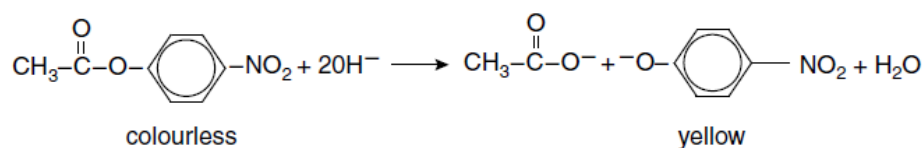


Q1 The ester 4-nitrophenyl ethanoate hydrolyses in alkaline solution according to the following equation.



(a) Suggest, and briefly describe, a suitable experimental technique for studying the rate of this reaction.

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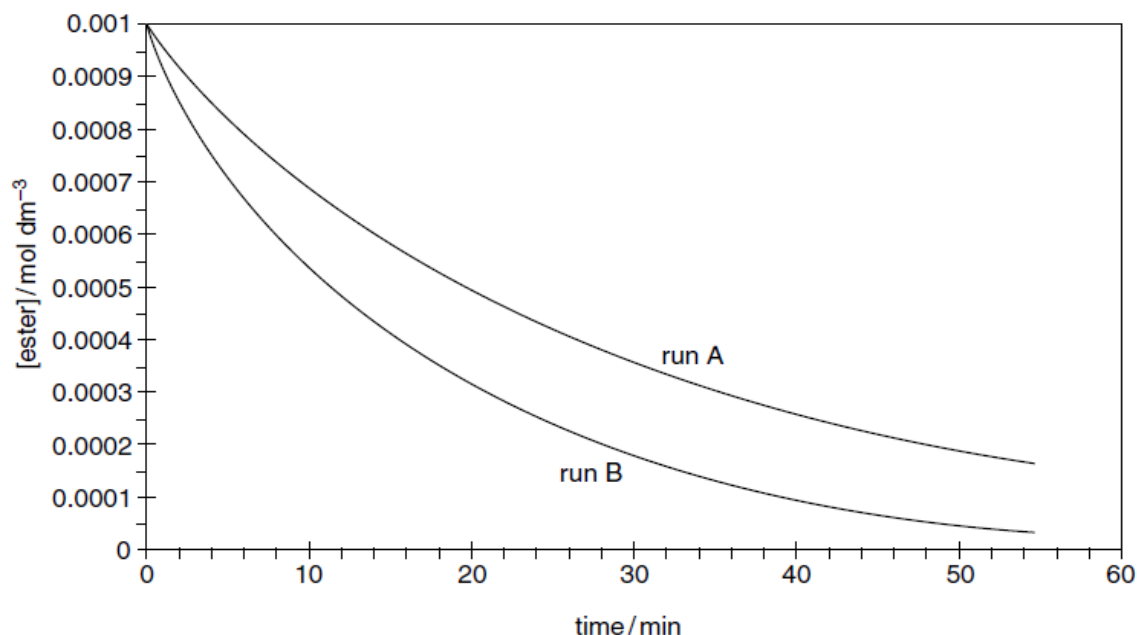
.....

(b) The reaction rate was studied using two solutions of different hydroxide ion concentrations.

run A: $[\text{OH}^-] = 0.20 \text{ mol dm}^{-3}$

run B: $[\text{OH}^-] = 0.40 \text{ mol dm}^{-3}$

The following graphs show how the concentration of the ester, 4-nitrophenyl ethanoate, varied over time in the two runs.



(i) By drawing tangents on the graphs, measure and calculate the initial rates of reaction during the two runs. Give the units in each case.

initial rate of run A

initial rate of run B

(ii) By using your results, calculate the overall order of reaction with respect to $[\text{OH}^-]$.

.....

(iii) From the curve of run B, determine the order of reaction with respect to $[\text{ester}]$.

.....

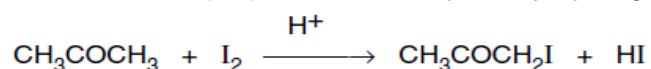
(iv) Explain how you arrived at your answer in (iii).

(v) Write a rate equation for the reaction.

(vi) Use your rate equation and the initial rates to calculate a value for the rate constant, including units.

(June 2002)

Q2 The reaction between iodine and propanone is catalysed by hydrogen ions.

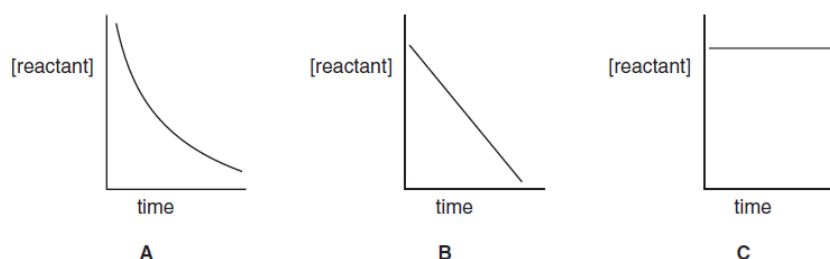


The reaction is found to be first order with respect to $[\text{CH}_3\text{COCH}_3]$ and with respect to $[\text{H}^+]$, and zero order with respect to $[\text{I}_2]$.

(a) What do you understand by the term *order of reaction*?

(b) Construct a rate equation for the reaction.

The following sketches show three ways in which the concentration of reagents might vary during the reaction.

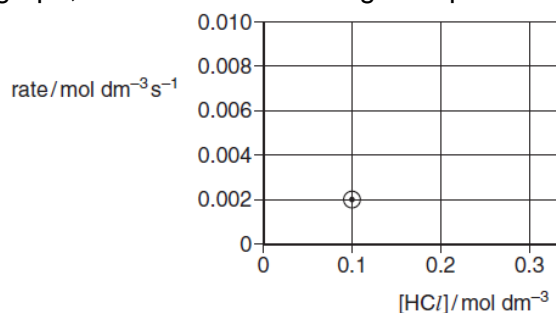


(c) Which of the above graphs correctly describes how the concentration of reactant changes with time for

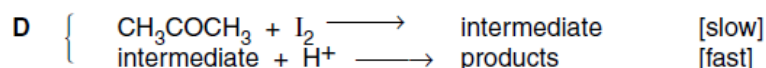
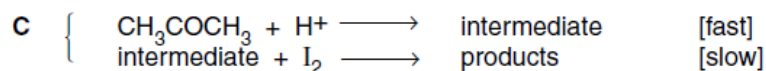
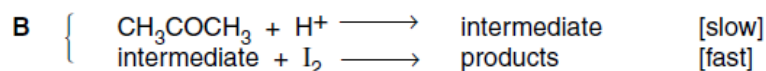
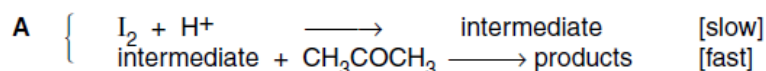
(i) the propanone concentration, _____

(ii) the iodine concentration? _____

(d) When carried out in $0.1 \text{ mol dm}^{-3} \text{ HC/}$ solution, the rate was found to be $0.002 \text{ mol dm}^{-3} \text{ s}^{-1}$. Predict the rate of reaction in $0.2 \text{ mol dm}^{-3} \text{ HC/}$ and in $0.3 \text{ mol dm}^{-3} \text{ HC/}$ solution. Plot your figures on the following graph, and draw a line through the points.



(e) Only one of the following outline reaction mechanisms is consistent with the observed kinetics.



Decide which mechanism is consistent, explaining the reasons for your choice.

Mechanism letter (A, B, C or D) _____

Reasons.....

.....

.....

(f) When the starting concentrations of propanone, iodine and H^+ were 0.20 mol dm^{-3} , 0.01 mol dm^{-3} and 0.5 mol dm^{-3} respectively, the rate of decrease of $[I_2]$ was found to be $3.3 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$.

(i) Suggest a method you could use to measure $[I_2]$.

.....

(ii) Use these figures and your rate equation in part (b) to calculate a value for the rate constant k .

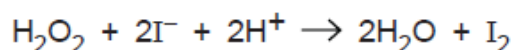
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(iii) What are the units of k ?

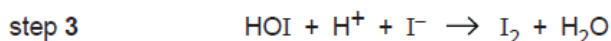
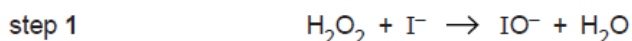
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(Nov 2003)

Q3 In the late 19th century the two pioneers of the study of reaction kinetics, Vernon Harcourt and William Esson, studied the rate of the reaction between hydrogen peroxide and iodide ions in acidic solution.



This reaction is considered to go by the following steps.



The general form of the rate equation is as follows.

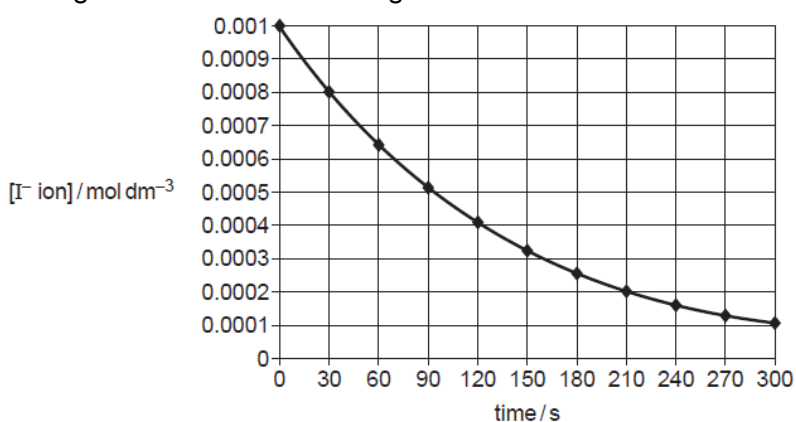
$$\text{rate} = k[H_2O_2]^a[I^-]^b[H^+]^c$$

(a) Suggest how the appearance of the solution might change as the reaction takes place.

(b) Suggest values for the orders a , b and c in the rate equation for each of the following cases.

case	numerical value		
	a	b	c
step 1 is the slowest overall			
step 2 is the slowest overall			
step 3 is the slowest overall			

A study was carried out in which both $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$ were kept constant at 0.05 mol dm^{-3} , and $[\text{I}^-]$ was plotted against time. The following curve was obtained.



To gain full marks for the following answers you will need to draw relevant construction lines on the graph opposite to show your working. Draw them using a pencil and ruler.

(c) Calculate the initial rate of this reaction and state its units.

rate = units

(d) Use half-life data calculated from the graph to show that the reaction is first order with respect to $[\text{I}^-]$.

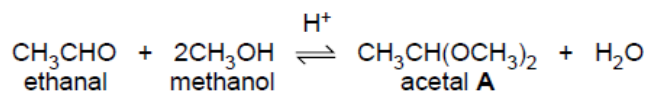
(e) Use the following data to deduce the orders with respect to $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$, explaining your reasoning.

$[\text{H}_2\text{O}_2] / \text{mol dm}^{-3}$	$[\text{H}^+] / \text{mol dm}^{-3}$	relative rate
0.05	0.05	1.0
0.07	0.05	1.4
0.09	0.07	1.8

order with respect to $[H_2O_2] = \dots\dots\dots$ order with respect to $[H^+] = \dots\dots\dots$
 (f) From your results, deduce which of the three steps is the slowest (rate determining) step.

.....
 (Nov 2008)

Q4 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.



(a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

experiment number	$[\text{CH}_3\text{CHO}]$ / mol dm ⁻³	$[\text{CH}_3\text{OH}]$ / mol dm ⁻³	$[\text{H}^+]$ / mol dm ⁻³	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

(i) Use the data in the table to determine the order with respect to each reactant.

order with respect to $[\text{CH}_3\text{CHO}] \dots\dots\dots$

order with respect to $[\text{CH}_3\text{OH}] \dots\dots\dots$

order with respect to $[\text{H}^+] \dots\dots\dots$

(ii) Use your results from part (i) to write the rate equation for the reaction.

.....
 (iii) State the units of the rate constant in the rate equation

(iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm⁻³.

relative rate =

(b) The concentration of the acetal product was measured when experiment number 1 was allowed to reach equilibrium. The result is included in the following table.

	$[\text{CH}_3\text{CHO}]$ / mol dm ⁻³	$[\text{CH}_3\text{OH}]$ / mol dm ⁻³	$[\text{H}^+]$ / mol dm ⁻³	[acetal A] / mol dm ⁻³	$[\text{H}_2\text{O}]$ / mol dm ⁻³
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20-x)			x	
at equilibrium				0.025	

(i) Complete the second row of the table in terms of **x**, the concentration of acetal **A** at equilibrium. You may wish to consult the chemical equation opposite.

(ii) Using the [acetal A] as given, $0.025 \text{ mol dm}^{-3}$, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.

(iii) Write the expression for the equilibrium constant for this reaction, K_c , stating its units.

$K_c = \dots\dots\dots$ units = $\dots\dots\dots$

(iv) Use your values in the third row of the table to calculate the value of K_c .

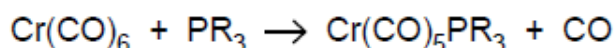
$K_c = \dots\dots\dots$

(Nov 2011 P42)

Q5 (a) (i) What is meant by the term *ligand* as applied to the chemistry of the transition elements?

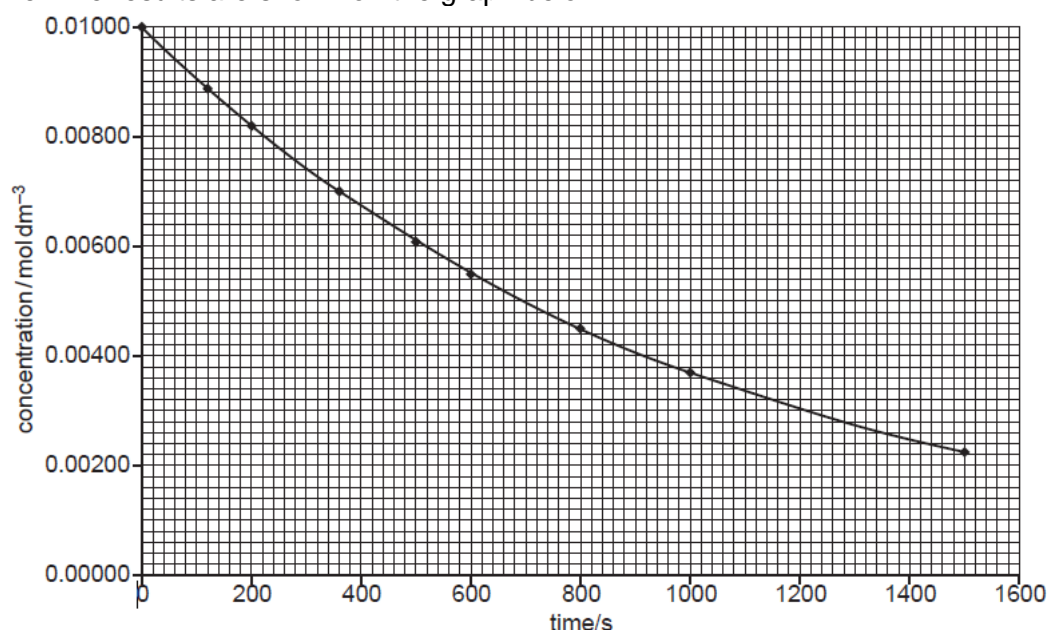
(ii) Describe the type of bonding that occurs between a ligand and a transition element.

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.



Two separate experiments were carried out to study the rate of this reaction.

In the first experiment, the ligand PR_3 was in a large excess and $[\text{Cr}(\text{CO})_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $\text{Cr}(\text{CO})_6$ was in a large excess, and $[\text{PR}_3]$ was measured with time. The following results were obtained.

time/s	$[\text{PR}_3]/\text{mol dm}^{-3}$
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

(ii) Use the graphs to determine the order of reaction with respect to $\text{Cr}(\text{CO})_6$ and PR_3 . In each case explain how you arrived at your answer.

$\text{Cr}(\text{CO})_6$

.....

PR_3

.....

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

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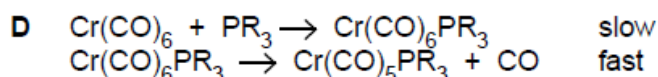
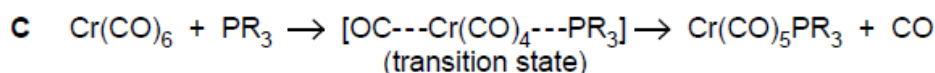
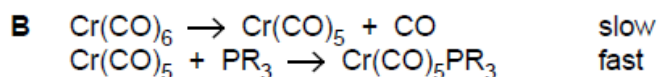
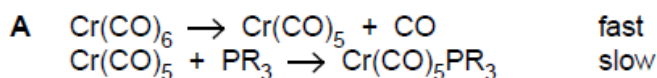
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(iv) State the units of the rate constant.

.....

(v) Four possible mechanisms for this reaction are given below. Draw a **circle** around the letter next to the **one** mechanism which is consistent with the rate equation you have written in (iii).



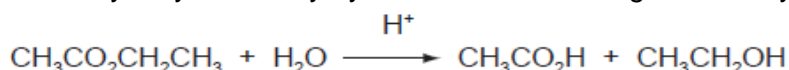
Explain your answer.

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(Nov 2011 P43)

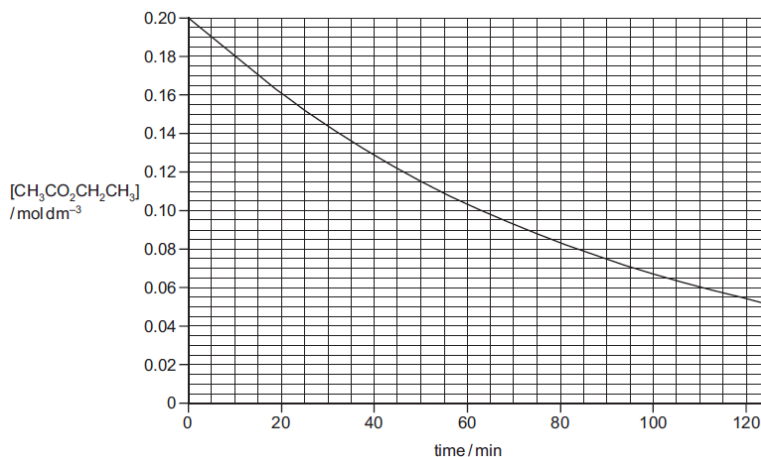
Q6 Ethyl ethanoate is hydrolysed slowly by water in the following acid-catalysed reaction.



The concentration of ethyl ethanoate was determined at regular time intervals as the reaction progressed.

Two separate experiments were carried out, with different $[\text{HC}]$ concentrations.

The following graph shows the results of an experiment using $[\text{HC}] = 0.1 \text{ mol dm}^{-3}$.



(a) When the experiment was carried out using $[HCl] = 0.2 \text{ mol dm}^{-3}$, the following results were obtained.

time/min	$[CH_3CO_2CH_2CH_3]$ /mol dm ⁻³
0	0.200
10	0.160
25	0.115
50	0.067
75	0.038
100	0.022
125	0.013

(i) Plot these data on the axes above, and draw a line of best fit.

(ii) Use one of the graphs to show that the reaction is first order with respect to $CH_3CO_2CH_2CH_3$. Show all your working, and show clearly any construction lines you draw on the graphs.

(iii) Use the graphs to calculate the order of reaction with respect to HCl .

Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

(b) (i) Why is it **not** possible to determine the order of reaction with respect to water in this experiment?

.....

(ii) Although $[CH_3CO_2CH_2CH_3]$ decreases during each experiment, $[HCl]$ remains the same as its initial value. Why is this?

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(June 2013 P43)