

Suggested Solutions to N2011 H2 Chemistry Paper 1 (9647/01)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
A	D	C	D	C	C	D	C	A	D	C	B	B	B	C	C	C	A	C	B
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
C	B	B	B	C	A	A	D	B	B	D	B	A	B	C	B	D	D	A	B

Working for Suggested Solutions to N2011 H2 Chemistry Paper 1 (9647/01)

Q1

Ti: 22 electrons

Ti⁴⁺: 22 – 4 = 18 electrons

Ans: A

Q2

First ionisation energy (1st I.E.) is the energy required to remove 1 mole of electrons from one mole of gaseous atoms in the ground state to form one mole of gaseous singly-charged cations.

Ionisation energy (I.E.) of an atom is influenced mainly by two factors:

1. Effective nuclear charge
2. Distance of the valence electron from the nucleus

Ne: 1s²2s²2p⁶

F: 1s²2s²2p⁵

Both F and Ne are in the same period, hence the shielding effect experienced by their valence electrons is approximately the same.

However, Ne has one more proton than F (i.e. greater nuclear charge), hence its valence electrons experience greater effective nuclear than those in F.

Ans: D

Note: Some students answered B. A complete octet does not make it harder to remove an electron.

Q3

Amt of C in CO₂ = 48 / 24000 = 0.00200 mol

Amt of C in (Na₂CO₃)_x.yH₂O = Amt of C in CO₂
 $x(10/1000 \times 0.100) = 0.00200$
 $x = 2$

Amt of H₂O₂ = y(10/1000 × 0.100) = 0.00100y

Amt of KMnO₄ = 24/1000 × 0.0500 = 0.00120

$$\frac{\text{Amt of H}_2\text{O}_2}{\text{Amt of KMnO}_4} = \frac{0.00100y}{0.00120} = \frac{2}{5}$$

$$y = 3$$

Ans: C

Q4

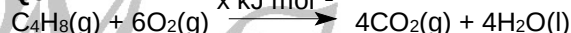
$$\frac{pV}{T} = nR = \text{constant}$$

$$\frac{pV}{T} = \frac{(2p)(V)}{T}$$

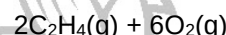
T = 600 K

Ans: D

Q5



y kJ mol⁻¹



$$2\Delta H_c^\circ [\text{C}_2\text{H}_4(\text{g})] = x + y \text{ kJ mol}^{-1}$$

Ans: C

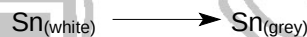
Q6

$$|LE| \propto \frac{q_+ q_-}{r_+ + r_-}$$

The magnitude of lattice energy is proportional to product of charges and inversely proportional to the sum of ionic radii.

Ans: C

Q7



$$\Delta H_f^\circ = -2090 - 0 = -2090 \text{ J mol}^{-1}$$

$$\Delta S_f^\circ = 44.1 - 51.4 = -7.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ = -2090 - (273+12)(-7.3)$$

$$= -2090 - (285)(-7.3)$$

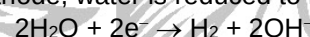
Ans: D

Q8: Equation in italics is out of syllabus

At the anode, chloride is oxidised to chlorine gas.



At the cathode, water is reduced to hydrogen gas.



Equation below not in syllabus

Chlorine disproportionates in cold NaOH.



Ans: C

Q9

The metal will dissolve in CO₂(aq), which is acidic, if

$$E^\circ(\text{H}^+/\text{H}_2) - E^\circ(\text{M}^{n+}/\text{M}) > 0.$$

As E°(Cu²⁺/Cu) is the most positive, Cu has the least tendency to be oxidised.

Ans: A

Q10

As the diagram shows apparatus needed to measure the standard electrode potential of Fe³⁺/Fe²⁺, X has to be an inert electrode, which is Pt, and Y should contain 1 mol dm⁻³ Fe²⁺(aq) and 1 mol dm⁻³ Fe³⁺(aq).

Ans: D

Q11

A buffer solution is one which is able to **resist a change in pH** (i.e. maintain an almost constant pH) upon the addition of a **small amount** of acid or base. Hence statements (A) and (D) are wrong. A mixture of sodium citrate and citric acid functions as an acidic buffer.

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{citrate}]}{[\text{citric acid}]}$$

When a small amount of base is added, citric acid will react with the base and form citrate. Hence, [citric acid] decreases while [citrate] increases. Hence, pH of the buffer solution will increase slightly. Ans: C

Q12

Let rate = $k[\text{NO}_2]^m[\text{SO}_2]^n$
Comparing expts 2 and 3, where $[\text{SO}_2] = \text{constant}$:
When $[\text{NO}_2]$ is increased by 1.33 times, the relative rate also increases by 1.33 times.
Hence, order of reaction wrt to $[\text{NO}_2]$ is 1 (i.e. $m=1$).
Comparing expts 1 and 2:

$$\frac{\text{Expt 2}}{\text{Expt 1}} = \frac{1.44}{1.00} = \frac{k[0.006]^1[0.006]^n}{k[0.005]^1[0.005]^n}$$

$$1.44 = (1.2)(1.2)^n$$

$$n = 1$$

Ans: B

Q13

rate = $k'[\text{C}_6\text{H}_5\text{N}_2^+]^a$, where $k' = k[\text{H}_2\text{O}]^b$.
Rate $\propto (V_{\text{gas}}/t)$. Since V_{gas} constant, rate $\propto (1/t)$.
As $1/t \propto k'[\text{C}_6\text{H}_5\text{N}_2^+]^a$, plot $[\text{C}_6\text{H}_5\text{N}_2^+] \text{ vs } (1/t)$.
Ans: B

Q14

(A) The element that has 4 atoms in its molecule is phosphorus (i.e. P_4), not sulfur. Sulfur exists as S_8 .
(B) Aluminium has the highest electrical conductivity as each Al atom contributes 3 electrons into the 'sea of delocalised electrons'.
(C) In period 3, the element with the highest melting point is silicon (giant molecular structure), not aluminium.
(D) The element with the largest anion is phosphorus, not chlorine. Trend in ionic radius is: $\text{Cl}^- < \text{S}^{2-} < \text{P}^{3-}$.
Ans: B

Q15

Thermal decomposition of HX involves breaking the H-X bond.
The strength of the covalent H-X bond is dependent on the effectiveness of the orbital overlap.
H-I is weaker than H-Cl bond since the electron cloud of I is more diffuse than that of Cl, hence the overlap of orbitals in HI is less effective.
Ans: C

Q16:

$\text{Ca}(\text{NO}_3)_2 \rightarrow \text{CaO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$: Given
Amt of $\text{Ca}(\text{NO}_3)_2 = 8.2 / 164 = 0.050 \text{ mol}$
Amt of $\text{O}_2 = 0.5 \times 0.050 = 0.025 \text{ mol}$
Vol. of $\text{O}_2 = 0.025 \times 24000 = 600 \text{ cm}^3$
Ans: C

Q17

In order to produce oxygen gas, H_2O_2 must undergo oxidation and this occurs only in acid solution. In alkaline solution, H_2O_2 will be reduced to water as it oxidises Cr^{3+} ions.
Ans: C

Q18

The enthalpy change of fusion of the period 3 elements is related to melting points of these elements. Trend in enthalpy change of fusion: $\text{X} > \text{W} > \text{Z} > \text{Y}$
Si has a giant covalent (or molecular) structure and has the highest melting point. Al, which has the 2nd highest melting point, has a giant metallic structure. S and P have simple molecular structures. The melting point of S is greater than that of P as the electron cloud of S_8 is larger and more polarisable than that of P_4 .
Ans: A

Q19

The terminal carbon atoms are sp^3 hybridised. (Note: options C and D are mutually exclusive)
Ans: C

Q20

$\text{C}_x\text{H}_{2x+2} + \frac{6x+2}{4}\text{O}_2 \rightarrow x\text{CO}_2 + \frac{2x+2}{2}\text{H}_2\text{O}$
 $y = \frac{6x+2}{4} = 1.5x + 0.5$
i.e. straight line with gradient 1.5
Ans: B

Q21

$\text{CH}_2=\text{CHCl}$ is unreactive to nucleophiles for 2 reasons.
(i) The electrons on the chlorine atom delocalise into the C-C π bond, giving the C-Cl bond double bond character, thus making it relatively stronger. Thus, the Cl will not be easily substituted.
(ii) Nucleophiles are electron-rich, and the carbon attached to the chlorine atom is in a C=C double bond, which is also electron-rich. Hence the carbon attached to the chlorine will not attract the nucleophile.
Ans: C

Q22

In an S_N1 mechanism (nucleophilic substitution with only 1 species in the rate determining step and is therefore a 2-step reaction), the halogen atom leaves the C, leaving a carbocation as the intermediate.

Note: Although this is a primary carbocation, the electrons from the benzene ring delocalise over the positively charged carbon, dispersing the positive charge and stabilising the cation.

On the other hand, option (D) shows the S_N2 mechanism (2 species in the rate determining step and hence a one-step reaction). The OH^- nucleophile and the halogen derivative react in the first step to form a species, at transition state, where the Br atom is just leaving as a bond is just forming between the nucleophile and the carbon atom.

Option (A) is an intermediate in a nucleophilic addition reaction while option (C) is an intermediate in an electrophilic substitution reaction.

Ans: B

Q23**Steam with H^+**

- can hydrolyse the ester (just as hot, dilute H_2SO_4 can hydrolyse an ester)
- can add water across an alkene (just as cold conc. H_2SO_4 , followed by warming with water, can add H_2O across an alkene)

Ans: B

Q24

CH_3CH_2COCl (an acyl halide) hydrolyses most readily in water since C is bonded to two very electronegative atoms.

Between $(CH_3)_3CBr$ and $(CH_3)_3CI$, the C–Br bond is stronger and thus rate of hydrolysis will be slower for Y than for Z.

C_6H_5Cl will have the slowest rate of hydrolysis as the C–Cl bond has double bond character.

Ans: B

Q25

Option (C) does not give the correct set of conditions as the Cl_2 should **NOT** be in aqueous medium.

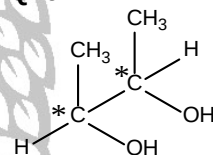
If Cl_2 is in the aqueous medium, then $AlCl_3$ will also dissolve in the aqueous medium and will dissociate to give Al^{3+} and Cl^- (and subsequently, Al^{3+} will hydrolyse water).

However, for the electrophilic substitution reaction to happen, we do not want $AlCl_3$ to hydrolyse in water. Instead, we want $AlCl_3$ to act as a Lewis acid to react in the following manner to form the electrophile Cl^+

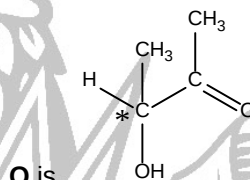
$$AlCl_3 + Cl_2 \rightleftharpoons AlCl_4^- + Cl^+ \text{ (this is what we want!)}$$

For this to happen, the reaction should be carried out in an anhydrous (no water) medium.

Ans: C

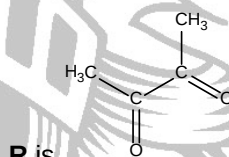
Q26

P (only P has 2 chiral centres)



Q is

. It only has 1 chiral centre.



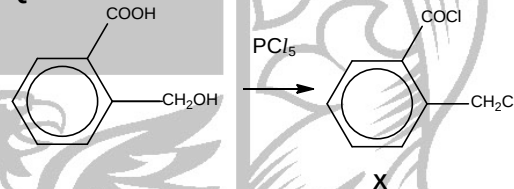
R is

. It has no chiral centre.

All 3 compounds, **P**, **Q** and **R**, give a positive iodoform

test as they have the $\begin{bmatrix} OH \\ | \\ -C-CH_3 \\ | \\ H \end{bmatrix}$ or $\begin{bmatrix} O \\ || \\ -C-CH_3 \end{bmatrix}$ structures required for the reaction with alkaline aqueous iodine to give tri-iodomethane.

Ans: A

Q27

Note: Carboxylic acids and alcohols react with PCl_5 .

Both the acyl halide and alkyl halide groups in X can react with NH_3 . The best answer is A, as after the NH_3 reacts with the acyl halide, an amide is formed. It is not possible to get the $-COO^-$ group in options (C) and (D). Option (B) is wrong as the alcohol would have reacted with PCl_5 .

Ans: A

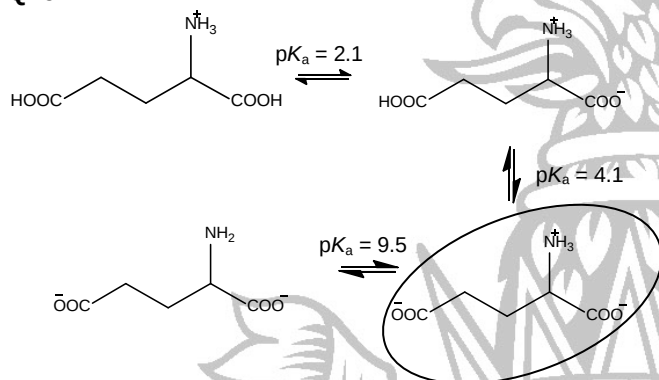
Q28

Reacts with Na to release $H_2 \rightarrow$ alcohol or carboxylic acid functional group must be present in all three compounds, X, Y and Z.

Only one of them reacts with 2,4-DNPH $\rightarrow$ only one of them is a carbonyl compound, i.e. has either an aldehyde group or a ketone group.

Ans: D

Q29



The species in the oval will be the major species present at pH 7.

Ans: B

Q30

The ester and amide functional groups will be hydrolysed when heated with HCl(aq) . Due to the acidic medium, the basic $-\text{NH}_2$ groups present will be protonated.

Ans: B

Q31

Statement 2 is wrong as M_r is compared to the mass of $1/12$ of a ^{12}C atom, not compared to a ^{12}C atom.

Statement 3 is incorrect as that is not the definition of M_r ; we do not compare with ^1H atoms.

Only option 1 is correct $\rightarrow$ Ans: D

Q32

1. Yes, H_2 gas has to be at 1 bar.
2. When resistance is infinite, the current passed will be effectively zero ($I = V/R$). When no current is passed, the potential difference between the standard hydrogen electrode and the half-cell being measured is the e.m.f.
3. At pH 1.0, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, which is not the required 1.0 mol dm^{-3} .

Options 1 and 2 are correct $\rightarrow$ Ans: B

Q33

1. Molecular formula (MF) of X: $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$, and MF of Z: $\text{C}_6\text{H}_5\text{NO}$. X and Z have the same empirical formula.
2. MF of Y is also $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$, i.e. same as X, so it is a structural isomer of X.
3. MF of Y is double the MF of Z.

Options 1, 2 and 3 are correct $\rightarrow$ Ans: A

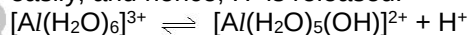
Q34

1. For a zero-order reaction, rate is independent of time. So, as time increases, rate remains constant.
2. The rate constant only changes when temperature changes or when a catalyst is used, so the rate constant is invariable with time.
3. The rate constant increases when temperature increases, so this option is wrong.

Options 1 and 2 are correct $\rightarrow$ Ans: B

Q35

1. Cl^- ions do not hydrolyse or react with water.
2. Al^{3+} has a high charge density. It hydrolyses water, giving an acidic solution.
3. Recall that one of the O–H bonds in H_2O is so polarised by the highly polarising Al^{3+} that it breaks easily, and hence, H^+ is released.



Options 2 and 3 are correct $\rightarrow$ Ans: C

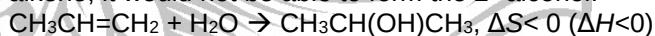
Q36: Out of syllabus for option 1 and 2

This is out of syllabus

This question integrates Group 17 and organic chemistry. When conc. H_2SO_4 and NaBr are placed together, HBr is produced in situ. The HBr produced then reacts with the alcohol to form an alkyl halide.

When conc. H_2SO_4 is added to NaBr , an acid-base reaction occurs first, forming HBr and NaHSO_4 . However, since Br^- is a good reducing agent, H_2SO_4 can be reduced to SO_2 while Br^- is oxidised to Br_2 . A redox reaction occurs and hence options 1 and 2 are by-products of the reaction.

If the 1° alcohol underwent dehydration to form an alkene, it would not be able to form the 2° alcohol.



The addition reaction needs to be carried out at low temperatures. Recall that, to add water to an alkene, we use **cold** conc. H_2SO_4 , followed by hot water. Therefore, at high temperatures, the 2° alcohol will not be formed. Option 3 is wrong.

Ans: B

Q37

1. Correct, it contains an amide group.
2. No, it only has 1 ester group.
3. No, it only has three chiral centres.

Only option 1 is correct $\rightarrow$ Ans: D

Q38

A catalytic converter oxidises hydrocarbons and carbon monoxide (to CO_2) and reduces oxides of nitrogen (to N_2). Only option 1 represents a possible reaction that takes place in a catalytic converter.

Ans: D

Q39

1. In the Baeyer's test, KMnO_4 loses its pink colour, so Mn(VII) in MnO_4^- is reduced.
2. In the Fehling's test, Cu^{2+} is reduced to copper(I) oxide.
3. In the Tollens' test, Ag^+ reduced to Ag .

All 3 options are correct $\rightarrow$ Ans: A

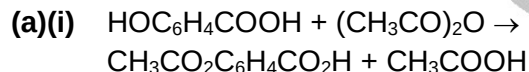
Q40: out of syllabus

For the 3° structure of spider silk, it involves R group interactions. R group in alanine is $-\text{CH}_3$. R group in glycine is $-\text{H}$. R group in serine is $-\text{CH}_2\text{OH}$. These R groups can form van der Waals' forces or hydrogen bonds, but not ionic bonds. Hence only options 1 and 2 are correct $\rightarrow$ Ans: B

**Suggested Solutions for N2011 H2 Chemistry Paper 2
(9647/02)**

Experimental Planning

1.



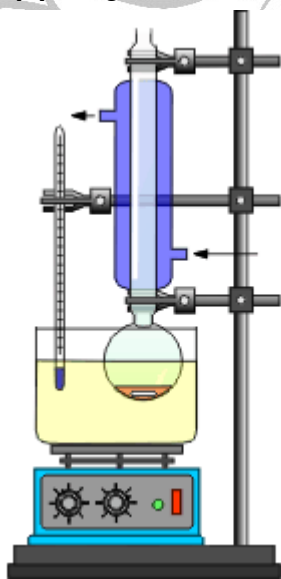
(ii) Amt of aspirin = $10 / 180 = 0.05556$ mol

Amt of 2-hydroxybenzenecarboxylic acid
required
= Amt of ethanoic anhydride
= $0.05556 \times 100/75$
= 0.07408 mol

Mass of 2-hydroxybenzenecarboxylic acid
required = 0.07408×138
= 10.2 g (3 s.f.)

Mass of ethanoic anhydride required
= 0.07408×102
= 7.56 g (3 s.f.)

(b) Diagram for reflux:



Note:
The direction for water in
and water out, the open
top and a safe way of
heating are important
marking points!

Note: As the anhydride is a corrosive liquid, it is not safe to take its mass on a weighing balance. Instead, its volume, which can be determined from its density and the mass calculated in a(ii), is used.

- 3) Using a dropper, add 8-10 drops of 85% phosphoric acid to the mixture carefully. Cool the reaction mixture in an ice bath placed inside a fumehood while this step is being carried out. **Note:** The round-bottomed flask should not be more than half-filled.
- 4) Set up the apparatus for reflux as shown. Heat the mixture gently for 15 minutes.
- 5) Detach the flask from the set-up. Using a dropper, add 2-3 cm³ of water dropwise to the mixture.
- 6) When the reaction has subsided, pour the mixture into a beaker containing 50 cm³ of cold water. Filter the crude product that is precipitated.
- 7) Transfer the residue into a small beaker. Carefully add hot water dropwise and stir until the aspirin just dissolves. A minimal volume of hot water should be used.
- 8) Filter the mixture to remove insoluble impurities while the mixture is still hot. The filter funnel should be hot and the filter paper dampened with hot water.
- 9) Crystals will start to grow as the solution cools. Cool the mixture in an ice bath to ensure all the aspirin has crystallised. Filter and dry the residue to obtain pure aspirin. Weigh the dried aspirin.
- 10) To test the purity, collect some crystals and determine the melting point. If the aspirin is pure, the melting point should be very close to 135 °C and the melting should be completed within a very small temperature range.

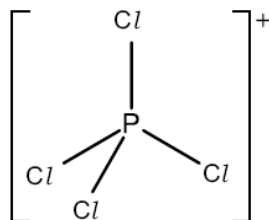
Procedure:

- 1) Weigh out accurately about 10.2 g of 2-hydroxybenzenecarboxylic acid using an electronic balance and transfer this to a round-bottomed flask.
- 2) In a fumehood, measure out 7 cm³ of ethanoic anhydride using a 10 cm³ measuring cylinder and add the anhydride to the round-bottomed flask while stirring with a glass rod.

(c) The anhydride and phosphoric acid are corrosive. Wear gloves and goggles when handling the chemicals / do the experiment in a fumehood. OR The solution may boil over when water is added to remove unreacted anhydride. Wear goggles and lab coat when performing this step. OR Organic compounds are flammable. Any heating should be done using a water bath and not with a naked flame.

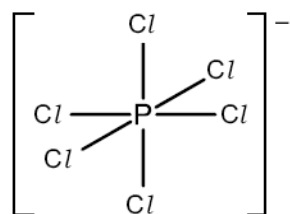
2. (a) $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$
units: mol dm⁻³

(b)

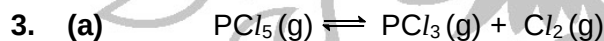


Shape: tetrahedral

A clear diagram of the bonding in each ion was required and not the 'dot-and-cross' diagram.



Shape: octahedral



Initial amt/mol	1.00	0	0
Change in amt/mol	-x	+x	+x
Eqm amt/mol	1.00 - x	x	x

Amount of H⁺ from hydrolysis of PCl₃
= 5x mol (H₃PO₃ is dibasic)
Amount of H⁺ from hydrolysis of PCl₅
= 7(1 - x)
= 7 - 7x mol
(H₃PO₄ is also dibasic)

Total amount of H⁺ = 7 - 2x mol

(b) (i) Amount of H⁺ in 25.0 cm³
= 37.4/1000 x 4.00
= 0.1496 mol

Amount of H⁺ in 1 dm³
= 0.1496/0.025
= 5.984 mol
= 5.98 mol (3 s.f.)

(ii) 7 - 2x = 5.984 mol
Hence, amount of Cl₂
= Amount of PCl₃ = x = 0.508 mol

Amount of PCl₅ = 1 - x = 0.492 mol

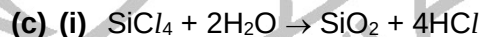
(c) $K_c = \frac{\left(\frac{0.508}{5}\right)^2}{\left(\frac{0.492}{5}\right)} = 0.105 \text{ mol dm}^{-3}$

4. (a) (i) Group 2 elements conduct electricity in the solid state. / They are ductile or malleable.

(ii) The melting point / boiling point of the element increases down Group 17. Down the group, the electron cloud size of the halogen molecules increases and becomes more polarisable. The strength of instantaneous dipole induced dipole interactions between the molecules increases and hence more energy is required to break the interactions in melting / boiling the elements.

(b) (i) Giant covalent or giant molecular or macromolecular structure

(ii) To melt the elements, strong covalent bonds between the atoms have to be broken. From C to Ge, the orbitals become bigger and more diffuse. The overlap of the orbitals becomes less effective. Bond strength decreases and hence less energy is required for melting.



(ii) C-Cl 340 kJ mol⁻¹
Si-Cl 359 kJ mol⁻¹

(iii) C does not have low-lying vacant orbitals to accommodate the lone pair from water during hydrolysis.

(d) (i)

Element	Cl	H	N	Pb
% mass	46.7	1.76	6.14	45.4
Amount in 100 g (% mass/ A_r)	1.315	1.76	0.4386	0.2191
Simplest ratio	6	8	2	1

The empirical formula is $\text{PbN}_2\text{H}_8\text{Cl}_6$.

(ii) Anion: $[\text{PbCl}_6]^{2-}$ Cation: NH_4^+

(iii) +4

(iv) octahedral

(e) $\text{Pb}^{4+} + 2\text{V}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + 2\text{VO}^{2+} + 4\text{H}^+$

$E^\ominus_{\text{cell}} = 1.69 - 0.34 = +1.35\text{V}$ (> 0 , reaction is thermodynamically feasible under standard conditions)

$\text{Pb}^{4+} + 2\text{VO}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + 2\text{VO}_2^+ + 4\text{H}^+$

$E^\ominus_{\text{cell}} = 1.69 - 1.00 = +0.69\text{V}$ (> 0 , reaction is thermodynamically feasible under standard conditions)

PbCl_4 will oxidise V^{3+} to VO_2^+ and then to VO_2^+ in an acidic medium.

5. (a)(i) C=C functional group is present since **K** undergoes electrophilic addition with aqueous bromine. Since the C:H ratio is 1:2, there is only one C=C double bond.

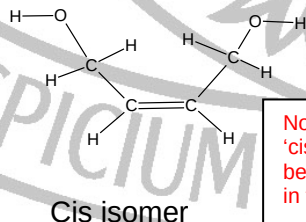
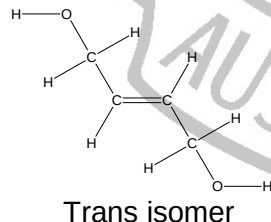
Note: "a double bond" is not acceptable as that could refer to a carbonyl group.

(ii) Alcohol functional group is present since **K** undergoes acid-metal / redox reaction with Na. As 1 mol of -OH group produces 0.5 mol of H_2 , and the mole ratio of K: H_2 is 1:1, there are two alcohol groups.

Note: "a hydroxyl group" is not acceptable when no distinction has been made between alcohols and carboxylic acids.

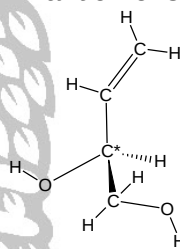
(b)

Cis-trans isomerism:

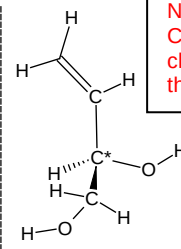


Note: The 'cis/trans' should be clearly labelled in the diagram.

Enantiomerism



Able to rotate plane polarised light



Note: The chiral C atom should be clearly labelled in the diagram.

Also able to rotate plane polarised light. Has similar chemical properties as its enantiomer, but behaves differently towards plane polarised light.

6.(a)(i) AgCl

(ii) Chloroalkane

(iii) Alcohol and phenol

(iv) The presence of the phenol functional group is confirmed. Phenols are soluble in NaOH but alcohols are not. Phenols are more acidic than alcohols because the lone pair on O delocalises into the benzene ring of phenoxide ions, dispersing the negative charge and stabilising the phenoxide. In contrast, the electron-donating R group of alkoxide intensifies the negative charge on O in the alkoxide ion and destabilises the ion.

(b) $\text{C}_7\text{H}_6\text{O}_3$. There is a side chain on the benzene ring which is oxidised to a carboxylic acid. The formula is for a hydroxybenzoic acid and fits the M_r data.

(c)(i) $\text{C}_7\text{H}_4\text{OC}/\text{Br}_3$. Since phenol is present, there can be up to 3 Br atoms incorporated.

$$\begin{aligned} \text{No. of Br atoms incorporated} &= \frac{379.2 - (7 \times 12.0 - 4 \times 1.0 - 16.0 - 35.5)}{79.9} = 3 \end{aligned}$$

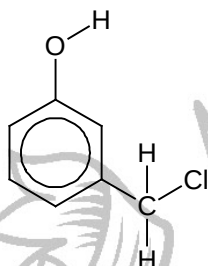
(ii) Electrophilic substitution

(iii) Compared to the original formula of **W**, it can be seen that 3 H atoms have been substituted by 3 Br atoms. Aromatic compounds undergo substitution. Aliphatic compounds with the same formula as **W** should undergo addition instead.

(iv) Phenol functional group.

(v) Reaction 3. The side chain on the benzene ring is oxidised.

(d)(i)



(ii) As phenol is 2- and 4- directing, and trisubstitution took place, the side chain is not on the 2-, 4- or 6- position. Reaction 1 shows that the chlorine atom is on the aliphatic side chain and not bonded to the ring.

(ii) Amount of $\text{S}_2\text{O}_3^{2-}$ used

$$= 6 / 1000 \times 0.005 = 3.0 \times 10^{-5} \text{ mol}$$

Amount of I_2

$$= \frac{1}{2} \times 3.0 \times 10^{-5} = 1.5 \times 10^{-5} \text{ mol}$$

Amount of N-chlorosuccinimide

$$= \text{Amount of HClO} = 1.5 \times 10^{-5} \text{ mol}$$

Mass of N-chlorosuccinimide

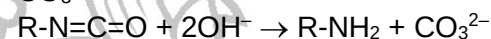
$$= 1.5 \times 10^{-5} \times 133.5 = 2.00 \times 10^{-3} \text{ g}$$

(d) (i) $\text{R-CONH}_2 + \text{Br}_2 \rightarrow \text{R-CONHBr} + \text{HBr}$

(ii) +1

(iii) 6 electrons

(iv) CO_3^{2-}



(e) Step V: Br_2 , anhydrous FeBr_3 , dark

Step VI: $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat

Step VII: SOCl_2

Step VIII: $\text{NH}_3(\text{g})$, room temperature

C: 4-bromobenzoic acid



D: 4-bromobenzamide

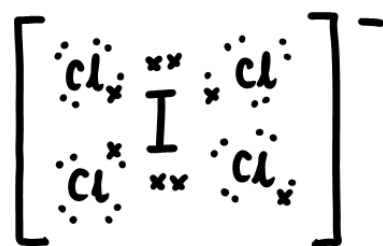
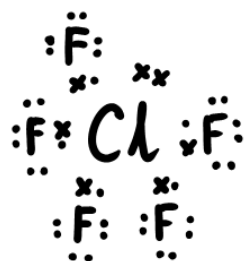


Suggested Solns for N2011 H2 Chemistry Paper 3

(9647/03)

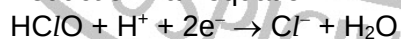
1 (a) oxidation number of iodine = +3

(b)

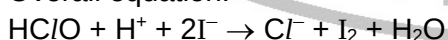


	ClF_3	ICl_4^-
Regions of electron density	6	6
Electron pair geometry	octahedral	octahedral
No. of lone pair of electrons	1	2
No. of bond pair of electrons	5	4
To minimise inter-electronic repulsion, the molecular geometry is	square pyramidal	square planar

(c) (i) Reduction half-equation:



Overall equation:



2(a)(i) Mass of gaseous products

$$= 1.00 - 0.438 = 0.562 \text{ g}$$

Using $pV = (\text{mass} / \text{molar mass})RT$

Average molar mass = $(\text{mass} \times RT) / (pV)$

$$= 0.562 \times 8.31 \times 298 / (10^5 \times 386 \times 10^{-6})$$

$$= 36.05 \text{ g mol}^{-1}$$

Average $M_r = 36.1$

(ii) CO_2

(iii) Volume of the other gas

$$= 386 - 193 = 193 \text{ cm}^3$$

Molar ratio of CO_2 : other gas = 1:1

M_r of the other gas

$$= (2 \times 36.05) - 44 = 28.1$$

The other gas is CO.

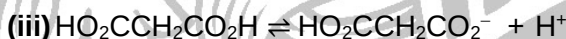
(iv) E is CaC_2O_4 .



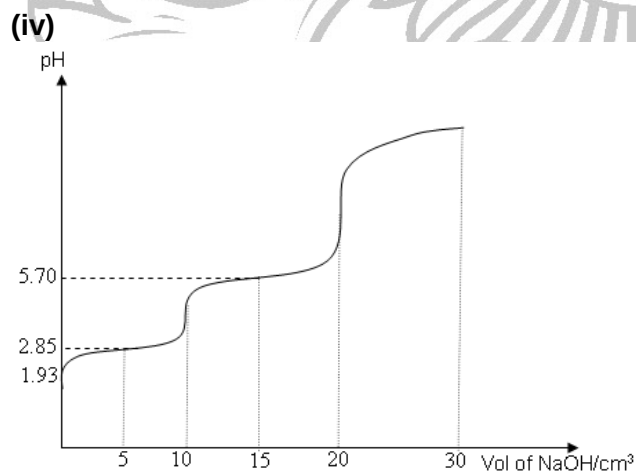
(b) (i) A stronger acid has a smaller pK value. As the additional $-\text{COOH}$ group in malonic acid is electron-withdrawing, it

stabilises the conjugate base formed by dispersing the negative charge of the carboxylate group. In addition, the conjugate base formed is further stabilised by the formation of an intramolecular hydrogen bond between the unionised $-\text{COOH}$ group and the $-\text{COO}^-$ group.

(ii) The $\text{p}K_2$ of malonic acid is higher because it is more difficult to remove an H^+ ion from an already negatively charged species than from a neutral ethanoic acid molecule. In addition, the intramolecular hydrogen bond that is formed in (b)(i) would be destroyed when the second $-\text{COOH}$ group ionises.



Initial conc.	0.10	0	0
Eqm conc.	$0.10 - x$	x	x
$K_a = x^2 / (0.10 - x) = 1.4125 \times 10^{-3}$			
$x = 1.1885 \times 10^{-2} \text{ mol dm}^{-3}$			
$\text{pH} = 1.93$			



At 0 cm^3 , initial $\text{pH} = 1.93$ (from (b)(ii))

At 5 cm^3 where $[\text{HO}_2\text{CCH}_2\text{CO}_2^-] = [\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}]$
 pH at 1st max buffer capacity = $\text{p}K_1 = 2.85$

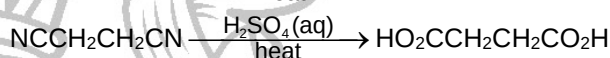
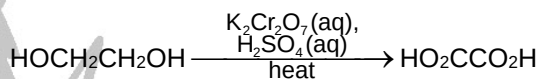
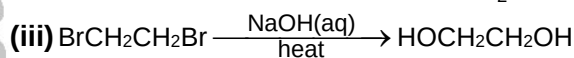
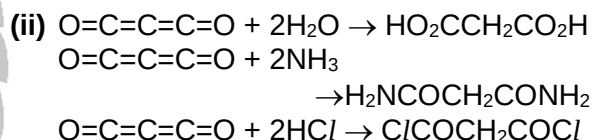
At 15 cm^3 where $[\text{HO}_2\text{CCH}_2\text{CO}_2^-] = [-\text{O}_2\text{CCH}_2\text{CO}_2^-]$
 pH at 2nd max buffer capacity = $\text{p}K_2 = 5.70$

At 30 cm^3 where $[\text{OH}^-] = [\text{unreacted NaOH}]$

$$[\text{OH}^-] = \frac{\frac{10}{1000} \times 0.10}{\frac{40}{1000}} = 0.025 \text{ mol dm}^{-3}$$

$$\text{pH} = 14 - \text{pOH} = 14 - (-\lg(0.025)) = 12.4$$

(c) (i) **F** is $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$ and is linear in shape.



3(a) (i)

ion	Concentration / g dm^{-3}	Concentration / mol dm^{-3}
Ca^{2+}	0.0080	1.99×10^{-4}
Mg^{2+}	0.0049	2.02×10^{-4}
Cl^-	0.0071	2.00×10^{-4}
HCO_3^-	0.0366	6.00×10^{-4}

$$[\text{Ca}^{2+}] = [\text{Mg}^{2+}]$$

Thus, the concentration of calcium salts will be equal to the concentration of the magnesium salts
 $[\text{Ca}(\text{HCO}_3)_2] = [\text{Mg}(\text{HCO}_3)_2]$ AND
 $[\text{CaCl}_2] = [\text{MgCl}_2]$

$$\text{However, } [\text{HCO}_3^-] = 3x[\text{Cl}^-]$$

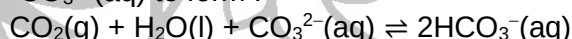
$$\text{Thus, } [\text{Mg}(\text{HCO}_3)_2] = 3[\text{MgCl}_2]$$

$$\text{And } [\text{Ca}(\text{HCO}_3)_2] = 3[\text{CaCl}_2]$$

Hence:

$$\text{CaCl}_2 : \text{MgCl}_2 : \text{Ca}(\text{HCO}_3)_2 : \text{Mg}(\text{HCO}_3)_2 = 1 : 1 : 3 : 3$$

(ii) The first solid to form is CaCO_3 . During evaporation, $\text{CO}_2(\text{g})$ is driven away from the solution. According to Le Chatelier's Principle, the position of the following equilibrium shifts left, causing more $\text{CO}_3^{2-}(\text{aq})$ to form :



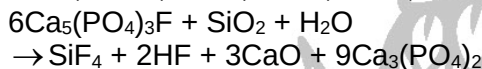
Since CaCO_3 is less soluble than MgCO_3 , the K_{sp} value of CaCO_3 is smaller. Thus, when $[\text{Ca}^{2+}] = [\text{Mg}^{2+}]$, the ionic product of CaCO_3 will surpass its K_{sp} value first. Hence, CaCO_3 will precipitate out first.

(iii) The rock probably contains a mixture of CaCO_3 , CaCl_2 , MgCO_3 and MgCl_2 .

(note: 3rd bullet pt mentions that the Group 2 hydrogen carbonates do not exist I solid state, thus upon removal of water, the carbonate forms instead) Rainwater enriched with CO_2 gas, when percolating through the rock, would convert the CO_3^{2-}

to HCO_3^- according to the equilibrium in part (a)(ii). This would then cause the insoluble carbonates to be converted to soluble hydrogencarbonates. CaCl_2 and MgCl_2 are both soluble in water, so they dissolve in the rainwater.

(b) (i) **a = 1, b = 1, c = 1, d = 2, e = 3, f = 9** (b)



(ii) $K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$, units: $\text{mol}^5 \text{dm}^{-15}$

(iii) solubility of $\text{Ca}_3(\text{PO}_4)_2 = s$ (mol dm^{-3})



$$1 \times 10^{-26} = (3s)^3(2s)^2 = 108s^5$$

$$[\text{Ca}^{2+}] = 3s$$

$$= 3(1 \times 10^{-26} / 108)^{1/5}$$

$$= 7.42 \times 10^{-6} \text{ mol dm}^{-3}$$

(c) (i) Pass dry chlorine gas into an excess of heated dry red phosphorus. Distill and collect the liquid PCl_3 .

Pass excess dry chlorine gas into a sample of liquid PCl_3 and heat to obtain PCl_5 .

(ii) **G** is POCl_3 .

$$[M_r \text{ of } \text{POCl}_3 = 31.0 + 16.0 + 3(35.5)]$$

shape of POCl_3 : tetrahedral

(iii) **H** is SO_2 .



4(a) (i) **4a and b not in syllabus**

The secondary structure of proteins refers to the way in which segments of the polypeptide backbone orientate into a regular pattern through hydrogen bonding between the C=O and N-H groups of the peptide groups in the polypeptide backbone.

The tertiary structure of proteins refers to the three-dimensional arrangement of the protein due to the folding of the secondary structural elements (α -helix or β -pleated sheet) together with the spatial disposition of the side-chains. Folding is due to R group interactions, i.e. van der Waals' forces, hydrogen bonds, disulfide bonds and ionic interactions.

The quaternary structure refers to the spatial arrangement and association of polypeptide subunits, which consist of two or more interacting polypeptide chains with characteristic tertiary structures.

Out of syllabus

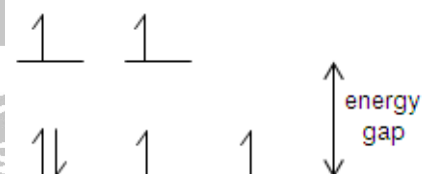
Since the reaction is spontaneous, ΔG must be negative.

As bonds are formed during the formation of secondary, tertiary and quaternary structures, heat is evolved and ΔH must be negative.

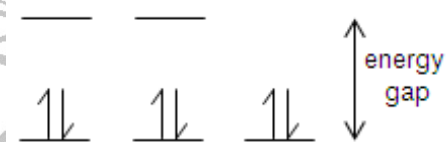
As the polypeptide chains coil or come together, the degree of disorder decreases. Thus, ΔS must be negative.

(c) (i) The ligands in haemoglobin causes the originally degenerate 3d orbitals in iron(II) to split into two sets of slightly different energy levels. As the 3d subshell of iron(II) is partially filled, electrons from the d-orbitals of lower energy can absorb energy from visible light and get promoted into the d-orbitals of higher energy. The observed colour (i.e. red) of haemoglobin is complementary to the colour of the light absorbed (i.e. green).

(ii)



'high spin' state



'low spin' state

(iii) When two electrons occupy an orbital, there is repulsion. To minimise inter-

electronic repulsion, electrons prefer to occupy orbitals singly.

(iv) Oxyhaemoglobin will contain the larger energy gap, E, between its d-orbitals. If the energy gap is larger, the energy required to overcome the energy gap is greater than the energy required to overcome inter-electronic repulsion (i.e. repulsion energy) between two electrons which are paired up in a d-orbital of lower energy. Hence, electrons will fill up the d-orbitals of lower energy before they occupy the d-orbitals of higher energy, i.e. the electronic configuration is in a 'low spin' state.

If the energy gap is smaller, the energy required to overcome the energy gap is less than the energy required to overcome the repulsion energy. Hence, electrons will occupy the d-orbitals singly before they pair up in the d-orbitals of lower energy, i.e. the electronic configuration is in a 'high spin' state.

4(d) (i) Heat the protein in HCl(aq) [or NaOH(aq)] for several hours.

(ii) met-asp-gly-ser-ala-gly-glu-ser-lys-tyr
 met-asp-gly-ser-ala-gly-glu-ser-lys-tyr
 met-asp-gly-ser-ala-gly-glu-ser-lys-tyr
 met-asp-gly-ser-ala-gly-glu-ser-lys-tyr
 met-asp-gly-ser-ala-gly-glu-ser-lys-tyr
 met-asp-gly-ser-ala-gly-glu-ser-lys-tyr
 met-asp-gly-ser-ala-gly-glu-ser-lys-tyr

met-asp-gly-ser-ala-gly-glu-ser-lys-tyr

5(a) $\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^-$

The relative acidity of a compound depends on the relative stability of its conjugate base (i.e. the anion). The more stable the conjugate base, the more acidic the compound is.

Water is neutral as $[\text{H}^+] = [\text{OH}^-]$.

As the p-orbital of the oxygen overlaps with the π orbitals of the benzene ring, the negative charge on the oxygen of the phenoxide ion is delocalised over the benzene ring. Since the phenoxide ion is resonance stabilised and is more stable than the hydroxide ion, phenol is more acidic than water.

reagent: $\text{HNO}_3(\text{aq})$
condition: room temperature

(c)

As the nitro group is electron withdrawing, the negative charge on the oxygen of the 4-nitrophenoxide ion will be dispersed to a greater extent than the negative charge on the oxygen of the phenoxide ion. Thus, the 4-nitrophenoxide ion is more stable than the phenoxide ion.

(d) (i)

step I: Sn, concentrated HCl, heat
Step II: NaOH(aq) **or** Na(s), room temperature
step IV: CH₃COCl **or** (CH₃CO)₂O, room temperature

(ii) met-asp-gly-ser-ala-gly-glu-ser-lys-tyr

(ii) **step I:** reduction **or** redox reaction
step II: acid-base reaction (if NaOH used) **or** redox reaction (if Na used)
step III: nucleophilic substitution
step IV: nucleophilic acyl substitution **or** acylation **or** condensation

(iii) The phenoxide ion in **K** is a stronger nucleophile than the phenol in **J**.

(e)

 $\text{Cl}_2(\text{aq})$

(f) (i)

Out of syllabus

$$3\text{Cl}_2(\text{aq}) + 6\text{NaOH}(\text{aq}) \rightarrow 5\text{NaCl}(\text{aq}) + \text{NaClO}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$

(ii) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^{-}$

$$\begin{aligned}\text{amt of Fe}^{2+} &= 11.3 \times 10^{-3} \times 0.500 \\ &= 0.00565 \text{ mol} \\ &\equiv \text{amt of e}^{-}\end{aligned}$$
$$\begin{aligned} \text{ClO}_x^- + 2x \text{H}^+ + 2x \text{e}^- &\rightarrow \text{Cl}^- + x \text{H}_2\text{O} \\ \text{amt of e}^- \text{ taken in by } \text{ClO}_x^- \\ &= (2x)[0.150 / (39.1 + 35.5 + 16.0x)] \\ &= 0.00565 \text{ mol} \\ \text{Hence, } x &= 2. \\ 4\text{Fe}^{2+} + \text{KClO}_2 + 4\text{H}^+ \\ &\rightarrow 4\text{Fe}^{3+} + \text{KCl} + 2\text{H}_2\text{O} \end{aligned}$$