Registration Number	ST group	Name

	NATIONAL JUNIOR COLLEGE Preliminary Examinations 2008	
CHEMISTRY Higher 2		9746/02
PAPER 2 10 Sept 2008		1 hour 30 min
Candidates are to ans Additional Materials: D	wer on the Question paper. Data Booklet	

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This question paper consists of **<u>14</u>** printed pages (including this page)

1 A section of the periodic table showing elements in periods 2 and 3 is shown below.

т		
W	X	Y

Element **X** has the following successive ionization energies.

IE/ kJmol ⁻¹	1011	1907	2914	4963	6273	21267	25431	29872
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(a) (i) Which group does element X belong to?

[1]

(ii) Do you expect the first ionization energy of element **Y** to be greater or smaller than that of **X**? Explain.

[2]

(b) (i) When dissolved in water, the chlorides of elements **W** and **X** produce solutions that turn blue litmus red. Explain. [2]

(ii) Deduce whether the same observation is seen for the chloride of element T.

[2]

(c) Element Z is in the same group as X but with a much greater proton number. The oxide of Z is seen to react with hydrochloric acid. Explain.

[2]

[Total: 9]

2 (a) (i) State two assumptions of the kinetic theory of gases.

- [2]
- (ii) Under what conditions is the behaviour of ammonia most nearly ideal? Explain your answer.

[2]

(b) The graph below shows experimental values of the product PV for a mass of ammonia against P at constant temperature.



Which graph (A, B or C) shows the relationship between the product PV and P for carbon dioxide? Explain your choice.

- (c) Ethylamine can be synthesized by reacting ammonia with chloroethane.
 - (i) State the reagents and conditions required for the reaction.

[1]

(ii) Chloroethane may be converted to dipropylamine by the following route:

 $CH_{3}CH_{2}CI \longrightarrow E \longrightarrow F \longrightarrow (CH_{3}CH_{2}CH_{2})_{2}NH$ Stage I Stage II Stage III

(I) Suggest reagents and conditions for Stages I and II.

Stage I:

Stage II:

[2]

(II) Draw the structural formulae of E and F.

Compound E

Compound F

(III) Describe the mechanism in Stage I.

[3]

(iii) Comment on the base strength of ammonia, ethylamine and dipropylamine.

[2]

[Total: 16]

- 3 Very often water contains various amounts of impurities which render it unsuitable for human consumption and other specific purposes. Thus, it is necessary to purify water before using it. The method of purification depends on how the water is to be used, or has been used.
 - (a) One of the methods involves the removal of excess iron from drinking water. This involves oxidation of the Fe²⁺ ions by chlorate(I) ion, OCI[−], followed by addition of a base. The precipitate formed will then be removed.
 - (i) Given OCI^- will be converted to CI^- , construct a balanced equation to show its reaction with Fe^{2+} .

(ii) The recommended percentage of iron permitted in drinking water in Singapore is 0.3 mg dm⁻³. Calculate the concentration of chlorate(I) ion in mg dm⁻³ needed to lower Fe²⁺(aq) from 15 mg dm⁻³ to the required safety level.

- (b) Steel boilers that convert water to steam can be easily corroded by the dissolved oxygen in the water. Fortunately, liquid hydrazine, N₂H₄, is an efficient oxygen scavenger and can be used to overcome the problem as it can remove the dissolved oxygen.
 - (i) Draw a 'dot-and-cross' diagram of N₂H₄.

[1]

(ii) Suggest the size of the bond angle in N_2H_4 .

[1]

(iii) Liquid N_2H_4 is a scavenger of dissolved oxygen as shown by

$$N_2H_4$$
 (I) + O_2 (aq) $\rightarrow N_2$ (g) + 2 H₂O (I)

Explain the feasibility of such method of removing dissolved oxygen from boiler water in terms of enthalpy and entropy changes. (No calculations are required.)

[2]

- (c) Hydrazine, N₂H₄, is not only useful for purifying water but also finds many applications in organic chemistry. One of such applications is the reaction with the carbonyl group.
 - (i) Draw the structure of the organic product formed when equimolar quantities of benzaldehyde (C_6H_5CHO) and hydrazine react.

[1]

(ii) Explain why the product from the reaction of benzaldehyde with hydrazine may exists as two stereoisomers but the product from $C_6H_5COC_6H_5$ with hydrazine does not have stereoisomers.

(d) Engineers in Japan are developing a fuel cell that uses hydrazine instead of hydrogen to power automobiles and other motorized vehicles.



Given that one of the products formed is nitrogen gas, write the half-cell equations occurring at the anode and the cathode, and hence the overall reaction of the fuel cell.

Anode:

Cathode:

Overall:

[2]

[Total: 13]

4 The solubilities of $PbCl_2$ in various concentrations of HCl at 25°C are as shown:

HCI /mol dm ⁻³	0	0.5	1.0	1.20	2.90	4.02	5.78
Solubility of PbCl ₂ (× 10^{-2} mol dm ⁻³)	6.60	5.10	4.91	4.93	5.90	7.48	14.0

(a) Explain the data as fully as you can.

(b) Calculate a value for the solubility product of $PbCl_2$ at $25^{\circ}C$.

[5]

[Total: 5]

- 5 When 0.158 g of a Group II ethanoate, (CH₃COO)₂M was heated strongly, 0.001 mol of a ketone, G, of molar mass 58.0 g mol⁻¹ was produced in addition to a white solid H and 24 cm³ of CO₂ (measured at room temperature and pressure).
 - (a) (i) Write a balanced equation for the thermal decomposition of the Group II ethanoate in terms of **M**.
 - (ii) Deduce the identity of **M** and hence the identity of the white solid **H**.

(b) The white solid H was dissolved in an excess of aqueous HCl, the solution was concentrated to a small volume and white crystals of MCl₂ were isolated. Write an equation for the chemical reaction that occurs when concentrated H₂SO₄ was added to the white crystals of MCl₂. (You may wish to leave the formula as MCl₂ if you did not manage to identify M in (a)(ii).)

[1]

(c) Describe and explain any difference in observations when concentrated H_2SO_4 was added to MBr_2 .

[2]

[Total: 7]

- **6** Mesaconic acid, $C_5H_6O_4$, is one of the components used in the manufacturing of fire retardants. It exists as a pair of geometric isomers. 0.65 g of mesaconic acid requires 25.0 cm³ of 0.20 mol dm⁻³ of sodium carbonate solution for complete reaction.
 - (a) Based on the above information, draw the structural formulae of mesaconic acid.

[2]

(b) Mesaconic acid can be converted into citramalic acid by the following scheme:



Compound J

(i) State the reagents and conditions needed for Stages I and II.

	Reagents and Conditions
Stage I	
Stage II	

(ii) Draw the structure of the organic compound **J** in the box above.

[1]

(iii) Describe the mechanism involved in Stage I.

[3]

(iv) Draw the structural formulae of the organic compounds formed when citramalic acid reacts with each of the following reagents.

Reagents	Organic compound
phosphorus pentachloride	
lithium aluminium hydride in dry ether	

[2]

[Total: 10]

Answer scheme

- 1 a i) Group V
 - ii) Smaller. Easier to remove paired electron in Y due to inter-electronic repulsion.
 - **b** i) Electronegative chlorine causes partial positive charge on W and X. Water molecules attack the central atom donating lone pair of electrons into empty d-orbitals. Cl is substituted by OH⁻ liberating HCl.
 - No. Carbon cannot expand its octet to accept lone pair of electrons from water to liberate H⁺.
 - **c** Lower down the group, valence electrons further from nucleus and thus easily lost to form ions. Oxide of Z is ionic and thus basic.
- 2 a (i) 1 Volume of gas particles is negligible compared to the volume of the gas.
 2 Negligible intermolecular forces of attraction between the gas particles.
 - (ii) High temperature: larger amount of kinetic energy as compared to intermolecular forces of attraction.
 Low pressure: gas particles are farer apart and hence negligible intermolecular forces of attraction.
 - **b** Graph B Carbon dioxide has only temporary dipole-induced dipole interaction as compared to ammonia which has hydrogen bonding which is a stronger interaction. CO₂ is a large molecule so the volume of the gas particle is not negligible.
 - c (i) Ethanol, heat in a sealed tube at high pressure
 - (ii) (I) Stage I: NaCN, ethanol, heat Stage II: LiAIH₄, dry ether OR H₂, Ni OR NaBH₄
 - (II) Compound E: CH_3CH_2CN Compound F: $CH_3CH_2CH_2NH_2$
 - (III) Nucleophilic substitution



(iii) Increasing basicity: $NH_3 < CH_3CH_2NH_2 < (CH_3CH_2CH_2)_2NH$

No. of electron-releasing alkyl groups attached to N increases from 0 in NH_3 to 1 alkyl group in $CH_3CH_2NH_2$ and 2 groups in $(CH_3CH_2CH_2)_2NH$, *Either* making the lone-pair on N more available for donation to proton, *OR* easing the positive charge on the cation to a greater extent, stablising the cation, hence basicity increases.

3 a (i)
$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

 $2H^{+} + OCI^{-} + 2e^{-} \rightarrow CI^{-} + H_2O$
 $2H^{+} + 2Fe^{2+} + OCI^{-} \rightarrow 2Fe^{3+} + CI^{-} + H_2O$

(ii) Concentration of Fe²⁺ to remove =
$$15 - 0.3 = 14.7 \text{ mg dm}^{-3}$$

= $\frac{14.7 \times 10^{-3}}{55.8}$
= $2.634 \times 10^{-4} \text{ mol dm}^{-3}$
Concentration of CIO⁻ = $\frac{2.634 \times 10^{-4}}{2}$ = $1.317 \times 10^{-4} \text{ mol dm}^{-3}$
= $1.317 \times 10^{-4} \times (35.5 + 16.0)$
= 6.78 mg dm^{-3}

b (i)

(ii) 107°

(iii)
$$\Delta S > 0 (S_{\text{final}} - S_{\text{initial}} > 0)$$

- $\Delta n = 1$

 Δ H < 0 - more energy is released in forming strong N=N

 $\Delta G = \Delta H - T\Delta S$ Since $\Delta S > 0$, $\Delta H < 0$, thus ΔG will be < 0. Hence reaction is feasible.

c (i) $H \\ C = N - N H$

(ii) Reaction of benzaldehyde with hydrazine yield a product that displays geometric isomerism as there are 2 different substituents group attached to the C=N double bond.



Reaction of $C_6H_5COC_6H_5$ with hydrazine does not yield a product that displays geometric isomerism as the same substituent, C_6H_5 , is attached to the C of the C=N double bond.

d Anode: $N_2H_4 + 4OH^- \rightarrow 4H_2O + N_2 + 4e^-$ Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall: $N_2H_4 + O_2 \rightarrow 2H_2O + N_2$

- **a** Due to common ion, Cl⁻ ions, from HCl, solubility of PbCl₂ decreases initially. As [HCl] increases, complex ion, PbCl₄²⁻ forms. [Pb²⁺] decreases thus solubility of PbCl₂ increases.
 - **b** $1.15 \text{ x}.10^{-3} \text{ mol}^3 \text{ dm}^{-9}$
- **5** a (i) Identity of ketone G: CH_3COCH_3 (Molar mass = 58.0 g mol⁻¹).

$$n_{CO_2} = \frac{24}{24 \times 10^{-3}} = 0.001 \text{ mol}$$

 $n_{CH_3COCH_3} = 0.001 \text{ mol}$

 $n_{CO_2} = n_{CH_3COCH_3}$ $(CH_3COO)_2M(s) \rightarrow CO_2(g) + CH_3COCH_3(I) + MO(s)$

Comments Since equimolar of CO_2 and CH_3COCH_3 are formed, their stoichiometric coefficients are 1. Thus. there are altogether 4 C and hence, the coefficient of $(CH_3COO)_2M$ is also 1. The other product is MO which is produced by most decomposition reactions.

(ii) From the above equation, no. of moles of $(CH_3COO)_2M = 0.001$ mol

 $M_r \text{ of } (CH_3COO)_2 M = \frac{0.158}{0.001} = 158$ Thus A_r of M = 158 - (12.0 + 3.0 + 12.0 + 16.0 + 16.0) = 40.0

M is Ca, H is CaO

b $CaCl_2(s) + 2 H_2SO_4(l) \rightarrow Ca(HSO_4)_2(s) + 2 HCl(g)$

Note: The product is $Ca(HSO_4)_2$, not $CaSO_4$. It is similar to the reaction when NaCl was used. State symbols are not (aq) as conc H_2SO_4 was used.

Also accepted: $CI^- + H_2SO_4 \rightarrow HSO_4^- + HCI$

c CaBr₂ (s) + 2 H₂SO₄ (l) → Ca(HSO₄)₂ (s) + 2 HBr (g) 2 HBr (g) + H₂SO₄ (l) → Br₂ (l) + SO₂ (g) + 2 H₂O (l)

Brown fumes of Br_2 and a pungent gas SO_2 will be evolved in addition to white fumes of HBr for $CaBr_2$. For $CaCl_2$, only white fumes of HCl evolved.

This is because Br^- has higher reducing strength than Cl^- , thus reduces H_2SO_4 to SO_2 (+6 to +4 state for S). Cl^- is unable to reduce H_2SO_4 .

Note:

- HCI and HBr are not oxidizing agents. DO NOT say that H₂SO₄ has a higher oxidizing strength than HBr but weaker than HCI.
- HBr are white fumes, not brown fumes.
- Only SOME of the HBr is oxidized to Br₂, it is incorrect to say that HBr will not be produced as they are oxidized to Br₂.

H CH₃ C C COOH

b (i) Stage I : $HCl(g) / HCl in CCl_4 / NaCl + conc H_2SO_4$ to generate HCl(g)

Stage II : NaOH(aq), heat under reflux

- (ii) Compound J H CI HOOC-C-C-COOH H CH₃
- (iii) Electrophilic addition

$$HOOC \xrightarrow{CH_3} + \xrightarrow{\delta^+ \quad \delta^-}_{H-Cl} \xrightarrow{\text{slow}} HOOC \xrightarrow{H \quad CH_3}_{H-Cl} \xrightarrow{H \quad CH_3}_{H} \xrightarrow{C} \xrightarrow{H \quad CH_3}_{H} \xrightarrow$$

⁶ a

