The problem sheets on the following pages are designed to show your understanding of some of the areas covered in the lecture course. Each week, you should attempt all of the questions prior to your tutorial. The answers will be provided on the ‘Resources’ page, accessed via WebCT or the unit area on the First Year Chemistry website, at the end of the week before the tutorial. These should be used to check your answers, correct minor errors and to provide you with an idea of topics which you need to build on. Your tutor will ask you at the start of the tutorial for the topics and questions to go over.

In addition, your tutor will go over a number of past examination questions from the list given on the next page. The past exam papers can be accessed via the relevant unit area on the First Year Chemistry website. Full solutions to these questions will not be provided online until the end of the semester.

Your performance in the tutorial quizzes and in the end of semester examination will be greatly enhanced by your attendance and involvement in the tutorial sessions.

In quiz weeks, you should attempt the sample quizzes, accessed via the ‘Tutorial Quizzes’ page on WebCT or on your unit area on the First Year Chemistry website. Your tutor will cover problems with these quiz questions prior to the actual quiz.

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<th>CHEM1102 Tutorials - Past Examination Questions</th>
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<td>• 2003-N-5 (ii)</td>
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<td>• 2005-J-6 (i), (vi) and (viii)</td>
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<td>• 2005-N-8 iv)</td>
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<td>• 2005-N-11 (ii)</td>
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<td>• 2004-J-6</td>
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<td><strong>Week 12</strong></td>
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<td><strong>Week 13</strong></td>
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<td>• 2005-N-3</td>
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<td>• 2005-N-4</td>
</tr>
</tbody>
</table>
1. Give the condensed structural formula and stick representation of the following molecules. In the stick representations do not show the C-H bonds but try to represent the appropriate bond angles in the rest of the molecule.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Condensed structural formula</th>
<th>Stick representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COCH₃</td>
<td><img src="image" alt="condensed structural formula" /></td>
<td><img src="image" alt="stick representation" /></td>
</tr>
<tr>
<td>CH₂CH₂CH₂CH₂OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CHBrCH₂Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂CHCH(CH₃)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂CCH₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂COOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃COOCH₂CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃COOCCOCH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzamide (C₆H₅CONH₂)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Determine molecular formulas and identify the functional groups in the following compounds:
3. Give the hybridisation of the atoms indicated by arrows in the following compounds.

4. Give approximate bond angles at the atoms indicated by arrows in the following compounds.
1. Give the stick structures of the following compounds.
   (a) 2,3,5-trimethyl-4-bromo-octane
   (b) cis-1,3-dimethylcyclobutane
   (c) 2-methyl-2-pentene

2. Name the following compounds.

3. Draw the structures of the following compounds.
   (a) 3-chloro-2,3-dimethyl-1-butene
   (b) 3-ethyl-3-hexene
   (c) (Z)-2-butene
   (d) (E)-2-butene
   (e) (Z)-2-methyl-3-hexene

4. All atoms, bonds and lone pairs are shown in the structures below. Use your knowledge of valency and arrow notation to add formal charges, $\oplus$ and $\ominus$, on the structures where it is appropriate. Add partial charges, $\delta\oplus$ and $\delta\ominus$, to the neutral reagents.

5. Classify the two starting materials (below) as electrophile, nucleophile or neither. What kind of reaction is this? Draw in appropriate partial charges $\delta\oplus$ and $\delta\ominus$ and curly arrows showing the mechanism of the reaction.
1. Consider the reaction below:

(a) Which species \( P - R \) is acting as the electrophile?
(b) Which species \( P - R \) is aromatic?
(c) Which species \( P - R \) is a carbocation intermediate?
(d) Draw in the curly arrows for this reaction.
(e) Classify this type of reaction.

2. What is the major product in the following reactions?

(a) \( \text{H} + \text{Br}_2 \)
(b) \( \text{HBr} \)
(c) \( \text{dilute H}_2\text{SO}_4 \)
(d) \( \text{C}_2\text{H}_4 + \text{H}_2 \) with Pd catalyst
(e) \( \text{C}_2\text{H}_3 + \text{HCl} \)
(f) \( \text{C}_2\text{H}_2 + 2\text{HBr} \)
(g) \( \text{C}_6\text{H}_6 + \text{Br}_2 \) with AlBr\(_3\) catalyst
3. What reagent would effect the following changes?

(a) \[ \text{alkene} \rightarrow \text{alkane} + \text{I}_2 \]
(b) \[ \text{alkene} \rightarrow \text{alkane} + \text{I} \]
(c) \[ \text{alkene} \rightarrow \text{alkane} \]
(d) \[ \text{cycloalkane} \rightarrow \text{cycloalkane} + \text{OH} \]

4. Low resolution mass spectrometry indicated a molecular ion at \( m/z = 58 \). The compound could be \( \text{C}_3\text{H}_6\text{O} \) or \( \text{C}_4\text{H}_{10} \) or \( \text{C}_2\text{H}_6\text{N}_2 \). High resolution mass spectrometry gave a value of \( m/z = 58.0530 \). Using the following more accurate atomic weight data determine which compound it is.

Data: \( ^1\text{H} 1.0078; ^{14}\text{N} 14.0031; ^{12}\text{C} 12.0000; ^{16}\text{O} 15.9949 \)

5. Consider the following six compounds A - F.

(a) Which compound(s) will give a molecular ion at \( m/z = 74 \) in the mass spectrum?
(b) Which compound(s) will show a strong absorption in the UV spectrum?
(c) Which compound(s) will show absorption around 1700 cm\(^{-1}\) in the infrared region?
(d) Which compound(s) will show absorption around 3500 cm\(^{-1}\) in the infrared region?
(e) Which compound(s) will not show absorption either around 1700 or 3500 cm\(^{-1}\) in the infrared region?
1. Which spectroscopic technique would most readily distinguish between the following pairs of compounds? Give a brief reason.

(a) \[ \text{O} \quad \text{OH} \]
(b) \[ \text{CH}_3 \quad \text{C} \quad \text{O} \quad \text{OH} \]
(c) \[ \text{CH}_3 \quad \text{C} \quad \text{O} \]
(d) \[ \text{CH}_3 \quad \text{C} \quad \text{O} \quad \text{H} \quad \text{C} \quad \text{O} \quad \text{OCH}_3 \]

2. Consider the following molecules, A - E.

(a) Which of the molecules would give three signals in the $^1$H NMR spectrum?
(b) Which of the molecules would possess a $^1$H NMR spectrum consisting of only one resonance?
(c) Which of the molecules would possess a $^1$H NMR spectrum consisting of two signals in the ratio 1:3?
(d) How many singlets would be observed in the $^1$H NMR spectrum of D?
(e) Which of the molecules would possess a $^1$H NMR spectrum containing a singlet, a triplet and a quartet signal?
(f) Examine the $^1$H NMR spectrum below. To which of the compounds does it belong? (Hint: See page E35-11 of the Laboratory Handbook for approximate chemical shifts.)

More than one answer may be correct. Give all correct answers.
3. Classify the following amines as either primary, secondary, tertiary or as a quaternary ammonium salt and draw the constitutional formula of the product formed when each of the compounds is treated with dilute acid.

![Amines with constitutional formulas]

4. Draw the major products of the following reactions. Write "NR" if there is no reaction.

![Reactions with products]

5. Mark each stereogenic centre in the following compounds with an asterisk (*).
1. Assign absolute configurations ($R$, $S$ nomenclature) to the following molecules.

![Chemical Structures]

2. Draw a three dimensional structural representation of $(3R, 5Z)$-2-methyloct-5-en-3-ol.

3. State whether the product of the following reactions is achiral, the ($R$)-enantiomer, the ($S$)-enantiomer, a *meso*-compound, or a racemic mixture?

   (a) 
   ![Chemical Reaction]  
   (b) 
   ![Chemical Reaction]  
   (c) 
   ![Chemical Reaction]  

4. Draw the constitutional formula of the major organic product formed in the following reactions. If there is no reaction, write "NR".

   (a) 
   ![Chemical Reaction]  
   (b) 
   ![Chemical Reaction]  
   (c) 
   ![Chemical Reaction]  
   (d) 
   ![Chemical Reaction]
5. Draw the constitutional formula of the major organic product formed in the following reactions. If there is no reaction, write "NR".

(a) \[ \text{Br}_2 + \]

(b) \[ \text{HCl} + \]

(c) \[ \text{HCl} + \]

(d) \[ \text{HI} + \]

(e) \[ \text{Cl}_2 + \]

(f) \[ \text{I} + \text{Mg} \text{ dry ether solvent} \]

6. Give the reagents required to carry out the following chemical conversions. Draw constitutional formulas for any intermediate compounds. More than one step is necessary in each case.

(a) \[ \]

(b) \[ \text{H}_2\text{C}≡\text{CH}_2 \rightarrow (\text{CH}_2\text{CH}_2)_4\text{NBr} \]

(c) \[ \text{Br} \rightarrow \text{CO} \]

(d) \[ \text{I} \rightarrow \]
1. Identify the following compounds as an aldehyde or a ketone. Then draw the formula of the major organic products formed on oxidation with acidified potassium dichromate solution and reduction with sodium borohydride followed by aqueous acid. If there is no reaction, write "NR".

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Functional Group</th>
<th>Oxidation Product</th>
<th>Reduction Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>CHO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td>O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Draw the constitutional formula of the major organic product formed in the following reactions. If there is no reaction, write "NR".

(a) \[ \text{O} \quad \text{H} \rightarrow \text{CH}_3\text{MgI} \rightarrow \text{H} \downarrow \text{H}_2\text{O} \]

(b) \[ \text{MgBr} \rightarrow \text{CO}_2 \rightarrow \text{H} \downarrow \text{H}_2\text{O} \]

(c) \[ \text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} \rightarrow \text{H} \downarrow \text{H}_2\text{O} \]
3. Identify the functional group in each of the starting materials below and give the constitutional formula of the major organic product(s) formed in the hydrolysis reactions shown.

(a)  
\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{dilute HCl} \\
\text{heat}
\end{array}
\]

(b)  
\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{dilute HCl} \\
\text{heat}
\end{array}
\]

(c)  
\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{H} \\
\text{conc. HCl} \\
\text{heat}
\end{array}
\]

(d)  
\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{dilute NaOH} \\
\text{heat}
\end{array}
\]

(e)  
\[
\begin{array}{c}
\text{O} \\
\text{Cl} \\
\text{water}
\end{array}
\]

(f)  
\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{dilute NaOH} \\
\text{heat}
\end{array}
\]

4. Give the constitutional formula of the major organic product(s) formed in the following reactions. If no reaction, write "NR".

(a)  
\[
\begin{array}{c}
\text{O} \\
\text{Cl} \\
\text{excess}
\end{array}
\]

(b)  
\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{OH}
\end{array}
\]

(c)  
\[
\begin{array}{c}
\text{OH} \\
\text{COOH}
\end{array}
\]

(d)  
\[
\begin{array}{c}
\text{NH}_2 \\
\text{O}
\end{array}
\]
Work through the four ChemCAL modules that deal with acids and bases: “Acids and bases”, “Weak acids and bases”; “Calculations with weak acids and bases” and “Acid/base titrations”. Revise the Self Help problems acids and bases (1) and (2) too.

1. Give the concentration of hydrogen ions present and hence calculate the pH of each of the following water solutions:
   
   (a) hydrochloric acid (0.14 M)  
   (b) nitric acid (0.0025 M)  
   (c) sodium hydroxide (0.048 M)  
   (d) barium hydroxide (3.7 × 10⁻³ M)

2. Complete the following table by giving the conjugate acid or conjugate base.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>HCO₃⁻</td>
<td>CH₃CH₂COOH</td>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>NH₃</td>
<td>CN⁻</td>
<td>CH₃CH₂NH₃⁺</td>
</tr>
</tbody>
</table>

3. Using the following $K_a$ values, arrange the bases CN⁻, NO₂⁻, F⁻, H₂O and Cl⁻ in order of increasing strength.
   
   $K_a$:  
   HNO₂ 4.0 × 10⁻⁴ M;  
   HF 7.2 × 10⁻⁴ M;  
   HCN 6.2 × 10⁻¹⁰ M

4. The pH of a 0.6 M solution of a weak acid is 4.0. What percentage of the acid has ionised?

5. The $K_a$ value for hydrazoic acid, HN₃, is 1.9 × 10⁻⁵ M. What is the equilibrium constant for the following reaction?
   
   $\text{N}_3^− + \text{H}_2\text{O}^+ \rightleftharpoons \text{HN}_3 + \text{H}_2\text{O}$

6. The p$K_a$ of acetic acid is 4.76. Calculate the pH of the following solutions:
   
   (a) 0.2 M acetic acid  
   (b) 0.2 M sodium acetate  
   (c) A buffer that is 0.2 M in acetic acid and 0.2 M in sodium acetate

7. What volumes of 0.200 M solutions of HNO₂ and KNO₂ are required to make 1.00 L of a buffer solution of pH 3.00? ($K_a$ for HNO₂ = 4.00 × 10⁻⁴ M)

8. Give the chemical equations and state whether the final solutions are acidic, neutral or basic when the following are dissolved in water.
   
   (a) Na₂O  
   (b) Cl₂O₇
1. Consider the phase diagram on the right.
   (a) Which point lies at the critical point?
   (b) Which point lies at the triple point?
   (c) Which point corresponds to conditions where the solid and gas phases are in equilibrium?
   (d) What phase transition accompanies moving from point G to point C?
   (e) What phases coexist at point B?
   (f) What phases coexist at point F?

2. A phase diagram of a pure compound has a triple point at 13 °C and 205 mmHg, a normal melting point at 17 °C, and a normal boiling point at 87 °C. Draw a phase diagram for this compound. Which of the following statements regarding this compound are correct?
   (a) The density of the solid is greater than that of the liquid.
   (b) If the pressure is reduced from 835 mmHg to 85 mmHg at a constant temperature of 11 °C, sublimation occurs.
   (c) At a constant pressure of 835 mmHg, evaporation occurs if the temperature is raised from 13 °C to 81 °C.

3. What percentage of the space within the unit cell is occupied by atoms in:
   (a) a face-centred cubic unit cell
   (b) a body-centred cubic unit cell
   (c) a simple cubic unit cell

4. If a metal crystallizes in a face-centred cubic lattice, how many “nearest” neighbours does each metal atom have?

5. In the unit cell to the right, element X is within the cell and element Y is at the corners. What is the formula for this compound?

6. Which intermolecular forces are present in CH₃Cl(s)?

7. Which intermolecular force or bond is responsible for the density of H₂O(s) being less than that of H₂O(l)?
CHEM1102 Problem Sheet 9 (Week 12)

The Self Help problems involving Complexes should also be revised.

1. The solubility of CaSO₄ is 2.1 g L⁻¹. What is the $K_{sp}$ of CaSO₄?

2. A solution is prepared that is 0.10 M in sodium chloride and 0.10 M in sodium chromate. A concentrated aqueous solution of silver nitrate is added dropwise with stirring.

\[ K_{sp} (AgCl) = 2 \times 10^{-10} \text{ M}^2 \quad K_{sp} (Ag_2CrO_4) = 3 \times 10^{-12} \text{ M}^3 \]

(a) What is the molar concentration of Ag⁺ when silver chloride first precipitates?
(b) What is the molar concentration of Ag⁺ when silver chromate first precipitates?
(c) What is the molar concentration of Cl⁻ when silver chromate first precipitates?
(d) What percentage of the Cl⁻ is precipitated before any silver chromate is precipitated?

3. Which one of the following statements is false?

(a) Solvation of ions is always accompanied by the release of energy.
(b) Dissolution of a solid is always accompanied by the release of enthalpy.
(c) Breaking up of a lattice structure always costs energy.
(d) The solubility depends on the lattice enthalpy and the solvation enthalpy.

4. What are the systematic names of (a) K₂[PtF₆] and (b) [CoCl₂(NH₃)₄]Cl·2H₂O?

5. What is the formula for (a) tetraamminezinc(II) sulfate-2-water and (b) tetraaquaoxalatochromium(III) ion?

6. How many isomers are possible for the square planar complex ion [Pt(NH₃)₂Cl]?

7. Which one of the following compounds is a coordination isomer of [Cr(H₂O)₅Cl]SO₄?

(a) [Cr(H₂O)₆]Cl₃
(b) [Cr(H₂O)₆]SO₄
(c) [Cr(H₂O)₅SO₄]Cl
(d) [Cr(H₂O)₅Cl]Cl₂
Work through the four ChemCAL modules that deal with reaction kinetics: “Reaction Rates and Chemical Kinetics 1”, “Reaction Rates and Chemical Kinetics 2”, “Thermal Energy, Collisions and Reactions” and “Reaction Mechanisms”. Also attempt some of the *Self Help problems* involving kinetics.

1. Without consulting data tables, write the ground state electronic configuration of the following atoms and ions. For example, Ti is \([\text{Ar}]4s^23d^2\).
   
   (a) Mn  
   (b) Cr  
   (c) Ni\(^{2+}\)  
   (d) Fe  
   (e) Fe\(^{3+}\)  
   (f) Cu\(^{2+}\)  
   (g) Zn\(^{2+}\)

2. Which one of the following properties is NOT characteristic of transition element compounds?
   
   (a) Many of them are paramagnetic.  
   (b) Many of them are coloured.  
   (c) Most of the metals exhibit multiple oxidation states.  
   (d) Most of the metals upon ionising lose the \(d\) electrons first.  
   (e) Most of the elements form many complexes.

3. Given the initial rate data below, what is the rate law for the following reaction?

   \[
   4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}
   \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([\text{Fe}^{2+}] / \text{mol L}^{-1})</th>
<th>([\text{O}_2] / \text{mol L}^{-1})</th>
<th>([\text{H}^+] / \text{mol L}^{-1})</th>
<th>Rate = (-d[\text{O}_2]/dt) / mol L(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1 \times 10^{-3})</td>
<td>(1 \times 10^{-3})</td>
<td>0.1</td>
<td>(5 \times 10^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>(2 \times 10^{-3})</td>
<td>(2 \times 10^{-3})</td>
<td>0.1</td>
<td>(8 \times 10^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>(2 \times 10^{-3})</td>
<td>(1 \times 10^{-3})</td>
<td>0.2</td>
<td>(8 \times 10^{-3})</td>
</tr>
<tr>
<td>4</td>
<td>(2 \times 10^{-3})</td>
<td>(2 \times 10^{-3})</td>
<td>0.2</td>
<td>(1.6 \times 10^{-2})</td>
</tr>
</tbody>
</table>

   (a) What is the rate equation for the reaction?  
   (b) What is the value of the rate constant, \(k\), for this reaction?  
   (c) What is the initial rate of formation of \(\text{Fe}^{3+}\) in experiment 3?  
   (d) Calculate the rate of loss of \(\text{Fe}^{2+}\) ions when \([\text{Fe}^{2+}] = [\text{O}_2] = 4 \times 10^{-3} \text{ mol L}^{-1}\) and \([\text{H}^+] = 0.1 \text{ mol L}^{-1}\).

4. The half-life for the first order decomposition of \(\text{N}_2\text{O}_5(\text{g})\) is \(6.00 \times 10^4\) s at 20 °C.

   (a) Calculate the rate constant, \(k\), at this temperature.  
   (b) What percentage of the \(\text{N}_2\text{O}_5\) molecules will have reacted after one hour?
5. Dinitrogen tetroxide decomposes according to the equation below.
At $30\, ^\circ\text{C}$, the value of $k$ is $5.1 \times 10^6 \, \text{s}^{-1}$. At $50\, ^\circ\text{C}$, the value of $k$ is $1.9 \times 10^7 \, \text{s}^{-1}$.
What are the activation energy, $E_a$, and pre-exponential factor, $A$, for this reaction?

\[ \text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g) \quad \text{Rate} = -\frac{d[\text{N}_2\text{O}_4(g)]}{dt} = k[\text{N}_2\text{O}_4(g)] \]

6. The reaction $2\text{A} + \text{B} \rightarrow \text{C}$ has the following mechanism.

\begin{align*}
\text{A} & + \text{B} \quad \text{D} \quad \text{(fast)} \\
\text{B} & + \text{D} \rightarrow \text{E} \quad \text{E} \quad \text{(slow)} \\
\text{A} & + \text{E} \rightarrow \text{B} + \text{C} \quad \text{(fast)}
\end{align*}

Show that this is consistent with the rate of formation of $\text{C}$ equalling $k[\text{A}][\text{B}]^2$. 