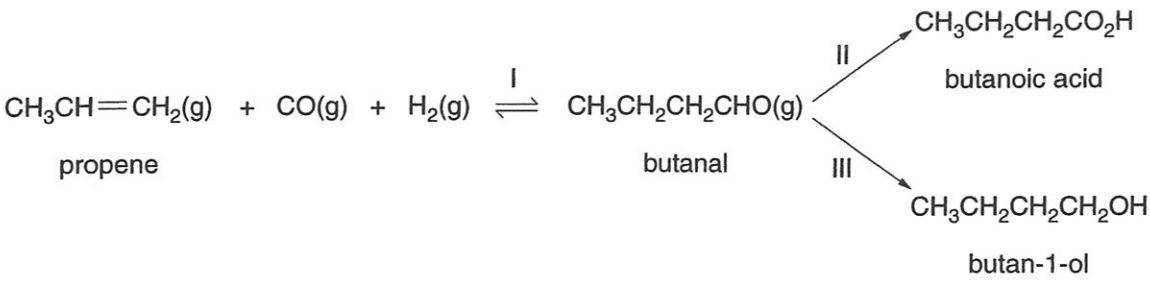
PAPER 3

Answer the following questions.

1 The "OXO" reaction (reaction I in the scheme below) is industrially important for making alcohols, aldehydes and carboxylic acids. For example, butan-1-ol, butanal and butanoic acid can all be synthesised from propene, C_3H_6, according to the following scheme.



(a) Write an expression for K_p for reaction I, stating its units. [2]

(b) When an equimolar mixture of C_3H_6, CO and H_2 at an initial total pressure of 120 atm is allowed to reach equilibrium at 500 K, the partial pressure of butanal is found to be 39.6 atm.

(i) Calculate the equilibrium partial pressures of C_3H_6, CO and H_2.

(ii) Hence calculate a value for K_p at 500 K.

(iii) Suggest, with a reason, whether or not a higher pressure would favour the formation of butanal. [3]

(2007 P3 Q1a,bi-iii)

2 **(a)** One molecule of haemoglobin can bind up to four molecules of oxygen, according to the following equation.

$$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$$

(i) Write an expression for K_c for this reaction, stating its units.

(ii) Experiments have shown that when the $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}, the concentrations of Hb and $Hb(O_2)_4$ are equal.

Use this information to calculate a value of K_c.

(iii) Use your value of K_c to calculate the $[O_2]$ necessary for 99% of the Hb to be converted to $Hb(O_2)_4$.

[6]

(b) Myoglobin, Mb, is an oxygen-carrier protein that occurs in muscle fibres. It has a higher affinity for O_2 than does Hb, but only binds one O_2 molecule per Mb molecule.

$$Mb(aq) + O_2(aq) \rightleftharpoons MbO_2(aq) \qquad K_c = 1 \times 10^6 \text{ mol}^{-1}\text{dm}^3$$

Calculate the percentage of MbO_2 in an Mb-MbO_2 mixture when $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}. [2]

(2009 P3 Q1c,d)

SECTION 1 PHYSICAL CHEMISTRY

TOPIC 7.2 Ionic Equilibria

PAPER 1

Section A

For each question there are four possible answers, A, B, C, and D. Choose the one you consider to be correct.

1 Values for the ionic product of water, K_w, at two different temperatures are given below.

temperature / °C	K_w / mol^2 dm^{-6}
25	1.00×10^{-14}
30	1.44×10^{-14}

What is correct for pure water at 30 °C?

A $[H^+] > [OH^-]$

B $[H^+] = 1.44 \times 10^{-7}$ mol dm^{-3}

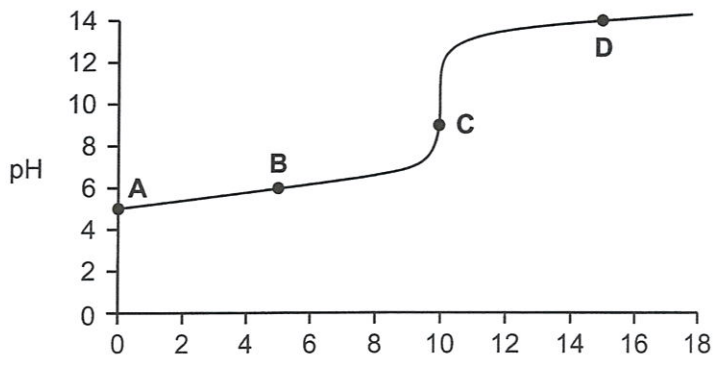
C pH < 7

D pH = 7

(2007 P1 A11)

2 The pH change when 0.100 mol dm^{-3} NaOH is added dropwise to 10.0 cm^3 of a 0.100 mol dm^{-3} solution of a weak acid is shown below.

Where on the graph does pH = pK_a where K_a is the acid dissociation constant of the weak acid?



(2007 P1 A12)

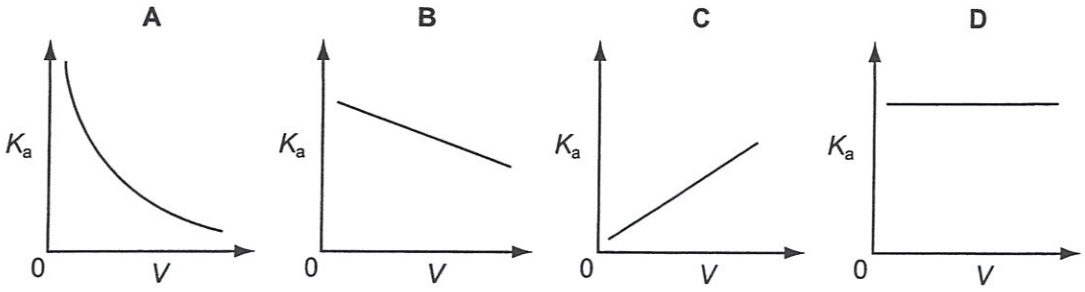
3 The pH of human blood is constant at about 7.40.

Which ion or molecule present in the human body will remove contaminating $H^+(aq)$ ions from the blood to keep the pH constant?

A CO_3^{2-} **B** HCO_3^- **C** H_2CO_3 **D** PO_4^{3-} **(2007 P1 A13)**

4 A 1 mol sample of ethanoic acid is diluted at constant temperature to a volume *V*.

Which diagram shows how K_a, the acid dissociation constant, varies with *V*?



(2008 P1 A11)

5 Soft drinks often have sodium citrate added to them to act as a buffer.

Which statement about buffer solutions is correct?

A The pH of a buffer solution changes slightly when very large amounts of acid or base are added.

B The pH of a buffer solution increases very slightly when small amounts of acid are added.

C The pH of a buffer solution increases very slightly when small amounts of base are added.

D The pH of a buffer solution remains unchanged when small amounts of acid or base are added.

(2011 P1 A11)

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

6 Two students separately have available equal volumes of 0.1 mol dm^{-3} silver nitrate, sodium ethanoate and potassium bromide.

The first student, on mixing the sodium ethanoate and silver nitrate, obtains a white precipitate. On adding potassium bromide to this mixture, the precipitate turns cream.

The second student adds the silver nitrate to the potassium bromide and obtains a cream precipitate. On adding the sodium ethanoate to this mixture, there is no further change.

Which statements about these observations are correct?

1 Silver ethanoate is insoluble.

2 Silver bromide is less soluble than silver ethanoate.

3 Ethanoate can oxidise bromide.

(2010 P1 B36)

PAPER 2

Answer all the questions in the space provided.

1 Silver forms a series of halides of general formula Ag*X*. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

salt	solubility /mol dm^{-3}	solubility product /mol^2 dm^{-6}
AgC*l*	1.4×10^{-5}	2.0×10^{-10}
AgBr	7.1×10^{-7}	to be calculated
AgI	8.9×10^{-9}	8.0×10^{-17}

In this question, give **each** of your numerical answers to **one** decimal place.

(a) Write an expression for the solubility product, K_{sp}, of silver bromide.

(b) From the data above, calculate a value for K_{sp} of silver bromide.

K_{sp} = ... mol^2 dm^{-6}

[2]

(2008 P2 Q2a)

PAPER 3

Answer the following questions.

1 **(a)** Write an expression for the acid dissociation constant, K_a, for the weak acid hydrocyanic acid, HCN.

(b) For HCN, $K_a = 4.9 \times 10^{-10}$ mol dm^{-3}. Use this value to calculate $[H^+]$ in a 0.100 mol dm^{-3} solution of HCN, and hence calculate the percentage of HCN molecules that are ionised.

(c) Explain how the addition of solid sodium cyanide, NaCN, will alter the percentage of HCN molecules ionised.

[5]

(2007 P3 Q4a)

2 This question is about hydroxyacids.
One of the simplest hydroxyacids is lactic acid, 2-hydroxypropanoic acid. It can be made in the laboratory by the following route.

$$CH_3CHO \xrightarrow{\text{I}} CH_3CH(OH)CN \xrightarrow{\text{II}} CH_3CH(OH)CO_2H$$

lactic acid

Lactic acid is a weak acid in water, with $K_a = 1.38 \times 10^{-4}$ mol dm^{-3}.

(a) Calculate the pH of a 0.20 mol dm^{-3} solution of lactic acid. [2]

(b) **(i)** Explain what is meant by a buffer solution.

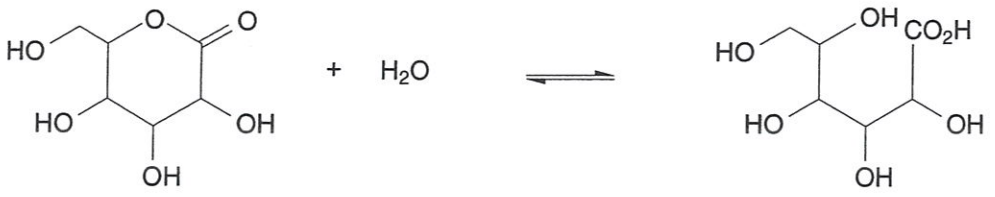
(ii) Calculate the pH of a buffer solution containing 0.20 mol dm^{-3} lactic acid and 0.30 mol dm^{-3} sodium lactate.

(iii) Write an equation for the reaction that occurs when a drop of HC*l* is added to this buffer solution.

[4]

(2008 P3 Q3b,c)

3 The addition of glucono-delta-lactone, GDL, to soy milk produces a soft form of dofu due to a gradual acidification of the mixture. In aqueous solution the following equilibrium is slowly set up.



GDL **gluconic acid**

When 1.00 g of GDL (M_r = 178) was dissolved in 50.0 cm^3 water and the solution allowed to reach equilibrium, the concentration of gluconic acid was found to be 0.0670 mol dm^{-3}.

Write an expression for K_c for the equilibrium above, and use the data given to calculate its value. You can assume that $[H_2O]$ = 55.5 mol dm^{-3} throughout. [2]

(2010 P3 Q2biv)

4 Dicarboxylic acids can ionise in stages.

$$HO_2C{-}(CH_2)_n{-}CO_2H \xrightarrow[pK_1]{-H^+} HO_2C{-}(CH_2)_n{-}CO_2^- \xrightarrow[pK_2]{-H^+} {}^-O_2C{-}(CH_2)_n{-}CO_2^-$$

The following table compares the pK_a values of one of these dicarboxylic acids with that of ethanoic acid.

acid	formula	pK_1	pK_2
ethanoic	CH_3CO_2H	4.76	–
malonic	$HO_2CCH_2CO_2H$	2.85	5.70

(a) Calculate the pH of a 0.10 mol dm^{-3} solution of malonic acid (ignore the effect of pK_2 on the pH). [2]

(b) Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid.
Briefly describe how you have calculated the various key points on the curve. [3]

(2011 P3 Q2biii,iv)

5 Parts of this question are concerned with the salts of the Group II elements. You may find the following information to be useful.

- Salts of Group II elements with divalent anions (i.e. those with a charge of 2–) tend to be insoluble.
- These salts become more insoluble down the group.
- Salts of Group II elements with monovalent anions tend to be soluble.
- The hydrogencarbonates of Group II elements do not exist in the solid state.
- Carbon dioxide reacts with solutions of carbonate ions according to the following equilibrium.

$$CO_2(g) + H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons 2HCO_3^-(aq)$$

You should use the above information and the ideas behind Le Chatelier's principle and solubility product, K_{sp}, to explain your answers.

(a) Mineral waters often contain the chlorides and hydrogencarbonates of Group II metals. Solutions of these salts are formed when rainwater percolates through the rocks of hills and mountains, and emerges as springs in the hillside.

One such mineral water has the following composition.

ion	concentration /g dm^{-3}
Ca^{2+}	0.0080
Mg^{2+}	0.0049
Cl^-	0.0071
HCO_3^-	0.0366

(i) Calculate the concentrations of these ions in mol dm^{-3}, and hence suggest the formulae of the salts that could exist in the solution, and their relative amounts.

When a sample of the mineral water was partially evaporated, a mixture of white solids was formed, and a solution containing a single salt remained.

(ii) Suggest the identity of the **first** solid to be precipitated. Explain your answer.

(iii) Suggest the composition of the rock through which the rainwater had percolated, and explain how the mineral water had been formed. [9]

(b) One of the most common phosphorus-containing rocks is fluorapatite, $Ca_5(PO_4)_3F$. The first step in the production of phosphate as a mineral supplement for animal feed is defluorination, which is achieved by heating the rock in a rotary kiln at 1500 °C with silica and steam.

The following equation represents this process.

$$\underset{\text{fluorapatite}}{6Ca_5(PO_4)_3F} + \boldsymbol{a}SiO_2 + \boldsymbol{b}H_2O \rightarrow \boldsymbol{c}SiF_4 + \boldsymbol{d}HF + \boldsymbol{e}CaO + \underset{\text{calcium phosphate}}{\boldsymbol{f}Ca_3(PO_4)_2}$$

(i) Complete the balancing of the above equation by deducing values for ***a***, ***b***, ***c***, ***d***, ***e*** and ***f***.

(ii) Write the expression for the solubility product of calcium phosphate, stating its units.

(iii) The value of K_{sp} for calcium phosphate is 1×10^{-26}. Calculate $[Ca^{2+}]$ in a saturated solution of calcium phosphate. Show your working clearly. [5]

(2011 P3 Q3a,b)

SECTION I PHYSICAL CHEMISTRY

TOPIC 8 Reaction Kinetics

PAPER 1

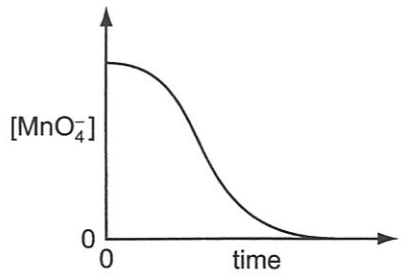
Section A

For each question there are four possible answers, A, B, C, and D. Choose the one you consider to be correct.

1 The reaction of manganate(VII) ions with ethanedioate ions in acid solution may be represented by the following equation.

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

The graph shows concentration of manganate(VII) ions against time for this reaction.



What does the shape of the graph suggest about this reaction?

A It is exothermic.

B It is endothermic.

C It shows first order kinetics.

D It produces its own catalyst. **(2007 P1 A14)**

2 Iodine-131 is a radioactive isotope with a half-life of 8 days. Following the nuclear power plant disaster at Chernobyl in 1986, it was stated that a cloud of vapour containing iodine-131 was formed which would not become safe for 80 days.

Given that radioactive decay is a first-order reaction, what fraction of the isotope would remain after that time?

A $\frac{1}{20}$ **B** $\frac{1}{160}$ **C** $\frac{1}{2^8}$ **D** $\frac{1}{2^{10}}$ **(2008 P1 A13)**