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 BaSO₄ in water. The [Ba²⁺(aq)] in a saturated solution of BaSO₄ is too low to cause problems of toxicity.

(i) Write an expression for the solubility product, $K_{sp}$, for BaSO₄, including its units.

(ii) The numerical value of $K_{sp}$ is $1.30 \cdot 10^{-10}$. Calculate [Ba²⁺(aq)] in a saturated solution of BaSO₄.

(iii) The numerical value of $K_{sp}$ for BaCO₃ ($5 \cdot 10^{-10}$) is not significantly higher than that for BaSO₄, but barium carbonate is very poisonous if ingested. Suggest a reason why this might be so.

(b) A useful commercial source of magnesium is sea water, where [Mg²⁺(aq)] is 0.054 moldm⁻³. The magnesium is precipitated from solution by adding calcium hydroxide.

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

(i) Write an expression for the $K_{sp}$ of Mg(OH)₂, including its units.

(ii) The numerical value for $K_{sp}$ is $2.00 \times 10^{-11}$. Calculate [Mg²⁺(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.

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

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

$$\text{MgCl}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^- (\text{aq})$$

<table>
<thead>
<tr>
<th>species</th>
<th>$\Delta H^{\circ}$/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂(s)</td>
<td>−641</td>
</tr>
<tr>
<td>Mg²⁺(aq)</td>
<td>−467</td>
</tr>
<tr>
<td>Cl⁻ (aq)</td>
<td>−167</td>
</tr>
</tbody>
</table>
(ii) Use your answer to explain why MgCl₂ is very soluble in water.

(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.

(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.

(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 cm³ 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 cm³ of 0.10 moldm⁻³ NaOH for neutralisation. Suggest a structure for A, showing your working.
(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 $\text{Na}_2\text{HPO}_4$ and $\text{NaH}_2\text{PO}_4$. These salts contain the $\text{HPO}_4^{2-}$ and $\text{H}_2\text{PO}_4^{-}$ ions respectively.

(ii) Write equations to show how this buffer reacts with H$^+$ ions, ................................................................................................................................................................................

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(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 $\text{Na}_2\text{HPO}_4$ and 0.005 moldm$^{-3}$ of $\text{NaH}_2\text{PO}_4$.

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(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.

<table>
<thead>
<tr>
<th>acid</th>
<th>$K_a$/mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{CO}_2\text{H}$</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{Cl}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\text{Cl}_2\text{CHCO}_2\text{H}$</td>
<td>$5.0 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
(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/CH$_2$CO$_2$H.

(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/CH$_2$CO$_2$H.

(c) (i) Write suitable equations to show how a mixture of ethanoic acid, CH$_3$CO$_2$H, 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.

\[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \quad \Delta H = +58 \text{ kJ mol}^{-1} \]

(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 mol dm\(^{-3}\) NaOH.

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Ammonia ionises slightly in water as follows.

\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]

The following expression applies to this equilibrium.

\[ [\text{H}_2\text{O}] \times K_c = [\text{NH}_4^+] [\text{OH}^-]/[\text{NH}_3] = 1.8 \times 10^{-5} \text{ mol dm}^{-3} \]

(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, CH₃CH(NH₂)CO₂H, behaves as a buffer in the presence of an acid such as HCl(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 cm³ of 0.100 mol dm⁻³ NaOH is added to 10.0 cm³ of 0.250 mol dm⁻³ CH₃CO₂H, whose pKₐ = 4.76.

(Nov 2011 P43)

Q6 A buffer solution is to be made using 1.00 mol dm⁻³ ethanoic acid, CH₃CO₂H, and 1.00 mol dm⁻³ sodium ethanoate, CH₃CO₂Na. Calculate to the nearest 1 cm³ the volumes of each solution that would be required to make 100 cm³ of a buffer solution with pH 5.50. Clearly show all steps in your working.

Kₐ(CH₃CO₂H) = 1.79 × 10⁻⁵ mol dm⁻³

volume of 1.00 mol dm⁻³ CH₃CO₂H = ......................... cm³

volume of 1.00 mol dm⁻³ CH₃CO₂Na = ......................... cm³

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

(i) added HCl/ .......................................................... ..........................................................

(ii) added NaOH .......................................................... ...................................................

(June 2013 P42)