2

Answer all the questions in the spaces provided.

1 The oxidation of nitrogen monoxide occurs readily according to the following equation.

\[ \text{NO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{NO}_2(g) \]

The following table shows how the initial rate of this reaction depends on the concentrations of the two reactants.

<table>
<thead>
<tr>
<th>[NO] / mol dm(^{-3})</th>
<th>[O(_2)] / mol dm(^{-3})</th>
<th>initial rate / mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0050</td>
<td>0.0050</td>
<td>0.02</td>
</tr>
<tr>
<td>0.0050</td>
<td>0.0075</td>
<td>0.03</td>
</tr>
<tr>
<td>0.0100</td>
<td>0.0075</td>
<td>0.12</td>
</tr>
</tbody>
</table>

(a) (i) Use the data to determine the order of reaction with respect to each of the reagents.

order with respect to NO ..............................................

order with respect to O\(_2\) ..............................................

(ii) Write the rate equation for the reaction, and use it to calculate a value for the rate constant, \(k\), stating its units.

rate equation ............................................................................................................

numerical value of \(k\) = ..............................................

units of \(k\) ..............................................

(iii) Use your rate equation in (ii) to calculate the rate of reaction when [NO] = [O\(_2\)] = 0.0025 mol dm\(^{-3}\).

rate of reaction =.............................................. [6]
(b) Nitrogen monoxide plays an important catalytic role in the oxidation of atmospheric SO$_2$ in the formation of acid rain.

(i) State the type of catalysis shown in this process.

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(ii) Explain the steps involved in this process by writing equations for the reactions that occur.

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[3]

[Total: 9]
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.

\[
\text{CaCO}_3(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CaSO}_4(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

(a) (i) Write an expression for the solubility product, \(K_{sp}\), of \(\text{CaSO}_4\), stating its units.

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(ii) The \(K_{sp}\) of \(\text{CaSO}_4\) has a numerical value of \(3 \times 10^{-5}\). Use your expression in (i) to calculate \([\text{CaSO}_4]\) in a saturated solution.

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(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 \(\text{CaSO}_4\).

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(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.

\[
(\text{NH}_2)_2\text{CO}(aq) + \text{H}_2\text{O}(l) \rightarrow 2\text{NH}_3(g) + \text{CO}_2(g)
\]

\[
\text{Ba(OH)}_2(aq) + \text{CO}_2(g) \rightarrow \text{BaCO}_3(s) + \text{H}_2\text{O}(l)
\]

Acid rain then converts the barium carbonate to its sulphate.

\[
\text{BaCO}_3(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

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

(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.

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[4]

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

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(ii) Predict, with a reason, how the lattice energy of BaSO$_4$ might compare with that of MgSO$_4$.

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[3]

[Total: 12]
3 (a) A transition element \( X \) has the electronic configuration \([Ar] 4s^2 3d^3\).

(i) Predict its likely oxidation states.

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(ii) State the electronic configuration of the ion \( X^{3+} \).

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(b) Potassium manganate(VII), \( \text{KMnO}_4 \), is a useful oxidising agent in titrimetric analysis.

(i) Describe how you could use a 0.0200 mol dm\(^{-3}\) solution of \( \text{KMnO}_4 \) to determine accurately the \([\text{Fe}^{2+}] \) in a solution. Include in your description how you would recognise the end-point in the titration, and write an equation for the titration reaction.

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(ii) A 2.00 g sample of iron ore was dissolved in dilute \( \text{H}_2\text{SO}_4 \) and all the iron in the salts produced was reduced to \( \text{Fe}^{2+}(\text{aq}) \). The solution was made up to a total volume of 100 cm\(^3\).

A 25.0 cm\(^3\) portion of the solution required 14.0 cm\(^3\) of 0.0200 mol dm\(^{-3}\) \( \text{KMnO}_4 \) to reach the end-point.

Calculate the percentage of iron in the ore.

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8
(c) High-strength low-alloy (HSLA) steels are used to fabricate TV masts and long span bridges. They contain very low amounts of phosphorus and sulphur, but about 1% copper, to improve resistance to atmospheric corrosion. When dissolved in nitric acid, a sample of this steel gives a pale blue solution.

(i) What species is responsible for the pale blue colour?

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(ii) Describe and explain what you would see when dilute aqueous ammonia is added to this solution.

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[4]  

[Total: 14]
4 The amino acids tyrosine, lysine and glycine are constituents of many proteins.

(a) State the reagents and conditions you could use to break proteins down into amino acids.

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(b) Draw a ring around each chiral centre in the above molecules.

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(c) In aqueous solution amino acids exist as zwitterions. Draw the zwitterionic structure of glycine.

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(d) For each of the following reactions, draw the structure of the organic compound formed.

(i) glycine + excess NaOH(aq)

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(ii) tyrosine + excess NaOH(aq)

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(iii) lysine + excess HCl (aq)
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(iv) tyrosine + excess Br₂(aq)
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(e) Draw the structural formula of a tripeptide formed from all three of these amino acids, showing clearly the peptide bonds.
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(f) The formula of part of the chain of a synthetic polyamide is shown below.

\[ \text{CH}_2\text{NH-CO-CH}_2\text{NH-CO-CH}_2\text{NH-CO-CH}_2\text{NH-CO-CH}_2\text{NH} \]

(i) Identify the repeat unit of the polymer by drawing square brackets around it on the above formula.

(ii) Draw the structures of the two monomers from which the polymer could be made.

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Benzocaine is an important local anaesthetic used in skin creams for sprains and other muscular pains. It can be made by the following route.

(a) Suggest reagents and conditions for each of the above four reactions.
   I ...........................................................................................................................................
   II ...........................................................................................................................................
   III ...........................................................................................................................................
   IV ............................................................................................................................................ [6]

(b) Draw steps to show the mechanism of reaction I.

(c) Another local anaesthetic is amylocaine, which can be made from compound X.

(i) Apart from the benzene ring, name two functional groups in the molecule of compound X.

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(ii) Explain whether compound X would be more or less basic than benzocaine.

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[3]

[Total: 11]