Equilibria

(c) The acid dissociation constant, K_a, of ethanoic acid is 1.75×10^{-5} mol dm^{-3}.

(i) Explain why this value of K_a is

- much larger than that of ethanol, CH_3CH_2OH,

.....

.....

- smaller than that of chloroethanoic acid, $ClCH_2CO_2H$.

.....

.....

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of ethanoic acid.

[4]

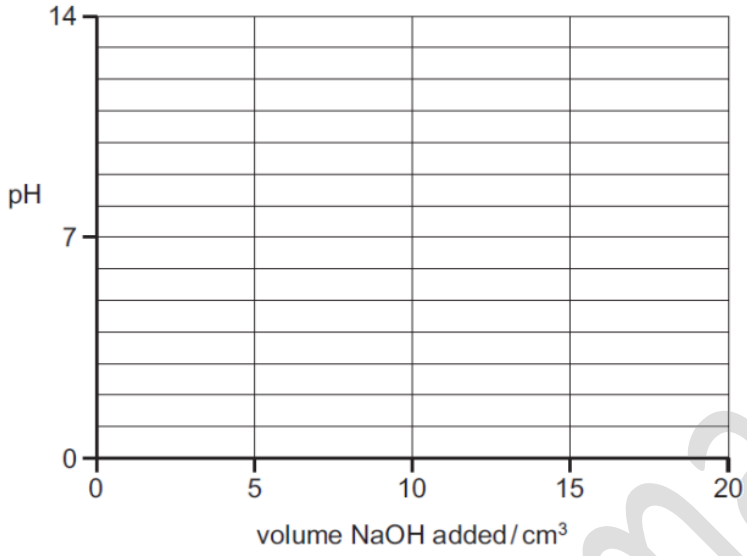
(d) 20.0 cm^3 of 0.100 mol dm^{-3} NaOH were slowly added to a 10.0 cm^3 sample of 0.100 mol dm^{-3} ethanoic acid, and the pH was measured throughout the addition.

(i) Calculate the number of moles of NaOH remaining at the end of the addition.

(ii) Calculate the $[OH^-]$ at the end of the addition.

(iii) Using the expression $K_w = [H^+][OH^-]$ and your value in **(ii)**, calculate $[H^+]$ and the pH of the solution at the end of the addition.

(iv) On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm^3 of 0.100 mol dm^{-3} NaOH. Mark clearly where the end point occurs.



(v) From the following list of indicators, put a tick in the box by the side of the indicator you consider most suitable for this titration.

indicator	pH at which colour changes	place **one tick only** in this column
malachite green	0 - 1	
thymol blue	1 - 2	
bromophenol blue	3 - 4	
thymolphthalein	9 - 10	

[7]

[Total: 15]

s/14/qp42

(ii) Write an expression for the solubility product, K_{sp}, of $PbCl_2$.

.....

(iii) Calculate the value of K_{sp}, including units.

K_{sp} = ... units .....

[5]

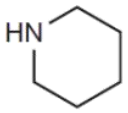
s/14/qp42

(c) **(i)** Write the expression for K_w.

.....

(ii) Use your expression and the value of K_w in the *Data Booklet* to calculate the pH of 0.150 mol dm^{-3} NaOH(aq).

(iii) The pH of a 0.150 mol dm^{-3} solution of piperidine is 11.9.



piperidine

Suggest why this answer differs from your answer in **(c)(ii)**.

.....

.....

(iv) How would you expect the basicity of piperidine to compare to that of ammonia? Explain your reasoning.

.....

.....

[5]

(d) 20.0 cm^3 of 0.100 mol dm^{-3} HC*l* was slowly added to a 10.0 cm^3 sample of 0.150 mol dm^{-3} piperidine. The pH was measured throughout the addition.

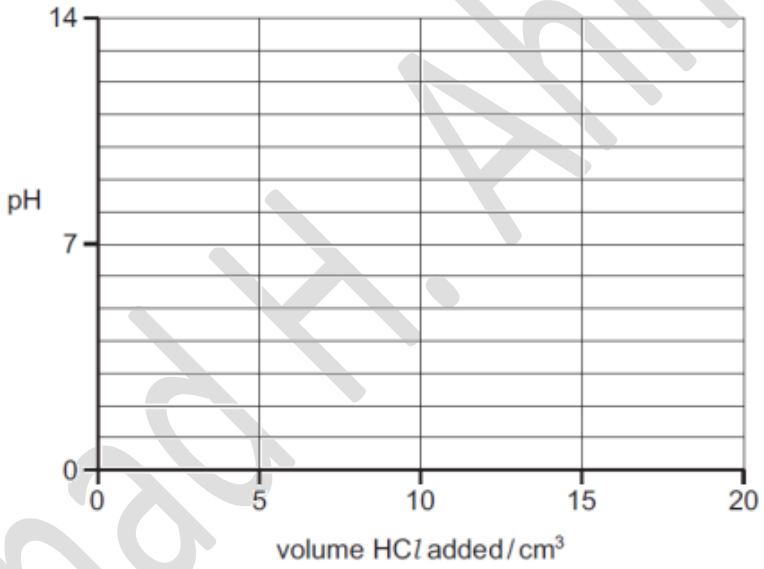
(i) Calculate the number of moles of HC*l* remaining at the end of the addition.

moles of HC*l* = ...

(ii) Hence calculate the $[H^+]$ and the pH at the end of the addition.

pH = ...

(iii) On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm^3 of 0.100 mol dm^{-3} HC*l*. Mark clearly where the end point occurs.



(iv) From the following list of indicators, put a tick in the box by the side of the indicator most suitable for this titration.

indicator	pH at which colour changes	place **one tick only** in this column
A	0 - 1	
B	3 - 4	
C	11 - 12	
D	13 - 14	

[6]

[Total: 16]

s/14/qp41

(b) A buffer solution is to be made using 1.00 mol dm^{-3} ethanoic acid, CH_3CO_2H, and 1.00 mol dm^{-3} sodium ethanoate, CH_3CO_2Na.
Calculate to the nearest 1 cm^3 the volumes of each solution that would be required to make 100 cm^3 of a buffer solution with pH 5.50.
Clearly show all steps in your working.
K_a (CH_3CO_2H) = 1.79×10^{-5} mol dm^{-3}

volume of 1.00 mol dm^{-3} CH_3CO_2H = ... cm^3

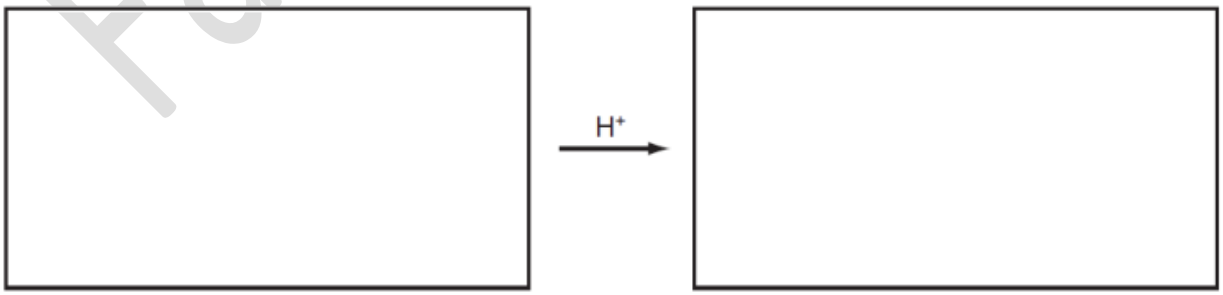
volume of 1.00 mol dm^{-3} CH_3CO_2Na = ... cm^3
[4]

(c) Write an equation to show the reaction of this buffer solution with each of the following.

(i) added HCl .....

(ii) added NaOH .....
[2]

(d) Choose **one** reaction in organic chemistry that is catalysed by an acid, and write the structural formulae of the reactants and products in the boxes below.



[3]

(c) The reaction between Fe^{3+} ions and I^- ions is an equilibrium reaction.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$$

(i) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this reaction.

.....

(ii) Hence state, with a reason, whether there will be more products or more reactants at equilibrium.

.....

.....

(iii) Write the expression for K_c for this reaction, and state its units.

K_c =

units .....

An experiment was carried out using solutions of $Fe^{3+}(aq)$ and $I^-(aq)$ of equal concentrations. 100 cm^3 of each solution were mixed together, and allowed to reach equilibrium.

The concentrations at equilibrium of $Fe^{3+}(aq)$ and $I_2(aq)$ were as follows.

$$[Fe^{3+}(aq)] = 2.0 \times 10^{-4}\ mol\ dm^{-3}$$
$$[I_2(aq)] = 1.0 \times 10^{-2}\ mol\ dm^{-3}$$

(iv) Use these data, together with the equation given in **(c)**, to calculate the concentrations of $Fe^{2+}(aq)$ and $I^-(aq)$ at equilibrium.

$[Fe^{2+}(aq)]$ = ... $mol\ dm^{-3}$

$[I^-(aq)]$ = ... $mol\ dm^{-3}$

(v) Calculate the K_c for this reaction.

K_c = ...

[8]

s/13/qp41

(d) Phosphate ions in water can be removed by adding a solution containing $Ca^{2+}(aq)$ ions, which form a precipitate of calcium phosphate, $Ca_3(PO_4)_2$.

(i) Write an expression for the K_{sp} of $Ca_3(PO_4)_2$.

K_{sp} =

(ii) The solubility of $Ca_3(PO_4)_2$ is 2.50×10^{-6} mol dm^{-3} at 298 K.

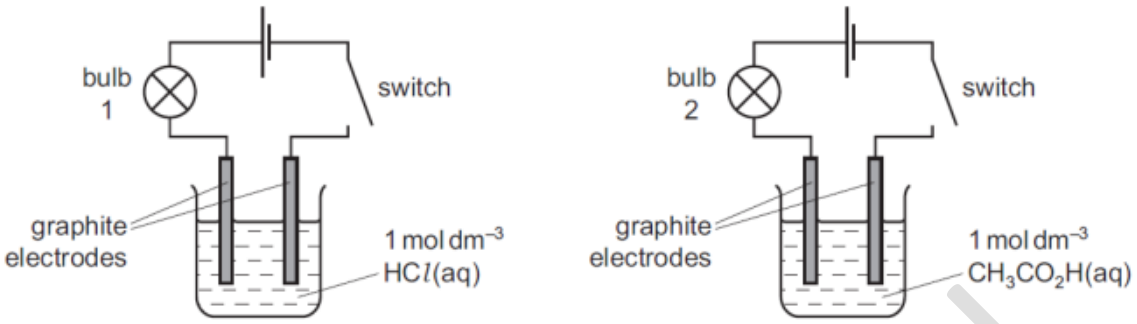
Calculate the solubility product, K_{sp}, of $Ca_3(PO_4)_2$ at this temperature. Include the units.

K_{sp} = ... units .....

[4]

w/14/qp41

4 **(a)** The following circuits were set up using aqueous hydrochloric and aqueous ethanoic acids as electrolytes. Assume that the two circuits were identical apart from the electrolyte.



When the switches were closed, bulb 1 was brighter than bulb 2. Explain why.

.....

.....

.....

..... [2]

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

.....

.....

(ii) Outline how a buffer solution can be prepared from ethanoic acid and a named base.

.....

.....

[4]

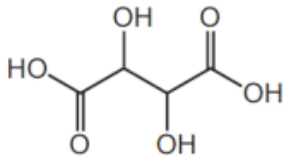
(c) Amino acids such as alanine, $CH_3CH(NH_2)CO_2H$, can act as a buffer solution.
Construct **two** equations to illustrate this.

equation 1

equation 2

[2]

(d) Tartaric acid is present in many plants.



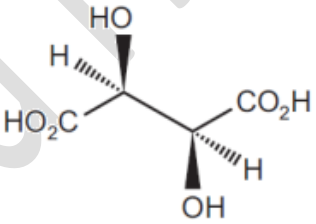
tartaric acid

(i) Tartaric acid has two dissociation constants, K_1 and K_2, for which the pK_a values are 2.99 and 4.40.
Suggest equations showing the two dissociations that give rise to these pK_a values.

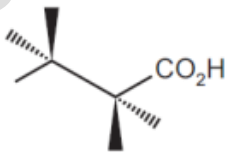
pK_a 2.99

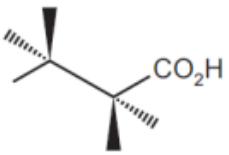
pK_a 4.40

(ii) One stereoisomer of tartaric acid is shown.



Complete the diagrams showing two other stereoisomers of tartaric acid.





[4]

[Total: 12]

w/14/qp43

3 **(a)** **(i)** Using the symbol **HZ** to represent a Brønsted-Lowry acid, write equations which show the following substances acting as Brønsted-Lowry bases.

NH_3 + →

CH_3OH + →

(ii) Using the symbol $\mathbf{B^-}$ to represent a Brønsted-Lowry base, write equations which show the following substances acting as Brønsted-Lowry acids.

NH_3 + →

CH_3OH + →

[4]

(b) State briefly what is meant by the following terms.

(i) reversible reaction

.....

(ii) dynamic equilibrium

.....

.....

[2]

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

.....

.....

.....

(ii) Explain how the working of a buffer solution relies on a reversible reaction involving a Brønsted-Lowry acid such as **HZ** and a Brønsted-Lowry base such as $\mathbf{Z^-}$.

.....

.....

.....

.....

[4]

(d) Propanoic acid, $CH_3CH_2CO_2H$, is a weak acid with $K_a = 1.34 \times 10^{-5}$ mol dm^{-3}.

(i) Calculate the pH of a 0.500 mol dm^{-3} solution of propanoic acid.

Buffer solution **F** was prepared by adding 0.0300 mol of sodium hydroxide to 100 cm^3 of a 0.500 mol dm^{-3} solution of propanoic acid.

(ii) Write an equation for the reaction between sodium hydroxide and propanoic acid.

.....

(iii) Calculate the concentrations of propanoic acid and sodium propanoate in buffer solution **F**.

[propanoic acid] = ... mol dm^{-3}

[sodium propanoate] = ... mol dm^{-3}

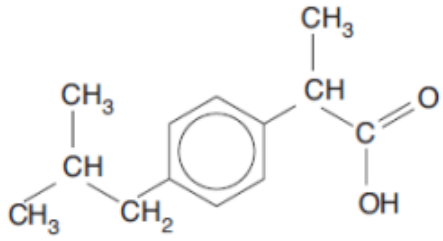
(iv) Calculate the pH of buffer solution **F**.

pH = ...

[6]

w/13/qp41

2 Ibuprofen is one of the most commonly used non-steroidal anti-inflammatory drugs, used to treat chronic arthritic pain caused by inflammation of the joints.



ibuprofen

(a) (i) Draw a circle around any chiral centre(s) in the above structure.

(ii) Write down the molecular formula of ibuprofen.

.....

(iii) Calculate the M_r of ibuprofen and use it to calculate how many grams are needed to make 100 cm^3 of a 0.15 mol dm^{-3} solution.

.....

.....

.....

(iv) Vigorous oxidation of ibuprofen produces a dibasic acid **A**. A solution containing 0.10 g of **A** required 12.0 cm^3 of 0.10 mol dm^{-3} NaOH for neutralisation.

Suggest a structure for **A**, showing your working.

.....

[7]

(b) The K_a value for ibuprofen is 6.3×10^{-6} mol dm^{-3}.

(i) Write an expression for K_a.

.....

(ii) Use the K_a value to calculate the pH of a 0.15 mol dm^{-3} solution of ibuprofen.

.....

.....

[3]

(c) To avoid problems with digestive irritation over a long period of use, research is being carried out into ways of administering ibuprofen using skin patches. For this use the compound is dissolved in a hydrophilic gel which acts as a buffer.

(i) What do you understand by the term *buffer*?

.....

.....

The buffer used in the pharmaceutical preparation is a solution containing Na_2HPO_4 and NaH_2PO_4. These salts contain the HPO_4^{2-} and $H_2PO_4^-$ ions respectively.

(ii) Write equations to show how this buffer reacts with

H^+ ions, ...

OH^- ions. .....

(iii) A buffer solution containing equal concentrations of the two sodium phosphate salts has a pH of 7.20.

Calculate the pH of a pharmaceutical preparation containing 0.002 mol dm^{-3} of Na_2HPO_4 and 0.005 mol dm^{-3} of NaH_2PO_4.

[5]

[Total: 15]

w/06/qp4

1 Sulphuric acid is a strong dibasic acid, which ionises in solution as follows.

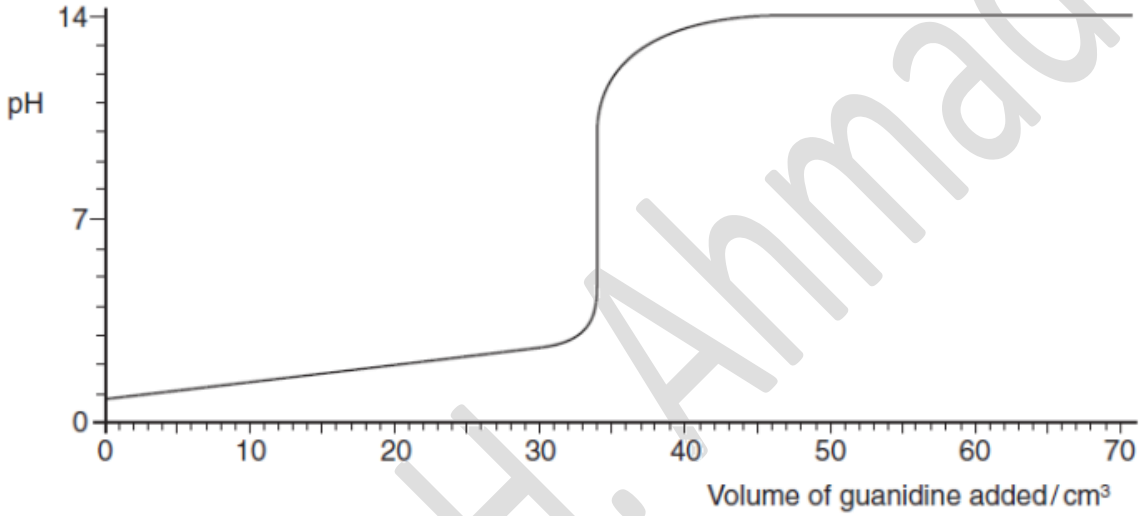
$$H_2SO_4(aq) \rightleftharpoons 2H^+(aq) + SO_4^{2-}(aq)$$

(a) The organic base guanidine contains carbon, nitrogen and hydrogen. Its reaction with acids can be represented as follows.

$$B(aq) + H^+(aq) \rightleftharpoons BH^+(aq)$$

where *B* represents the molecule of guanidine.

When a 25.0 cm^3 sample of dilute sulphuric acid was titrated against a solution of guanidine, the following titration curve was obtained.



Use this curve to answer the following questions.

(i) Is guanidine a strong or a weak base? Explain your answer.

.....

.....

(ii) The pH at the start of the titration was 0.70. Calculate the $[H^+]$, and hence the concentration of sulphuric acid, at the start of the titration.

.....

.....

.....

.....

(iii) Calculate the concentration of guanidine in the solution in mol dm^{-3}.

.....

.....

.....

(iv) The guanidine solution contained 8.68 g of the base per dm^3. Use your answer to **(iii)** calculate the M_r of guanidine.

..... [6]

(b) One of the major industrial uses of sulphuric acid is to convert phosphate rock (calcium fluorophosphate(V)) into 'superphosphate' for use as a fertiliser. The process can be represented by the following partially balanced equation.

$$2\,Ca_5(PO_4)_3F + 7H_2SO_4 \longrightarrow \text{.....}\,CaSO_4 + \text{.....}\,\underset{\text{'superphosphate'}}{Ca(H_2PO_4)_2} + \text{.....}\,HF$$

(i) Balance the above equation.

(ii) Use your balanced equation to calculate the mass of H_2SO_4 required to manufacture 1.0 kg of superphosphate fertiliser.

.....

.....

.....

..... [4]

(c) Solutions of hydrogenphosphates make useful buffers for biochemical experiments.

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

(i) Explain what is meant by the term *buffer solution*.

.....

.....

(ii) Calculate the pH of a buffer solution that contains 0.20 mol dm^{-3} NaH_2PO_4 and 0.10 mol dm^{-3} Na_2HPO_4. [K_a ($H_2PO_4^-$) = 6.3×10^{-8} mol dm^{-3}]

.....

.....

..... [3]

[Total: 13]

2 **(a)** Methanoic acid, HCO_2H, is a weak acid, with $K_a = 1.77 \times 10^{-4}$ mol dm^{-3}.

(i) Write an expression for the K_a of methanoic acid.

.....

(ii) Use your expression to calculate the $[H^+]$ in a 0.0500 mol dm^{-3} solution of methanoic acid.

.....

(iii) Calculate the percentage of HCO_2H molecules that are ionised in this solution.

(iv) Calculate the pH of this solution.

.....

[4]

(b) Calculate the pH of a 0.0500 mol dm^{-3} solution of the strong acid HCl.

.....[1]

(c) Both HCO_2H and HCl react with powdered magnesium metal, giving off hydrogen gas. For a fixed amount of magnesium, the rate equation for the reaction is as follows.

$$\text{rate} = k[H^+(aq)]$$

(i) Write an equation for the reaction between HCO_2H and Mg.

.....

When 20.0 cm^3 of a 0.0500 mol dm^{-3} solution of either acid is reacted with an excess of powdered magnesium, the same volume of hydrogen is given off, but the methanoic acid solution reacts much more slowly than the hydrochloric acid.

(ii) Calculate the volume of hydrogen given off.

.....

(iii) Explain why the hydrogen is evolved more slowly from the methanoic acid solution.

.....

.....

(iv) Explain why, eventually, the methanoic acid solution produces just as much hydrogen as the hydrochloric acid solution.

.....

.....

.....[5]

[Total : 10]

w/03/qp4

2 Monuments made of marble or limestone, such as the Taj Mahal in India and the Mayan temples in Mexico, are suffering erosion by acid rain. The carbonate stone is converted by the acid rain into the relatively more soluble sulphate.

$$CaCO_3(s) + \underset{\text{acid rain}}{H_2SO_4(aq)} \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

(a) (i) Write an expression for the solubility product, K_{sp}, of $CaSO_4$, stating its units.

.....

(ii) The K_{sp} of $CaSO_4$ has a numerical value of 3×10^{-5}. Use your expression in **(i)** to calculate $[CaSO_4]$ in a saturated solution.

.....

(iii) Hence calculate the maximum loss in mass of a small statue if 100 dm^3 of acid rain falls on it. Assume the statue is made of pure calcium carbonate, and that the acid rain becomes saturated with $CaSO_4$.

.....

.....

.....

[5]

(b) The life of such monuments is now being extended by treating them with a mixture of urea and barium hydroxide solutions. After soaking into the pores of the carbonate rock, the urea gradually decomposes to ammonia and carbon dioxide. The carbon dioxide then reacts with the barium hydroxide to form barium carbonate.

$$(NH_2)_2CO(aq) + H_2O(l) \longrightarrow 2NH_3(g) + CO_2(g)$$

$$Ba(OH)_2(aq) + CO_2(g) \longrightarrow BaCO_3(s) + H_2O(l)$$

Acid rain then converts the barium carbonate to its sulphate.

$$BaCO_3(s) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + H_2O(l) + CO_2(g)$$

Barium sulphate is much less soluble than calcium sulphate. A saturated solution contains $[Ba^{2+}] = 9.0 \times 10^{-6}$ mol dm^{-3}.

(i) Explain why barium sulphate is less soluble than calcium sulphate.

.....

.....

.....

.....

(ii) Write an expression for the K_{sp} of barium sulphate and use the data to calculate its value.

.....

.....

[4]

(c) (i) Explain what is meant by the term *lattice energy.*

.....

.....

(ii) Predict, with a reason, how the lattice energy of $BaSO_4$ might compare with that of $MgSO_4$.

.....

.....

.....

[3]

s/06/qp4

5 **(a)** Give an expression for K_a as applied to the weak acid RCO_2H.

.....

..... [1]

(b) The K_a values for three carboxylic acids are listed in the table below.

acid	K_a / mol dm^{-3}
CH_3CO_2H	1.8×10^{-5}
$ClCH_2CO_2H$	1.4×10^{-3}
Cl_2CHCO_2H	5.5×10^{-2}

(i) Describe and explain the trend in acid strength illustrated by these values.

.....

.....

.....

.....

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of $ClCH_2CO_2H$.

.....

.....

.....

(iii) Calculate the pK_a value for Cl_2CHCO_2H.

.....

..... [5]

s/05/qp4

2 **(a)** Barium ions are poisonous. Patients with digestive tract problems are sometimes given an X-ray after they have swallowed a 'barium meal', consisting of a suspension of $BaSO_4$ in water. The $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$ is too low to cause problems of toxicity.

(i) Write an expression for the solubility product, K_{sp}, for $BaSO_4$, including its units.

.....

(ii) The numerical value of K_{sp} is 1.30×10^{-10}. Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.

.....

.....

(iii) The numerical value of K_{sp} for $BaCO_3$ (5×10^{-10}) is not significantly higher than that for $BaSO_4$, but barium carbonate is **very** poisonous if ingested. Suggest a reason why this might be so.

.....

.....

[3]

(b) A useful commercial source of magnesium is sea water, where $[Mg^{2+}(aq)]$ is $0.054\,mol\,dm^{-3}$. The magnesium is precipitated from solution by adding calcium hydroxide.

$$Mg^{2+}(aq) + Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + Mg(OH)_2(s)$$

(i) Write an expression for the K_{sp} of $Mg(OH)_2$, including its units.

.....

(ii) The numerical value for K_{sp} is 2.00×10^{-11}. Calculate $[Mg^{2+}(aq)]$ in a saturated solution of $Mg(OH)_2$.

.....

.....

(iii) Hence calculate the maximum percentage of the original magnesium in the seawater that this method can extract.

.....

.....

[5]

s/03/qp4

(f) A solution containing a mixture of tartaric acid and its sodium salt is used as a buffer in some pre-prepared food dishes.
Calculate the pH of a solution containing 0.50 mol dm^{-3} of tartaric acid and 0.80 mol dm^{-3} sodium tartrate.
[K_a(tartaric acid) = 9.3×10^{-4} mol dm^{-3}]

pH = ...
[2]

w/12/qp43

(c) **(i)** Write an expression for K_{sp} of silver sulfate, Ag_2SO_4, including units.

K_{sp} = ... units .....

Using a similar experimental set-up to that illustrated opposite, it is found that [Ag^+] in a saturated solution of Ag_2SO_4 is 1.6×10^{-2} mol dm^{-3}.

(ii) Calculate the value of K_{sp} of silver sulfate.

K_{sp} = ...
[3]

w/12/qp41

(e) Solutions of amino acids are good buffers.

(i) What is meant by the term *buffer*?

.....

(ii) Write an equation to show how a solution of alanine, $CH_3CH(NH_2)CO_2H$, behaves as a buffer in the presence of an acid such as HC*l*(aq).

.....

(iii) Briefly describe how the pH of blood is controlled.

.....

.....

.....

(iv) Calculate the pH of the buffer formed when 10.0 cm^3 of 0.100 mol dm^{-3} NaOH is added to 10.0 cm^3 of 0.250 mol dm^{-3} CH_3CO_2H, whose pK_a = 4.76.

pH = ...

[7]

w/11/qp43

---

2 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.

$$\underset{\text{ethanal}}{CH_3CHO} + \underset{\text{methanol}}{2CH_3OH} \overset{H^+}{\rightleftharpoons} \underset{\text{acetal } \mathbf{A}}{CH_3CH(OCH_3)_2} + H_2O$$

(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.

	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	[acetal **A**] / mol dm^{-3}	$[H_2O]$ / 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 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 = ... units = ...

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

K_c = ...

[9]

w/11/qp41

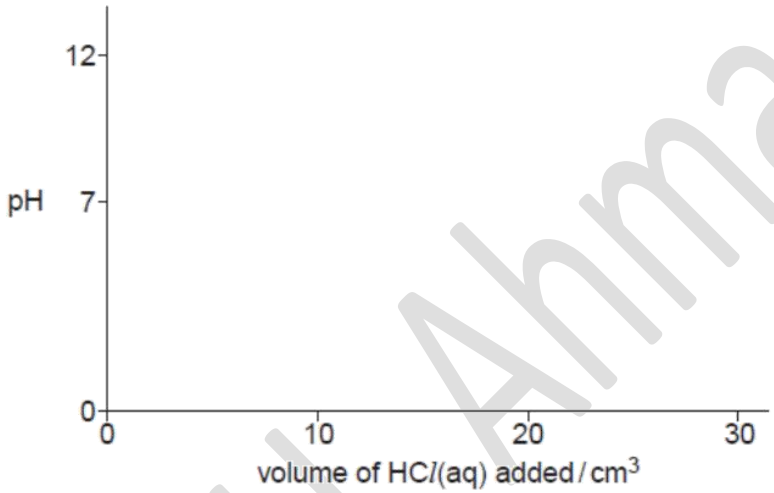
7 When an aqueous solution of compound **G**, $NH_2CH_2CH_2CH_2NH_2$, is titrated with HC*l*(aq), two successive acid-base reactions take place.

(a) Write equations for these two acid-base reactions.

.....

..... [2]

(b) A 0.10 mol dm^{-3} solution of **G** has a pH of 11.3. When 30 cm^3 of 0.10 mol dm^{-3} HC*l* is added to 10 cm^3 of a 0.10 mol dm^{-3} solution of **G**, the final pH is 1.6.
Using the following axes, sketch the pH changes that occur during this addition of HC*l*(aq).



[2]

[Total: 4]

w/10/qp43

(c) Lead(II) chloride is slightly soluble in water.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 2.0 \times 10^{-5}$$

(i) Write an expression for the solubility product, K_{sp} for lead(II) chloride and state its units.

K_{sp} = ... units .....

(ii) Calculate $[Pb^{2+}(aq)]$ in a saturated solution of $PbCl_2$.

.....

.....

An excess of $PbCl_2(s)$ is stirred with $0.50\,mol\,dm^{-3}$ $NaCl$ until equilibrium has been established. The excess $PbCl_2(s)$ is then filtered off.

(iii) Assuming $[Cl^-]$ remains at $0.50\,mol\,dm^{-3}$ throughout, calculate the $[Pb^{2+}(aq)]$ in the remaining solution.

.....

.....

(iv) Suggest an explanation for the difference between this value and the value that you calculated in **(ii)**.

.....

[4]

w/10/qp41

(b) Describe how the use of aqueous silver nitrate and aqueous ammonia can distinguish between aqueous solutions containing chloride, bromide or iodide ions by filling in the following table.

halide	observation when $AgNO_3(aq)$ is added	observation when dilute $NH_3(aq)$ is added	observation when concentrated $NH_3(aq)$ is added
chloride			
bromide			
iodide			

[3]

(c) Silver bromide is sparingly soluble in water.

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5 \times 10^{-13}\ mol^2\ dm^{-6}$$

(i) Calculate $[Ag^+(aq)]$ in a saturated aqueous solution of AgBr.

$[Ag^+(aq)]$ = ... mol dm^{-3}

(ii) State and explain whether AgBr will be less or more soluble in 0.1 mol dm^{-3} KBr than it is in pure water.

.....

.....

[2]

(d) Silver ions form complexes with ammonia and with amines.

$$Ag^+(aq) + 2RNH_2(aq) \rightleftharpoons [Ag(RNH_2)_2]^+(aq)$$

(i) Write an expression for the K_c for this reaction, and state its units.

K_c = ... units .....

K_c has the numerical value of 1.7×10^7 when R = H.

(ii) Using your expression for K_c calculate the $[NH_3(aq)]$ needed to change the $[Ag^+(aq)]$ in a 0.10 mol dm^{-3} solution of silver nitrate to the value that you calculated in **(c)(i)**.

$[NH_3(aq)]$ = ... mol dm^{-3}

(iii) Explain whether you would expect the K_c for the reaction where R = C_2H_5 to be greater or less than that for the reaction where R = H.

.....

.....

[5]

w/09/qp42

(c) Copper forms a complex with chlorine according to the following equilibrium.

$$Cu^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons [CuCl_4]^{2-}(aq)$$

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

K_c = ... units .....

(ii) The numerical value of K_c is 4.2×10^5.
Calculate the $[[CuCl_4]^{2-}]/[Cu^{2+}]$ ratio when $[Cl^-] = 0.20\,mol\,dm^{-3}$.

.....

.....

[3]

[Total: 12]

w/09/qp41

(c) The solubility product, K_{sp}, of magnesium hydroxide has a numerical value of 2.0×10^{-11}.

(i) Write an expression for the K_{sp} of magnesium hydroxide, stating its units.

.....

(ii) Use the value of K_{sp} given to calculate the concentration of $Mg(OH)_2$ in a saturated solution.

.....

.....

(iii) Explain whether magnesium hydroxide would be more or less soluble in $0.1\,mol\,dm^{-3}$ $MgSO_4(aq)$ than in water.

.....

.....

[5]

w/07/qp4

1 **(a)** Use the general formula of a carboxylic acid, RCO_2H, to write equations to explain the following terms.

(i) K_a .....

(ii) pK_a .....

[2]

(b) The pK_a values of four carboxylic acids are listed in the table below.

acid	formula of acid	pK_a
1	$CH_3CH_2CO_2H$	4.9
2	$CH_3CHClCO_2H$	2.8
3	$CH_3CCl_2CO_2H$	1.4
4	$CH_2ClCH_2CO_2H$	4.1

(i) Describe and explain the trend in acid strength shown by acids 1, 2 and 3.

.....

.....

.....

.....

(ii) Suggest an explanation for the difference in the pK_a values for acids 2 and 4.

.....

.....

(iii) Calculate the pH of a 0.010 mol dm^{-3} solution of propanoic acid (acid 1).

.....

.....

.....

[6]

w/07/qp4

1 **(a)** Hydrogen fluoride, HF, behaves as a weak acid in water, with $K_a = 5.6 \times 10^{-4}$ mol dm^{-3}.

Calculate the pH of a 0.050 mol dm^{-3} solution of HF.

pH = ...[2]

(b) Gaseous ammonia and hydrogen fluoride react together to give solid ionic ammonium fluoride.

$$NH_3(g) + HF(g) \rightleftharpoons NH_4F(s) \qquad \Delta H = -147 \text{ kJ mol}^{-1}$$

(i) What *type of reaction* is this?

.....

(iv) The reaction between NH_3 and HF is reversible. What conditions of temperature and pressure would favour the **reverse** reaction, i.e. the dissociation of NH_4F? Explain your answer.

.....

.....

.....

[9]

s/11/qp43

The oxidation takes place in two steps. The initial reaction is that between NO_2 and SO_2.

reaction 1 $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$ $\Delta H = -168\,kJ\,mol^{-1}$

(ii) Write an equation to show how the NO_2 is regenerated in the second step of the oxidation.

.....

(iii) Write an expression for the equilibrium constant, K_p for *reaction 1*, stating its units.

K_p =

units .....

(iv) If equal amounts of $NO_2(g)$ and $SO_2(g)$ are allowed to react at room temperature, it is found that 99.8% of the gases have been converted into products at equilibrium. Calculate a value for K_p.

K_p = ...

(v) The temperature of the atmosphere decreases with height. How will this affect the position of the equilibrium in *reaction 1*? Explain your answer.

.....

.....

[7]

s/11/qp41

2 **(a)** State briefly what is meant by the following terms.

(i) reversible reaction

.....

(ii) dynamic equilibrium

.....

.....

[2]

(b) Water ionises to a small extent as follows.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H = +58\,kJ\,mol^{-1}$$

(i) Write an expression for K_c for this reaction.

.....

(ii) Write down the expression for K_w, the ionic product of water, and explain how this can be derived from your K_c expression in **(i)**.

.....

.....

(iii) State and explain how the value of K_w for hot water will differ from its value for cold water.

.....

.....

[3]

(c) K_w can be used to calculate the pH of solutions of strong and weak bases.

(i) Use the value of K_w in the *Data Booklet* to calculate the pH of $0.050\,mol\,dm^{-3}$ NaOH.

pH = ...

Ammonia ionises slightly in water as follows.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The following expression applies to this equilibrium.

$$[H_2O] \times K_c = [NH_4^+][OH^-]/[NH_3] = 1.8 \times 10^{-5}\,mol\,dm^{-3}$$

(ii) Calculate $[OH^-(aq)]$ in a $0.050\,mol\,dm^{-3}$ solution of NH_3. You may assume that only a small fraction of the NH_3 ionises, so that $[NH_3]$ at equilibrium remains at $0.050\,mol\,dm^{-3}$.

$[OH^-(aq)]$ = ...

(iii) Use the value of K_w in the *Data Booklet*, and your answer in **(ii)**, to calculate $[H^+(aq)]$ in $0.050\,mol\,dm^{-3}$ $NH_3(aq)$.

$[H^+(aq)]$ = ...

(iv) Calculate the pH of this solution.

pH = ...

[6]

[Total: 11]

s/11/qp41

(c) Calcium hydroxide, $Ca(OH)_2$, is slightly soluble in water.

(i) Write an expression for K_{sp} for calcium hydroxide, and state its units.

K_{sp} = units .....

(ii) 25.0 cm^3 of a saturated solution of $Ca(OH)_2$ required 21.0 cm^3 of 0.0500 mol dm^{-3} HC*l* for complete neutralisation.

Calculate the $[OH^-(aq)]$ and the $[Ca^{2+}(aq)]$ in the saturated solution, and hence calculate a value for K_{sp}.

$[OH^-(aq)]$ = ...

$[Ca^{2+}(aq)]$ = ...

K_{sp} = ...

(iii) How would the solubility of $Ca(OH)_2$ in 0.1 mol dm^{-3} NaOH compare with that in water?
Explain your answer.

.....

.....

[6]

s/10/qp43

1 **(a)** Explain what is meant by the *Bronsted-Lowry* theory of acids and bases.

.....

.....

..... [2]

(b) The K_a values for some organic acids are listed below.

acid	K_a/mol dm^{-3}
CH_3CO_2H	1.7×10^{-5}
$ClCH_2CO_2H$	1.3×10^{-3}
Cl_2CHCO_2H	5.0×10^{-2}

(i) Explain the trend in K_a values in terms of the structures of these acids.

.....

.....

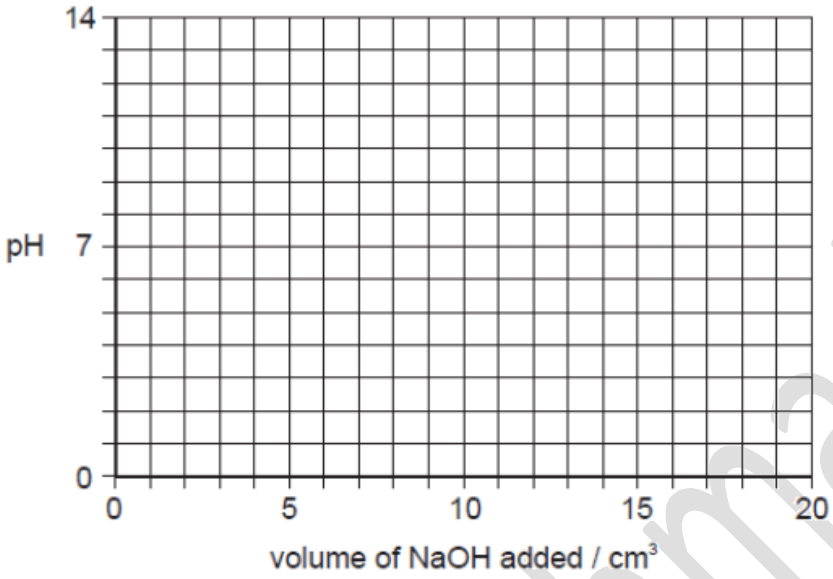
.....

.....

(ii) Calculate the pH of a 0.10 mol dm^{-3} solution of $ClCH_2CO_2H$.

pH = ...

(iii) Use the following axes to sketch the titration curve you would obtain when 20 cm^3 of 0.10 mol dm^{-3} NaOH is added gradually to 10 cm^3 of 0.10 mol dm^{-3} $C\ell CH_2CO_2H$.



[8]

(c) **(i)** Write suitable equations to show how a mixture of ethanoic acid, CH_3CO_2H, and sodium ethanoate acts as a buffer solution to control the pH when either an acid or an alkali is added.

.....

.....

(ii) Calculate the pH of a buffer solution containing 0.10 mol dm^{-3} ethanoic acid and 0.20 mol dm^{-3} sodium ethanoate.

pH = ...

[4]

[Total: 14]

s/09/qp4

CO_2 dissolves in water to form a weakly acidic solution containing the hydrogencarbonate ion.

(iii) Write an equation for the reaction of CO_2 with water, and write an expression for the equilibrium constant, K_c.

.....

.....

(iv) Explain the role of the hydrogencarbonate ion in controlling the pH of blood, illustrating your answer with relevant equations.

.....

.....

.....

[7]

1 **(a)** Write an expression for K_w.

..... [1]

(b) Use your expression to help you calculate the pH of 0.200 mol dm^{-3} NaOH(aq).

.....

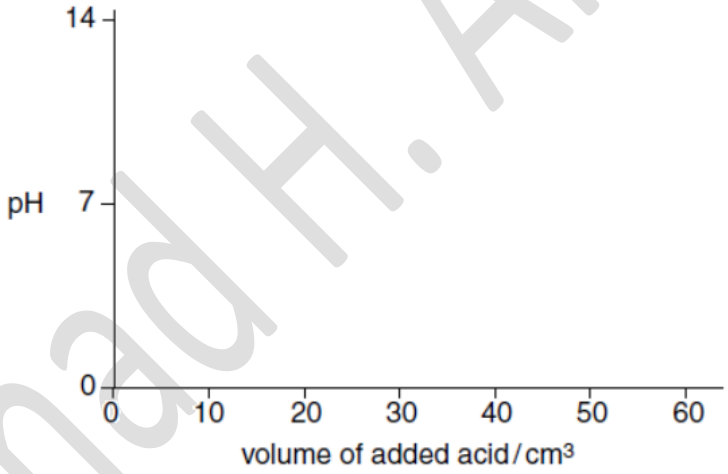
..... [2]

(c) The pH of 0.200 mol dm^{-3} NH_3(aq) is 11.3. Explain why this answer differs from your answer in **(b)**.

.....

..... [1]

(d) A 20.0 cm^3 sample of 0.200 mol dm^{-3} NH_3(aq) was titrated with 0.100 mol dm^{-3} HC*l*. On the following axes, sketch how the pH changes during this titration. Mark clearly where the end point occurs.



[3]

(e) From the following list of indicators, put a tick in the box by the side of the indicator you consider most suitable for this titration.

indicator	pH at which colour changes	place **one tick only** in this column
methyl violet	0.0 - 1.6	
methyl orange	3.1 - 4.4	
bromothymol blue	6.0 - 7.6	
phenolphthalein	8.3 - 10.0	

[1]

(f) A solution containing $NH_3(aq)$ and $NH_4Cl(aq)$ acts as a buffer solution, resisting changes in pH when acids or alkalis are added.

Explain with the help of equations how this mixture acts as a buffer.

.....

.....

.....

..... [2]

[Total: 10]

s/02/qp4