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NZQA
NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2014
Chemistry

9.30 am Monday 10 November 2014
Time allowed: Three hours
Total marks: 40

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

You should answer ALL the questions in this booklet.

Resource Sheet S–CHEMR is included in your pack.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–20 in the correct order and that none of these pages is blank.

You are advised to spend approximately 35 minutes on each question.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

Question	Mark
ONE	
TWO	
THREE	
FOUR	
FIVE	
TOTAL	/40

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QUESTION ONE

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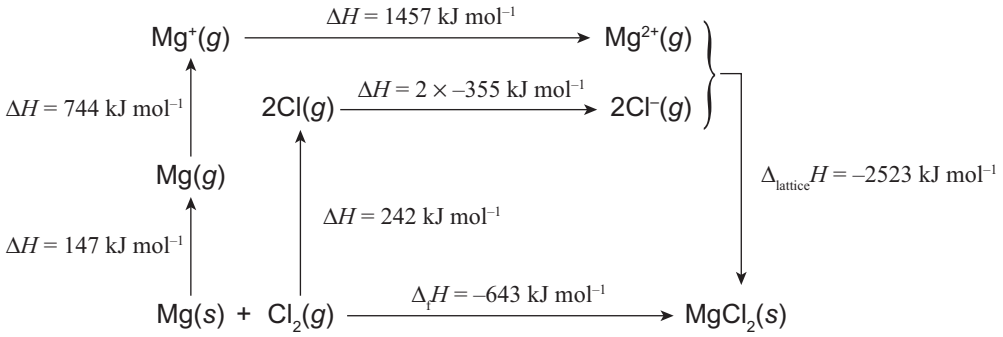
(a) Magnesium metal and chlorine gas react spontaneously to produce solid magnesium chloride.

The following diagram gives the enthalpy changes for the steps in a Hess's Law cycle for the formation of $MgCl_2(s)$ from its elements.



(i) A similar cycle could be drawn for the formation of NaCl(*s*) from its elements.

$\Delta_f H(NaCl) = -411$ kJ mol^{-1}

Account for the difference in the values for the enthalpy of formation for the two compounds, $MgCl_2$ and NaCl, by comparing and contrasting the enthalpy changes for the steps in the Hess's Law cycles.

You are not expected to know the actual values for the NaCl steps, but you should use your knowledge of structure and bonding to discuss why the enthalpy changes would be larger or smaller than for those in the $MgCl_2$ cycle.

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(ii) Use the information in the Hess's Law cycle given to discuss the relative stability of $MgCl_2$ and MgCl.

The theoretical value for $\Delta_{lattice}H(MgCl) = -753$ kJ mol^{-1}

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(b) Observations of a well-known chemical phenomenon are given below, along with potential misconceptions of the chemistry involved.

Observations: Energy from the sun is used in the process of photosynthesis, resulting in the formation of glucose and oxygen from carbon dioxide and water. During the process of respiration, glucose and oxygen are converted to carbon dioxide and water to provide energy for cell reactions.

Common misconceptions: *Energy from the sun is stored in the bonds of the glucose molecules and released when these bonds are broken.*

Data:

	Standard Enthalpy of Formation/kJ mol^{-1}
Glucose ($C_6H_{12}O_6(s)$)	–1271
Water ($H_2O(\ell)$)	–286
Carbon dioxide ($CO_2(g)$)	–394

Give an account of the enthalpy and entropy of the processes described, and discuss the errors in the misconceptions, including a more correct interpretation of the evidence.

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QUESTION TWO

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Sodium hypochlorite is used, on a large scale, for water disinfection, including the water in swimming pools. It is also the active ingredient in household bleach.

In the water purification industry, **percent available chlorine** is a unit of concentration used for hypochlorite-based bleaches. One gram of a 100% available chlorine bleach has the same bleaching power as one gram of chlorine. The term 'available chlorine' is used because most commercial bleaches contain substantial amounts of chloride ions, which have no bleaching properties.

(a) A bottle of household bleach contains the following information:

Active ingredients: Sodium hypochlorite 42 g L^{-1} (available chlorine 4.0% m/V), available chlorine by 'use by date' 2.0% m/V, sodium hydroxide 9 g L^{-1}.

(i) The following procedure is carried out to determine the extent of the decomposition of the contents of the bottle of household bleach described above.

A 20.00 mL sample of the bleach is diluted to 250.00 mL, using a volumetric flask.

Excess potassium iodide is added to a 10.00 mL sample of the diluted bleach solution, along with 10 mL of dilute sulfuric acid.

$$H^+ + 2I^- + OCl^- \rightarrow I_2 + Cl^- + OH^-$$

The liberated iodine is titrated with a standard sodium thiosulfate ($Na_2S_2O_3$) solution of concentration 0.04562 mol L^{-1}. The end point is determined by the change of colour of a starch indicator.

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

The titration data is given below.

Titre	Final volume/mL	Initial volume/mL
1	16.88	0.16
2	33.56	16.88
3	16.98	0.02
4	33.64	16.98

Determine the extent of the decomposition of the bleach by comparing the available chlorine (% m/V) in the bottle, with that given on the label.

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(ii) The decomposition of bleach is a disproportionation reaction, where an atom in a particular oxidation state acts as both an oxidant and a reductant.

Use the following data to explain why the hypochlorite ion might decompose in a disproportionation reaction.

$E°(ClO_3^-/ClO^-) = +0.50$ V $E°(ClO^-/Cl^-) = +0.89$ V in basic conditions

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(b) Production of sodium hypochlorite is part of the chlor-alkali industry and involves electrolysis of a brine solution, which contains dissolved sodium chloride.

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

When electrolysis takes place in aqueous solution, the strongest oxidant in the solution reacts at one electrode, and the strongest reductant at the other. However, the electrode potential of a half cell is dependent on the concentration of the cell components. When a concentrated solution of sodium chloride is used, as in the chlor-alkali cell, chlorine gas is formed at one electrode, and hydrogen gas and hydroxide ions at the other.

Unless the two electrolytic half cells are separated, chlorine and hydroxide ions can react to form hypochlorite:

$$OH^- + Cl_2 \rightarrow H^+ + OCl^- + Cl^-$$

Discuss the oxidation-reduction processes that occur during the preparation of hypochlorite in relation to the species involved, the movement of electrons, and the spontaneity of the reactions. Standard reduction potentials are provided below.

Redox couple	$E°$ /V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.36
$2HOCl + 2e^- \rightleftharpoons Cl_2 + 2OH^-$	0.42
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	0.40

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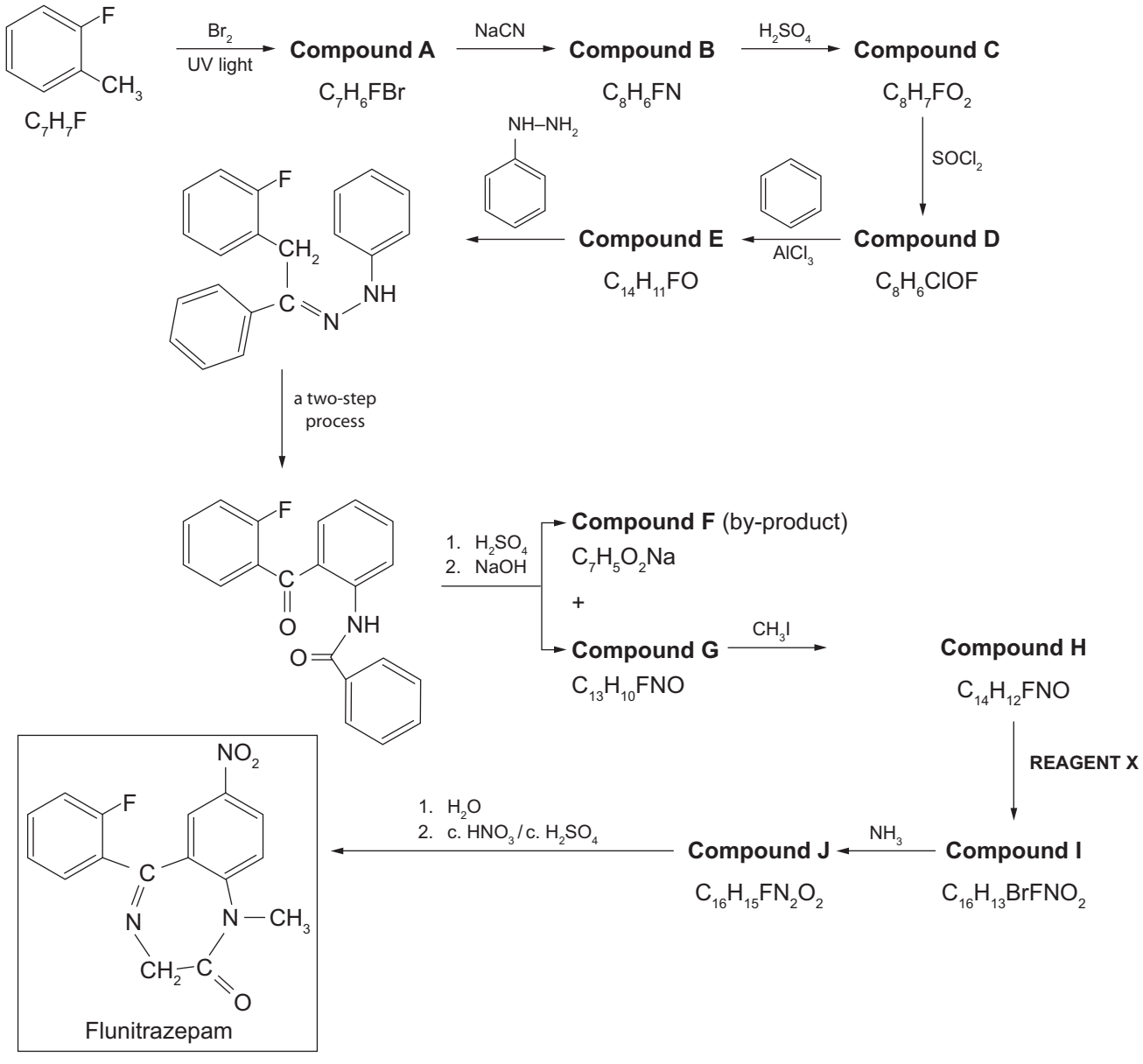
QUESTION THREE

Rohypnol is a trade name for the compound **flunitrazepam**. It is a controversial sedative which has sometimes been used to 'spike' people's drinks. The molecular structure for flunitrazepam is given in the box at the bottom of the scheme. Flunitrazepam was first synthesised from 2-fluoro-1-methylbenzene, as outlined in the scheme below. Some useful information is provided to help you interpret this scheme.

USEFUL INFORMATION

1. Compounds containing the $-C\equiv N$ functional group are called nitriles. They can be formed when a primary bromoalkane reacts by substitution with a cyanide ion (CN^-). Reaction with warm dilute sulfuric acid converts a nitrile to a carboxylic acid and an ammonium ion.
2. The benzene ring does not undergo the usual alkene reactions. The most common reaction of benzene rings is substitution of one of the hydrogen atoms.

   For example:
   - Substitution by Br will take place using Br_2 in the presence of a $FeBr_3$ catalyst.
   - Substitution by NO_2 is carried out using a mixture of concentrated nitric and sulfuric acids.
   - Substitution by an alkyl (eg $-CH_3$) or acyl group (eg $-\overset{\overset{O}{\|}}{C}-CH_3$) can be carried out using alkyl or acyl chloride in the presence of an $AlCl_3$ catalyst.



Complete the reaction scheme by providing structures for **Compounds A** to **J**, and identifying **Reagent X**. Note that some parts of the scheme have been completed for you.

You may not be familiar with all the chemistry involved, but the added information given in the box opposite can be used to interpret the data given.

Draw your structures in the box below.

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Structures for **Compounds A** to **J**, and identify **Reagent X**.

QUESTION FOUR

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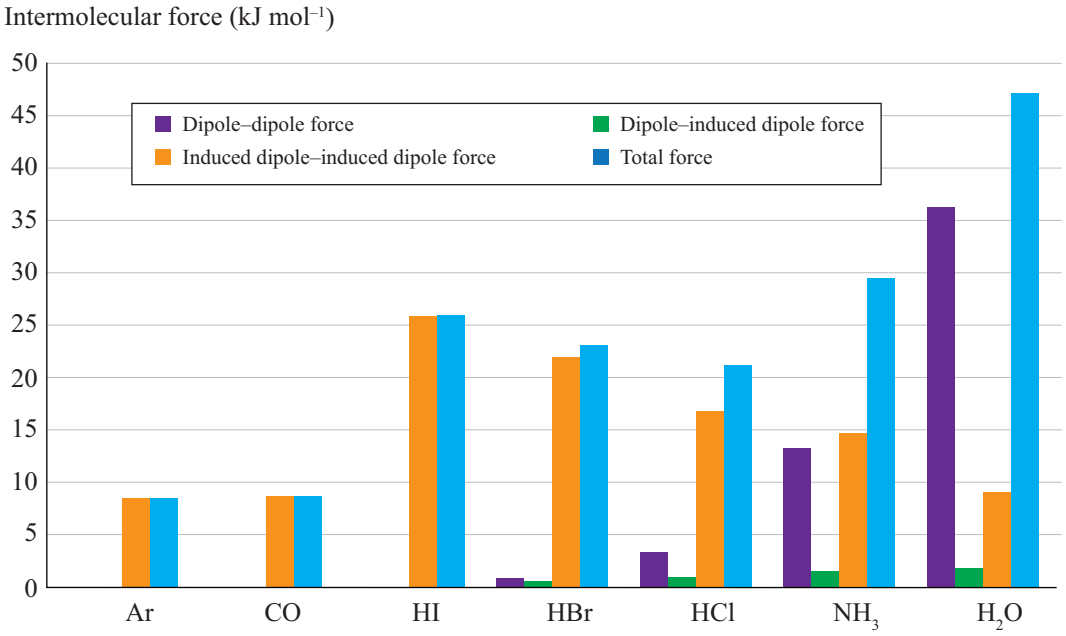
The bar graph below shows the relative importance of the different kinds of intermolecular forces of various substances.



Discuss the similarities, differences, and trends in the intermolecular forces **documented in the graph** for the substances given. (Assume that the inter-particle forces between the argon atoms come into the category of intermolecular forces.)

The dipole moments of the molecules are given below (units are debye, D).

Molecule	Dipole moment / D
CO	0.12
HI	0.38
HBr	0.83

Molecule	Dipole moment / D
HCl	1.05
NH_3	1.42
H_2O	1.85

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QUESTION FIVE

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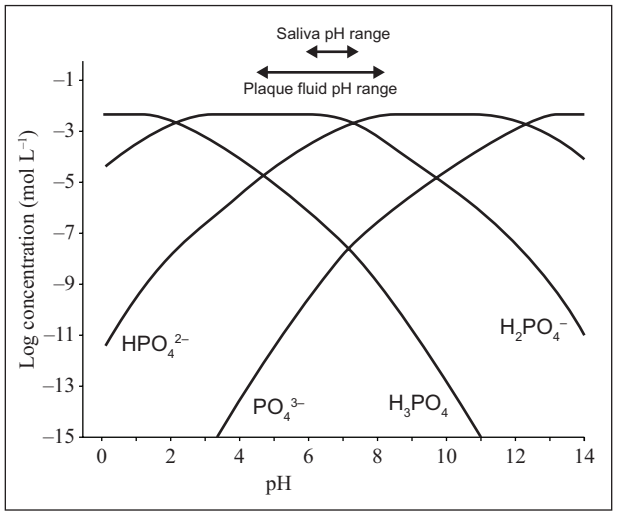
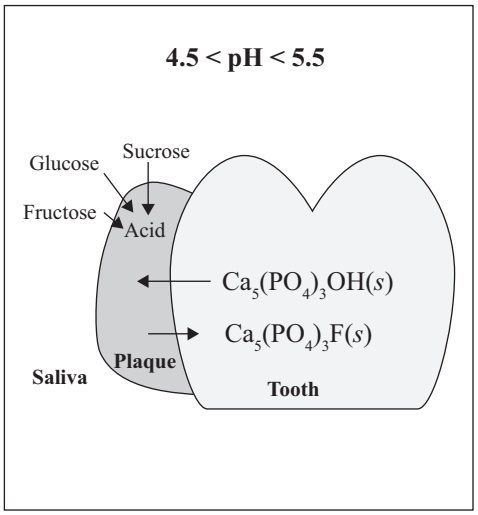
(a) Hydroxyapatite, $Ca_5(PO_4)_3OH$, is the naturally occurring mineral found in bone and teeth. Fluorapatite, $Ca_5(PO_4)_3F$, is a closely related mineral with a structure that allows it to co-deposit with hydroxyapatite. Fluorapatite is formed on the surface of teeth in the presence of fluoride ions (eg from toothpaste or fluoride-treated water).

(i) Hydroxyapatite in tooth enamel is preserved by being bathed in saliva, which has a pH between 6 and 7, and is saturated in dissolved calcium ions and inorganic phosphate. The form of the phosphate present in a solution is dependent on the pH of the solution, as shown in the graph below.

The effect of pH on the phosphate species in saliva





Plaque, a biofilm layer that can form on the outside of a tooth, also contains calcium ions and inorganic phosphate. When sugars are present, the pH of the plaque is lowered as the action of bacteria on the sugars produces acid. If the pH drops below 5.5, hydroxyapatite will dissolve. However, at this pH, a small concentration of F^- ions present in plaque allows the mineral fluorapatite to be deposited on the tooth. The removal of sugars or plaque will raise the pH, allowing hydroxyapatite and fluorapatite to be co-deposited on the tooth.

Use equilibrium principles to account for the observations described above.

$K_s(Ca_5(PO_4)_3OH) = 6.80 \times 10^{-37}$, $K_s(Ca_5(PO_4)_3F) = 1.00 \times 10^{-60}$, $pK_a(HF) = 3.17$

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(ii) Show that the pK_a of water is 15.74.

Use this value to compare the basicities of the OH^- and F^- ions, and hence explain why fluorapatite is more stable toward the acidic conditions that can arise from consumption and bacterial digestion of some foods.

Density of water = 1 g mL^{-1}, pK_a(HF) = 3.17

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(b) Gravimetric analysis can be used to determine the amount of an ion present by precipitating the ion as an insoluble salt, collecting the precipitate, usually by filtration, and then measuring the mass of isolated material.

The following procedure determines the strontium ion content of a water-soluble solid by precipitation of $SrHPO_4$ ($K_s = 1.2 \times 10^{-7}$).

1. Weigh accurately a sample of the solid that contains approximately 0.50 millimoles of strontium(II).
2. Dissolve the sample in water and make up to a 60.0 mL solution.
3. Add 20.0 mL of 0.500 mol L^{-1} KH_2PO_4 solution and heat until boiling $pK_a(H_2PO_4^-) = 7.21$.
4. Add a drop of bromocresol purple indicator ($pK_a = 6.3$) and add 1.00 mol L^{-1} KOH solution dropwise until the indicator just changes colour.
5. Boil the solution until the initial precipitate becomes crystalline, between 30 and 60 minutes, and then allow it to stand for 1 hour.
6. Collect the precipitate, wash with a little cold water, and dry to constant weight.

(i) Discuss the chemistry involved in steps 3 and 4, with reference to the species present in the solution.

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(ii) The effectiveness of the precipitation process can be determined by calculating the concentration of strontium ions left in solution after precipitation is complete.

Calculate the concentration of strontium ions left in the solution at the end of the procedure, and use your answer to comment on the effectiveness of the process.

Assume that:

- the initial amount of Sr^{2+} is 0.500 millimoles
- after the addition of KOH, the pH of the solution is 6.0
- heating is done under reflux so that no water is lost from the solution (hence the final volume is determined by the volumes of KH_2PO_4 and KOH solutions, and water).

Question Five continues on the following page.

(iii) Explain how the effectiveness of the process will be affected if methyl orange ($pK_a = 3.7$) is used as the indicator.

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Extra paper if required.
Write the question number(s) if applicable.

QUESTION NUMBER

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Extra paper if required.
Write the question number(s) if applicable.

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