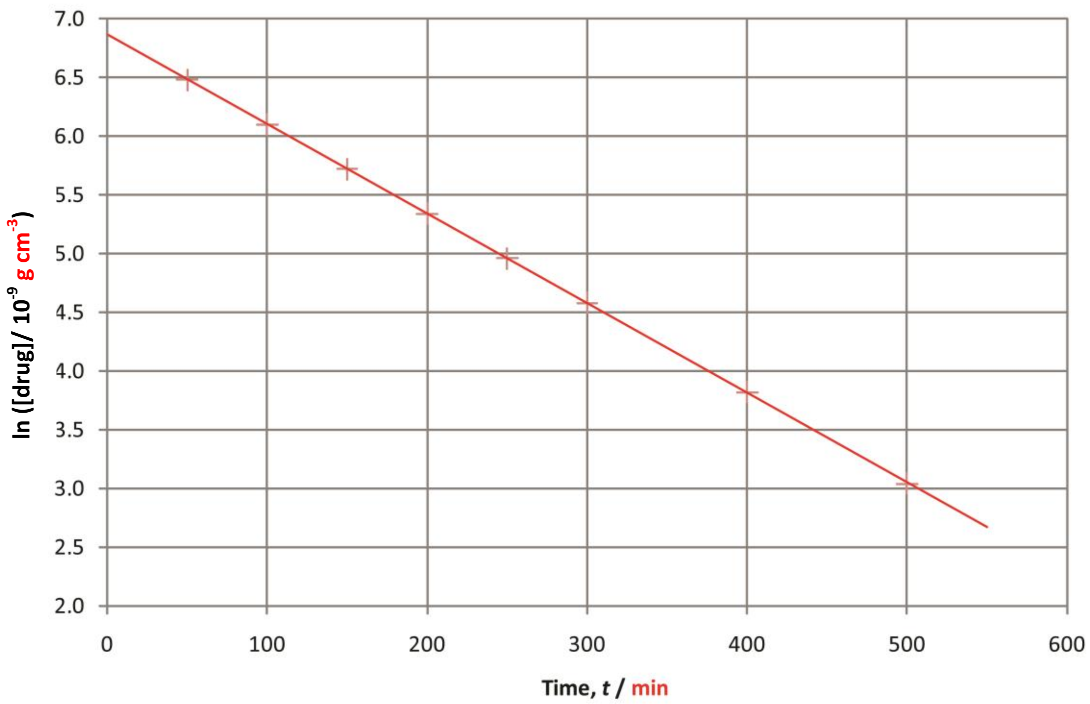
(a) Using Equation 9.6a, if the reaction is first order, then

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

Draw up a table with values of ln [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
ln ([drug]/ 10^{-9} g cm^{-3})	6.48	6.10	5.72	5.34	4.96	4.58	3.82	3.04

and plot a graph of ln [drug] against t.



The plot is a straight line.

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

Use Equation 9.7b to confirm that the reaction is not second order.

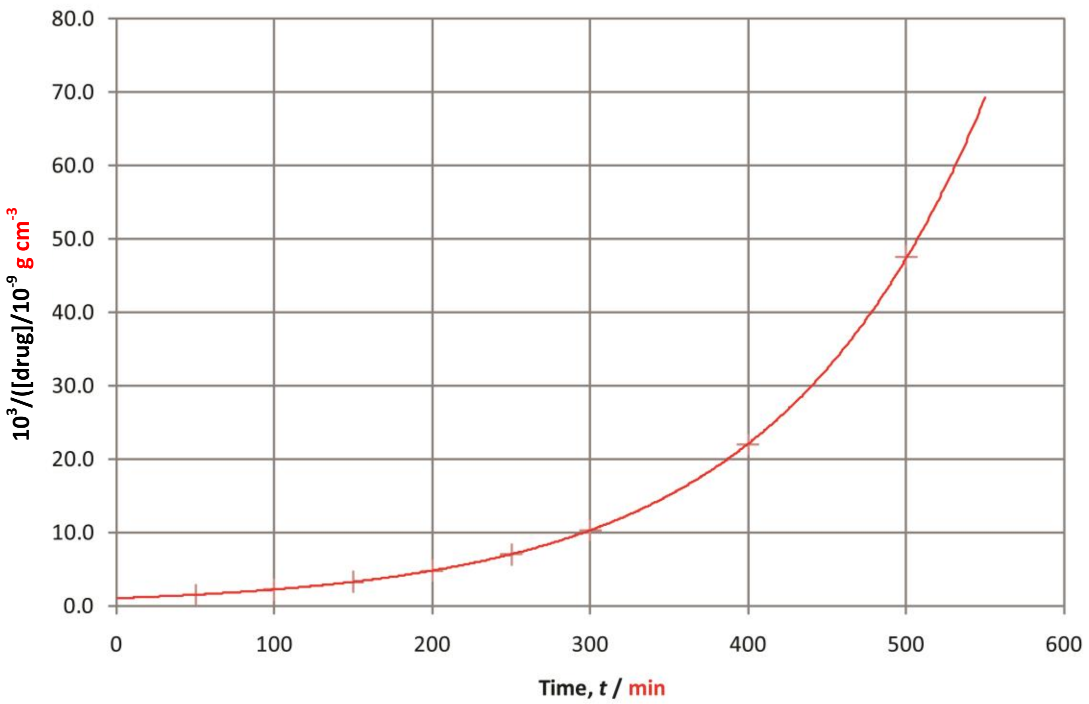
$$\frac{1}{[\text{drug}]_t} = \frac{1}{[\text{drug}]_0} + 2kt$$

Draw up a table with values of 1/[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

∗ The values have been multiplied by 1000 to give manageable numbers to plot.

and plot a graph of 1000/[drug]against *t.*



The plot is a curve, not a straight line, demonstrating that the process is not second order with respect to the drug.

(b) From the gradient of the first order plot, $k = 0.0076\ \text{min}^{-1} = 1.27 \times 10^{-4}\ \text{s}^{-1}$

Using Equation 9.9, p.392

$$t_{½} = \frac{\ln 2}{k} = \frac{0.639}{1.27 \times 10^{-4}\,\text{s}^{-1}} = 5460\ \text{s} = 91\ \text{min}\ (1.5\ \text{hr})$$

(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.

29*. The reaction between hydrogen and iodine is a complex reaction.

$$H_2 + I_2 \rightarrow 2HI$$

Kinetics experiments show that the reaction is first order with respect to H_2 and first order with respect to I_2. The following mechanism has been proposed

1 $$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I^\bullet \qquad \text{Equilibrium constant } K_1$$

2 $$H_2 + I^\bullet \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2I^\bullet \qquad \text{Equilibrium constant } K_2$$

3 $$H_2I^\bullet + I^\bullet \xrightarrow{k_3} 2HI$$

where each step is an elementary reaction. Reaction 3 is the rate-determining step and both reactions 1 and 2 form pre-equilibria.

(a) Assuming reaction 1 is at equilibrium, obtain an expression for $[I^\bullet]$ in terms of $[I_2]$ and the rate constants k_1 and k_{-1}.

(b) Assuming reaction 2 is at equilibrium, obtain an expression for $[H_2I^\bullet]$ in terms of $[H_2]$, $[I^\bullet]$ and the rate constants k_2 and k_{-2}.

(c) Write down the rate equation for reaction 3 and substitute in this the expressions for $[I^\bullet]$ and $[H_2I^\bullet]$ you obtained in (a) and (b).

(d) Compare the rate equation you have derived from the reaction mechanism with that found experimentally and write an expression for the rate constant, k, for the overall reaction.

Strategy

(a) and (b) Write rate equations for the forward and backward reaction. When the reaction comes to equilibrium, the rates of the forward and backward reactions are equal. Alternatively, you can use Equation 9.14 (p.414)

$$K_c = \frac{k_1}{k_{-1}} \tag{9.14}$$

Solution

(a) Reaction 1 is a dynamic equilibrium. The rate of the forward reaction must therefore be the same as the rate of the backward reaction

$$k_1[I_2] \;=\; k_{-1}[I^\bullet]^2$$

Rearranging to give an expression for $[I^\bullet]$

$$[I^\bullet] \;=\; \left(\frac{k_1}{k_{-1}}\,[I_2]\right)^{\frac{1}{2}}$$

(You can arrive at the same expression using Equation 9.14:

$$K_c(\text{Reaction 1}) = \frac{\left[\text{I}^\bullet\right]^2}{\left[\text{I}_2\right]} = \frac{k_1}{k_{-1}} \quad)$$

(b) In the same way for Reaction 2

$$K_c(\text{Reaction 2}) = \frac{\left[\text{H}_2\text{I}^\bullet\right]}{[\text{H}_2]\left[\text{I}^\bullet\right]} = \frac{k_2}{k_{-2}},\ \text{so}$$

$$[\text{H}_2\text{I}^\bullet] = \frac{k_2}{k_{-2}}[\text{H}_2][\text{I}^\bullet]$$

(c) For Reaction 3

rate of reaction = $k_3\,[\text{H}_2\text{I}^\bullet][\text{I}^\bullet]$

$$= k_3 \times \frac{k_2}{k_{-2}}[\text{H}_2][\text{I}^\bullet] \times [\text{I}^\bullet] = k_3 \times \frac{k_2}{k_{-2}}[\text{H}_2] \times \frac{k_1}{k_{-1}}[\text{I}_2]$$

$$\text{So, rate of reaction} = k_3\,\frac{k_2}{k_{-2}}\,\frac{k_1}{k_{-1}}\,[\text{H}_2][\text{I}_2]$$

(d) The rate equation derived from the reaction mechanism is first order with respect to H_2 and first order with respect to I_2, so agrees with the experimentally determined kinetics:

rate of reaction = $k\,[\text{H}_2][\text{I}_2]$

The rate constant for the overall reaction, $k = k_3 \dfrac{k_2}{k_{-2}} \dfrac{k_1}{k_{-1}}$

30*. The dissociation of propane in which a C–C bond breaks to form a methyl radical and an ethyl radical is a *unimolecular* reaction.

$$C_3H_8 \rightarrow CH_3^{\bullet} + C_2H_5^{\bullet}$$

The rate of formation of $CH_3^{\bullet}$ (and of $C_2H_5^{\bullet}$) is given by

$$\frac{d[CH_3^{\bullet}]}{dt} = k_{\text{overall}}\,[C_3H_8]$$

where k_{overall} is the unimolecular rate constant for the reaction.

The propane molecules obtain sufficient energy to dissociate by colliding with other molecules, M, where M may be an unreactive gas such as nitrogen. The mechanism for this process can be written as

$$C_3H_8 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_3H_8^{*} + M$$

$$C_3H_8^{*} \xrightarrow{k_2} CH_3^{\bullet} + C_2H_5^{\bullet}$$

where $C_3H_8^{*}$ is a propane molecule in a high energy state, which has sufficient energy to dissociate.

(a) Explain what is meant by the term *unimolecular*.

(b) By applying the steady state approximation to $C_3H_8^{*}$, derive an expression for $[C_3H_8^{*}]$. Since the rate of formation of CH_3^{*} is equal to $k_2[C_3H_8^{*}]$, show that

$$k_{overall} = \frac{k_1k_2[M]}{k_{-1}[M]+k_2}$$

(c) Show that (i) when [M] is very large, $k_{\text{overall}} \simeq \dfrac{k_1k_2}{k_{-1}}$

(ii) when [M] is very small, $k_{\text{overall}} \simeq k_1[M]$

(d) What are the rate-determining stages in the mechanism under each of the conditions in (c)(i) and (c)(ii)? Sketch a graph to show the dependence of k_{overall} on [M].

(e) It is always better to find a linear expression to analyse experimental data. Show that

$$\frac{1}{k_{\text{overall}}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1[\text{M}]}$$

A plot of $1/k_{\text{overall}}$ (y-axis) against 1/[M] (x-axis) is a straight line. What are the gradient and the intercept on the y-axis at 1/[M] = 0?

Strategy

The high energy propane molecule, $C_3H_8{}^*$, is very short lived. so you can use the steady state approximation, Equation 9.15 (p.416). Work through the parts in the problem using the general approach in Section 9.6 (p.415-419).

Solution

(a) In a unimolecular reaction, the transition state involves just one molecule of the reactant in a high energy state.

(b) Using Equation 9.15 to apply the steady state approximation

$$\frac{d[C_3H_8{}^*]}{dt} = (\text{rate of formation of } C_3H_8{}^*) - (\text{rate of consumption of } C_3H_8{}^*) = 0$$

$$\frac{d[C_3H_8{}^*]}{dt} = k_1[C_3H_8][\text{M}] - k_{-1}[C_3H_8{}^*][\text{M}] + k_2[C_3H_8{}^*]$$

$$= k_1[C_3H_8][\text{M}] - (k_{-1}[\text{M}] + k_2)[C_3H_8{}^*] = 0$$

Rearranging the equation to obtain an expression for $[C_3H_8{}^*]$

$$k_1[C_3H_8][\text{M}] = (k_{-1}[\text{M}] + k_2)[C_3H_8{}^*]$$

$$[C_3H_8{}^*] = \frac{k_1[C_3H_8][\text{M}]}{k_{-1}[\text{M}] + k_2}$$

Rate of formation $CH_3{}^\bullet$ $= k_2[C_3H_8{}^*]$

$$= \frac{k_1k_2[C_3H_8][M]}{k_{-1}[M] + k_2} = k_{\text{overall}}[C_3H_8]$$

$$\text{So, } k_{\text{overall}} = \frac{k_1k_2[M]}{k_{-1}[M] + k_2}$$

(c) (i) When [M] is very large, $k_{-1}[M] >> k_2$

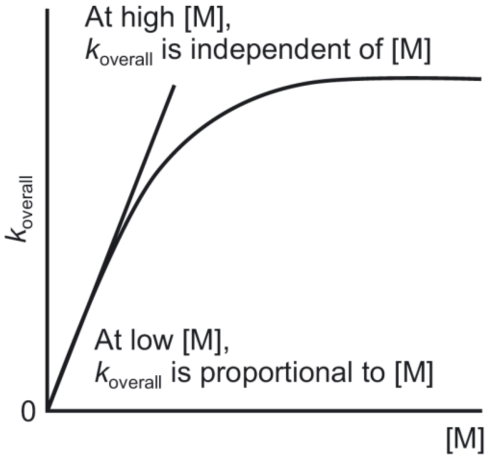
$$k_{\text{overall}} \simeq \frac{k_1k_2[M]}{k_{-1}[M]} \simeq \frac{k_1k_2}{k_{-1}}$$

(ii) When [M] is very small, $k_2 >> k_{-1}[M]$

$$k_{\text{overall}} \simeq \frac{k_1k_2[M]}{k_2} \simeq k_1[M]$$

(d) (i) The overall rate of reaction is independent of [M] and proportional to $[C_3H_8]$, so the second stage, the dissociation of $[C_3H_8^*]$, is rate-determining.

(ii) The overall rate of reaction is proportional to both [M] and $[C_3H_8]$, so the first stage, the collision of C_3H_8 and M, is the rate-determining stage in the mechanism.



(e) $$k_{\text{overall}} = \frac{k_1k_2[M]}{k_{-1}[M] + k_2}$$

Taking a reciprocal of each side

$$\frac{1}{k_{\text{overall}}} = \frac{k_{-1}[M] + k_2}{k_1k_2[M]}$$

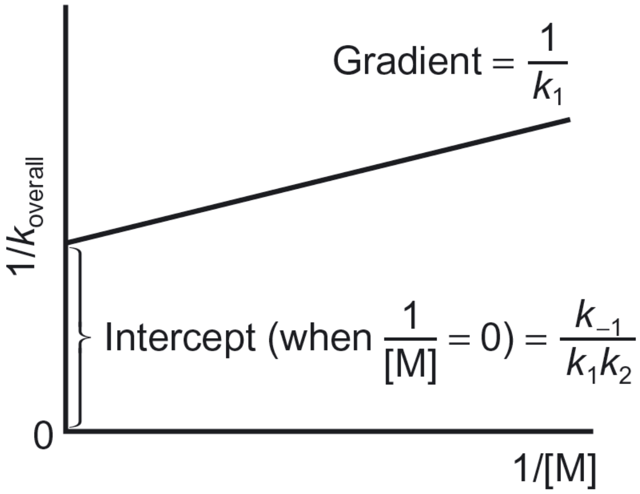
$$= \frac{k_{-1}[\mathrm{M}]}{k_1k_2[\mathrm{M}]} + \frac{k_2}{k_1k_2[\mathrm{M}]}$$

$$= \frac{k_{-1}}{k_1k_2} + \frac{1}{k_1[\mathrm{M}]}$$

This corresponds to the equation for a straight line: $y = mx + c$

So a plot of $1/k_{\text{overall}}$ against $1/[\mathrm{M}]$ is a straight line.

Intercept on y-axis (at $1/[\mathrm{M}] = 0$) is $\frac{k_{-1}}{k_1k_2}$



31. At *low substrate concentrations*, the initial rate of an enzyme-catalysed reaction was found to be directly proportional to the initial substrate concentration, $[\mathrm{S}]_0$, and directly proportional to the initial enzyme concentration, $[\mathrm{E}]_0$.

(a) Outline the series of experiments that led to these results.

(b) Write a rate equation for the reaction under these conditions and explain the observed kinetics in terms of the mechanism for the reaction. What is the rate-determining step under these conditions?

At *much higher substrate concentrations*, the initial rate was found to be constant and independent of the initial substrate concentrations. The initial enzyme concentration was the same in each experiment.

(c) Write a rate equation for the reaction under these conditions and explain the observed kinetics in terms of the mechanism for the reaction. What is the rate-determining step under these conditions?

Strategy

(a) Use the initial rate method. You will need two series of experiments. Think about which concentrations are kept constant and which varied in each series.

(b) and (c) Use the reaction mechanism for an enzyme catalysed reaction on p.435. Think about the consequences of all the active sites of the enzyme being filled by substrate molecules.

Solution

(a) In each experiment, the concentrations of the substrate (or the product) are measured at different times in the reaction and a kinetic profile plotted. The initial rate in each experiment is found from the gradient of a tangent drawn to the curve at $t = 0$. A series of experiments is carried out for different initial values of $[S]_0$, for a constant value of $[E]_0$. In a second series of experiments, $[E]_0$ is varied and $[S]_0$ is kept constant.

(b) At low substrate concentrations, rate of reaction = $k[S][E]$.

The mechanism of the reaction is

$$E + S \rightleftharpoons ES \longrightarrow E + P$$

If the substrate concentration is low enough, not all the enzyme active sites will have a substrate molecule bound to them. The reaction of E + S to form the complex ES is the rate determining step. The overall rate of reaction depends on how frequently the substrate molecules encounter active sites, which depends on both the concentration of the substrate and the concentration of the enzyme. The reaction is then first order with respect to the substrate and first order with respect to the free enzyme.

(c) At high substrate concentrations, rate of reaction = constant.

When the maximum rate is reached, all the active sites on the enzyme molecules have substrates attached. The rate determining step is now the conversion of ES to form E + P and the overall rate of reaction is independent of [S]. The reaction is zero order with respect to the substrate.