Topics in the June 2010 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2010-J-2:

- Intermolecular Forces and Phase Behaviour
- Hydrolysis of Metal Ions
- Physical States and Phase Diagrams

2010-J-3:

- Physical States and Phase Diagrams
- Solubility Equilibrium

2010-J-4:

- Coordination Chemistry

2010-J-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2010-J-6:

- Crystal Structures

2010-J-7:

- Kinetics

2010-J-8:

- Kinetics

2010-J-9:

- Stereochemistry

2010-J-10:

- Alkenes
- Alcohols
- Aldehydes and Ketones

2010-J-11:

- Carboxylic Acids and Derivatives

2010-J-12:

- Stereochemistry

2010-J-13:

- Alkenes

2010-J-14:

- Synthetic Strategies

	Marks
• Explain why hydrogen bonding is significant in H_2O (bp 100 °C), but not in H_2Se (bp –41°C) despite both oxygen and selenium being in Group 16 of the Periodic Table.	**2**

O is very small and has a high effective nuclear charge for its size: it is a very electronegative atom. The O-H bonds are thus extremely polar giving the H atoms a large partial positive charge and the O atom a large negative partial charge.

The small size of O and these charge leads to the formation of strong H-bonds in $H_2O(l)$.

Selenium is a much larger atom with a much lower electronegativity. The H-Se bonds are not sufficiently polar for H-bonding to occur between H_2Se molecules.

• Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3}, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9}.	**2**

The Fe^{3+} ion is much smaller and has a much higher charge density than the Fe^{2+} ion. This results in a stronger Fe–O bond and a weakening of the O–H bonds. The high charge density on the Fe^{3+} ion pulls electron density from the attached OH_2 ligands. This leads to the release of $H^+(aq)$.

As the O–H bonds are weaker, it is more acidic: it has a much *greater* value for K_a.

• Which of the following are allotropes? Explain your answer. $^{16}O, {}^{18}O, O_2, O_3, O^-, O^{2-}, O_2^-, O_2^{2-}, H_2O, H_2S, H_2O_2.$	**1**

Allotropes are different structural forms of an *element*.

The only allotropes in the list are O_2 and O_3.

	Marks

- The solid-liquid curve in the phase diagram of a particular compound slopes to the left. Can the compound sublime? Explain your answer.

Marks 1

The slope of the solid-liquid curve is irrelevant as sublimation is the phase change from solid to gas.

As long as there is an equilibrium line between these phases then the compound can sublime.

(The sloping of the solid-liquid to the left indicates that the solid is less dense than the solid and applying pressure has the effect of pushing the substance towards the liquid phase.)

- Following blood donation, a solution of sodium oxalate is added to remove Ca^{2+} ions (as calcium oxalate, $CaC_2O_4 \cdot H_2O$, K_{sp} 2.3×10^{-9}), which cause the blood to clot. If the concentration of Ca^{2+} ions in blood is 9.7×10^{-5} g mL^{-1}, and 100.0 mL of 0.1550 M $Na_2C_2O_4$ is added to a 104 mL sample of blood, what will be the concentration (in mol L^{-1}) of Ca^{2+} ions remaining in the blood?

4

The amount of Ca^{2+} present in 100.0 mL is 9.7×10^{-3} g. As its molar mass is 40.08 g mol^{-1}, this corresponds to:

    number of moles = mass / molar mass =
        = (9.7×10^{-3} g) / (40.08 g mol^{-1}) = 2.4×10^{-4} mol

The number of moles of $C_2O_4^{2-}$(aq) added is:

    number of moles = concentration × volume
        = (0.1550 mol L^{-1}) × (0.1000 L) = 0.01550 mol

When this is added to the blood, the total volume increases to (100.0 + 104) mL = 204 mL. The concentration of $C_2O_4^{2-}$(aq) is now:

    concentration = number of moles / volume
        = (0.01550 mol) / (0.204 L) = 0.0760 mol L^{-1}

For $CaC_2O_4.H_2O$(s), the solubility product is for the reaction:

    $CaC_2O_4.H(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq) + H_2O(l)$
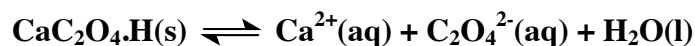
    $K_{sp} = [Ca^{2+}(aq)][C_2O_4^{2-}(aq)]$

The amount of $C_2O_4^{2-}$ is *much* larger than the amount of Ca^{2+} present so precipitation of $CaC_2O_4.H_2O$(s) does not reduce its concentration significantly. Hence:

    $[Ca^{2+}(aq)] = K_{sp} / [C_2O_4^{2-}(aq)] = (2.3 \times 10^{-9} / 0.0760)$ M = 3.0×10^{-8} M

Answer: **3.0×10^{-8} M**

	Marks
• Complete the following table. $NCS^- =$ isothiocyanate ion	**5**

bipy = 2,2'-bipyridine = $(C_5H_4N)_2$ =
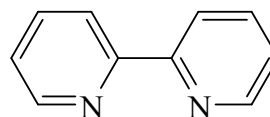
Formula	$K_2[Zn(CN)_4]$	$[Co(bipy)(NH_3)_4]Cl_3$	$[Co(bipy)_2(NCS)_2]$
Oxidation state of transition metal ion	**+2 or II**	**+3 or III**	**+2 or II**
Coordination number of transition metal ion	**4**	**6**	**6**
Number of *d*-electrons in the transition metal ion	**10**	**6**	**7**
Coordination geometry of the complex ion	**tetrahedral**	**octahedral**	**octahedral**
List all the ligand donor atoms	**4 × C**	**2 × N (from bipy)** **4 × N (from NH₃)**	**4 × N (from bipy)** **2 × N (from NCS⁻)**

- A 20.0 mL solution of nitrous acid (HNO_2, pK_a = 3.15) was titrated to its equivalence point with 24.8 mL of 0.020 M NaOH. What is the concentration of the HNO_2 solution?

The number of moles of OH⁻ added at the equivalence point is:

> number of moles = concentration × volume
> = (0.020 mol L⁻¹)(0.0248 L) = 0.00050 mol

This must also be equal to the number of moles of HNO_2 present in 20.0 mL. Its concentration is therefore:

> concentration = number of moles / volume
> = (0.00050 mol) / (0.020 L) = 0.025 M

Answer: **0.025 M**

What was the pH at the start of the titration?

As HNO_2 is a weak acid, [H⁺(aq)] must be calculated by considering the equilibrium:

	HNO_2(aq)	⇌	NO_2^-(aq)	H⁺(aq)
initial	0.025		0	0
change	-x		+x	+x
final	0.025 – x		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[HNO_2^-(aq)][H^+(aq)]}{[HNO_2]} = \frac{x^2}{(0.025-x)}$$

As pK_a = 3.15, K_a = 10⁻³·¹⁵. K_a is very small so 0.025 – x ~ 0.025 and hence:

$$x^2 = 0.025 \times 10^{-3.15} \quad \text{or} \quad x = 0.0042 \text{ M} = [\text{H·(aq)}]$$

Hence, the pH is given by:

$$pH = -\log_{10}[\text{H·(aq)}] = -\log_{10}[0.0042] = 2.38$$

pH = **2.38**

ANSWER CONTINUES ON THE NEXT PAGE

What was the pH after (a) 12.4 mL and (b) 24.8 mL of the NaOH had been added?

When OH⁻ reacts with HNO_2, the amount of HNO_2 decreases *and* the amount of its conjugate base, NO_2^-, increases.

(a)　12.4 mL represents the half equivalence point. When this much OH⁻ is added, the amount of HNO_2 is reduced to half its initial value and an *equal* amount of NO_2^- is produced. With $[HNO_2(aq)] = [NO_2^-(aq)]$, the Henderson-Hasselbalch equation gives the pH as:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 3.15 + \log(1) = 3.15$$

(b)　24.8 mL represents the equivalence point. When this much OH⁻ is added, the amount of HNO_2 is reduced zero and all of the initial HNO_2 is now present as NO_2^-. From above, the amount of NO_2^- is therefore 0.00050 mol. The total volume is now (20.0 + 24.8) mL = 44.8 mL so:

$[NO_2^-(aq)] = (0.00050 \text{ mol}) / 0.0448 \text{ L}) = 0.0112 \text{ M}$

As $NO_2^-(aq)$ is a weak base, the pH must be calculated using a reaction table:

	$NO_2^-(aq)$	$H_2O(l)$	$\rightleftharpoons$	$HNO_2(aq)$	$OH^-(aq)$
initial	0.0112	large		0	0
change	-y	negligible		+y	+y
final	0.0112 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[HNO_2(aq)][OH^-(aq)]}{[NO_2^-(aq)]} = \frac{y^2}{(0.0112-y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 - 3.15 = 10.85$

As $pK_b = 10.85$, $K_b = 10^{-10.85}$. K_b is very small so $0.0112 - y \sim 0.0112$ and hence:

$y^2 = 0.0112 \times 10^{-10.85}$ or $y = 0.000000397 \text{ M} = [OH^-]$

Hence, the pOH is given by:

$pOH = -\log_{10}[OH^-] = \log_{10}[0.000000397] = 6.40$

Finally, pH + pOH = 14.00 so pH = 14.00 – 6.40 = 7.60

(a) 12.4 mL: pH = **3.15** 　　　　　　　(b) 24.8 mL: pH = **7.60**

ANSWER CONTINUES ON THE NEXT PAGE

Qualitatively, how would each of these three pH values be affected if 5 mL of water were added to the 20.00 mL of nitrous acid before beginning the titration?

The initial pH would increase slightly as the nitrous acid solution would be more dilute.

The pH at half-equivalence point would *not* change (as pH = pK_a).

The final pH would decrease slightly as the NO_2^- solution produced would also be more dilute.

•   The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. The unit cell dimension (edge length, *a*) for this alloy is 0.36 nm.
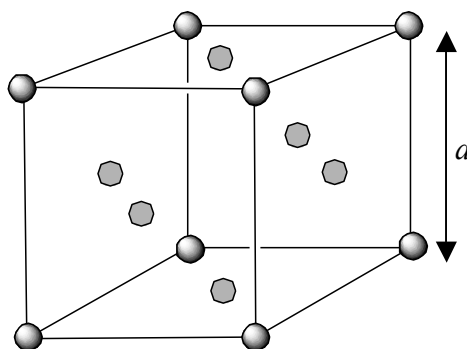
⬤ = Au   ⬡ = Cu

What is the chemical formula of the alloy?

There are 8 Au atoms on the corners. Each of these contribute 1/8 to the unit cell:

  number of Au atoms = 8 × 1/8 = 1

There are 6 Cu atoms on the face. Each of these contribute 1/2 to the unit cell:

  number of Cu atoms = 6 × 1/2 = 3

The ratio of Cu to Au atoms is therefore 3 : 1 and the formula is Cu_3Au.

Answer: **Cu_3Au**

Pure gold is 24 carat, whilst gold alloys consisting of 75 % gold by weight are termed 18 carat gold. What carat gold is this alloy?

The molar mass of Cu_3Au is:

  molar mass = (3 × 63.55 (Cu) + 1 × 196.97 (Au)) g mol⁻¹ = 387.62 g mol⁻¹.

1 mol of Cu_3Au contains 1 mol of Au, the percentage by weight of gold in Cu_3Au is:

  percentage by weight $= \dfrac{196.97}{387.62} \times 100\ \% = 50\ \%$

As a 100 % alloy is 24 carat and a 75% alloy is 18 carat, a 50 % alloy is 12 carat.

Answer: **12 carat**

What is the volume (in cm³) of the unit cell?

As the unit cell is cubic:

  volume = (side length)³ = a^3 = (0.36 × 10⁻⁹ m)³ = 4.7 × 10⁻²⁹ m³

                        = 4.7 × 10⁻²³ cm³

Answer: **4.7 × 10⁻²³ cm³**

ANSWER CONTINUES ON THE NEXT PAGE

What is the density (in g cm^{-3}) of the alloy?

From above, the unit cell contains 1 Au atom and 3 Cu atoms:

mass of gold = 196.97 g mol^{-1} / 6.022 × 10^{23} mol^{-1} = 3.271 × 10^{-22} g

mass of copper = 3 × 63.55 g mol^{-1} / 6.022 × 10^{23} mol^{-1} = 3.166 × 10^{-22} g

mass of unit cell = (3.271 × 10^{-22} + 3.166 × 10^{-22}) g = 6.437 × 10^{-22} g

The density is therefore:

density = mass / volume

= 6.437 × 10^{-22} g / 4.7 × 10^{-23} cm^3 = 1.4 × 10^1 g cm^{-3}

Answer: **14 g cm^{-3}**

Marks
4

- In the reaction of Cl_2 with Br_2 in CCl_4 solution, BrCl forms according to the equation:

$$Br_2 + Cl_2 \rightarrow 2BrCl \qquad K_c = 2$$

With initial concentrations of $[Br_2] = 0.6$ M, $[Cl_2] = 0.4$ M and $[BrCl] = 0.0$ M, which of the following concentration versus time graphs represents this reaction? Explain qualitatively why you rejected each of the other three graphs.
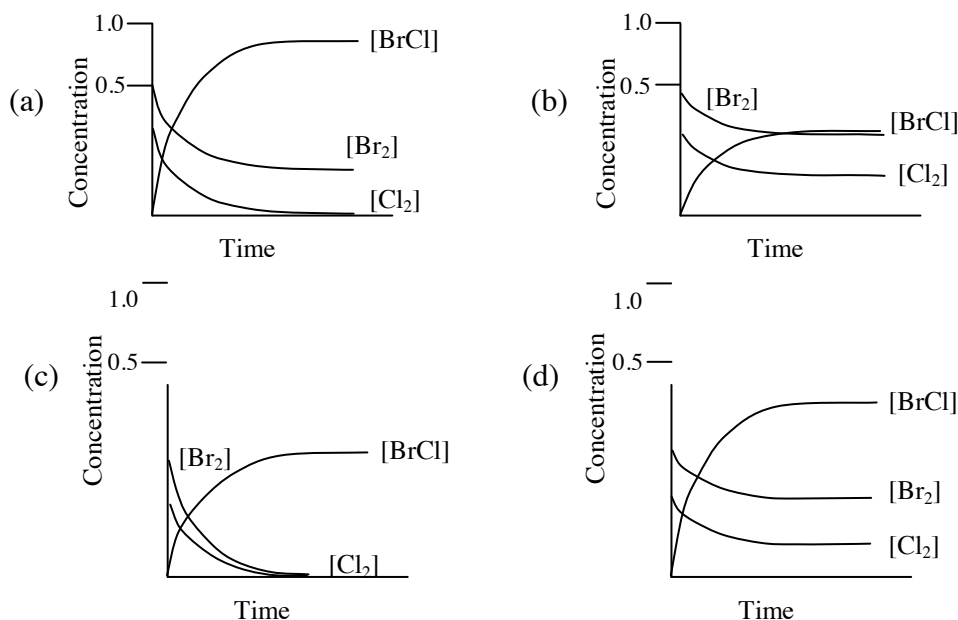
Graph B is correct.

Graphs A and C: As $K_c = 2$, the reaction does not go anywhere near to completion. At equilibrium, the concentrations of reactants and products are both significant. Graphs A and C can therefore be rejected because at least one reagent in both these graphs has dropped to 0. Also, in Graph C, the rates of change of $[Br_2]$ and $[Cl_2]$ are different, at variance with the stoichiometry of the reaction.

Graph D: Cl_2 is the limiting reagent, so the maximum [BrCl] that can form is twice the initial $[Cl_2]$. But as only half the Cl_2 has been used, the maximum [BrCl] that can form is $0.2 \times 2 = 0.4$ M.

- Hydrogenation of NO to N_2 and water is a potential means of reducing smog-forming NO_x gases:

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$
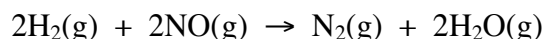
The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0).

Experiment	P_0 H_2 (kPa)	P_0 NO (kPa)	Rate (kPa s^{-1})
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

What is the order of the reaction? Show all working.

The rate law is in the form:

rate = $k(P(H_2))^n(P(NO))^m$

The order of the reaction is equal to $n + m$.

Between experiments (1) and (2), $P(H_2)$ is constant. $P(NO)$ is decreased from 40.0 kPa to 20.3 kPa. It is almost halved. This causes the rate to drop from 0.137 kPa s^{-1} to 0.033 kPa s^{-1}. It is decreases by (0.033 / 0.137) % = 24.1 %

As halving the amount of NO reduces the rate by a factor of 4, $m = 2$.

Between experiments (3) and (4), $P(NO)$ is constant. $P(H_2)$ is decreased from 38.5 kPa to 19.6 kPa. It is almost halved. This causes the rate to drop from 0.213 kPa s^{-1} to 0.105 kPa s^{-1}. It is decreases by (0.105 / 0.213) % = 49.2 %

As halving the amount of NO reduces the rate by a factor of 2, $n = 1$.

The order of the reaction is equal to $n + m$ so is 3.

Answer: **3**

What is the value of the rate constant?

From above, the rate law is:

rate = $k(P(H_2))(P(NO))^2$
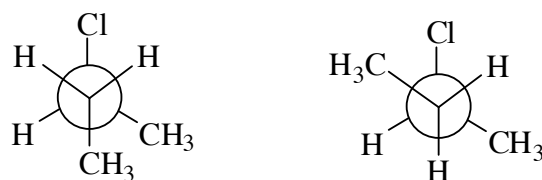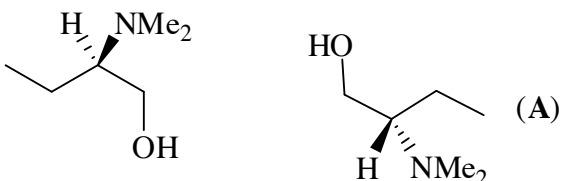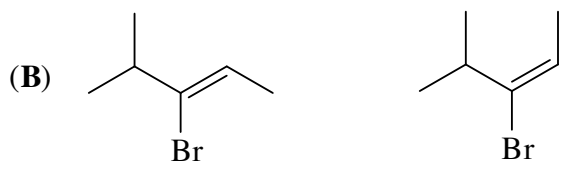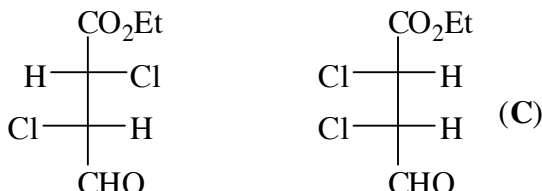
From experiment (1), rate = 0.137 kPa s^{-1} when $P(H_2)$ = 53.3 kPa and $P(NO)$ = 40.0 kPa. Hence:

k = rate / [$(P(H_2))(P(NO))^2$]

= (0.137 kPa s^{-1}) / (53.3 kPa)(40.0 kPa)^2

= 1.61×10^{-6} kPa^{-2} s^{-1}

**(Note that the units can be derived from the equation and would be required to gain the marks in this question.)**

Answer: **1.61×10^{-6} kPa^{-2} s^{-1}**

Marks
8

•   Consider the following pairs of compounds. Indicate the isomeric relationship that exists between the compounds in each set.

	constitutional isomers **(different connectivity)**
	conformational isomers **(related by a rotation about a C-C bond)**
(A)	**enantiomers** **(non-superimposable mirror images)**
(B)	**diastereoisomers** **(different arrangement in space but not enantiomers)**
(C)	**diastereoisomers** **(different arrangement in space but *not* enantiomers – the molecules are not mirror images of one another)**

What is the configuration of the stereogenic centre in compound (**A**)?

(*S*). The groups have the priorities shown below. With the lowest priority group at the back, the other groups are in an anticlockwise order.
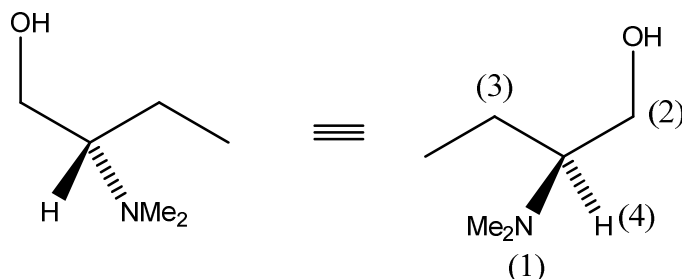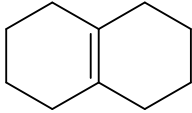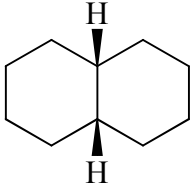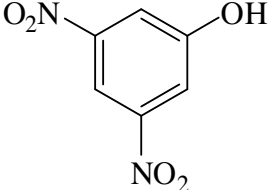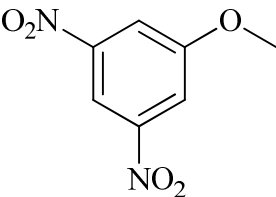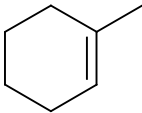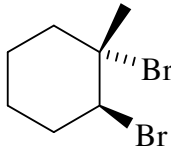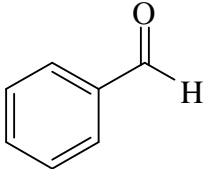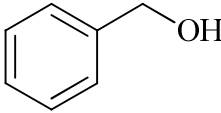

Give the full name of compound (**B**) that unambiguously describes its stereochemistry.

(*Z*)-3-bromo-4-methylpent-2-ene

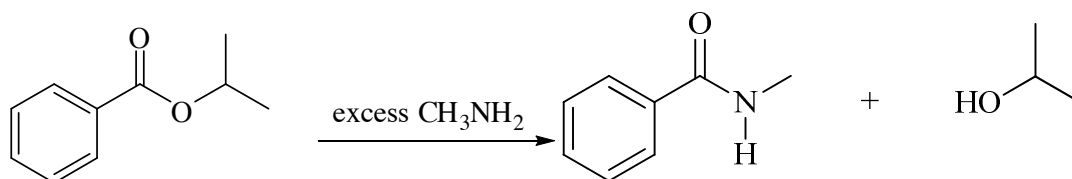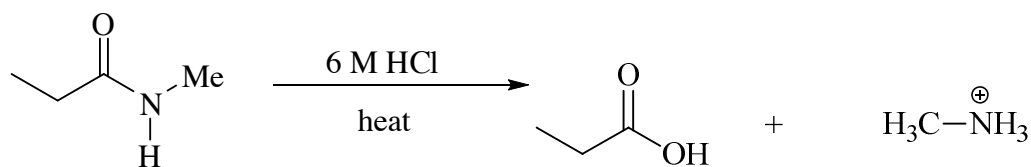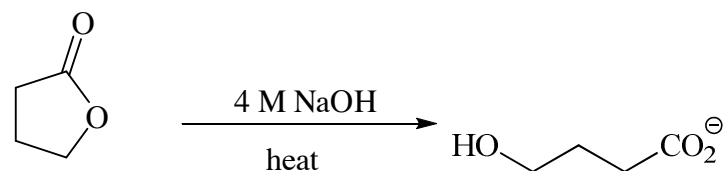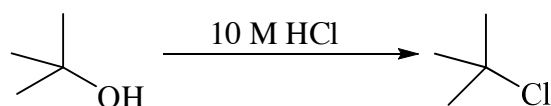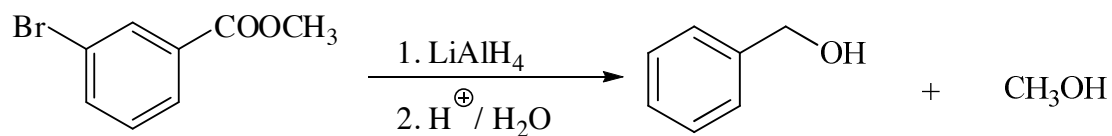Is compound (**C**) a *meso* isomer? Give a reason for your answer.
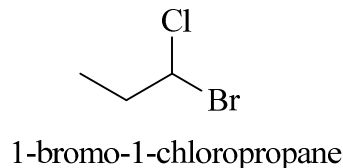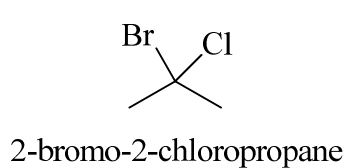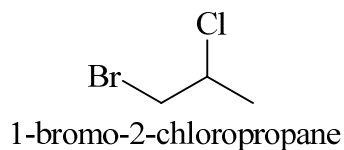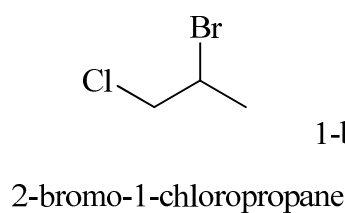
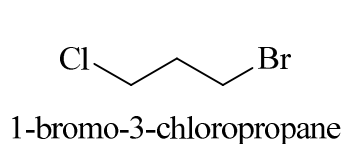**No. It has no plane of symmetry.**

- Complete the following table. Make sure you indicate any relevant stereochemistry.

Marks
4

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	H_2/Pd/C (catalyst)	
	1. NaOH 2. CH_3Br	
	Br_2	
	1. $NaBH_4$ 2. $H^{\oplus}$/ H_2O	

	Marks
• Give the constitutional formula(s) of the major organic product(s) formed in each of the following reactions.	**7**

Br—⟨benzene ring⟩—COOCH₃ $\xrightarrow[\text{2. H}^{\oplus}/\text{H}_2\text{O}]{\text{1. LiAlH}_4}$ ⟨benzene ring⟩—CH₂OH   +   CH₃OH

(CH₃)₃C—OH $\xrightarrow{\text{10 M HCl}}$ (CH₃)₃C—Cl

γ-butyrolactone $\xrightarrow[\text{heat}]{\text{4 M NaOH}}$ HO–CH₂CH₂CH₂–CO₂⁻

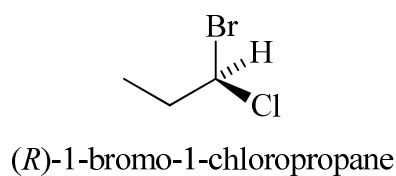CH₃CH₂C(=O)–N(H)–Me $\xrightarrow[\text{heat}]{\text{6 M HCl}}$ CH₃CH₂C(=O)–OH   +   H₃C–$\overset{\oplus}{N}$H₃

Ph–C(=O)–O–CH(CH₃)₂ $\xrightarrow{\text{excess CH}_3\text{NH}_2}$ Ph–C(=O)–N(H)–CH₃   +   HO–CH(CH₃)₂

- Draw the constitutional formulas of all isomers of C_3H_6BrCl.

Cl⌄⌄⌄Br

1-bromo-3-chloropropane

Br | Cl⌄⌄

2-bromo-1-chloropropane

Cl | Br⌄⌄

1-bromo-2-chloropropane

Br⌄Cl

2-bromo-2-chloropropane

Cl⌄⌄Br

1-bromo-1-chloropropane

A number of the above isomers are optically active. For all such compounds, draw the two enantiomers.

Cl, H, Br

(*S*)-1-bromo-1-chloropropane

Br, H, Cl

(*S*)-2-bromo-1-chloropropane

Cl, H, Br

(*S*)-1-bromo-2-chloropropane

Br, H, Cl

(*R*)-1-bromo-1-chloropropane

Cl, H, Br

(*R*)-2-bromo-1-chloropropane

Br, H, Cl

(*R*)-1-bromo-2-chloropropane
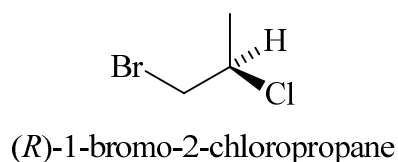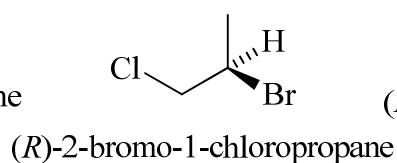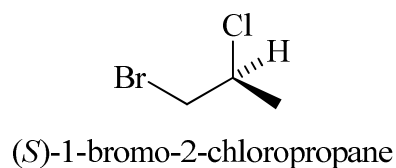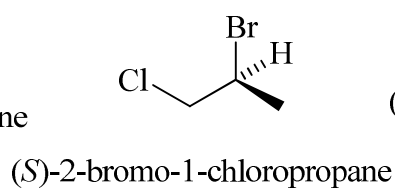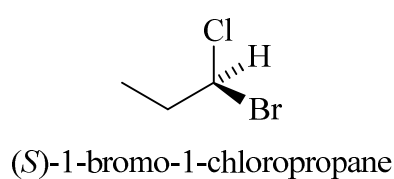
Select any **one** of the structures you have drawn on this page and write its full systematic name just below it. **See above.**

	Marks 3
• Complete the mechanism for the following reaction. Give the structure of the carbocation intermediate and indicate (using curly arrows) all the bonding changes that occur.	
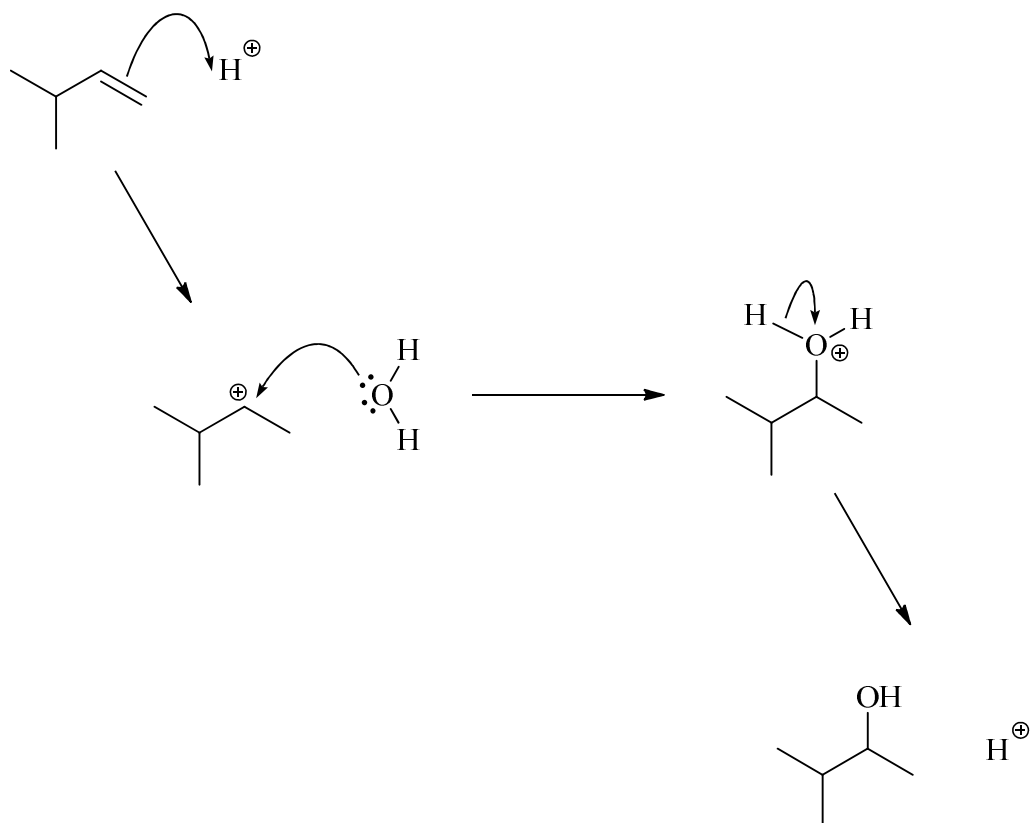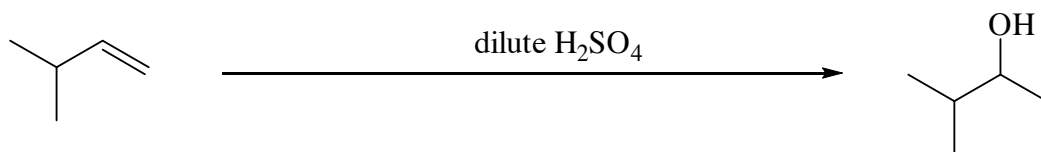
	Marks
• Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.	6