Topics in the November 2014 Exam Paper for CHEM1002

Click on the links for resources on each topic.

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- Strong Acids and Bases
- Weak Acids and Bases
- Calculations Involving pK_a

2014-N-3:

- Metal Complexes
- Coordination Chemistry
- Entropy

2014-N-4:

- Metal Complexes
- Coordination Chemistry
- Kinetics

2014-N-5:

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- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams

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2014-N-8:

- Alkenes
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2014-N-9:

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2014-N-10:

- Representations of Molecular Structure
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- Carboxylic Acids and Derivatives

2014-N-12:

- Synthetic Strategies
- Stereochemistry

Marks
3

- Above what concentration of H_3O^+ is a solution considered to be acidic at 25 °C?

Neutral at 25 °C corresponds to $[H_3O^+(aq)] = 10^{-7}$ M and pH = 7.0. Acidic solutions have pH < 7.0 and $[H_3O^+(aq)] > 10^{-7}$ M

	Answer: 10^{-7} M

At 95 °C the auto ionisation constant of water, K_w, is 45.7×10^{-14}. What is the pH of a neutral solution at 95 °C?

K_w refers to the auto ionisation reaction, $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ so that $K_w = [H_3O^+(aq)][OH^-(aq)]$. As the solution is neutral, $[H_3O^+(aq)] = [OH^-(aq)]$. Hence:

$K_w = [H_3O^+(aq)][OH^-(aq)] = [H_3O^+(aq)]^2 = 45.7 \times 10^{-14}$
$[H_3O^+(aq)] = 6.76 \times 10^{-7}$ M
pH $= -\log_{10}[H_3O^+(aq)] = -\log_{10}(6.76 \times 10^{-7}) = 6.17$

	pH = **6.17**

- Calculate the pH of a 0.020 M solution of lactic acid, $HC_3H_5O_3$, at 25 °C. The pK_a of lactic acid is 3.86.

5

As lactic acid is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	$HC_3H_5O_3$	H_2O	$\rightleftharpoons$	H_3O^+	$C_3H_5O_3^-$
initial	**0.020**	**large**		**0**	**0**
change	**-x**	**negligible**		**+x**	**+x**
final	**0.020 –x**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{x^2}{0.020-x}$$

As pK_a = -$\log_{10}K_a$, $K_a = 10^{-3.86}$ and is very small, $0.010 – x \sim 0.010$ and hence:

$x^2 = 0.020 \times 10^{-3.86}$ or $x = 1.7 \times 10^{-3}$ M = $[H_3O^+]$

Hence, the pH is given by:

pH $= -\log_{10}[H_3O^+] = -\log_{10}(1.7 \times 10^{-3}) = 2.78$

	pH = **2.78**

ANSWER CONTINUES ON THE NEXT PAGE

A 1.0 L solution of 0.020 M lactic acid is added to 1.0 L of 0.020 M sodium hydroxide solution. Write the ionic equation for the reaction that occurs.

$HC_3H_5O_3(aq) + OH^-(aq) \rightarrow C_3H_5O_3^-(aq) + H_2O(l)$
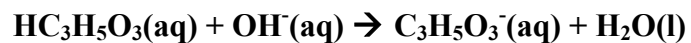
Is the resulting solution acidic, basic or neutral? Give a reason for your answer.

All of the lactic acid will have reacted as the number of moles of sodium hydroxide added equals the number of moles of lactic acid originally present.

The solution contains lactate ions, $C_3H_5O_3^-(aq)$, which is the conjugate base. The solution contains a weak base so is basic.

	Marks
• Transition metals are often found in coordination complexes such as $[NiCl_4]^{2-}$. What is a complex?	**8**

A complex contains a metal cation surrounded by ligands which bond to the cation using one or more lone pairs. The complex can be positive, negative or neutral depending on the charges on the metal and ligands.

How does the bonding in the complex $[NiCl_4]^{2-}$ differ from the bonding in CCl_4?

In CCl_4, the C-Cl bonds are polar covalent; each involves the sharing of 1 electron from C and 1 electron from Cl to make a 2 electron bond.

In $[NiCl_4]^{2-}$, the Ni-Cl bonds also involve 2 electrons. However, both originate on the Cl^- ion which donates a lone pair to the Ni^{2+} ion to make the bond. This type of bond is sometimes called a 'dative' or 'coordinate' bond.

What is a chelate complex?

Some ligands have more than one atom with a lone pair and can bond to a metal ion more than once. An example of this type of ligand is ethylenediamine (en) which has the formula $NH_2CH_2CH_2NH_2$. As there is a lone pair on each of the N atoms, it can bond twice to a metal ion.

Complexes containing ligands which do this are called chelate complexes.

Why is a chelate complex generally more stable than a comparable complex without chelate ligands?

When a chelate ligand bonds to a metal ion, it releases other ligands: if the chelate can bond twice to a metal ion, it will release two ligands and if the chelate can bond three times to a metal ion, it will release three ligands.

If the bond strengths are similar, the enthalpy change is small. However, the release of ligands increases the entropy of the system and this favours the formation of the chelate complex.

For example, en can bond twice to a metal ion so in the reaction below, it can replace $2NH_3$ ligands:

$$[Ni(NH_3)_6]^{2+}(aq) + en(aq) \rightarrow [Ni(en)(NH_3)_4]^{2+}(aq) + 2NH_3(aq)$$

The reaction involves breaking 2 Ni-N bonds and making 2 Ni-N bonds, so the enthalpy change is small. There are 2 reactant molecules and 3 product molecules so the entropy has increased.

**Marks
2**

- An aqueous solution of iron(III) nitrate is pale yellow/brown. Upon addition of three mole equivalents of potassium thiocyanate (KSCN) a bright red colour develops. Draw the metal complex responsible for the red colour, including any stereoisomers.

Thiocyanate, SCN⁻, has a lone pair on both the S and N ends and so can form Fe-SCN and Fe-NCS complexes, which are linkage isomers.

Fe^{3+}(aq) contains octahedral $[Fe(OH_2)_6]^{3+}$ ions and addition of 3 SCN⁻ will lead to $[Fe(OH_2)_3(SCN)_3]$. There are 2 possible stereoisomers (i.e. ignoring possible linkage isomers):

fac   *mer*

4
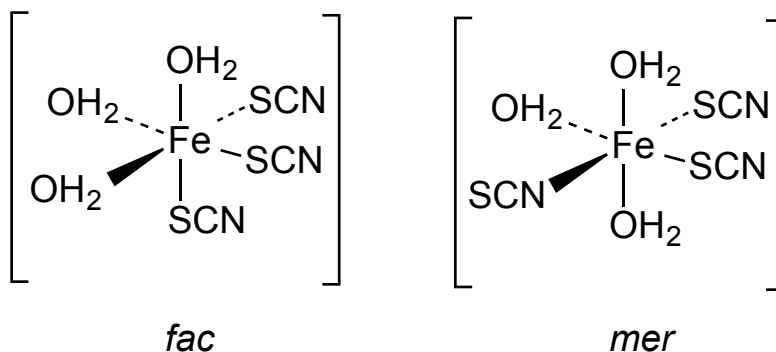
- The reaction order for a chemical reaction is given by the sum of the powers in the rate law. Why is the reaction order usually given by a small positive integer, *i.e.* 2 or less?

The rate of a reaction is determined by the slowest step (the rate determining step). This step usually involves 2 species colliding or a single species spontaneously undergoing a change. The rate law for this step then depends on the concentrations on the species involved in this step.

If 2 species are involved, then the rate will be proportional to the concentration of each giving an overall order of 1 + 1 = 2. If 1 species is involved, then the rate will be proportional to its concentration so the overall order will be 1.

Are zero order reactions possible? Explain your answer using examples if possible.

A zero order reaction is one in which the rate does not depend on the concentration of the reactant(s). These are known and typically occur when the reaction is dependent on the availability of a catalyst. For example:

- **A reaction of a gas which occurs on the surface of a metal will become independent of the concentration of the gas if all of the metal surface is saturated with reactants.**
- **A reaction of a substrate on an enzyme will become independent of the concentration of the substrate if the active centres in the enzyme are saturated.**

**Marks
2**

- The cubic form of boron nitride (borazon) is the second-hardest material after diamond and it crystallizes with the structure shown below. The large spheres represent nitrogen atoms and the smaller spheres represent boron atoms.
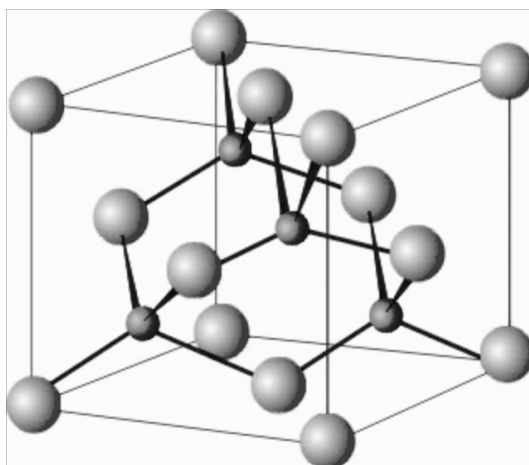
From the unit cell shown above, determine the empirical formula of boron nitride. Show your working.

There are N atoms on the corners and on the faces of the unit cell:

- **There are 8 N atoms on the corners. These contribute 1/8 to the unit cell giving a total of $8 \times 1/8 = 1$ N atom.**
- **There are 6 N atoms on the faces. These contribute 1/2 to the unit cell giving a total of $6 \times 1/2 = 3$ N atoms.**
- **There are a total of $1 + 3 = 4$ N atoms in the unit cell.**

There are B atoms inside the unit cell:

- **There are 4 B atoms completely inside the cell. These contribute only to this unit cell giving a total of $4 \times 1 = 4$ B atoms.**

The formula is therefore B_4N_4 which simplifies to BN.

Answer: **BN**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

• Consider the pressure/temperature phase diagram of H_2O shown below.
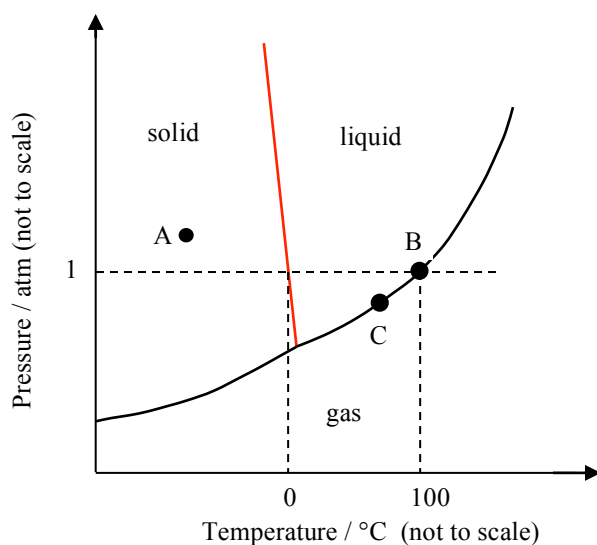
Which phase exists at the point labelled A? | **Solid**

What are the temperature and pressure for the normal boiling point of water?

Temperature = 100 ^{o}C or 373 K. Pressure = 1 atm. This is labelled as point B.

Use the phase diagram to explain why it takes longer to hard boil eggs on the top of a 4000 m high mountain rather than at sea level.

The pressure at 4000 m is considerably lower than at sea level. At lower pressure, the water boils at the temperature corresponding to the new position on the liquid – gas line in the phase diagram, represented as point C.

The boiling point at lower pressure is lower: water boils at a lower temperature on the mountain. It is not possible to heat the water above this temperature, as it boils away. Because the water used to cook the egg is at a lower temperature, it takes longer to cook it.

Use the phase diagram to explain why ice cubes float in water.

The equilibrium line between solid and liquid slopes slightly to the left. Increasing the pressure lowers the melting point: the liquid phase is favoured over the solid phase by increasing pressure.

This behaviour results from the solid occupying more volume than the liquid. If the pressure increases, the system responds by favouring the liquid as it takes up less space.

The solid has a lower density than the liquid form.

Marks
7

- Write the equation for the dissolution of lead(II) chloride, $PbCl_2$, in water.

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

Write the expression for the solubility product constant, K_{sp}, for $PbCl_2$.

$K_{sp} = [Pb^{2+}(aq)][Cl^-(aq)]^2$

What $[Cl^-]$ is needed to reduce the $[Pb^{2+}]$ to the maximum safe level of 0.015 mg L^{-1}? $K_{sp}(PbCl_2) = 1.6 \times 10^{-6}$

The molar mass of Pb is 207.2 g mol^{-1} so 0.015 mg corresponds to:

number of moles = mass / molar mass
= 0.015×10^{-3} g / 207.2 g mol^{-1} = 7.2×10^{-8} mol

The maximum safe value for $[Pb^{2+}(aq)]$ = 7.2×10^{-8} mol L^{-1}. As K_{sp} = 1.6×10^{-6}, the value of $[Cl^-(aq)]$ can be calculated:

$K_{sp} = [Pb^{2+}(aq)][Cl^-(aq)]^2 = (7.2 \times 10^{-8}) \times [Cl^-(aq)]^2 = 1.6 \times 10^{-6}$

$[Cl^-(aq)]$ = 4.7 mol L^{-1}

$[Cl^-]$ = 4.7 mol L^{-1}

The solubility of sodium chloride is 359 g L^{-1}. If a reservoir of 50,000 L is saturated with lead(II) chloride, can sodium chloride be used to reduce the $[Pb^{2+}]$ to a safe level? If so, what mass of sodium chloride (in kg) would be needed?

The molar mass of NaCl is:

molar mass = (22.99 (Na) + 35.45 (Cl)) g mol^{-1} = 58.44 g mol^{-1}

359 g corresponds to:

number of moles = mass / molar mass
= 359 g / 58.44 g mol^{-1} = 6.14 mol

The maximum concentration of $[Cl^-(aq)]$ from NaCl is therefore 6.14 mol L^{-1}. As this is greater than that required to keep the lead concentration at a safe level, it could be used.

The minimum concentration of $Cl^-(aq)$ needed is 4.7 mol L^{-1}. The number of moles required to achieve this concentration in 50,000 L is therefore:

number of moles = concentration × volume
= 4.7 mol L^{-1} × 50000 L = 24000 mol

ANSWER CONTINUES ON THE NEXT PAGE

The mass of NaCl that corresponds to this is:

mass = number of moles × molar mass
      = 24000 mol × 58.44 g mol^{-1} = 1.4 × 10^7 g = 14 tonnes
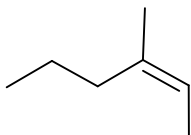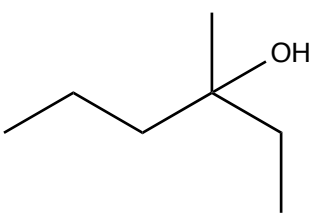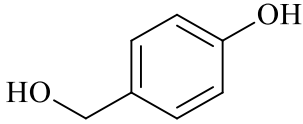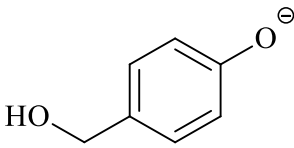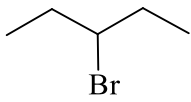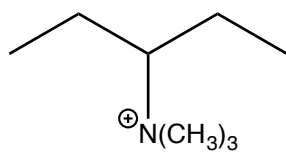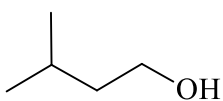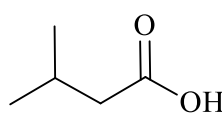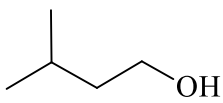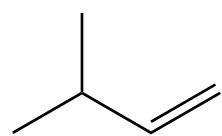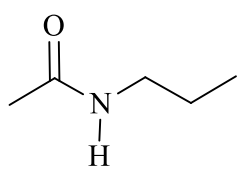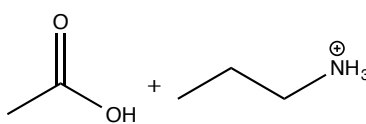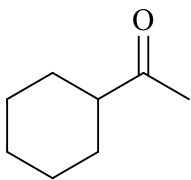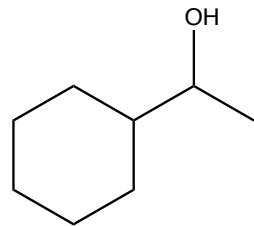
Answer: **1.4 × 10^7 g or 14 tonnes**

Would the water in the reservoir be fit for drinking? Explain your answer.

It would be too salty to drink and is likely to exceed safe levels of Na$^+$(aq) and Cl$^-$(aq).

- Complete the following table. Make sure you give the name of the starting material where indicated.

**Marks
10**

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
Name: **(Z)-3-methyl-2-hexene**	dilute H_2SO_4	
Name: 3-bromopentane	$N(CH_3)_3$	
	$Cr_2O_7{}^{2-}$ / H^+	
	concentrated H_2SO_4	
	$H^{\oplus}$ / H_2O / heat	
	1. $LiAlH_4$ 2. $H^{\oplus}$ / H_2O	

Marks
8

• Consider compound **A**, whose structure is shown below.
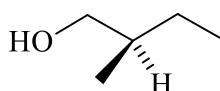
A

List the substituents on the stereogenic (chiral) carbon in compound **A**, in descending order as determined by the sequence rules.
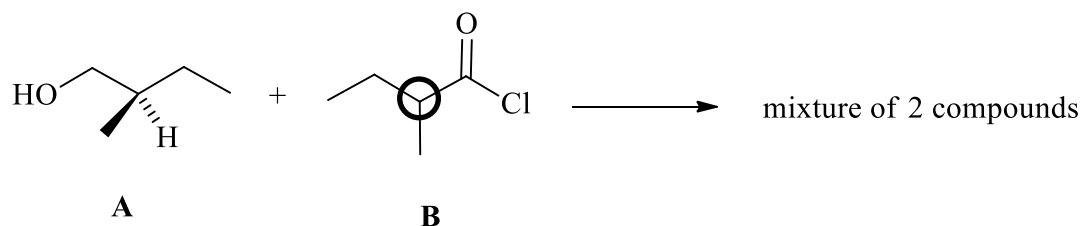
Highest priority   Lowest priority

-CH₂OH	**-CH₂CH₃**	**-CH₃**	**-H**

Give the full name that unambiguously describes the stereochemistry of compound **A**.
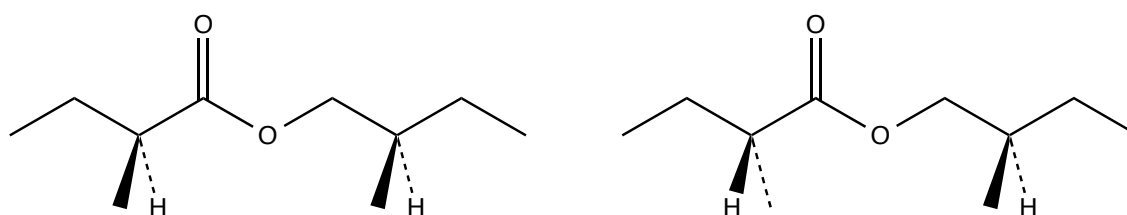
(*R*)-2-methylbutan-1-ol   or (*R*)-2-methyl-1-butanol

When compound **A** is reacted with racemic compound **B**, two compounds are formed as shown below.

Circle the stereogenic centre in compound B.

Draw the stick structures of the two compounds formed in this reaction. Make sure you clearly show all of the stereochemistry in your structures.


Are the two compounds formed in this reaction enantiomers, constitutional isomers or diastereoisomers?

They are diastereoisomers (stereoisomers which are not mirror images).

Marks
8

• The tropane alkaloid (–)-hyoscyamine is found in certain plants of the *Solanaceae* family. It is an anticholinergic agent that works by blocking the action of acetylcholine at parasympathetic sites in smooth muscle, secretory glands and the central nervous system.
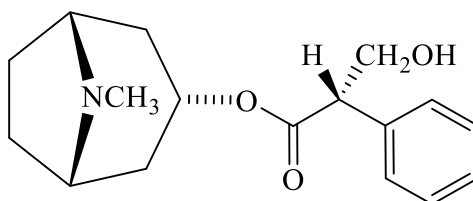
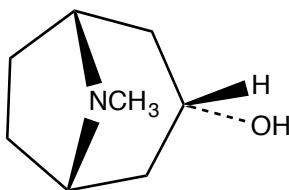Give the molecular formula of (–)-hyoscyamine.

$C_{17}H_{23}O_3N$

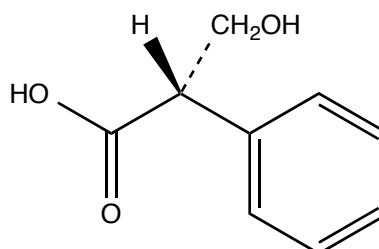List the functional groups present in (–)-hyoscyamine.

Tertiary amne, ester, primary alcohol and aromatic ring.

Hydrolysis of (–)-hyoscyamine results in two fragments, tropine and tropic acid. Draw each of these fragments.

tropine	tropic acid

What is the stereochemistry at the tropic acid stereocentre? Write (*R*) or (*S*). | **(*S*)**

Is tropine optically active? Explain your answer.

Tropine is not optically active. It has no chiral centre and is identical to its mirror image.

	Marks
• The amino acids alanine and phenylalanine can be reacted together to form two dipeptides. Draw the structures of the two possible dipeptides.	**3**

alanine   phenylalanine
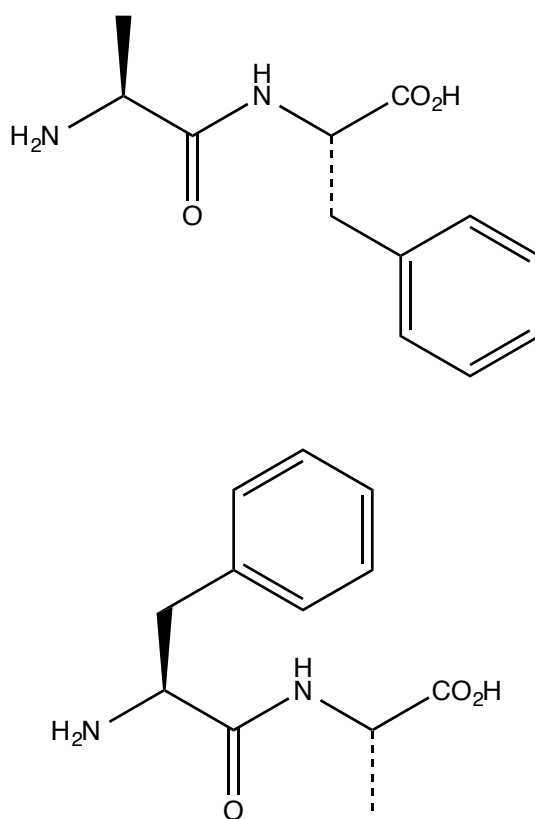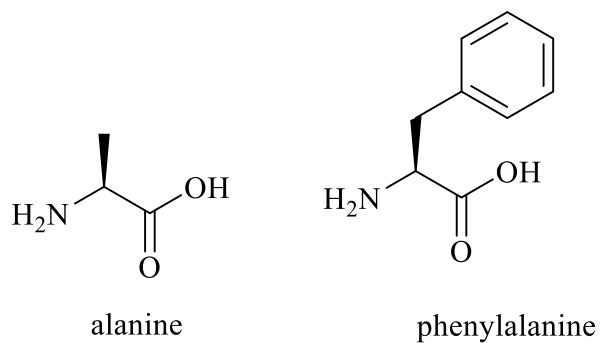
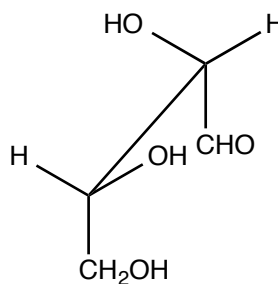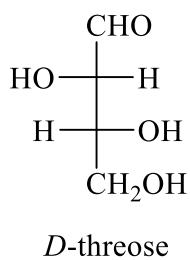**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

- Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structure of any intermediate compounds formed.

(i) NaBH$_4$
(ii) H$_3$O$^+$

HCl

concentrated H$_2$SO$_4$ / heat
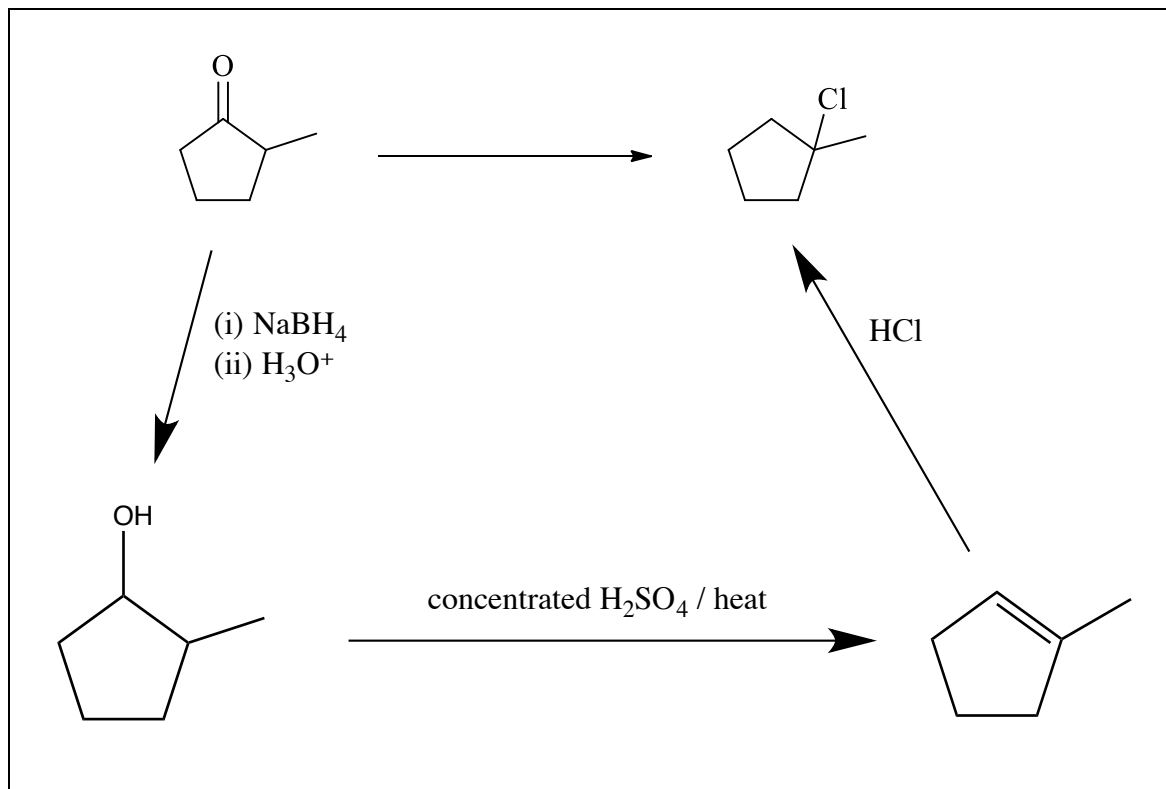
- Convert the following structure into a sawhorse projection.

3

CHO
HO——H
H——OH
CH$_2$OH

D-threose

What does the *D* in the name *D*-threose designate?

The OH on the last stereogenic carbon on the Fischer projection (i.e. the third carbon from the top) is on the right hand side.