Paper 1	Qn No	Answer	Qn No	Answer	Qn No	Answer	Qn No	Answer
	1	С	11	D	21	В	31	А
	2	С	12	D	22	С	32	D
	3	С	13	С	23	А	33	С
	4	С	14	В	24	D	34	В
	5	D	15	В	25	В	35	С
	6	А	16	В	26	С	36	В
	7	В	17	А	27	С	37	D
	8	С	18	С	28	D	38	С
	9	А	19	В	29	С	39	D
	10	С	20	В	30	В	40	В

# CJC H2 Chem Preliminary Exam 2008 Answers

### Paper 2

**1** (a) S [Ne]  $3s^2 3p_x^2 3p_y^1 3p_z^1$  P [Ne]  $3s^2 3p_x^1 3p_y^1 3p_z^1$ S has a lower 1<sup>st</sup> I.E. than P due to the inter-electron repulsion between paired electrons in a 3p orbital of S.

- (b)  $CO_2$  exists as simple covalent molecules with weak van der Waals' forces of attraction between molecules. SiO<sub>2</sub> has a giant molecular structure with strong covalent bonds between atoms  $\therefore$  SiO<sub>2</sub> has a much higher melting point than CO<sub>2</sub>.
- (c) 2-nitrophenol is able to form intra-molecular hydrogen-bonding between the –OH and –NO<sub>2</sub> groups. Hence its inter-molecular hydrogen bonding is less extensive than that of 4-nitrophenol. Less energy is required to break the intermolecular forces of attraction and it has a lower melting point.
- (d) Boiling point is dependent on the intermolecular forces of attraction.
   Down the group, boiling points of the hydrogen halides generally increase due to stronger van der Waals' forces of attraction between

Down the group, boiling points of the hydrogen halides generally increase due to stronger van der Waals' forces of attraction between molecules as the number of electrons increases (with increase in  $M_r$ ). However, HF has the highest boiling point (an exception) due to the presence of strong hydrogen bonding between molecules.

(e) P is more electronegative than As. The bond pair electrons in PCl<sub>3</sub> are closer to the central P atom as compared to that in AsCl<sub>3</sub>. There is more repulsion between the electrons / greater bond pair-bond pair repulsion and hence the bond angle increases.

**2** (a) +5

(b) (i) 
$$BiO_3^- + 6 H^+ + 2 e^- \rightarrow Bi^{3+} + 3 H_2O$$
  
(ii)  $2 Mn^{2+} + 5 BiO_3^- + 14 H^+ \rightarrow 2 MnO_4^- + 5 Bi^{3+} + 7 H_2O$ 

(c) 
$$Fe^{2^+} \rightarrow Fe^{3^+} + e^-$$
  
 $MnO_4^- + 5 Fe^{2^+} + 8 H^+ \rightarrow Mn^{2^+} + 5 Fe^{3^+} + 4 H_2O$   
 $\therefore MnO_4^- \equiv 5 Fe^{2^+}$   
no. of mol of Mn in sample = no. of mol of MnO\_4^- required  
 $= \frac{1}{5} \times No.$  of mol of  $Fe^{2^+}$   
 $= \frac{1}{5} \times (0.10 \times \frac{36.00}{1000})$   
 $= 0.000720 \text{ mol}$   
 $\therefore$  mass of Mn in sample = 0.000720 × A<sub>r</sub> of Mn  
 $= 0.000720 \times 55$ 

∴ % of Mn in sample = 
$$\frac{0.0396}{1.00} \times 100$$
  
=  $\frac{3.96 \%}{1.00}$ 

(d) (i)  $E_{cell}^{e} = E_{red}^{e} - E_{oxd}^{e}$ 

Reactants	Products	<b>Ε</b> <sup>θ</sup> <sub>cell</sub> / V	Can reaction occur? (Y/N)	
Mn & SO <sub>4</sub> <sup>2-</sup>	Mn <sup>2+</sup> & SO <sub>2</sub>	<i>E</i> <sup>θ</sup> <sub>cell</sub> = +0.17 - (-1.18)	Yes	
		= <u>+1.35</u>		
Mn <sup>2+</sup> & SO <sub>4</sub> <sup>2-</sup>	MnO <sub>4</sub> & SO <sub>2</sub>	<i>E</i> <sup>θ</sup> <sub>cell</sub> = +0.17 - (+1.52)	No	
		= <u>-1.35</u>		
Fe <sup>2+</sup> & SO <sub>4</sub> <sup>2-</sup>	Fe <sup>3+</sup> & SO <sub>2</sub>	<i>E</i> <sup>θ</sup> <sub>cell</sub> = +0.17 - (+0.77)	No	
		= <u>-0.60</u>		
ii) <u>Yes</u> , sulphuric acid is a suitable replacement for nitric acid in this experiment.				

Yes, sulphuric acid is a suitable replacement for nitric acid in this experiment.
 <u>Reason</u>: H<sub>2</sub>SO<sub>4</sub> can oxidise Mn to Mn<sup>2+</sup> but cannot further oxidise Mn<sup>2+</sup> to MnO<sub>4</sub><sup>-</sup>. Also, it does not oxidise Fe<sup>2+</sup> to Fe<sup>3+</sup>.
 ⇒ H<sub>2</sub>SO<sub>4</sub> does not interfere with the redox reaction.



(ii) initial dose = 
$$(2 \times 500)$$
 = 1000 mg

$$1000 \xrightarrow{t_{\frac{1}{2}}} 500 \xrightarrow{t_{\frac{1}{2}}} 250 \xrightarrow{t_{\frac{1}{2}}} 125$$

∴ time taken = 3 
$$t_{\frac{1}{2}}$$
  
= (3 × 2.7) hrs  
= 8.1 hrs

- (iii) Curve must show faster reaction (i.e. steeper).
- (iv) pH of body fluid or body temperature

(b) (i)  $Cl \longrightarrow CHClCH_3$ 

(ii) Cl<sub>2</sub>, presence of ultra-violet light

(iii)



(iv) Only <u>one</u> of the C/ (on the alkyl side-chain) is hydrolysed.  $M_r$  of **V**, C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub> = 8(12.0) + 8(1.0) + 2(35.5) = 175 mol of AgC/ppt = mol of **V** =  $\frac{1.75}{175}$  = 0.010 mol  $M_r$  of AgCl = 108 + 35.5 = 143.5 ∴ mass of AgC/ppt = (0.010 × 143.5) g = 1.435 g

4 (a) (i) mole ratio C : H =  $\frac{92.3}{12.0}$  :  $\frac{100 - 92.3}{1.0} = \frac{92.3}{12.0}$  :  $\frac{7.7}{1.0} = 7.8$  : 7.7 = 1 : 1 ∴ empirical formula of W is <u>CH</u>. Amount of CO<sub>2</sub> =  $\frac{1.76}{12.0 + 2(16.0)} = \frac{1.76}{44.0} = 0.0400$  mol ∴ mole ratio W : CO<sub>2</sub> = 0.005 : 0.0400 = 1 : 8

(or  $W \equiv 8 \text{ CO}_2$ )  $\Rightarrow 8 \text{ C}$  atoms in one molecule of **W**.

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 $\therefore$  Molecular formula of **W** is <u>**C**</u><sub>8</sub>**H**<sub>8</sub>.



(iv) Geometric isomerism/cis-trans isomerism or optical isomerism



(b) Ni has smaller atomic size due to higher effective nuclear charge.

In Ni, electrons are added to d-subshells, which provide poor shielding. However Ni has higher nuclear charge than Ca and so, electrons in Ni are more strongly held by the nucleus / greater electrostatic forces of attraction between electrons and nucleus.

Ni has much higher melting point due to stronger metallic bonding.

In Ni, both 3d and 4s electrons are delocalised for metallic bonding (since 3d and 4s orbitals have similar energy levels). In Ca, only two valence electrons (4s<sup>2</sup>) are available for delocalisation in forming metallic bonds.

**5** (a)  $M_{\rm r}$  of SO<sub>2</sub>Cl<sub>2</sub> = 32.1 + 2(16.0) + 2(35.5) = 135.1

Using ideal gas equation, 
$$pV = nRT$$
  
 $p = \frac{nRT}{V} = \frac{\frac{6.7}{135.1} \times 8.31 \times 375}{1 \times 10^{-3}} \times \frac{1}{1.01 \times 10^{5}} = 1.53 \text{ atm}$ 

(b) 
$$SO_2Cl_2(g) \Rightarrow SO_2(g) + Cl_2(g)$$
  
initial / atm 1.53 0 0  
equil / atm 1.53 - x x x x  
i.e. at equilibrium,  $p_{SO_2} = p_{Cl_2}$  and  $p_{SO_2Cl_2} = 1.53 - p_{SO_2}$   
 $\therefore K_p = \frac{p_{SO_2} \times p_{Cl_2}}{p_{SO_2Cl_2}} = \frac{(p_{SO_2})^2}{1.53 - p_{SO_2}}$   
 $\mathcal{K}_p = \frac{(p_{SO_2})^2}{1.53 - p_{SO_2}}$   
 $2.4 = \frac{(p_{SO_2})^2}{1.53 - p_{SO_2}}$   
 $\Rightarrow p_{SO_2} = p_{Cl_2} = 1.06 \text{ atm}$   
 $p_{SO_2Cl_2} = 1.53 - 1.06 = 0.47 \text{ atm}$   
(c)  $SO_2Cl_2(g) \Rightarrow SO_2(g) + Cl_2(g)$   
initial / atm 1.53 0 1.0  
equil / atm 1.53 - x x 1.0 + x  
i.e. at equilibrium,  $p_{Cl_2} = p_{SO_2} + 1.0$   
and  $p_{SO_2Cl_2} = 1.53 - p_{SO_2}$   
 $\therefore K_p = \frac{p_{SO_2} \times p_{Cl_2}}{p_{SO_2Cl_2}}$   
 $2.4 = \frac{p_{SO_2} \times p_{Cl_2}}{p_{SO_2Cl_2}}$   
 $\Rightarrow p_{SO_2} = 0.86 \text{ atm}$   
 $p_{SO_2Cl_2} = 1.53 - 0.86 = 0.67 \text{ atm}$ 

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6 (a) Y burns with a sooty flame and reacts with aqueous NaOH but not Na<sub>2</sub>CO<sub>3</sub>.  $\Rightarrow$  unsaturated  $\Rightarrow$  acidic but not RCO<sub>2</sub>H

Deduction: Y has a phenol group

Y rotates plane polarised light.

Deduction: Y has a chiral carbon

**Y** gives a yellow precipitate when warmed with aqueous alkaline  $I_2$ .

<u>Deduction</u>: **Y** has <u>CH<sub>3</sub>CH(OH)</u> or CH<sub>3</sub>C=O group. Yellow precipitate is **CHI**<sub>3</sub>.

Y decolourises 2 mol of aqueous  $Br_2$  to give steamy white fumes and a white precipitate.  $\Rightarrow$  only 2 position free for rxn  $\Rightarrow$  substitution rxn

<u>Deduction</u>: CH<sub>3</sub>CH(OH)– is at <u>-2 or -4 position</u> with respect to phenol. (Electrophilic substitution takes place, steamy white fumes is HBr.)

**Y** reacts with hot excess conc  $H_2SO_4$  to give **Z**,  $C_9H_{10}O$ , which can exist as stereoisomers.  $\Rightarrow$  dehydration rxn  $\Rightarrow$  cis-trans

Deduction: Y undergoes dehydration to form an alkene Z.

**Y**:



**Z**:



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- (b) (i) By-products (SO<sub>2</sub> and HCI) being gases do not contaminate the product.
  - (ii)  $\Delta S$  is positive. There are 2 mol of gaseous products formed, which resulted in higher disorder.

(iii)  $\Delta G = \Delta H - T \Delta S$ 

Since both  $\Delta S$  and  $\Delta H$  are positive,  $\Delta G$  will become more negative / less positive as temperature increases.

This reaction is spontaneous ( $\Delta G < 0$ ) at high temperatures.

[The reaction should be carried out at high a temperature so that  $\Delta G$  will be < 0, or else "spontaneity" will be lost.]

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### Paper 3 Essay

**1** (a) (i) Electrophilic addition

 $NaCI + H_2SO_4 \rightarrow HCI + Na_2SO_4$ 

Formation of carbocation.



The CI<sup>-</sup> ion attacks the intermediate carbocation to give the addition product.



(ii) The carbocation is <u>planar</u>, hence there is equal probability the nucleophile may attack it from the top or the bottom to give either stereoisomer (optical isomer).

(b) (i) CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub> → Cl<sub>2</sub> uv light CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CHCICH<sub>3</sub> 2-chloro-3-methylbutane (intermediate)

$$CH_3CH_2CH(CH_3)CHCICH_3 \xrightarrow{NaOH(aq)} CH_3CH_2CH(CH_3)CH(OH)CH_3$$
  
3-methylpentan-2-ol

(ii) It is difficult to obtain 2-chloro-3-methylbutane as the major product during free radical substitution (or there are many other by-products formed).



### (d) (i) Mg + $\frac{1}{2}O_2 \rightarrow MgO$

Mg reacts with air to form magnesium oxide which acts as a protective layer and so, prevents the magnesium from reacting with the organic compounds.

## (ii) pH = 6.5

 $\begin{array}{l} MgCl_{2}(s) + 6H_{2}O \ \rightarrow \ \left[Mg(H_{2}O)_{6}\right]^{2+}(aq) + 2CI^{-}(aq) \\ \left[Mg(H_{2}O)_{6}\right]^{2+}(aq) \ \rightarrow \ \left[Mg(H_{2}O)_{5}(OH)\right]^{+} + H^{+} \end{array}$ 

The Grignard reagent will react with water instead of the starting material to form other side-products.

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	MgO	SiO <sub>2</sub>	SO <sub>2</sub> or SO <sub>3</sub>
structure	Giant ionic	Giant covalent	Simple molecular
Bonding	Strong ionic/electrostatic forces of attraction between oppositely charged ions	Strong covalent bonds between atoms	Strong covalent bonds between atoms, weak vdw forces of attraction between molecules.

**2 (a)** Reaction 1: NO(g) + CO(g)  $\rightarrow \frac{1}{2}N_2(g) + CO_2(g) \Delta H_1$ 

$$\Delta H_1 = \Sigma \Delta H_f (\text{products}) - \Sigma \Delta H_f (\text{reactants})$$
  
=  $\frac{1}{2}(0) + (-394) - (+90) - (-111)$   
= -373 kJ mol<sup>-1</sup>

• <u>Reaction 2</u>:  $NO(g) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$   $\Delta H_2$ 

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\Delta H_2 = \Sigma \Delta H_f (\text{products}) - \Sigma \Delta H_f (\text{reactants})= \frac{1}{2}(0) + \frac{1}{2}(0) - (+90)= -90 \text{ kJ mol}^{-1}
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Since  $\Delta H_1$  is more exothermic than  $\Delta H_2$ , reaction 1 occurs more readily and hence, is more efficient as a method of removing NO than decomposing it to its elements.

(b) (i) Comparing Expt 1 & 2, [O<sub>2</sub>] constant. When [NO] doubles, the initial rate increases 4 fold. Hence, the reaction is second order of reaction with respect to NO.

Let the rate equation be rate =  $k [NO]^2 [O_2]^n$ 

From Expt 2 & 3,

$$\frac{2.80 \times 10^{-3}}{12.60 \times 10^{-3}} = \frac{k(0.002)^2 (0.1)^n}{k(0.003)^2 (0.2)^n} \implies n = 1$$

Hence, the reaction is first order of reaction with respect to  $O_2$ .

$$\therefore$$
 rate equation is rate =  $k [NO]^2 [O_2]$ 

(ii) rate constant  $k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]}$ From Expt 1,  $k = \frac{0.7 \times 10^{-3}}{(0.001)^2(0.1)} = 7000 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ 

(iii) When temp. falls, rate of reaction decreases and so rate constant k is decreased.

Or From Arrhenius equation,  $k = Ae^{-Ea/RT}$   $\Rightarrow k \propto T$  $\therefore$  When temperature falls, *k* is decreased.

NO has an unpaired electron / single electron and so, is reactive and can combine readily to form N<sub>2</sub>O<sub>2</sub>.



(iii) Nucleophilic substitution



- **3** (a) (i) Green precipitate Fe(OH)<sub>2</sub> Brown precipitate Fe(OH)<sub>3</sub>  $Fe^{2^+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$   $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$   $E^{\circ}_{cell} = +0.40 - (-0.56) = +0.96 V (> 0 \Rightarrow rxn is feasible)$ 
  - (ii)  $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$ Brown solution is  $I_2(aq)$  or  $I_3^{-}(aq)$  $E^{\circ}_{cell} = +0.77 - (+0.54) = +0.23 \text{ V} (> 0 \Rightarrow rxn \text{ is feasible})$

In the presence of CN<sup>-</sup> ligands,  $[Fe(CN)_6]^{3+}(aq) + I^{-}(aq) \rightarrow \text{ no rxn}$   $E^{\circ}_{cell} = +0.36 - (+0.54) = -0.18 \text{ V} (< 0 \implies rxn \text{ is not feasible})$ 

- (b) (i)  $2 Zn (s) + O_2 (g) + 2H_2O (I) \Rightarrow 2 Zn^{2+} (aq) + 4OH^{-} (aq) [or 2 Zn(OH)_2 (s)]$  $E_{cell}^{e} = +0.40 - (-0.76) = +1.10 V$ 
  - (ii) When pH decreases, [OH<sup>-</sup>] falls and so, position of equilibrium shifts to the <u>right</u>.  $\therefore E^{\circ}_{cell}$  increases.

(iii) Amount of 
$$Zn = \frac{5}{65.4} = 0.0765 \text{ mol}$$
  
 $Zn \rightarrow Zn^{2+} + 2 e^-$   
Amount of electrons = 2 × amt of Zn  
 $= 2 \times 0.0765 = 0.153 \text{ mol}$   
Since charge on 1 mol of electron = 96500 C  
 $\therefore$  charge = 0.153 × 96500 = 14755 C  
 $t = \frac{Q}{I} = \frac{14755}{4 \times 10^{-5}} = 3.69 \times 10^8 \text{ s} = 4269 \text{ days}$ 

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(c)  $Fe^{2+}$  [Ar]  $3d^6$   $Zn^{2+}$  [Ar]  $3d^{10}$ 

Fe<sup>2+</sup> has partially filled d-subshell. Zn<sup>2+</sup> has a completely filled d-subshell, hence d-d\* electronic transition cannot occur. On forming complexes, the d-orbitals of Fe<sup>2+</sup> become non-degenerate. This allows d-d\* electronic transition to take place when an electron moves from a d-orbital of lower energy to one of higher energy. Radiations in the visible light region will be absorbed. Hence the colours of transition element complexes observed will be complementary to the colours absorbed.

- (d) (i) Homogeneous catalysis. Co is able to exist in variable oxidation states.
  - (ii)  $2\text{Co}^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2\text{Co}^{3+}(aq) + 2\text{SO}_4^{2-}(aq)$  $E^{\circ}_{\text{cell}} = +2.01 - (+1.82) = +0.19 \text{ V} (>0 \Rightarrow \text{rxn is feasible})$

 $2\text{Co}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow 2\text{Co}^{2+}(\text{aq}) + \text{I}_{2}(\text{aq})$  $E^{\circ}_{\text{cell}} = +1.82 - (+0.54) = +1.28 \text{ V} (>0 \implies \text{rxn is feasible})$ 









(ii) Primary Structure – amide / peptide linkage
 Secondary Structure – hydrogen bonds between C=O & N-H groups
 Tertiary Structure – R group interactions (e.g. ionic, disulphide linkages, hydrogen bonding or van der Waals interactions)
 Quaternary Structure – van der Waal forces (& ionic)

- (iii) minimum possible molar mass =  $\frac{100}{0.34} \times 55.8 = 1.64 \times 10^4$  g There are 4 iron atoms per haemoglobin molecule, or 4 polypeptides in the quaternary structure of haemoglobin.
- (iv) van der Waals interactions.

**5** (a) (i)



- (ii) Down the group,
  - The size of cation *increases*, thus charge density *decreases*, leading to lower polarising power.
  - Therefore, the anion (OH<sup>-</sup>) is polarised (distorted) to a *smaller* extent.
  - Decomposition (to form oxide) occurs with greater difficulty.
  - Thermal stability of the hydroxides increases, with higher decomposition temperatures

(c) (i) When small amount of  $OH^-$  is added, HCIO +  $OH^- \rightarrow CIO^- + H_2O$ 

> When small amount of  $H^+$  is added, KCIO +  $H^+ \rightarrow K^+$  + HCIO (or)  $CIO^-$  +  $H^+ \rightarrow$  HCIO

(ii) By considering salt hydrolysis,  

$$CIO^{-} + H_2O \Rightarrow HCIO + OH^{-}$$
  
 $K_b = \frac{10^{-14}}{10^{-7.4}} = 2.51 \times 10^{-7} \text{ mol dm}^{-3}$   
Let concentration of OH<sup>-</sup> be x mol dm<sup>-3</sup>.  
 $2.51 \times 10^{-7} = x^2/0.01$   
 $x = 5.01 \times 10^{-5} \text{ mol dm}^{-3}$   
 $pOH = -log_{10} (5.01 \times 10^{-5}) = 4.3$   
 $pH = 14 - 4.3 = 9.7$   
(iii)  $pH = pK_a + log_{10} \text{ [salt]/[acid]}$   
 $[acid] = \frac{(250/1000)x0.1}{0.25 + 0.30}$   
 $= 0.0455 \text{ mol dm}^{-3}$   
 $[salt] = \frac{(300/1000)x0.2}{0.25 + 0.30}$   
 $= 0.109 \text{ mol dm}^{-3}$   
 $pH = 7.4 + lg(0.109/0.0455)$ 

=7.78

(iv) Reagent/Condition: KOH(aq), Cold / At room temperature  $Cl_2(g) + 2 \text{ KOH}(aq) \rightarrow \text{KCI}(aq) + \text{KCIO}(aq) + H_2O(I)$ Type of reaction: Disproportionation

(d) Ionic product of Ag<sub>2</sub>CO<sub>3</sub> = [Ag<sup>+</sup>]<sup>2</sup>[CO<sub>3</sub><sup>2-</sup>]  
= 
$$(\frac{1 \times 0.001}{1.001})^{2}(\frac{1 \times 1}{1.001})$$
  
= 9.97 x 10<sup>-7</sup> mol<sup>3</sup> dm<sup>-9</sup>

Ionic product  $> K_{sp}$  (Ag<sub>2</sub>CO<sub>3</sub>) Precipitation occurs.

lonic product of AgCH<sub>3</sub>CO<sub>2</sub> = [Ag<sup>+</sup>][CH<sub>3</sub>CO<sub>2</sub>] =  $(\frac{1 \times 0.001}{1.001})(\frac{1 \times 1}{1.001})$ = 9.97 x 10<sup>-4</sup> mol<sup>2</sup> dm<sup>-6</sup>

lonic product <  $K_{sp}$  (AgCH<sub>3</sub>CO<sub>2</sub>) Precipitation does not occur.