2008 H2 Chemistry Preliminary Examinations Paper 2 Mark Scheme

1 **(a)** On heating, Group I metal nitrates such as sodium nitrate(V) decompose giving the metal nitrate(III) and oxygen, while Group II metal nitrates, for example magnesium nitrate(V), decompose giving different products.

(i) Write balanced equations for the decomposition of sodium nitrate(V) and magnesium nitrate(V) respectively.

$$\mathbf{NaNO_3 \longrightarrow NaNO_2 + \tfrac{1}{2}O_2}$$
$$\mathbf{Mg(NO_3)_2 \longrightarrow MgO + 2NO_2 + \tfrac{1}{2}O_2}$$

15.35 g of a mixture of sodium nitrate(V) and magnesium nitrate(V) was heated in a fume cupboard until no more gases were evolved.

The water soluble part of the residue was dissolved in water to prepare 1.00 dm^3 of solution.

10.00 cm^3 of this solution was reacted with 20.00 cm^3 (in excess) of 0.0200 mol dm^{-3} potassium manganate(VII) solution, acidified with dilute sulphuric acid.

(ii) The nitrate(III) half equation is
$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$.

Write a balanced equation for the reaction between nitrate(III) ions and manganate(VII) ions.

$$\mathbf{2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O}$$

The excess potassium manganate(VII) required 12.00 cm^3 of 0.0500 mol dm^{-3} ethanedioic acid solution for complete reaction.

$[\,2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O]$

(iii) Calculate the amount in moles of the nitrate(III) ions in the 10.00 cm^3 solution.

no of mols of $C_2O_4^{2-}$ ions in 12.00 cm^3 = 0.012 x 0.05 = 6.00 x10^{-4}
no of mols of excess MnO_4^- = (2/5) x 0.0006 = 2.40 x 10^{-4}
no of mols of MnO_4^- in 20.00 cm^3 = 0.02 x 0.02 = 4.00 x 10^{-4}

no of mols of MnO_4^- reacted with NO_2^- in 10.00 cm^3
= 4 x 10^{-4}-2.40 x 10^{-4}
= 1.60 x 10^{-4} l
no of mols of NO_2^- in 10.00 cm^3
= (5/2) x 1.60 x 10^{-4} = 4.00x 10^{-4}

(iv) Hence, calculate the mass of each nitrate in the mixture.

$NaNO_3 \equiv NaNO_2$

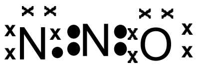
mass of $NaNO_3$ in 1 dm^3
= (1000/10) x 4.00 10^{-4} x (23.0+14.0+16.0x3)
= 0.0400 x 85 = 3.40g

mass of $Mg(NO_3)_2$ = 15.35-3.40 =12.0g (3s.f.) (or 11.95 g)

(b) Magnesium nitrate(V) and strontium nitrate(V) decompose similarly on heating. Magnesium nitrate decomposes at a lower temperature than strontium nitrate.
Explain why these two nitrates decompose at different temperatures.

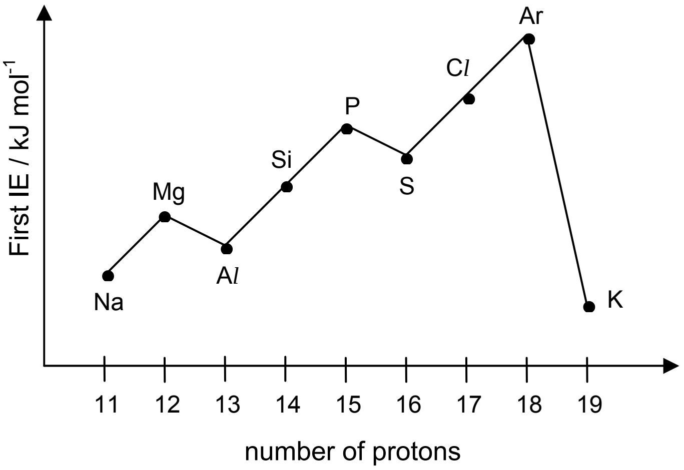
- **Mg^{2+} has a smaller ionic radius than Sr^{2+}**
- **higher charge density and greater polarising power**
- **hence Mg^{2+} distorts electron cloud around NO_3^- to a greater extent, thus decomposing at a lower temperature**.

(c) Ammonium nitrate(V) decompose to produce nitrous oxide, **N_2O**. Nitrous oxide is relatively inert at room temperature but at 500°C, it decomposes to oxygen, nitrogen and nitric oxide, **NO**. In the spaces provided, draw the dot and cross diagrams of these two oxides of nitrogen.

Formula	Nitrogen oxidation state	Dot and Cross Diagram
N_2O	+1	 OR 
NO	+2	 OR 

2 The first ionisation energies of nine elements from sodium to potassium are shown in the sketch below.

(a)



Give reasons for:

(i) the general trend across the period from Na to Ar.

**First IE <u>increases</u> across a period.
Across a period, <u>number of protons increases</u>.
<u>Shielding effect remains the same</u> as number of inner shell electrons is the same. Hence <u>effective nuclear charge on valence electrons is stronger</u> across a period. Atomic size is also smaller. More energy is required to remove an outermost electron due to increasing electrostatic attraction.**

(ii) the discontinuity between Mg and Al.

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$
Al $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

A*l* has a lower first IE. Less energy is required to remove a 3p electron in Al than a 3s electron in Mg since <u>3p electron is further away from the nucleus</u>.

(iii) the discontinuity between P and S.

P $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$ **OR** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
S $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

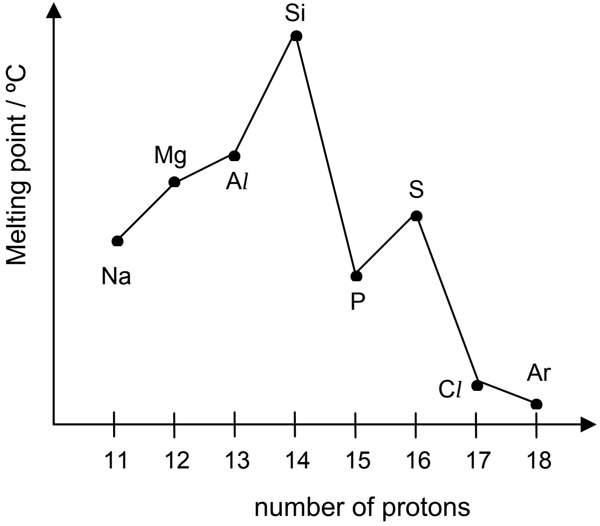
S has a lower first IE. Less energy is required to remove an electron from paired 3p electrons in S since <u>inter-electron repulsion</u> is experienced between the paired electrons.

(iv) the difference between the first ionisation energies of Na and K.

Na $1s^2\ 2s^2\ 2p^6\ 3s^1$
K $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

K has a lower first IE than Na. Less energy is required to remove a 4s electron in K than a 3s electron in Na since <u>4s electron is further away from the nucleus</u>.

(b) **(i)** Sketch the melting point trend of elements in period 3.



(ii) Explain the difference in melting points for sodium and silicon in terms of their structures and bondings.

Silicon has <u>higher melting point</u> than sodium.
Silicon has <u>covalent bond</u> and <u>giant molecular structure</u>.
Sodium has <u>metallic bond</u> and giant <u>lattice</u> structure .
<u>More energy</u> is required to break the relatively stronger bonds in silicon than in sodium.
atomic radius of silicon is smaller than atomic radius of sodium; hence silicon atoms are more closely packed together.

(c) Sodium was first produced commercially in 1855 by thermal reduction of sodium carbonate with carbon in what is known as the Deville process.

$Na_2CO_3(l) + 2C(s) \rightarrow 2Na(g) + 3CO(g)$

The standard entropy change of reaction, ΔS_r^{θ}, is +549 J K^{-1} mol^{-1}

(i) Explain why the entropy change of above reaction is positive.

Change in phase: $S_{gas} >> S_{liquid} >> S_{solid}$

There is a <u>change in phase from solid or liquid reactants to gaseous products</u>. Entropy of a gas is much greater than that of a liquid or solid as its particles are free to move and system becomes more disorderly.

Entropy increases as the <u>number of gaseous particles increases</u> and system becomes more disorderly.

(ii) Determine the range of temperatures for the above reaction to be feasible.

	$Na_2CO_3(l)$	CO(g)	Na(g)
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	-1103	-111	+107

$$\Delta H_r^{\ominus} = \sum n\Delta H_f^{\ominus}(\text{products}) - \sum m\Delta H_f^{\ominus}(\text{reactants})$$
$$= 2\,\Delta H_f^{\ominus}(Na) + 3\,\Delta H_f^{\ominus}(CO) - \Delta H_f^{\ominus}(Na_2CO_3) - 2\,\Delta H_f^{\ominus}(C)$$
$$= (2)(107) + (3)(-111) - (-1103) - 0$$
$$= +984 \text{ kJ mol}^{-1}$$

Assume that ΔH and ΔS remain constant.
For reaction to be feasible, $\Delta G_r < 0$
$\Delta H_r - T\Delta S_r < 0$
$+984{,}000 - (T)(549) < 0$
$T > 1792$ K

3 (a) (i) Calcium is a fairly soft, silvery-grey metal which quickly tarnishes in air; hence metallic calcium has no commercial uses. However titanium is a commercially important engineering metal.

State two physical properties which make titanium a very useful material in the aircraft industry and **suggest** another property that allows titanium to be used in artificial hip joints.

(Low density/ light) ; (strong/high tensile strength)
Does not corrode

(ii) Calcium can only exist as Ca^{2+} ions in its compounds but titanium forms ions with different charges (+2,+3 and +4) in its solid compounds.
$TiCl_3$ is coloured while TiF_4 (an ionic compound) is a white powder.

Unlike calcium, explain why titanium can exhibit several oxidation states in its compounds and suggest why TiF_4 is not coloured.

Ti : [Ar]$3d^24s^2$. As both 4s and 3d electrons are close in energy, it can use both 4s and 3d electrons for bond formation leading to several possible oxidation states.

In the +4 oxidation state, Ti has no 3d electron and hence d-d transition is not possible.

(b) Vanadium was named after Vanadis, the Scandinavian goddess of beauty and it forms many coloured compounds. Using the following data, choose a reagent which will convert vanadium(V) to vanadium(IV) but not to vanadium(III). Write a balanced equation for the conversion.

	E^θ/V
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+}$ H2O	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77

$$\mathbf{VO_2^+ + 2H^+ + Fe^{2+} \longrightarrow VO^{2+} + Fe^{3+} + H_2O}$$
$E_{cell} = +1.00 - 0.77 = +0.23V > 0$

(c) Some data for iron and ruthenium are given below.

	Proton number	Electronic configuration
Fe	26	$1s^22s^22p^63s^23p^63d^64s^2$
Ru	44	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^75s^1$

$[Ru(H_2O)_6]^{3+} + e^- \rightleftharpoons [Ru(H_2O)_6]^{2+}$ $E^\theta = +0.23V$

$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$ $E^\theta = +0.77V$

(i) Write the electronic configuration of Ru^{2+}(aq) and hence explain why Ru^{2+}(aq) is less stable than Ru^{3+}(aq).

$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^6$

In +2 oxidation state, there is a pair of electrons in one of the 4d orbitals which results in inter-electronic repulsion.

(ii) $[Ru(H_2O)_6]^{3+}$ can be made from the complex $[Cl_5Ru\text{-}O\text{-}RuCl_5]^{4-}$. What is the oxidation state of ruthenium in $[Cl_5Ru\text{-}O\text{-}RuCl_5]^{4-}$?
+4

(iii) Cyanide ligands can form a very stable complex with Fe^{2+} ions. How can the formation of this very stable complex explain the highly poisonous nature of the cyanide ion?

Fe^{2+} is important as an O_2 carrier in haemoglobin. CN^- binds to it preventing O_2 from being carried, causing suffocation.

(d) **(i)** 2,3-dihydroxybutanedioate ions are oxidised by hydrogen peroxide to carbon dioxide and water. The reaction is catalysed by Co^{2+}(aq). The solution is pink at the beginning and end of the reaction, but green during it.
The redox reaction between 2,3-dihydroxybutanedioate ions and hydrogen peroxide is represented by the following half-equations:

$(CHOHCO_2^-)_2(aq) + 2H_2O(l) \rightleftharpoons 4CO_2(g) + 8H^+(aq) + 10e^-$

$2H^+(aq) + H_2O_2(aq) + 2e^- \rightleftharpoons 2H_2O(l)$

Suggest the mechanism by which Co^{2+}(aq) ions catalyse this reaction.

Step 1
$2Co^{2+} + 2H^+ + H_2O_2 \longrightarrow 2Co^{3+} + 2H_2O$

Step 2
$(CHOHCO_2^-)_2 + 2H_2O + 10Co^{3+} \longrightarrow 4CO_2 + 8H^+ + 10Co^{2+}$

(ii) The typical blue colour of the famous Delft pottery is due to the Co^{2+} ions which are incorporated in the thin layer of glaze on the pottery. Explain why cobalt compounds are usually coloured.

- **In cobalt compounds, the five 3d orbitals/ 3d subshell are split into two energy levels with an energy difference ΔE corresponding to that of visible light energy**
- **When 3d e^- from the lower 3d orbital is promoted to a vacancy in the upper 3d orbital, visible light energy ΔE is absorbed.**
- **The colour seen is complementary to the colour absorbed.**

4 (a) 1.00 g of magnesium ammonium phosphate, $MgNH_4PO_4$, was added to 50 cm^3 of a 1.00 mol dm^{-3} aqueous solution of sodium hydroxide. The mixture was then boiled.
(The values of K_{sp} of magnesium hydroxide = 1.0×10^{-11} and of K_b of ammonia = 1.0×10^{-5})

(i) Predict whether a precipitate of magnesium hydroxide would form in the mixture above.

M_r of $MgNH_4PO_4$, = 137.3
Amt of $MgNH_4PO_4$, = 1/137.3 = 0.00728 mol
$[Mg^{2+}]$ = 0.00728 / 0.05 mol dm^{-3} = 0.146 mol dm^{-3}

$[Mg^{2+}][OH^-]^2$ = 0.146 x $(1.00)^2$
= 0.146 >> K_{sp} of $Mg(OH)_2$.
A ppt would form
(Taking into account the amount of NaOH that reacts with NH_4^+, the $[OH^-]_{remaining}$ works out to be 0.85 mol dm^{-3}. Using this value to work out the IP of $Mg(OH)_2$ is absolutely correct albeit tedious. The approximate value of $[OH^-]$= 1.00 mol dm^{-3} in the above calculation does not detract much from the actual value)

(ii) If all the ammonia liberated from the mixture were completely dissolved in water to give a 50.0 cm^3 solution, what volume of 0.20 mol dm^{-3} aqueous hydrochloric acid would be needed for complete reaction with the aqueous ammonia solution?
$NH_3 \equiv HCl \equiv Mg^{2+}$
Amt of HCl needed = 0.00728
Vol of acid needed = 0.00728 / 0.20 = 0.0364 dm^3 (or 36.4 cm^3)

(iii) Hence, calculate the pH value of the mixture in **(ii)** after hydrochloric acid has completely reacted with it.

Total vol = 50 +36.4 = 86.4 cm^3
$[NH_4^+(aq)]$ = 0.00728 mol / 0.0864

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+(aq)]\,[NH_3\,aq)]}{[NH_4^+(aq)]}$$

$$= \frac{[H_3O^+(aq)]^2}{[NH_4^+(aq)]}$$

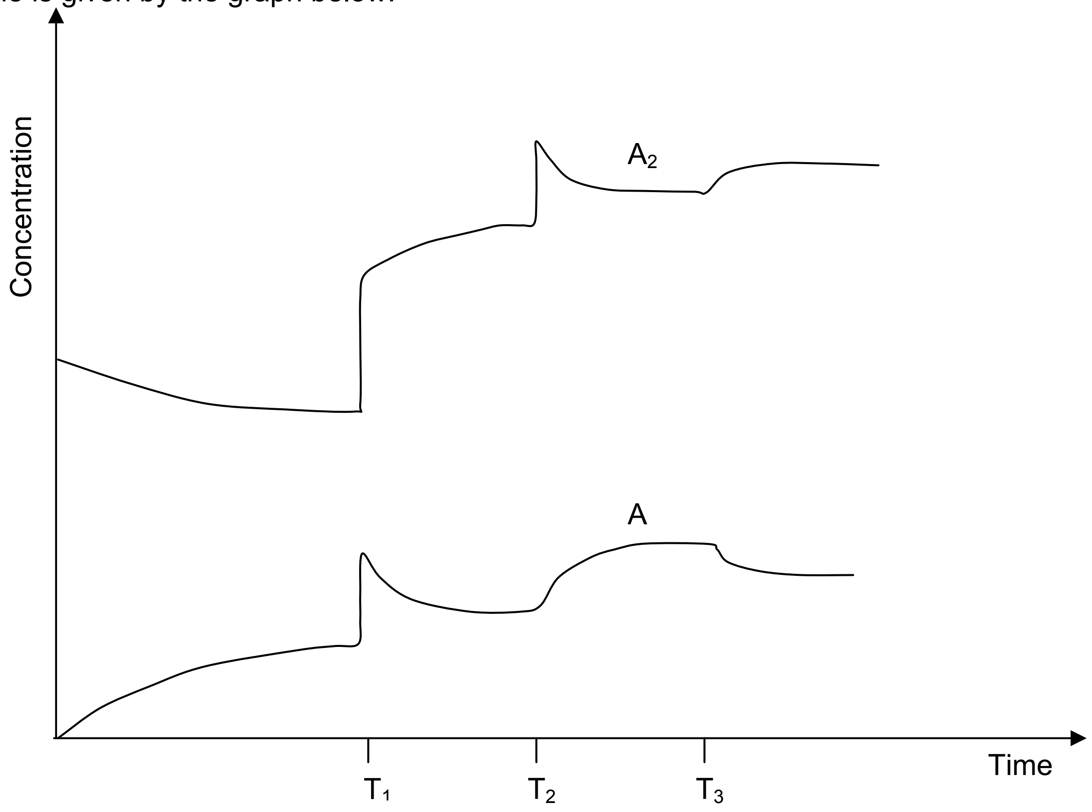
$[H_3O^+(aq)]^2$ = $(10^{-14} / 10^{-5})$ (0.00728 mol / 0.0864)

$[H_3O^+(aq)]$ = 9.18×10^{-6} pH = 5.04

(b) The conversion of A_2 is as follows:

$A_2(g) \rightleftharpoons 2A(g)$

The conversion was studied using a fixed amount of A_2 in a reaction vessel. At different times during the experiment, changes were made to the conditions in the reaction vessel. The change in the concentrations in the equilibrium mixture with time is given by the graph below:



Suggest the change in condition that caused the change at time

(i) T_1.

The volume of the mixture was reduced/ the mixture was compressed

(ii) T_2

A_2 was added to the mixture at equilibrium

(iii) Explain whether you expect the conversion of A_2 to A to be exothermic or endothermic. Sketch on the graph above the changes in the concentrations of A_2 and A when the mixture was cooled at time T_3.

Endothermic. Involves bond breaking

5 **(a)** An organic compound **X** (spirit of amber) plays an important biochemical role in the Krebs cycle. It is also produced in the fermentation of sugar and gives wine a characteristic flavour.

(i) Compound **X** has the following composition by mass.

C, 40.7%; H, 5.1%; O, 54.2%

Calculate the empirical formula of **X**.

Assume 100 gram of sample

	C	**H**	**O**	
Mass / g	**40.7**	**5.1**	**54.2**	
Amount / mol	**3.39**	**5.1**	**3.39**	
Simplest Mole Ratio	**1**	**1.5**	**1**	
	2	**3**	**2**	

Empirical Formula of **X**: **$C_2H_3O_2$**

(Incomplete presentation of table: -1m)

(ii) When a 0.204g sample of compound **X** was vapourised in a suitable apparatus, the vapour occupied 74.2 cm^3 at 250 °C and 101 kPa.

Calculate the M_r of compound **X**.

Assume X is an ideal gas

PV = nRT

$$(101{,}000)(74.2\times10^{-6}) = \left(\frac{0.204}{\text{Mr}}\right)(8.31)(250+273)$$

$M_r = 118.3$

(iii) Determine the molecular formula of **X**.
Let molecular formula of X be $(C_2H_3O_2)_n$

[(2 x 12) + (3 x 1) + (2 x 16)] n = 118.3
n = 2
Molecular formula of **X**: **$C_4H_6O_4$**

(b) The following tests are carried out on compound **X**. State all deductions about compound **X** in each case.

(i) When aqueous sodium carbonate is added to compound **X**, effervescence occurs. Colourless gas forms white precipitate in lime water.

X is a **carboxylic acid.**

(ii) Compound **X** gives white fumes when treated with thionyl chloride, $SOCl_2$.

X has **–OH or –COOH groups**.

(iii) On heating compound **X** under reflux with potassium manganate (VII), purple colour of solution remains.

X is **neither an alkene, an aldehyde nor (primary or secondary alcohol).**

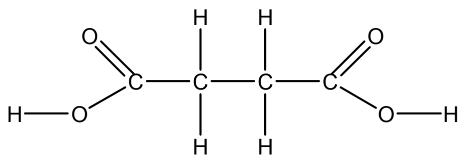
(iv) Compound **X** does not give yellow precipitate with aqueous alkaline iodine.

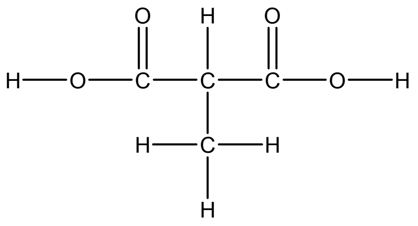
X does not have this structure: CH_3CO– or $CH_3CH(OH)$–

(v) Compound **X** does not give orange precipitate with 2,4-dinitrophenylhydrazine.

X is **neither a ketone nor aldehyde (or not a carbonyl compound).**

(c) (i) Draw two possible displayed formulae of compound **X**.





(ii) Given that compound **X** can be obtained from an alkene, suggest reagents and conditions for the reaction.

Reagent: $KMnO_4$, dilute H_2SO_4
Condition: Heat under reflux

(d) Compound **Y** has the same molecular formula as compound **X**. If compound **Y** undergoes positive tests in **(b)(i) to (b)(v)**, suggest a structural formula for it.

$CH_3CH(OH)COCOOH$ or $CH_3COCH(OH)COOH$