H2 Chemistry 9647

2014 'A' Level P3 Suggested Solutions

1 (a) (i)
$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq); pH = 13 (accept 14)$$
 [1]
(ii) $P_4O_6(s) + 6H_2O(l) \longrightarrow 4H_3PO_3(aq); pH \approx 2$ [1]
(b) (i) amount of $Na_2S_2O_3$ reacted $= \frac{16.70}{1000} \times 0.200$
 $= 3.34 \times 10^{-3} \text{ mol}$
 $\frac{n(Na_2S_2O_3)}{n(Na_2O_2)} = \frac{2}{1}$ [1]
amount of Na_2O_2 present $= 1.67 \times 10^{-3} \text{ mol}$
mass of Na_2O_2 present $= 1.67 \times 10^{-3} \times [2(23.0) + 2(16.0)]$
 $= 0.131 \text{ g}$ [1]
mass of Na_2O present $= \frac{0.370}{[2(23.0) + 16.0]}$
 $= 5.97 \times 10^{-3} \text{ mol}$
 $\frac{n(Na_2O)}{n(Na_2O_2)} = \frac{5.97 \times 10^{-3}}{1.67 \times 10^{-3}}$
 $= 3.57$ [1]

<u>Comments</u>:

(a) Students are expected to include state symbols in the equation. Some thought that P_4O_6 was a liquid or a gas, or that H_3PO_3 was gaseous. Several gave H_2 as one of the products with Na_2O , and H_3PO_4 or O_2 as popular incorrect products with P_4O_6 .

(c) (i) Compound with a lower pK_a is the stronger acid.

 $\begin{array}{c} H_2 O \rightleftharpoons HO^- + H^+ \\ H_2 O_2 \rightleftharpoons HOO^- + H^+ \end{array}$

In the 2nd equilibrium, the <u>highly electron–withdrawing oxygen</u> attached to the [1] $-O^-$ will <u>disperse the negative charge on the O atom</u>, <u>stabilising</u> it. The <u>position of</u> equilibrium will lie more to the right as compared to the 1st eqm, making <u>H₂O₂ a</u> stronger acid with lower pK_a compared to water.

(ii)
$$\begin{array}{c} O \\ CH_3 - C - OH \end{array} \xrightarrow{O} CH_3 - C - O^- + H^+ \\ O \\ CH_3 - C - O - OH \end{array} \xrightarrow{O} CH_3 - C - O - O^- + H^+ \end{array}$$

In the first equilibrium, The p-orbital of the C atom <u>overlaps sideways</u> with the [1] <u>p-orbitals</u> of the <u>2 neighbouring O atoms</u>. The negative charge on the carboxylate ion is <u>distributed equally</u> between the two O atoms. This will <u>stabilise the CH₃CO₂⁻</u>, hence making <u>CH₃CO₂H a stronger acid</u>.

In the second equilibrium, this stabilisation by <u>resonance of the $-CO_2^-$ structure</u> is impossible due to an intervening O atom, hence making <u>CH₃CO₃H a weaker</u> acid. (or the <u>negative charge on the O atom is localised</u> as there is <u>absence of p</u> <u>orbital on the adjacent sp³ O atom</u>, hence making <u>CH₃CO₃H a weaker acid</u>.) [1]

Comments:

Those who had successfully argued the H_2O_2 case often incorrectly used the same arguments with CH_3CO_3H . Some thought that the more oxygen atoms there were, the more stabilisation by delocalisation. Other students wrongly suggested that CH_3CO_3H ionised to give OH^- (or OH^+), rather than H^+ .

(d) (i) B.E.(C-C) + 2B.E.(C-O) =
$$350 + 2(360)$$
 [1]
= +1070 kJ mol⁻¹

(ii) $\Delta H_r = B.E.(C=C) + 4B.E.(C-H) - [4B.E.(C-H) + B.E.(C-C) + 2B.E.(C-O)]$ -354 = +610 - [B.E.(C-C) + 2B.E.(C-O)]sum of B.E.(C-C) and 2B.E.(C-O) = +964 kJ mol⁻¹ [1]

In a 3-membered ring where each sp³ hybridised C atom has only an angle of [1] 60° (<<109.5°), the ring in epoxyethane experiences <u>severe bond strain</u>, resulting in <u>bond weakening</u>. This explains the much lower sum of the C–C and 2 x C–O actual bond energies than the theoretical value.

Comments:

Fewer students were able to explain the difference in the values. Most students wrote about either heat being lost to the surroundings, non–standard conditions or average bond energies were used. Some students appreciated that the difference was significantly larger than one might expect from using average bond energies.

(e) (i)
$$H OHH$$
 $H H$ $H H$ [2]
 $CH_3 - C - C - CH_2$ $CH_3 - C = C - CH_3$ $CH_3 - C = CH_2$
 CH_3H CH_3 CH_3 CH_3
 CH_3 CH_3

[1]: correct structure for C[1]: correct structures for E and F (structures can be swopped)

Thinking process

Given that CH_3COCH_3 and CH_3CO_2H are formed when one of the alkenes, **E** or **F** are treated with hot/MnO₄⁻, you can deduce the identity of one of the alkenes to be $(CH_3)_2C=CHCH_3$ (labelled as **E**, in this case).

Since the alkene is obtained from dehydration of the alcohol **C**, you can add back the –H and –OH across the C=C of the alkene deduced to form **C**. Here, you need to also take note that the alcohol **C** formed must have the structure $CH_3CH(OH)R$ so that it can give a positive iodoform test.

After which, you can then deduce the structure of alkene F.

Comments:

Although most gave structures with five carbon atoms, there were a number who suggested straight chain compounds rather than branched chain ones. The idea that **E** and **F** must have the same overall carbon skeleton was not appreciated by some students. Many gave straight chain alkenes thus only incorporating part of their evidence and some gave **C** as a primary alcohol, which could not have given a positive tri–iodomethane reaction.



(vi) O CH_2 CH_2 CH_2 CH_3 CH_3

An easier way to deduce A is to derive the ester B first and then remove the -O-atom to get ketone A.

2 (a)

[2]

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By Hess' Law, LE = (−90.5) – [159.5 + 519 + ½ (436) + (−73)] = **−914 kJ mol**⁻¹

[1]: correct substitution of relevant values from question and from *Data Booklet*

[1]: final answer with correct units

Comments:

For this question, students are expected to extract relevant data from the question and Data Booklet.

Students can first tackle the question by writing the equation that represents lattice energy of LiH(s). Next, identify the enthalpy changes from the question and data booklet that can be linked to the reactants $[Li^+(g) \& H^-(g)]$ and product [LiH(s)]. The determination of L.E. can subsequently be done by completing the energy cycle.

Note: ΔH_{atm} (H) = $\frac{1}{2}$ B.E.(H–H), all the energy terms should be quoted and the signs of the enthalpy changes should be correct.

(b) $4\text{LiH}(s) + A/Cl_3(s) \longrightarrow \text{LiA}/H_4(s) + 3\text{LiC}/(s)$

 $\Delta H_{\rm f}^{\ominus} = \Sigma \Delta H_{\rm f}^{\Theta} \text{ (products)} - \Sigma \Delta H_{\rm f}^{\Theta} \text{ (reactants)}$ $-276 = \Delta H_{\rm f}^{\Theta} \text{ (LiA}/H_4) + 3(-408.5) - [4(-90.5) + (-704)]$ $\Delta H_{\rm f}^{\ominus} \text{ (LiA}/H_4) = -116.5 \text{ kJ mol}^{-1}$

[1]: balanced equation

- [1]: correct substitution into mathematical expression
- [1]: final answer with units

Comments:

It is important to be able to first extract the reactants and products correctly from the question, before balancing the equation for the reaction.

Since enthalpy change of reaction is given in the question, and all data available from the question are enthalpy change of formation, students can use the mathematical expression " $\Delta H_{\rm f}^{\rm o} = \Sigma \Delta H_{\rm f}^{\rm o}$ (products) – $\Sigma \Delta H_{\rm f}^{\rm o}$ (reactants)" to determine $\Delta H_{\rm f}^{\rm o}$ (LiA*l*H₄) without drawing any energy cycle. Students should take note of both the signs and multipliers in the calculation of the enthalpy change.

(c) (i) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ},$ $(-27.68) = (+3.46) - (298)\Delta S^{\circ}$ $\Delta S^{\circ} = +0.104 \text{ kJ mol}^{-1} \text{ K}^{-1} \text{ or } +104 \text{ J mol}^{-1} \text{ K}^{-1}$

 ΔS° is positive as the reaction results in an increase in <u>number of moles of</u> gaseous particles which increases disorder / brings about more ways of arranging / distributing the particles in the system.

[1]: final answer with units[1]: correct explanation

(ii) O.N. of H in LiA*I*H₄ = -1

O.N. of A*l* in $Li_3AlH_6 = +3$ [1]

(iii) octahedral

[2]

[1]

[1]

4

Comments:

(i) Students should state the units for ΔS° correctly. If the substitution of values for ΔH° and ΔG° are in kJ mo⁺¹, the calculated value should be in kJ mo⁺¹ K⁻¹, not J mo⁺¹ K⁻¹. Do not omit the K⁻¹. As this question required students to comment on why ΔS° is positive "with respect to the equation", students should link the explanation to the equation given in the question.

(ii) Note: O.N. of Li = +1 and O.N. of H in hydrides = -1 (not +1). Hence, O.N. of Al is +3 (not -3, -9) Calculation of O.N. of H: 0 = (+1)+(+3)+4(x), x = -1, where x is the O.N. of H Calculation of O.N. of Al: 0 = 3(+1)+y+6(-1), y = +3, where y is the O.N. of Al

(iii) The anion complex should have the formula $[AlH_6]^{3-}$ and the coordination number of Al^{3+} in $[AlH_6]^{3-} = 6$.



symmetry and is bonded to four different groups.

M is not chiral as there is a plane of symmetry in **M**. All the C atoms have $\underline{2}$ identical groups bonded to it (either 2 H or 2 –CH₂CH₂OH groups).

Comments:

(i) It is good to know that NaBH₄ can only reduce ketones or aldehyde but not carboxylic acid and its derivatives whilst LiAlH₄ can reduce ketones, aldehyde, carboxylic acid and its derivatives.

Given that	Type of reaction	Deduction about structure
No. of C < 6		All 3 unknowns do not contain benzene ring.
<i>H, J</i> and <i>K</i> reacts with alkaline aqueous iodine	oxidation	 <i>H</i> can contain either CH₃CO– or CH₃CH(OH)– group <i>J</i> and <i>K</i> contains CH₃CH(OH)– group (as <i>J</i> and <i>K</i> are products of reduction, they should not be carbonyl compounds)
H, J and K reacts with Na	redox	 H, J contains either alcohol group or carboxylic acid group. (as carboxylic acid cannot be reduced by NaBH₄) K contain alcohol functional group (LiAlH₄ can reduce both alcohol and carboxylic acid if H contains carboxylic acid group).
<i>H</i> and <i>J</i> reacts with Na ₂ CO ₃ , but not <i>K</i> .	Only H and J undergoes acid–base reaction	 <i>H</i> and <i>J</i> contain carboxylic acid functional group. <i>K</i> does not contain carboxylic acid functional group.

Students can use the following table to help them determine the structure of H, J and K.

(ii) NaBH₄ reduces <u>only</u> the ketone group, but not the ester group. Ketone is reduced to a secondary alcohol in **L**. Thus there should <u>not</u> be 2 - OH group bonded to the same carbon in **L**.

LiAlH₄ reduces <u>both the ketone and ester</u> functional group. As the ester functional group is reduced, **M** should no longer be a cyclic compound. It is also <u>not</u> possible to have 2 - OH group bonded to the same carbon in **M**.

If we only consider the reduction of the ester group, the process of reduction can be simplified into two stages:



(iii) It is incorrect to think that a cyclic compound is not chiral.

(e) (i) 1:
$$LiA/H_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2$$

2: $LiOH + HCl \longrightarrow LiCl + H_2O$ and $Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

[1]: balanced equation for each process

[2]

(ii) $n(\text{LiA}/\text{H}_4) = \frac{2.00}{(6.9 + 27.0 + 4 \times 1.0)} = 0.05277 \text{ mol}$ $n(\text{H}_2) = 4 \times 0.05277 = 0.2111 \text{ mol}$ volume of H₂ at r.t.p. = 0.2111 x 24 = **5.07 dm**³

[1]: correct calculation of n(H₂)[1]: correct final answer with units

Comments:

(i) Students should deduce from the 2 bullet points given in the question that both hydrogen and a mixture of metal hydroxides (not oxides) are produced when water is added to $LiAlH_4$.

3	(a)	(i)	$NaX + H_3PO_4 \longrightarrow HX + NaH_2PO_4$	(X = Cl or I)	[1]
			$NaX + H_2SO_4 \longrightarrow HX + NaHSO_4$	(X = Cl or I)	

When sodium chloride / sodium iodide is heated with either concentrated H_3PO_4 or concentrated H_2SO_4 , HCl(g) / HI(g) will be produced in the <u>acid–base</u> [1] <u>reaction</u>. [1]

 $8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$

However, HI being a <u>stronger reducing agent</u> than HC*l*, will be <u>oxidised</u> by concentrated H₂SO₄ to give I₂. H₃PO₄ is a <u>weaker oxidising agent</u> than concentrated H₂SO₄, thus no oxidation of HI occurs. Therefore, only H₃PO₄ can be used to make a pure sample of HI from NaI. Both H₃PO₄ and H₂SO₄ can be used to prepare HC*l*.

- (b) (i) A sample of PCl_3 is prepared by <u>heating</u> solid phosphorus with chlorine gas. [1] The product is purified by <u>distillation</u>.
 - (ii) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$ PCl_3 reacts with H_2O in the moist air to produce white <u>fumes of HCl</u>.

Comments:

Note that the product is **not** H_3PO_4 (oxidation number of P is $+5 \neq +3$).

(c) (i) POCl₃ [1] (ii) CH₃CH=C=CHCH₃ or CH₃C=CCH₂CH₃ [1] (iii) H 120° 120° H H 180° [2] —Н H--H [1]: correct displayed formula [1]: correct bond angles

[1]

[1]



The loss of both chlorine atoms does not occur because of the <u>bond strain</u> caused by having 2 C=C double bonds / having a C=C on the same carbon in the cyclic ring if further elimination were to occur.

<u>Comments</u>:

(iii)The H–C–C bond angles are not required in this question. Note that a bond angle must involve three atoms.

(iv) The question is asking why further elimination did not occur and not asking to explain why the (C–Cl) bond in chlorobenzene is strong.

(d)	(i)		Р	Ν	Cl	
		mass in 100g / g	20.5	9.2	70.3	
		A _r	31.0	14.0	35.5	
		no. or moles / mor		0.007	3.01	[1]
		Smallestratio	1.01		0.01	[,]
		Empirical formula of Molecular formula of	$S = PNCl_3$ $S = P_2N_2Cl_6$			[1] [1]
		C <i>l</i> —	$Cl \qquad Cl \\ \downarrow \qquad \downarrow \\ P = N - N = P - Cl$			[1]
		Structure of S :	Cl Cl			
	(ii)	$P_2N_2Cl_6 + 12NH_3 - $	$\rightarrow P_2H_{12}N_8 + 6NH_4($	Cl		[2]
	(iii)	NH ₂ N	IH ₂			[1]
			P—NH ₂			
		│ NH₂ N	H_2			
		L	L			
Con	<u>iment</u>	<u>s</u> : d T is obtained by sub	stituting the _Cl ato	ns in substance S by		
0011	ipouri		$Cl \qquad Cl$		-11112.	
		C <i>l</i> —F	P-N-N-P-C <i>l</i>			
Alter	mative	e structure of S :	\mathbf{C}_{l} \mathbf{C}_{l}			
			NH ₂ NH ₂			
		NH ₂ —	- P N P NH	2		
and	the co	orresponding T	NH ₂ NH ₂			
Alth	ough a	these are possible alte	ernatives based on a	the information given	by the question, th	ey are
less	likely	to be correct if you	I look at the struc	tures of PCl_5 and F	H_2N-NH_2 and using	g your
know	vleda	e of the chemistry bety	veen PCl ₅ and wate	r (nucleophile)		

Chlorine is a highly electronegative atom which will exert an electron-4 (a) (i) [1] withdrawing effect on the carboxylate ion C/CH₂CO₂⁻. This increases the dispersal of negative charge, hence stabilising the ion. The [1] dissociation of the acid molecule to give H⁺ ions is thus favoured, which results in [1] C/CH_2CO_2H being a stronger acid and hence the smaller pK_a value as compared to CH₃CO₂H.

(ii)
$$K_a = \frac{[H^+][A^-]}{[HA]}$$
 [3]

For CH₃CO₂H: $\frac{[A^{-}]}{[HA]} = \frac{10^{-4.76}}{10^{-3.8}}$ $\frac{[A^{-}]}{[HA]} = 0.110$

For C/CH₂CO₂H: $\frac{[A^{-}]}{[HA]} = \frac{10^{-2.87}}{10^{-3.8}}$ $\frac{[A^{-}]}{[HA]} = 8.51$

[1] each correct ratio obtained [1] quoting answers to 3 s.f.

Step 1: dilute H₂SO₄, heat Step 2: K₂Cr₂O₇, dil. H₂SO₄, heat (accept KMnO₄)

[1]: for intermediate U [1]: correct reagents and conditions for each step

(ii)

Step 1: dilute HCl, heat Step 2: KMnO₄, dil. H₂SO₄(aq), heat (do not accept K₂Cr₂O₇)

[1]: for intermediate V

[1]: correct reagents and conditions for each step

[3]

[3]



Step 1: KMnO₄, dil. H_2SO_4 , heat under reflux Step 2: warm with $I_2(aq)$ and NaOH(aq) followed by acidification with dilute HC*l*

[1]: for intermediate W[1]: correct reagents and conditions for each step

(c) (i)
$$H_3^+ H_3 - CH - CO_2^-$$
 [1]



(iii)
$$H_3^+ H_- CH_- CO_2^-$$
 [1]

(d) (i) aspartic acid: <u>ionic linkages</u> between the <u>charged</u> $-CO_2^-$ and the $-NH_3^+$ groups [1]

(ii) valine: <u>van der Waals' interactions</u> between the <u>non-polar</u> $-CH(CH_3)_2$ and the - [1] $CH_2-C_6H_5$ groups

5 (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ [1]

(ii)
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$$
 [1]

(b) Blue solution of $Cu^{2+}(aq)$ contain Cu^{2+} in its hexaaqua complex, $[Cu(H_2O)_6]^{2+}$. [4]

In aqueous solution, the weak base NH_3 undergoes partial ionisation, producing OH^- ions.

When a small amount of $NH_3(aq)$ is added, the $OH^-(aq)$ undergoes acid-base reaction with $[Cu(H_2O)_6]^{2+}(aq)$ to produce a blue precipitate of $Cu(OH)_2$.

[3]

[1]

 $[Cu(H_2O)_6]^{2+}(aq) + 2OH^{-}(aq) \iff [Cu(OH)_2](s) + 6H_2O(l) \qquad \dots \dots (1)$ blue solution blue ppt

When excess $NH_3(aq)$ is added, ligand exchange reaction occurs and the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is formed.

 $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \implies [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(I) \qquad \dots \dots (2)$ blue solution deep blue solution

The increasing addition of NH₃(aq) shifts the position of equilibrium (2) to the <u>right</u>, forming a deep blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$. As the concentration of $[Cu(H_2O)_6]^{2+}(aq)$ <u>decreases</u>, the position of equilibrium (1) shifts <u>left</u>, causing the blue precipitate of Cu(OH)₂ to <u>dissolve</u>.

[1]: correct observations
[1]: role of NH₃
[1]: equation for formation of copper(II)hydroxide
[1]: equation for formation of soluble complex

(c)	(i)	Cu²+ + 2e 🗮 Cu	+0.34V
. ,	.,	Ni ²⁺ + 2e 💳 Ni	-0.25V

 $E^{\bullet}_{cell} = +0.34 - (-0.25)$ = +0.59 V

(ii) The voltage will become more positive.

 $Ni^{2+} + 2e \longrightarrow Ni$ -0.25V When $[Ni^{2+}]$ is decreased, position of equilibrium <u>shifts left</u> to <u>favour oxidation</u> of Ni to Ni^{2+}. $E^{\bullet}(Ni^{2+}/Ni)$ becomes <u>more negative</u>, hence E^{\bullet}_{cell} becomes <u>more positive</u>.

<u>Comments</u>: Values were often incorrectly described as 'higher' or 'lower'.

(d)	Ag⁺ + e 득 Ag	+0.80V
	Cu²+ + 2 e ≕ Cu	+0.34V
	Ni ²⁺ + 2 e ≕ Ni	-0.25V

At the anode, Cu and Ni <u>dissolve</u> to form Cu^{2+} (aq) and Ni²⁺ (aq) respectively. These [1] metals are oxidised as they have the <u>least positive E° values</u>.

Ag has a <u>more positive E^{\bullet} value</u> than Cu, thus is <u>remains undissolved</u>. It separates out [1] as <u>anode sludge</u> beneath the anode.

 Cu^{2+} and Ni^{2+} ions migrate to the cathode. Ni^{2+} ions are <u>less easily reduced</u> than Cu^{2+} due to its less positive E^{\oplus} value. Hence, Ni^{2+} <u>remains in solution</u> while <u> Cu^{2+} is</u> [1] preferentially discharged.

(e) (i) quantity of charge =
$$2.00 \times 23 \times 60$$

= 2760 C

. 1

[1]

[1]

[1]

$$n_{e} = \frac{2760}{96500}$$

= 0.0286 mol
$$Cu^{2+} + 2e \longrightarrow Cu$$

$$n_{Cu} = \frac{1}{2} \times 0.0286$$

= 0.0143 mol
expected increase in mass = 0.0143 \times 63.5
= 0.908 g

$$n_{\text{Ni}} = \frac{0.492}{58.7 + 2[4(12.0) + 7(1.0) + 2(14.0) + 2(16.0)]}$$

= 1.704 x 10⁻³ mol





Ω



Comments:			
Evidence	Deduction	Type of reaction (fyi)	
Both X and Y react with Na	-OH group (alcohol or carboxylic	redox	
	acid) is present in X and Y .		
but only Y reacts with Na_2CO_3	Y only.	acid-Base	
Both X and Y do not react with	Carbonyl and unsaturated carbon-	condensation	
either 2,4–DNPH	carbon bonds are absent in both X	electrophilic addition	
or aqueous bromine.	and Y		
Both Z and Ω form salts with	Acidic – COOH and basic – NH ₂	acid-base	
HC/ and with Na ₂ CO ₃ .	groups are present in both Z and Ω .		

Note: At room temperature, alkenes (C=C), alkynes (C≡C), carbonyls (C=O) and nitriles (C≡N) are

(f)

[1]

[1]

[1]

[4]

reduced. Aromatic ring is only reduced upon heating. Carboxylic acids are not reduced by H_2/Ni even upon heating.