INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 20 pages of examinable material.

- Complete the written section of the examination paper in INK.

- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.

- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.

- Each new question of the short answer section begins with a *. 

- Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.

- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheet.

- Pages 18, 22 & 24 are for rough working only.

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Multiple choice section

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Short answer section

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• Regulation of our blood's pH value is of vital importance for our health. In a healthy person the blood pH does not vary by more than 0.2 from the average 7.4. How does our body regulate the pH of blood?

During exercise, CO₂ is produced at a rapid rate in muscle tissue. What effect does this have on the pH of blood? Why?

Hyperventilation (rapid and deep breathing) can occur during intense exertion. What effect does hyperventilation have on the pH of blood? Why?
• A lecture demonstration showed that a loop of wire with a weight attached can cut through a block of ice (solid water) without the block falling apart. Explain this phenomenon.

• The half-life for the first order decomposition of $\text{N}_2\text{O}_5(g)$ is $6.00 \times 10^4$ s at 20 °C. Calculate the rate constant, $k$, at this temperature.

\[ k = \] 

What percentage of the $\text{N}_2\text{O}_5$ molecules will have reacted after one hour?

Answer:
• Carbon has a number of allotropes, the two major ones being graphite and diamond. What are allotropes?

Give an example of a pair of allotropes not involving carbon.

The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions?

• Complete the following table.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Oxidation state of transition metal</th>
<th>Coordination number of transition metal</th>
<th>Number of d-electrons in metal in complex ion</th>
<th>Species formed upon dissolving in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂[Ni(CN)₄]</td>
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<td></td>
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<tr>
<td>[Cr(NH₃)₅Cl]Cl₂</td>
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<td></td>
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<tr>
<td>[Co(en)₃]Br₃</td>
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</tr>
</tbody>
</table>

en = ethylenediamine = NH₂CH₂CH₂NH₂
• Find the concentration of H$_3$O$^+$ in a 0.60 M aqueous solution of nitrous acid. The acid dissociation constant of HNO$_2$ is $K_a = 7.1 \times 10^{-4}$ M.

Answer:

• An aqueous solution of a weak acid has [H$_3$O$^+$] = 2.54 $\times$ 10$^{-4}$ M. Find the pH and pOH of the solution.

pH = pOH =
In a major industrial process alumina, Al$_2$O$_3$, is isolated from bauxite, a mineral consisting of mainly Al$_2$O$_3$ and Fe$_2$O$_3$. The first step of the process is treatment of the ore with concentrated NaOH solution. Describe how this step allows separation of the two compounds. Use chemical equations as part of your explanation.

In a second step CO$_2$ is used to precipitate Al$_2$O$_3$ from solution. Write a chemical equation for this step.

What property of Al$_2$O$_3$ is exploited in these two steps?
- Draw the constitutional formula(s) of the major organic product(s) formed in each of the following reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product(s)</th>
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</table>
| \[
\text{CH}_3\text{C}-\text{Cl} + \text{OH} \rightarrow
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product(s)</th>
</tr>
</thead>
</table>
| \[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{1. \text{Na}^+ \text{NH}_2} \text{CH}_3\text{CH}_2\text{I} \rightarrow
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product(s)</th>
</tr>
</thead>
</table>
| \[
\text{HBr} \rightarrow
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product(s)</th>
</tr>
</thead>
</table>
| \[
\text{concentrated H}_2\text{SO}_4 \rightarrow
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product(s)</th>
</tr>
</thead>
</table>
| \[
\text{Cr}_2\text{O}_7^{2-} / \text{H}^+ / \text{H}_2\text{O} \rightarrow
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product(s)</th>
</tr>
</thead>
</table>
| \[
\text{excess CH}_3\text{NH}_2 \rightarrow
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product(s)</th>
</tr>
</thead>
</table>
| \[
\text{conc. KOH} / \text{heat} \rightarrow
\]
• Compound X was isolated as a derivative of a natural product.

What is the stereochemistry about the C6-C7 double bond? Write (E) or (Z).

Carbon 3 of X is a stereogenic centre. List the substituents attached to C3 in descending order of priority according to the sequence rules.

Highest priority

Lowest priority

What is the stereochemistry at C3? Write (R) or (S).

Oxidation of X with Cr2O7^2-/H^+ produces a new compound Y. Give the constitutional formula for compound Y.

Is compound Y obtained as an (R)-enantiomer, an (S)-enantiomer, a racemic mixture or an achiral compound?
• Draw the constitutional formula of the major organic product formed in the following reactions.

1. \( \text{CH}_3\text{CH}_2\text{MgBr} \)  
   2. \( \text{H}^+ / \text{H}_2\text{O} \)

\[
\text{PhCHO} \xrightarrow{1. \text{CH}_3\text{CH}_2\text{MgBr}} \xrightarrow{2. \text{H}^+ / \text{H}_2\text{O}}
\]

2. \( \text{H}_2 / \text{Pd} \)

\[
\begin{array}{c}
\text{CH}_3
\
\end{array} \xrightarrow{\text{H}_2 / \text{Pd}}
\]

3. \( \text{NaBH}_4 \)
   1. \( \text{H}_2\text{O} \)

\[
\text{CH}_3\text{OH} \xrightarrow{1. \text{NaBH}_4} \xrightarrow{2. \text{H}^+ / \text{H}_2\text{O}}
\]

• Show clearly the reagents you would use to carry out the following chemical conversions. Draw constitutional formulas for any intermediate compounds. NOTE: More than one step is necessary.

\[
\begin{array}{c}
\text{C}-\text{NH}_2
\
\end{array} \xrightarrow{\text{H}_2\text{O}} \xrightarrow{\text{H}_2 / \text{Pd}}
\]

\[
\begin{array}{c}
\text{C}-\text{OH}
\
\end{array}
\]

\[
\text{CH}_3\text{OH}
\]
• Draw the repeating unit of the polymer formed in the following reactions.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
+ & \\
\text{H}_2\text{N} & \text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \text{Cl} \\
\rightarrow & \\
\text{HO} & \text{O}
\end{align*}
\]

• The incomplete proposed mechanism for the reaction of acetyl chloride with two equivalents of \(\text{OH}^-\) is shown below. The reaction occurs in three steps. In each step, complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.

\[
\begin{align*}
\text{CH}_3 & \text{C} \quad \text{Cl}^+ \\
\rightarrow & \\
\text{CH}_3 & \text{C} \\
\text{H} & \text{O}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{C} \quad \text{Cl}^+ \\
\rightarrow & \\
\text{CH}_3 & \text{C} \\
\text{H} & \text{O}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{C} \quad \text{Cl}^+ \\
\rightarrow & \\
\text{CH}_3 & \text{C} \\
\text{H} & \text{O}
\end{align*}
\]
DATA SHEET

Physical constants
Avogadro constant, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Faraday constant, $F = 96485 \text{ C mol}^{-1}$
Planck constant, $h = 6.626 \times 10^{-34} \text{ J s}$
Speed of light in vacuum, $c = 2.998 \times 10^{8} \text{ m s}^{-1}$
Rydberg constant, $E_R = 2.18 \times 10^{-18} \text{ J}$
Boltzmann constant, $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
\[ = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \]

Properties of matter
Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L
Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L
Density of water at 298 K = 0.997 g cm$^{-3}$

Conversion factors
1 atm = 760 mmHg = 101.3 kPa
0 °C = 273 K
1 L = 10$^{-3}$ m$^3$
1 Å = 10$^{-10}$ m
1 eV = 1.602 × 10$^{-19}$ J
1 Ci = 3.70 × 10$^{10}$ Bq
1 Hz = 1 s$^{-1}$

\[ \begin{array}{|c|c|c|} \hline \text{Decimal fractions} & \text{Decimal multiples} \\ \hline \text{Fraction} & \text{Prefix} & \text{Symbol} & \text{Multiple} & \text{Prefix} & \text{Symbol} \\ \hline 10^{-3} & \text{milli} & m & 10^3 & \text{kilo} & k \\ 10^{-6} & \text{micro} & \mu & 10^6 & \text{mega} & M \\ 10^{-9} & \text{nano} & n & 10^9 & \text{giga} & G \\ 10^{-12} & \text{pico} & p & & & \\ \hline \end{array} \]
## Standard Reduction Potentials, $E^\circ$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^\circ$ / V</th>
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<tbody>
<tr>
<td>$\text{Co}^{3+}(\text{aq}) + e^- \rightarrow \text{Co}^{2+}(\text{aq})$</td>
<td>+1.82</td>
</tr>
<tr>
<td>$\text{Ce}^{4+}(\text{aq}) + e^- \rightarrow \text{Ce}^{3+}(\text{aq})$</td>
<td>+1.72</td>
</tr>
<tr>
<td>$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-(\text{aq})$</td>
<td>+1.36</td>
</tr>
<tr>
<td>$\text{O}_2 + 4\text{H}^+(\text{aq}) + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>+1.23</td>
</tr>
<tr>
<td>$\text{Pd}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pd(s)}$</td>
<td>+0.92</td>
</tr>
<tr>
<td>$\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag(s)}$</td>
<td>+0.80</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$</td>
<td>+0.77</td>
</tr>
<tr>
<td>$\text{Cu}^+(\text{aq}) + e^- \rightarrow \text{Cu(s)}$</td>
<td>+0.53</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu(s)}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$\text{Sn}^{4+}(\text{aq}) + 2e^- \rightarrow \text{Sn}^{2+}(\text{aq})$</td>
<td>+0.15</td>
</tr>
<tr>
<td>$2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g})$</td>
<td>0 (by definition)</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Fe(s)}$</td>
<td>−0.04</td>
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<td>$\text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb(s)}$</td>
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<tr>
<td>$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Fe(s)}$</td>
<td>−0.44</td>
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<td>$\text{Cr}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Cr(s)}$</td>
<td>−0.74</td>
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<tr>
<td>$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn(s)}$</td>
<td>−0.76</td>
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<tr>
<td>$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$</td>
<td>−0.83</td>
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<tr>
<td>$\text{Cr}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cr(s)}$</td>
<td>−0.89</td>
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<tr>
<td>$\text{Al}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Al(s)}$</td>
<td>−1.68</td>
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<tr>
<td>$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mg(s)}$</td>
<td>−2.36</td>
</tr>
<tr>
<td>$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na(s)}$</td>
<td>−2.71</td>
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</table>
**Useful Formulas**

**Quantum Chemistry**

\[ E = h\nu = hc/\lambda \]
\[ \lambda = h/mu \]
\[ 4.5k_B T = hc/\lambda \]
\[ E = Z^2 E_R (1/n^2) \]

**Thermodynamics & Equilibrium**

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]
\[ \Delta G = \Delta G^\circ + RT \ln Q \]
\[ \Delta G^\circ = -RT \ln K \]
\[ K_p = K_c (RT)^\Delta n \]

**Kinetics**

\[ k = A e^{-E_a/RT} \]
\[ t_{1/2} = \ln2/k \]
\[ \ln[A] = \ln[A]_o - kt \]

**Radioactivity**

\[ A = \lambda N \]
\[ \ln(N_0/N_i) = \lambda t \]
\[ ^{14}C \text{ age} = 8033 \ln(A_0/A_t) \]

**Gas Laws**

\[ PV = nRT \]
\[ (P + n^2a/V^2)(V - nb) = nRT \]

**Acids and Bases**

\[ pK_w = \text{pH} + \text{pOH} = 14.00 \]
\[ pK_w = pK_a + pK_b = 14.00 \]
\[ \text{pH} = pK_a + \log\{[A^-]/[HA]\} \]

**Colligative Properties**

\[ \pi = cRT \]
\[ p = kc \]
\[ P_{\text{solute}} = X_{\text{solute}} \times P_{\text{solvent}}^\circ \]
\[ \Delta T_f = K_m m \]
\[ \Delta T_b = K_b m \]

**Electrochemistry**

\[ \Delta G^\circ = -nFE^\circ \]
\[ \text{Moles of } e^- = It/F \]
\[ E = E^\circ - \frac{(RT/nF) \ln Q}{1 + 2.303 \log Q} \]
\[ E = E^\circ - \frac{0.0592}{n} \ln Q \text{ (at } 25 \degree C) \]

**Polymers**

\[ R_g = \sqrt{\frac{nl_0^2}{6}} \]

**Mathematics**

If \( ax^2 + bx + c = 0 \), then \( x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \)
\[ \ln x = 2.303 \log x \]
# Periodic Table of the Elements

<table>
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<td>Lithium (Li)</td>
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<td>Beryllium (Be)</td>
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<td>Sodium (Na)</td>
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<td>Magnesium (Mg)</td>
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<td>22</td>
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<tr>
<td>Strontium (Sr)</td>
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<td>38</td>
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<td>42</td>
<td>43</td>
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<td>50</td>
<td>51</td>
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<td>Rubidium (Rb)</td>
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<td>Caesium (Cs)</td>
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<td>102</td>
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</tr>
</tbody>
</table>

**Lanthanides:**

- Lanthanum (La)
- Cerium (Ce)
- Praseodymium (Pr)
- Neodymium (Nd)
- Promethium (Pm)
- Samarium (Sm)
- Europium (Eu)
- Gadolinium (Gd)
- Terbium (Tb)

**Actinides:**

- Actinium (Ac)
- Thorium (Th)
- Protactinium (Pa)
- Uranium (U)
- Np
- Pu
- Am
- Cm
- Bk
- Cf
- Es
- Fm
- Md
- No
- Lr

**Atomic Masses:**

- Hydrogen: 1.008
- Helium: 4.003
- Lithium: 6.941
- Beryllium: 9.012
- Sodium: 22.99
- Magnesium: 24.31
- Potassium: 39.10
- Calcium: 40.08
- Strontium: 87.62
- Rubidium: 85.47
- Caesium: 132.91
- Barium: 137.34
- Francium: 223.0
- Lanthanum: 138.91
- Cerium: 140.12
- Praseodymium: 140.91
- Neodymium: 144.24
- Promethium: 144.9
- Samarium: 150.4
- Europium: 151.96
- Gadolinium: 157.25
- Terbium: 158.93
- Actinium: 227.0
- Thorium: 232.04
- Protactinium: 231.0
- Uranium: 238.03
- Np: 238.4
- Pu: 243.1
- Am: 247.1
- Cm: 252.1
- Bk: 252.1
- Cf: 252.1
- Es: 252.1
- Fm: 252.1
- Md: 256.1
- No: 259.1
- Lr: 260.1

**November 2004**