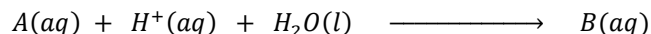


ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

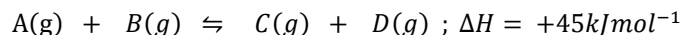
CHAPTER 9: CHEMICAL KINETICS

1. Substance A undergoes the following reaction in aqueous solution.



The reaction is acid catalysed and is first order with respect to each of the reacting species.

- (a). (i). Write an expression for the rate of reaction
(ii). What would be the effect of doubling the catalyst concentration on the rate of the reaction?
- (b). Under certain conditions, the reaction is overall first order
(i). State the conditions
(ii). Write the corresponding rate equation
(iii). If the rate constant, K is $2.0 \times 10^{-5} s^{-1}$, calculate the time required for the concentration of A decreases to a third of its original value.
- (c). (i). Explain what is meant by the term activation complex
(ii). Draw a potential energy diagram for a chemical reaction and label it fully
(iii). What is the effect of a catalyst on the rate of the chemical reaction?
2. (a). For a reversible reaction;

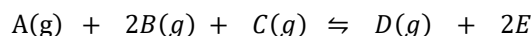


The activation energy for the forward reaction is $195 kJ mol^{-1}$. The following data was experimentally obtained on the rates of reaction under different conditions at 298K

Experiment number	[A]/ $mol l^{-1}$	[B]/ $mol l^{-1}$	Rate / $mol l^{-1} s^{-1}$
1	2.0×10^{-2}	1.0×10^{-2}	1.0×10^2
2	2.0×10^{-2}	2.0×10^{-2}	2.0×10^2
3	4.0×10^{-2}	1.0×10^{-2}	4.0×10^2

Write the expression for the rate equation using the data given in the above table.

- (b). Calculate the rate constant and state its units
(c). Calculate the activation energy for the backward reaction
3. The following kinetic data was obtained for the reaction

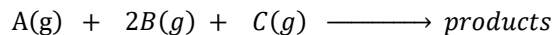


Experiment number	[A]/ $mol l^{-1}$	[B]/ $mol l^{-1}$	[C]/ $mol l^{-1}$	Rate / $mol l^{-1} s^{-1}$
1	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}	2.0×10^2
2	2.0×10^{-2}	1.0×10^{-2}	2.0×10^{-2}	2.0×10^2
3	4.0×10^{-2}	4.0×10^{-2}	2.0×10^{-2}	8.0×10^2
4	2.0×10^{-2}	4.0×10^{-2}	1.0×10^{-2}	1.0×10^2

- (a). Write the rate equation

- (b). Determine the rate of formation of E in experiment 2 given that, that in the table was of D.
- (c). Hence find the rate of consumption of B in experiment 3

4. The kinetic data for the reaction is shown below.



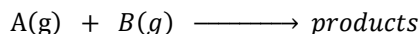
Experiment number	[A]/ mol ⁻¹	[B]/ mol ⁻¹	[C]/ mol ⁻¹	Rate /mol ⁻¹ s ⁻¹
1	0.2	0.3	0.1	2.0×10^2
2	0.4	0.3	0.1	4.0×10^2
3	0.2	0.6	0.1	8.0×10^2
4	0.2	0.3	0.2	2.0×10^2

- (a). Determine the rate equation
- (b). What is the overall order of reaction?
5. Substance B reacts with potassium iodide to form iodine. The iodine is titrated with standard sodium thiosulphate solution. The volume of sodium thiosulphate is the measure of the concentration of B remaining at a given time, t.

Volume (cm ³)	24.70	17.80	12.90	9.25	5.50	3.60
Time (minutes)	0	60	120	180	240	300

- (a). Plot a graph of volume against time
- (b). From the graph in (a), deduce the time taken for the concentration of B to
- Reduce to half of the original value
 - Reduce to a quarter of the original value.
- (c). What is the order of reaction with respect of B
- (d). Write the rate equation for the reaction.
- (e). Determine the rate constant.
6. (a). Draw a fully labelled potential energy versus reaction coordinate diagram for an endothermic reaction
- (b). Explain the effect of temperature on the rate of a chemical reaction.
- (c). Distinguish between order of reaction and molecularity
- (d). Discuss the role of a catalyst in speeding up the rate of a reaction.

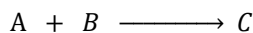
7. The data below was obtained for the reaction



Experiment number	[A]/ moldm ⁻³	[B]/ moldm ⁻³	Rate /moldm ⁻³ s ⁻¹
1	0.1	0.1	1.6×10^{-3}
2	0.1	0.2	3.2×10^{-3}
3	0.1	0.3	4.8×10^{-3}
4	0.2	0.1	6.4×10^{-3}
5	0.3	0.1	y

- (a). Determine the
- Order of reaction with respect to B
 - Value of y in the table
- (b). Write the rate equation for the reaction
- (c). Calculate the value of the rate constant and state its units

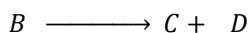
8. The following data was obtained for the reaction



Experiment	Initial [A]/ mol dm^{-3}	Initial [B]/ mol dm^{-3}	Initial rate / $\text{mol dm}^{-3}\text{min}^{-1}$
1	0.1	0.1	1.0×10^{-4}
2	0.1	0.3	9.0×10^{-4}
3	0.1	0.3	2.7×10^{-3}

- (a). Determine the order of reaction with respect to
- A
 - B
- (b). Write the rate equation for the reaction.
- (c). If the initial concentration of both A and B are 0.4M, calculate the initial rate of formation of C.

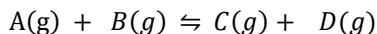
9. Compound B is converted to C and D according to the equation.



The data below was obtained for the reaction

time (minutes)	0.0	7.2	18.0	36.0	72.0	108.0
[B]/ mol dm^{-3}	100	91	79	63	40	25

- (a). Plot a graph of concentration of B against time
- (b). Using your graph, determine the
- Half-life of the reaction
 - Order of reaction
 - Rate constant of the reaction and state its units.
10. For a reversible reaction indicated below, the activation energy, E_a , and the enthalpy change, ΔH , for the forward reaction are +180 and +40 kJ mol^{-1} respectively.

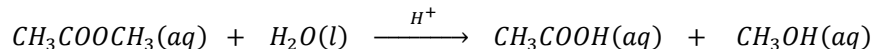


- (a). The following data was obtained experimentally on the rates of reaction under different conditions at 298K

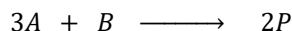
Experiment	[A]/ mol dm^{-3}	[B]/ mol dm^{-3}	Rate / $\text{mol dm}^{-3}\text{s}^{-1}$
1	2.0×10^{-2}	1.0×10^{-2}	1.0×10^2
2	2.0×10^{-2}	2.0×10^{-2}	4.0×10^2
3	6.0×10^{-2}	1.0×10^{-2}	3.0×10^2

- (i). Write an expression for the rate equation using the data in the table above
- (ii). Calculate the rate constant and give its units
- (b). (i). Sketch a fully labelled diagram showing the energy versus reaction coordinate for this reaction.
- (ii). Determine the activation energy for the backward reaction
- (c). How do you expect the
 - (i). Equilibrium constant for the reaction to change if temperature was raised
 - (ii). Rate of the reaction to change if temperature was raised
- (d). Sketch on the same diagram the variation of the concentration of D with time during the reaction after A and B are mixed for two temperatures T_1 and T_2 where $T_1 > T_2$

11. (a). State what is meant by the term order of reaction.
- (b). Methyl ethanoate is hydrolysed in water in the presence of an acid according to the equation

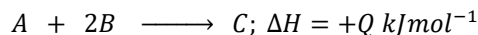


- (i). State the molecularity of the reaction
 - (ii). Determine the order of the reaction
 - (iii). State the conditions under which the reaction can be overall first order
- (c). The table below shows some kinetic data for the reaction



Experiment	[A]/ moldm ⁻³	[B]/ moldm ⁻³	Rate / moldm ⁻³ s ⁻¹
1	0.2	0.2	1.2×10^{-8}
2	0.2	0.6	1.2×10^{-8}
3	0.4	0.6	4.8×10^{-8}

- (i). Write the overall rate equation
 - (ii). Calculate the rate constant for the reaction and state its units
12. (a). Differentiate between order of reaction and molecularity of a reaction.
- (b). The table below shows some data for the reaction



Experiment	[A]/ moldm ⁻³	[B]/ moldm ⁻³	Rate / moldm ⁻³ s ⁻¹
1	1.00×10^{-2}	2.80×10^{-3}	2.1
2	1.00×10^{-2}	5.60×10^{-3}	4.3
3	5.00×10^{-3}	2.80×10^{-3}	1.1

- (i). Determine the order of reaction with respect to A and B
- (ii). Write the rate equation for the reaction

- (iii). Calculate the rate constant for the reaction and give its units
- (iv). Calculate the rate of reaction when the concentration of A and B are 8.5×10^{-3} and $3.83 \times 10^{-3} \text{ moldm}^{-3}$ respectively.
- (c). State what would happen to the order of the reaction in above if B was in large excess. Explain your answer.
- (d). Draw a fully labelled potential energy diagram for the reaction
13. (a). Derive an expression for the half-life of a first order reaction. $2.303 \log \left(\frac{a_0}{a_0 - x} \right) = kt$.
Where a_0 is the initial concentration and $(a_0 - x)$ is the concentration after time, t.
- (b). The half-life of a first order reaction is 100s.
- (i). Calculate the rate constant
- (ii). Determine the percentage of the reactants that reacted in 250 seconds.
14. (a). Briefly describe how you would determine the rate of the following reactions
- (i). Decomposition of hydrogen peroxide
- (ii). Reaction of sodium thiosulphate and dilute hydrochloric acid
- (iii). Iodination of propanone catalysed by sulphuric acid
- (b). For each of the following reactions describe experiments to show that
- (i). The decomposition of hydrogen peroxide is a first order reaction
- (ii). The reaction of hydrochloric acid with sodium thiosulphate is a first order reaction with respect to hydrochloric acid
- (iii). The acid catalysed reaction of iodine and propanone is zero order with respect to iodine.
15. (a). Explain what is meant by
- (i). Rate equation
- (ii). Order of reaction
- (iii). Rate constant
- (b). The following results were obtained for two compounds A and B reacting to form product C.

Initial [A]/ moldm^{-3}	Initial [B]/ moldm^{-3}	Initial rate / $\text{moldm}^{-3}\text{s}^{-1}$
2.0×10^{-1}	2.4×10^{-1}	2.0×10^{-4}
4.0×10^{-1}	2.4×10^{-1}	8.0×10^{-4}
4.0×10^{-1}	4.8×10^{-1}	16.0×10^{-4}

- (i). Deduce the rate equation
- (ii). Calculate the rate constant and indicate its units
16. (a). A gas decomposes according to the following equation
- $$X_2(g) \longrightarrow 2X(g); \Delta H = -ve$$
- Sketch a graph to show how the concentration of X_2 and X vary with time
- (b). Using the same scale, sketch another graph to show how the concentration of X_2 varies with time, showing what happens under similar conditions in which the
- (i). Temperature is raised

- (ii). Pressure is lowered.
Comment on the results in each case.
- (c). The following results were obtained for the decomposition of dinitrogen tetraoxide.

<i>Time (s)</i>	0	250	300	750	1000	1500	2000	2500
<i>Concentration (mol dm⁻³)</i>	2.33	1.95	1.68	1.42	1.25	0.95	0.70	0.50

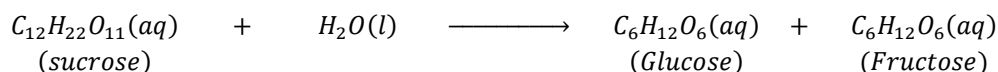
- (i). Plot a graph of concentration against time
(ii). Use your graph to determine the order of reaction
(iii). Calculate the rate constant and state its units
17. (a). Distinguish between order of reaction and molecularity
(b). (i). Define a catalyst
(ii). Explain the effect of a catalyst on the rate of reaction
(c). For a reaction with between P, Q and R, the rate equation is given as $Rate = [P]^2[Q][R]$. State how the rate of reaction would be altered if;
(i). [P] and [Q] are kept constant but [R] doubled
(ii). [P] and [R] are kept constant but [Q] halved
(iii). [Q] and [R] are kept constant but [P] doubled.
(iv). Concentration of all species are doubled.
- (d). Ammonia decomposes on a hot tungsten surface into nitrogen and hydrogen. The following data was obtained

<i>Initial pressure of NH₃ (kPa)</i>	38.0	19.0	9.5
<i>Half - life (s)</i>	490	250	130

- (i). Write the equation for the decomposition of ammonia
(ii). Using the above table, explain the term **half-life**.
(iii). Plot a suitable graph and use the graph to determine the order and rate constant of the reaction.
18. (a). Distinguish between
(i). Reaction rate and rate constant.
(ii). Homogeneous and heterogeneous catalyst
(b). The table below was obtained during the hydrolysis of sucrose. The initial concentration was 1.00M.

<i>Time (minutes)</i>	0	60	90	130	180
<i>Sucrose reacted (mol dm⁻³)</i>	0.00	0.195	0.277	0.373	0.478

The hydrolysis of sucrose is as shown in the equation below



- (i). Plot a suitable graph to show that the order of reaction with respect to sucrose is one
(ii). Determine the half-life and rate constant for the reaction.

- (iii). State the effect of halving the initial concentration of sucrose on the value of the half-life and rate constant
- (iv). Explain why the reaction is first order yet water is a reactant in the stoichiometric equation
- (c). The following data was obtained during the hydrolysis of 2-chloro-2-methylpropane by sodium hydroxide

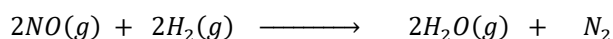
Experiment	1	2	3	4	5
[2-chloro-2-methylpropane] (Mol dm^{-3})	0.1	0.1	0.075	0.050	0.025
[OH] (Mol dm^{-3})	0.5	0.25	0.25	0.25	0.25
Initial rate ($\text{Mol dm}^{-3} \text{s}^{-1}$)	0.0020	0.0020	0.0015	0.0010	0.0005

- (i). Determine the order of the reaction with respect to 2-chloro-2-methylpropane and sodium hydroxide
- (ii). Calculate the value of the rate constant and state its units
- (iii). Suggest a mechanism for the reaction
- (d). The following results were obtained for the decomposition of dinitrogen pentoxide

Temperature ($^{\circ}\text{C}$)	25	35	45	55	65
Rate constant; K (s^{-1})	1.74×10^{-5}	6.6×10^{-5}	2.51×10^{-4}	7.59×10^{-4}	2.0×10^{-3}

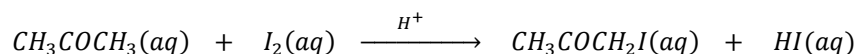
- (i). Plot a graph of $\log K$ against $\frac{1}{\text{Temp}}$
- (ii). Use your graph to determine the activation energy of the reaction.
 (take slope = $\frac{-E_a}{2.303R}$) where $R = 8.314$ and E_a is activation energy.

19. (a). The data below was obtained from the following reaction



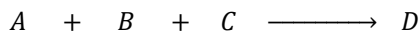
Experiment	1	2	3	4
[NO] (Mol dm^{-3})	0.5	0.5	0.1	0.1
[H ₂] (Mol dm^{-3})	0.1	0.2	0.5	0.5
Rate of formation of N_2 ($\text{Mol dm}^{-3} \text{s}^{-1}$)	0.045	0.09	0.09	0.36

- (i). Determine the rate equation
- (ii). Calculate the rate constant and state its units
- (iii). State the effect on the reaction if the concentration of nitrogen monoxide is halved while that of hydrogen remains constant
- (iv). What is the effect on the rate of the reaction by doubling the concentration of nitrogen monoxide and increasing the concentration of hydrogen by three times?
20. (a). Propanone and iodine react in the presence of an acid according to the equation



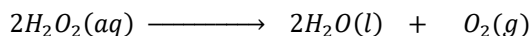
The reaction is first order with respect to propanone and is independent of the concentration of iodine

- (i). Write the expression for the rate law
 (ii). Describe briefly how the order with respect to iodine can be determined
 (b). The following data was obtained for the reaction



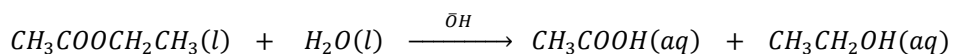
Experiment	Initial [A] (mol dm ⁻³)	Initial [B] (mol dm ⁻³)	Initial [C] (mol dm ⁻³)	Initial rate (mol dm ⁻³ min ⁻¹)
1	0.1	0.1	0.1	1.0×10^{-4}
2	0.1	0.3	0.1	9.0×10^{-4}
3	0.3	0.3	0.1	2.7×10^{-3}
4	0.1	0.1	0.3	1.0×10^{-4}

- (i). Determine the order of reaction with respect to A, B and C. explain how you arrive at your answer.
 (ii). Write the rate equation for the reaction
 (iii). If the initial concentration of A, B, and C are each 0.4 mol dm⁻³. Calculate the initial rate of reaction.
21. (a). Hydrogen peroxide decomposes in the presence of iron(III) chloride according to the equation.



The decomposition is first order reaction with respect to hydrogen

- (i). Write the rate law
 (ii). Describe briefly how the order with respect to hydrogen peroxide can be determined
 (b). The following data show the hydrolysis of ethyl ethanoate catalysed by sodium hydroxide



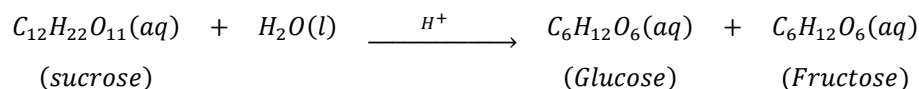
The initial concentration of the ethyl ethanoate being 0.05M

Time (seconds)	100	200	300	400	600
Percentage of ester hydrolysed	29.5	44.2	55.5	62.2	70.3

- (i). Plot a suitable graph and from it determine the order of reaction
 (ii). Hence determine the rate constant K
22. The following kinetic data was obtained for a reaction in which a certain compound W was converted to Y at 25°C.

Time (minutes)	0	9	18	27	40	54	72	105	118
[W] (mol dm ⁻³)	0.106	0.096	0.086	0.077	0.065	0.054	0.043	0.030	0.025

- (a). Plot a graph of concentration against time
 (b). From the graph, deduce the time taken for the concentration of W to reduce to
 (i). Half of the original value
 (ii). Quarter of the original value
 What is the order of reaction with respect to W.
 (c). Write the rate equation for the reaction in which W is changed to Y.
 (d). Determine the rate constant and state its units.
23. In the presence of an acid, sucrose is converted to a mixture of glucose and fructose according to the equation.

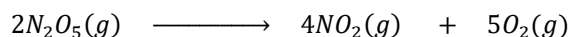


The following data was obtained at 25°C.

[sucrose] (mol dm ⁻³)	0.08	0.06	0.04	0.02
Rate (mol dm ⁻³ s ⁻¹)	0.004	0.003	0.002	0.001

Draw a suitable graph and use it to determine the

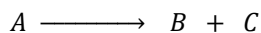
- (i). Order of reaction
 (ii). Rate constant
 (iii). Rate of reaction when the concentration of sucrose is 0.12 mol dm⁻³.
24. The following data refers to the reaction at 6°C.



Time (seconds)	0	20	45	73	105	140	185	243	325
Partial pressure of N ₂ O ₅ (Pa)	100	90	80	70	60	50	40	30	20

Plot a graph of partial pressure against time and use it to determine the

- (a). Order of reaction with respect to N₂O₅
 (b). Rate constant.
25. Compound A is converted to compounds B and C according to the equation.

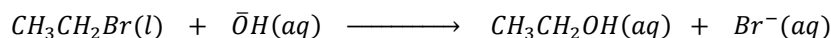


Time (minutes)	0.0	7.2	18.0	36.0	71.0	108.0
[A] (mol l ⁻¹)	100	91	79	63	40	25

- (a). Plot a graph of concentration of A against time
 (b). Use your graph to determine the time taken for the concentration of A to decrease from
 (i). 80 to 40 mol l⁻¹

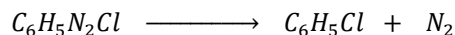
- (ii). 60 to 30 mol⁻¹
- (c). Determine the
 - (i). Half-life of the reaction
 - (ii). Order of the reaction
 - (iii). Rate constant and state its units.

26. Bromoethane reacts with sodium hydroxide according to the equation.



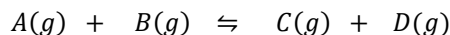
The overall reaction is bimolecular.

- (a). Draw a fully labelled diagram of energy versus reaction path for the reaction
 - (b). Explain what is meant by the terms
 - (i). Bimolecular reaction
 - (ii). Activated complex
 - (c). Write the rate equation for the reaction.
 - (d). Outline the mechanism for the reaction.
27. (a). Write an equation to show how benzene diazonium chloride can be prepared in the laboratory.
- (b). Benzene diazonium chloride decomposes according to the equation when heated.



The reaction is first order with respect to benzene diazonium chloride

- (i). Write an expression for the rate equation for the decomposition of benzene diazonium chloride
 - (ii). Sketch a graph to show the variation in concentration of benzene diazonium chloride with time
 - (iii). Use the graph to show how the order of reaction can be determined by half-life method
28. (a). For a reversible reaction indicated below; the enthalpy of reaction; ΔH is +50kJmol⁻¹ and the activation energy; E_a ; is +200kJmol⁻¹ both for the forward reaction.



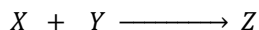
The following data were obtained experimentally on the rates of reaction under different conditions at 300K

[A] (mol ⁻¹)	[B] (mol ⁻¹)	Rate (mol ⁻¹ s ⁻¹)
2.0×10^{-2}	1.0×10^{-2}	1.0×10^2
2.0×10^{-2}	2.0×10^{-2}	2.0×10^2
4.0×10^{-2}	2.0×10^{-2}	4.0×10^2

- (i). Write down an expression for the experimental rate equation using the data above.

- (ii). Calculate the rate constant at 300K and give its units
- (b). (i). Sketch a diagram showing the energy versus the reaction path for this reaction. Label the diagram carefully and indicate the ΔH and E_a .
- (ii). What is the activation energy for the backward reaction?
- (c). Explain how you would expect the
- (i). Equilibrium constant for the reaction to change if the temperature was raised
- (ii). Rate of reaction to change if the temperature was raised
- (d). Sketch on the same diagram, the variation of the concentration, C, with time during the reaction at two temperatures T_1 and T_2 where $T_2 > T_1$
29. 2-bromo-2-methylpropane reacts with aqueous sodium hydroxide to form 2-methylpropan-2-ol.
- (a). Write down an equation for the reaction
- (b). Draw an energy diagram for the reaction
- (c). Write a mechanism for the reaction
- (d). State the
- (i). Rate determining step of the reaction
- (ii). Technique used to study the reaction

30. The table below shows how the initial rate of reaction between reactants X and Y varies with different starting concentrations of X and Y



[X] (mol ⁻¹)	[Y] (mol ⁻¹)	Initial rate (mol ⁻¹ s ⁻¹)
0.2	0.2	4.0×10^{-3}
0.2	0.4	4.0×10^{-3}
0.4	0.2	16.0×10^{-3}

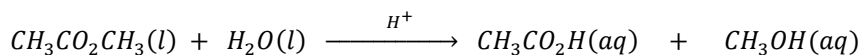
- (a). Determine the order of the reaction with respect to X and Y
- (b). Write the rate equation for the reaction
- (c). Calculate the
- (i). Rate constant
- (ii). Rate of reaction when the concentration of X and Y are 0.1 and 0.2 respectively.
31. The results of hydrolysis of 2-bromo-2-methylpropane by aqueous sodium hydroxide at 25°C is shown below.

$[(CH_3)_3C - Br]$ (mol ⁻¹)	$[OH^-]$ (mol ⁻¹)	Initial rate of hydrolysis (mol ⁻¹ s ⁻¹)
0.100	0.500	0.0020
0.100	0.250	0.0020
0.050	0.250	0.0010
0.025	0.250	0.0005

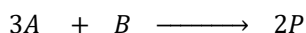
- (a). Deduce the order of reaction with respect to
- (i). 2-bromo-2-methylpropane
- (ii). Sodium hydroxide

- (b). Write the rate equation for the reaction
 (c). Calculate the rate constant, K, for the reaction and state its units

32. (a). State what is meant by the term order of reaction
 (b). Methyl ethanoate is hydrolysed by water in the presence of an acid according to the following equation



- (i). State the molecularity of the reaction
 (ii). Determine the order of the reaction
 (iii). Under which conditions can the overall order be the first order.
 (c). The table below shows some kinetic data for the reaction



[A] (mol ⁻¹)	[B] (mol ⁻¹)	Initial rate (mol ⁻¹ s ⁻¹)
0.2	0.2	1.2×10^{-8}
0.2	0.6	1.2×10^{-8}
0.4	0.6	4.8×10^{-8}

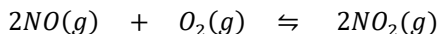
- (i). Write the overall rate equation
 (ii). Calculate the rate constant and give its units

32. The kinetics data for the reaction between P and sodium hydroxide is shown below

[P] (mol dm ⁻³)	0.105	0.088	0.074	0.051	0.037	0.026	0.016	0.010
Time (hour)	0.0	3.5	7.0	14.5	20.0	27.0	35.5	45.0

- (a). Plot a graph of concentration of P against time
 (b). Determine
 (i). The half-life of P.
 (ii). The order of the reaction.
 (iii). The rate constant for the reaction.

33. Nitrogen(II) oxide combines with oxygen at 80°C and 200atm.



- (a). The kinetic data for the reaction is shown below

Initial rate (Nm ⁻² s ⁻¹)	6.8	27.2	61.2	108
P_{NO}^2 (N ² m ⁻⁴)	0.04	0.16	0.36	0.64

- P_{NO} = the partial pressure of NO
 (i). Plot a graph of initial rate against P_{NO}^2
 (ii). Using your graph, determine the order of the reaction with respect to nitrogen(II) oxide
 (iii). Give a reason for your answer in (a) (ii) above
 (b). When the partial pressure of oxygen was doubled to a new constant value, the value of the gradient of the graph in a (i) above doubled.

- (i). Determine the order of the reaction with respect to oxygen. Explain your answer.
- (ii). Write the rate equation for the reaction in (b)
- (iii). Calculate the rate constant when the initial rate = $170 \text{ Nm}^{-2}\text{s}^{-1}$; $P_{\text{NO}} = 0.1 \text{ Nm}^{-2}$ and $P_{\text{O}_2} = 1.36 \text{ Nm}^{-2}$ and state its units.
- (c). State the effect of the following on the rate of this reaction.
- (i). Having P_{NO} and O_2 that of is kept constant.
- (ii). Doubling the P_{O_2} and that of P_{NO} .

34. The rate equation for a certain reaction is; Rate = $K[\text{P}][\text{Q}]^2[\text{R}]$

- (a). State what would happen to the rate of the reaction if
- (i). [P] and [Q] are kept constant but [R] doubled
- (ii). [P], [Q] and [R] all halved
- (iii). [P], [Q] and [R] all doubled
- (b). The following results were obtained in a study of a reaction between peroxodisulphate and iodide ions

$[\text{S}_2\text{O}_8^{2-}]$ (mol $^{-1}$)	$[\text{I}^-]$ (mol $^{-1}$)	Initial rate (mol $^{-1}\text{s}^{-1}$)
0.024	0.024	9.6×10^{-6}
0.048	0.024	1.92×10^{-5}
0.048	0.012	9.6×10^{-6}

- (i). Write the rate equation
- (ii). Calculate the rate constant and state its units.

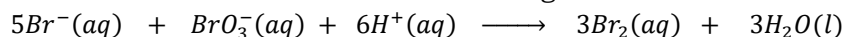
35. The kinetic data for a reaction between X and Y are given below

[X] (mol $^{-1}$)	[Y] (mol $^{-1}$)	Initial rate (mol $^{-1}\text{s}^{-1}$)
0.30	0.15	1.5×10^{-2}
0.30	0.30	3.0×10^{-2}
0.60	0.30	6.0×10^{-2}
0.60	0.60	1.2×10^{-1}

- (a). Determine the order of the reaction with respect to
- (i). X
- (ii). Y
- (b). Determine the overall order of the reaction
- (c). Calculate the rate constant for the reaction and indicate its units

36. (a). Differentiate between order of reaction and molecularity

(b). The table below shows kinetics data for the following reaction



Volume of BrO_3^- (cm 3)	3.0	4.0	5.0	6.0	8.0	10.0
Time; t (s)	69.0	45.0	35.0	31.0	24.0	18.5

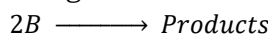
- (i). Plot a graph of $\frac{1}{t}$ against volume of bromate(V); BrO_3^-

- (ii). Determine the order of reaction with respect to bromate(V) and give a reason for your answer
- (iii). Determine the rate constant for the reaction and state its units
- (iv). Write equation for the rate of reaction in terms of concentration of bromate(V)
- (c). The kinetic data for the reaction between substances X and Y are shown below

[X] (mol ⁻¹)	[Y] (mol ⁻¹)	Initial rate (mol ⁻¹ s ⁻¹)
5.0×10^{-3}	5.0×10^{-3}	3.0×10^{-3}
1.0×10^{-2}	1.0×10^{-2}	2.4×10^{-2}
5.0×10^{-3}	1.0×10^{-2}	6.0×10^{-3}

Determine the

- (i). Rate equation for the reaction
- (ii). Value of rate constant and state its units
- (iii). Initial rate of the reaction when the concentration of X and Y are 1.5×10^{-2} and 7.5×10^{-3} moldm⁻³ respectively.
- (d). Explain how the following factors that affect the rate of a reaction
- (i). Temperature
- (ii). Concentration
- (iii). Surface area
37. (a). State what is meant by the following terms order of a reaction and half-life of a reaction.
- (b). A compound B decomposes according to the following equation

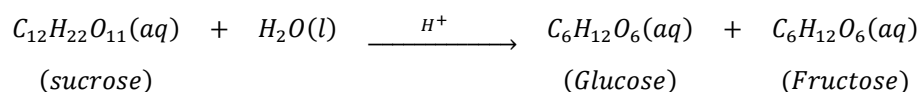


The table below shows the concentration of B at variation time

Time (minutes)	2.0	4.0	7.0	10.0	14.0	20.0
[B] (moldm ⁻³)	0.820	0.670	0.490	0.372	0.240	0.141

Draw a graph of a $\log_{10}[B]$ against time

- (c). Using your graph, determine the
- (i). Original concentration of B
- (ii). Order of the reaction
- (iii). Rate constant for the reaction
- (iv). Half-life for the reaction
- (d). (i). Using the same axes, draw a labelled diagram for energy-reaction coordinate for a catalysed and uncatalysed reaction
- (ii). State the difference in your diagrams
- (iii). State how a catalyst increases the rate of a reaction.
38. Sucrose is hydrolysed in dilute acid to give a mixture of glucose and fructose



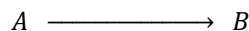
The table below shows the concentration of sucrose; [S] remaining at different time intervals

Time (minutes)	10	20	30	40	50	60
[S] (mol dm ⁻³)	1.25	1.04	0.87	0.73	0.60	0.50

- (a). Plot a graph of $\ln[S]$ against time
- (b). Using your graph, determine the
- Original concentration of sucrose
 - Order of reaction
 - Rate constant for the reaction
 - Half-life for the reaction
- (c). State the conditions under which the reaction in (a) can be overall first order
39. (a). Sodium thiosulphate solution reacts with dilute hydrochloric acid according to the following equation
- $$Na_2S_2O_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$
- The rate equation for the reaction is given by $Rate = K[HCl]^2[Na_2S_2O_3]$
- State and explain how the rate of reaction would be affected if
- $[HCl]$ is doubled while $[Na_2S_2O_3]$ is kept constant
 - $[Na_2S_2O_3]$ is halved while the $[HCl]$ is kept constant
 - $[HCl]$ is halved while the $[Na_2S_2O_3]$
 - $[HCl]$ and $[Na_2S_2O_3]$ are both halved
- (b). Describe an experiment to show that the order of reaction in (a) is first order reaction with respect to sodium thiosulphate
- (c). The table below shows how the rate constant; K varies with temperature for a reaction between hydrogen and iodine to form hydrogen iodide

Temperature (K)	500	550	600	650	700
Rate constant; K (mol ⁻¹ l ³ s ⁻¹)	6.81×10^{-4}	2.64×10^{-2}	0.56	7.31	66.67

- Plot a graph of $\log_{10} K$ against $\frac{1}{Temp}$
 - Use your graph to determine the activation energy, E_a , for the reaction
- (d). State how a catalyst increases the rate of a chemical reaction
40. The information in the table below gives the time taken for a substance S to form with different concentration of the reactant R
- | | | | | | |
|------------------------------|-------|-------|-------|-------|-------|
| Time; t (s) | 0.96 | 0.64 | 0.48 | 0.39 | 0.32 |
| $[R]$ (mol l ⁻¹) | 0.447 | 0.548 | 0.632 | 0.707 | 0.775 |
- Plot a graph of $\frac{1}{t}$ against $[R]^2$
 - Use your graph to determine the
 - Order of reaction with respect to R. Give a reason for your answer
 - Rate constant and state its units
 - Write the rate equation for the reaction
41. The table below shows the amount of the reactant, A, remaining at different time intervals in a reaction in which A is converted into a product B.



Time; $t(\text{minutes})$	0.5	1.0	1.5	2.0	2.5
$[A](\text{moll}^{-1})$	0.067	0.045	0.030	0.020	0.014

- (a). Plot a graph of $\ln[A]$ against time
 (b). Use your graph to determine the
 (i). Original concentration of A
 (ii). Rate constant for the reaction
 (iii). Order of the reaction with respect to A
 (iv). Half-life of A
 (c). Write the rate equation for the reaction

42. The table below shows how the concentration of a given reactant, K, varies with time.

Time(minutes)	0.0	2.0	4.0	6.0	8.0	10.0
$[K](\text{moll}^{-1})$	1.20	0.72	0.46	0.26	0.14	0.06

- (a). Draw a graph of
 (i). Concentration of K against time
 (ii). $\log_{10} \left(\frac{[K]_t}{[K]_0} \right)$ against time
 (b). Using each graph; determine the
 (i). Rate constant for the reaction
 (ii). The order of reaction with respect to K
 (iii). The half-life for the reaction

43. X and Y react to form W according to the equation



The table below shows the rates of reaction when various concentrations of X and Y were used at 298K

$[X] (\text{moll}^{-1})$	$[Y] (\text{moll}^{-1})$	Initial rate ($\text{moll}^{-1}\text{s}^{-1}$)
2.0×10^{-2}	1.0×10^{-2}	1.0×10^2
2.0×10^{-2}	2.0×10^{-2}	2.0×10^2
4.0×10^{-2}	2.0×10^{-2}	4.0×10^2

- (a). (i). Differentiate between 'order of reaction' and 'rate constant'
 (ii). Determine the order of reaction with respect to X and Y
 (iii). Write the expression for the rate equation
 (iv). Calculate the rate constant for the reaction at 298K and state its units
 (b). (i). Distinguish between activation energy and enthalpy of reaction
 (ii). Draw a fully labelled potential energy versus reaction coordinate for the reaction between X and Y
 (iii). Calculate the activation energy for the backward reaction (the activation energy for the forward reaction is $+200\text{kJmol}^{-1}$)

- (c). State how you would expect the
- Activation energy for the reaction to change if a catalyst is used. Give a reason for your answer
 - Rate of reaction to change if the reaction was carried out at a temperature above 298K. give a reason for your answer.
- (d). The react was carried out at temperatures T_1 and T_2 where T_2 is greater than T_1 . Sketch on the same axes graphs to show how the concentration of W varies with time during the reactions at T_1 and T_2

44. Various concentrations of X and Y were reacted at a constant temperature. The table below shows the initial concentration of X and Y and their initial rates for the reaction.

[X] (mol dm ⁻³)	[Y] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
0.2	0.2	3.5×10^{-4}
0.4	0.4	1.4×10^{-3}
0.8	0.4	5.6×10^{-3}

- State the order of reaction with respect to
 - X
 - Y
 - Give reasons for your answer in (a)
 - Determine the overall order of the reaction
 - Calculate the value for the rate constant
45. (a). The rate of a chemical reaction can be affected by the concentration of the reactants. State two other factors that can affect the rate of a chemical reaction.
- (b). Describe an experiment to determine the rate of decomposition of hydrogen peroxide.
- (c). The table below shows variation in the concentration of sodium thiosulphate with time when a fixed volume of hydrochloric acid was added to sodium thiosulphate of various concentrations

Concentration of sodium thiosulphate (mol dm ⁻³)	0.2	0.16	0.12	0.08	0.04
Time; t (s)	24	29	39	60	138
$\frac{1}{t}$ (s ⁻¹)					

- Copy the table and fill in the values of $1/t$
- Plot a graph of $1/t$ against concentration of sodium thiosulphate.
- What is the order of the reaction? Give a reason for your answer.
- Calculate the rate constant of the reaction and indicate its units.
- Determine the time taken for the concentration of sodium thiosulphate to decrease from 0.2 mol dm³ to 0.1 mol dm³