Q1 **(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.

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

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(iii) The numerical value of K_{sp} for $BaCO_3$ ($5 \cdot 10^{-10}$) 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.

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(b) A useful commercial source of magnesium is sea water, where $[Mg^{2+}(aq)]$ is 0.054 $moldm^{-3}$. 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 $Mg(OH)_2$.

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.....

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

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(c) The magnesium ions in seawater are mainly associated with chloride ions.

(i) Use the following $\Delta H_f^{\ominus}$ values to calculate a value for the $\Delta H^{\ominus}$ of the following reaction.

$$MgCl_2(s) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

species	$\Delta H_f^{\ominus}$ /kJ mol^{-1}
$MgCl_2(s)$	–641
$Mg^{2+}(aq)$	–467
$Cl^-(aq)$	–167

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(ii) Use your answer to explain why $MgCl_2$ is very soluble in water.

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(d) All the chlorides of Group II elements are soluble in water. The same is not true of their sulphates. These become less soluble as the group is descended.
Explain qualitatively the variation in solubility of the sulphates of the elements in Group II down the Group from magnesium to barium.

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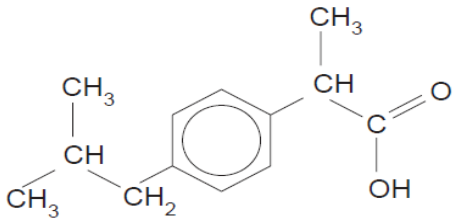
(June 2003)

Q2 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 $moldm^{-3}$ 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 $moldm^{-3}$ NaOH for neutralisation.
Suggest a structure for **A**, showing your working.

(b) The K_a value for ibuprofen is $6.3 \cdot 10^{-6} moldm^{-3}$.
(i) Write an expression for K_a.

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

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.....

(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*?

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.....

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 moldm^{-3} of Na_2HPO_4 and 0.005 moldm^{-3} of NaH_2PO_4.

(Nov 2006)

Q3 **(a)** Explain what is meant by the *Bronsted-Lowry* theory of acids and bases.

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(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.

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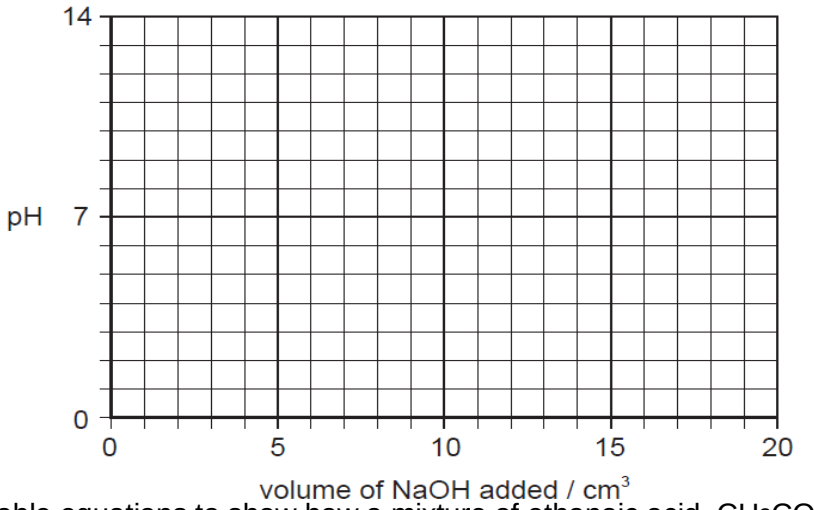
(ii) Calculate the pH of a 0.10 mol dm^{-3} solution of C*l* CH_2CO_2H.

(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*l* CH_2CO_2H.



(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.

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

(June 2009)

Q4 **(a)** State briefly what is meant by the following terms.
(i) reversible reaction

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(ii) dynamic equilibrium

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(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.

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(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)**.

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

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(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 $moldm^{-3}$ NaOH.

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}.

(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} $NH_3(aq)$.

(iv) Calculate the pH of this solution.

(June 2011 P41)

Q5 Solutions of amino acids are good buffers.
(i) What is meant by the term *buffer*?

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(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).

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

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(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.

(Nov 2011 P43)

Q6 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.
$K_a(CH_3CO_2H) = 1.79 \times 10^{-5}$ 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

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

(i) added HC*l* .....

(ii) added NaOH .....

(June 2013 P42)