	NATIONAL JUNIOR COLLEGE SH2 PRELIMINARY EXAMINATION Higher 2	
CANDIDATE NAME		
SUBJECT CLASS	REGISTRATION NUMBER	
CHEMISTRY		9647/01

Paper 1 Multiple Choice Additional Materials:

Multiple Choice Answer Sheet Data Booklet

9647/01 Thu 17 Sep 2015 1 hour

READ THESE INSTRUCTIONS FIRST

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Write in soft pencil.

Write your name, subject class and registration number on the Optical Answer Sheet (OAS) in the spaces provided unless this has been done for you.

There are **40** questions in this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Optical

Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

This booklet consists of **19** printed pages and **1** blank page.

Section A

For each question there are four possible answers, A, B, C, and D. Choose the one you consider to be correct.

1 When scientists research on atomic nuclei, they often correlate the stability of isotopes with the proton to neutron ratio.

Which isotope has the same proton to neutron ratio as ${}^{18}_{8}$ O?

$$A = \frac{9}{5}B \qquad B = \frac{26}{12}Mg \qquad C = \frac{36}{16}S \qquad D = \frac{52}{24}Cr$$
Given: $\frac{p}{n}$ ratio of $\frac{18}{8}O = \frac{8}{18-8} = \frac{4}{5}$
 $\frac{p}{n}$ ratio of $\frac{9}{5}B = \frac{5}{4} \neq \frac{4}{5}$; $\frac{p}{n}$ ratio of $\frac{26}{12}Mg = \frac{12}{14} = \frac{6}{7} \neq \frac{4}{5}$; $\frac{p}{n}$ ratio of $\frac{52}{24}Cr = \frac{24}{28} = \frac{6}{7} \neq \frac{4}{5}$
 $\frac{p}{n}$ ratio of $\frac{36}{16}S = \frac{16}{20} = \frac{4}{5} \Rightarrow$ ans is C

A_xO_y, a gaseous oxide of an element A, gives an acidic gas AO₂ on combustion with 2 excess oxygen.

When 10 cm³ of A_xO_y is burnt in 40 cm³ oxygen (in excess), the total volume of gas after cooling to the original temperature is unchanged. On shaking with excess aqueous potassium hydroxide, the volume is reduced to 20 cm³. All volumes are measured at the same temperature and pressure.

What are the values of **x** and **y**?



After burning, total volume = 50 cm³ = vol of unreacted O_2 + vol of AO_2 Since O₂ does not react with KOH(aq), AO₂ is the acidic gas that reacts with KOH(aq) Vol. of unreacted $O_2 = 20 \text{ cm}^3$ Vol. of $AO_2 = 30 \text{ cm}^3$

A_xO_y	+ $(X - \frac{1}{2})$	$y)O_2 \rightarrow$	x A O ₂
10	40		0
0	20		30
10	20		30
1	2		3
= 2	½ v = 1	v = 2	
	A _x O _y 10 0 10 1 = 2	$A_{x}O_{y} + (x - \frac{1}{2})$ 10 40 0 20 10 20 1 2 = 2 ¹ / ₂ y = 1	$A_{x}O_{y} + (x - \frac{1}{2}y)O_{2} \rightarrow$ 10 40 0 20 10 20 1 2 = 2 ¹ / ₂ y = 1 y = 2

3 The diagram below shows the first ionisation energy of some elements with atomic numbers less than 20.



Based on the trend of the 1st IE of elements given; L must be N (in Group V, Period 2) and M must be P (in Group V, Period 3).

Both N and P form trichlorides. P can form pentachloride but not N as the latter cannot expand its octet configuration when forming compounds. Thus, answer is D.

4 The figure below shows the stable oxidation numbers of five consecutive elements, P to T, plotted against their atomic numbers.



Α

Consider atomic no given in option A:

Atomic no	1	2	3	4	5
element	Н	He	Li	Be	В
Known stable O.N. of atom in	+1 or –1	does not form compound	+1	+2	+3
compounds					

Thus option **A** is **not** the answer.

Consider atomic no given in option B:

U					
Atomic no	3	4	5	6	7
element	Li	Be	В	С	Ν
Known stable O.N. of atom in	+1	+2	+3	from -4 to +4	from -3 to +5
compounds					

Thus option **B** is **not** the answer.

Consider atomic no given in option C:

Atomic no	11	12	13	14	15
element	Na	Mg	Al	Si	Р
Known stable O.N. of atom in	+1	+2	+3	+4	+3, +5
compounds					
		•	•		•

Thus option **C** is **not** the answer.

Consider atomic no given in option **D**:

Atomic no	19	20	21	22	23
element	K	Ca	Sc	Ti	V
Known stable O.N. of atom in	+1	+2	+3	+2, +3, +4	+2, +3, +4, +5
compounds					

Thus option **D** is the answer.

5 When a sample of gas is compressed at constant temperature from 20 atm to 80 atm, its volume changes from 67.0 cm³ to 15.5 cm³.

Which is a possible explanation of this behaviour?

- A The gas particles are adsorbed onto the vessel walls.
- **B** The gas particles dimerised.
- **C** The gas particles dissociated.
- **D** The gas is liquefied at 80 atm.

For the same amount of an ideal gas at constant T, $P_2V_2 = P_1V_1 = nRT$ From given info, $P_2V_2 = 80 \times 15.5 = 1240$; $P_1V_1 = 20 \times 67.0 = 1340$ $P_2V_2 < P_1V_1 \implies gas is non-ideal$

For A: If the gas is adsorbed onto the vessel walls, $\eta_2 < \eta_1$ as the amount of free moving gas particles decreases $\Rightarrow P_2V_2 < P_1V_1$; thus option A is the ans

For **B**: If the gas dimerised completely, $\eta_2 = \frac{1}{2}\eta_1 \Rightarrow P_2V_2 = \frac{1}{2}P_1V_1$; thus option **B** is not the ans

For **C**: If the gas dissociates, $\eta_2 > \eta_1 \Rightarrow P_2V_2 > P_1V_1$; thus option **C** is the not ans

For D: If the gas is liquefied, P_2 will be very low $\Rightarrow P_2V_2 \iff P_1V_1$; thus option D is not the ans

6 The shapes of two species, D and E, are linear and T-shaped respectively.What could D and E be?



Based on VSEPR theory,

SO ₂ is bent in shape (2 bp's + 1 lp around S)	BH ₃ is trigonal planar (only 3 bp's around B)
I ₃ ⁻ is linear (2 lp's and 3 bp's around I) :I-II (lp e's occupy equatorial positions so as to minimise their mutual repulsion due to lp-lp > lp - bp > bp - bp);	BrCl ₃ is T-shaped (3 bp's + 2 lp's around Br) \vdots \vdots \vdots \vdots \vdots (lp e's occupy equatorial positions so as to minimise their mutual repulsion due to lp- lp > lp - bp > bp - bp)
CS_2 is linear (only 2 bp's around C) s=c=s	AsCl ₃ is trigonal pyramidal (3 bp's + 1 lp around As) :ü:As:ü:
H ₂ S is bent (2 bp's + 2 lp's around S) H H H	IC l_3 is T-shaped (3 bp's + 2 lp's around I) Cl Cl Cl Cl Cl Cl Cl Cl Cl Cl

7 Some enthalpy changes of combustion are given below.

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$
 -283

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$
 -286

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
 -715

What is the enthalpy change of the following reaction?

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

 $\Lambda H_{\rm c}$ / kJ mol⁻¹



By Hess' law: $\Delta H_r = -283 + 2(-286) - (-715) = -140$ kJ mol⁻¹ (**B**)

8 When a large current was passed through acidified aqueous nickel(II) sulfate, there was a simultaneous liberation, at the cathode, of x mol of a grey solid and y dm³ of a diatomic gas (measured at s.t.p.).

How many moles of electrons passed through the cell?

A
$$x + \frac{y}{22.4}$$
 B $x + \frac{y}{11.2}$ **C** $2x + \frac{y}{22.4}$ **D** $2x + \frac{y}{11.2}$

Eqn for reactions at cathode: [R] $Ni^{2+} + 2e^- \rightarrow Ni$ and [R] $2H^+ + 2e^- \rightarrow H_2$ Total no of mol of e^- passed through solution = 2(no of mol of $Ni^{2+} + no$ of mol of H_2)

$$= 2x + 2(\frac{y}{22.4}) = 2x + \frac{y}{11.2}$$

(molar gas vol at stp = 22.4 dm^3) Thus ans is **D**. 9 The equation below shows the reaction of ethanoic acid with ethanol.

$$\mathsf{CH}_3\mathsf{CO}_2\mathsf{H}(l) + \mathsf{C}_2\mathsf{H}_5\mathsf{OH}(l) \qquad \rightleftharpoons \qquad \mathsf{CH}_3\mathsf{CO}_2\mathsf{C}_2\mathsf{H}_5(l) + \mathsf{H}_2\mathsf{O}(l)$$

ethyl ethanoate

Which statement is true when the above reaction has attained equilibrium?

- **A** The equilibrium constant, K, is equal to 1.
- **B** The reaction between the acid and the alcohol has stopped.
- **C** The concentrations of the products and reactants are the same.
- **D** The rate of formation and the rate of hydrolysis of ethyl ethanoate are the same.

The value of equilibrium constant (ratio of concentrations of reactants and concentrations of products raised to appropriate power terms as the stoichiometric ratio) varies from a system to another and can't be predicted; thus **A** and **C** are NOT the answer.

An equilibrium system is a dynamic one in that reactants react continually to form products while the products continually decompose to reform the reactants at the same rate; thus **B** is wrong, but **D** is true.

10 A student wanted to determine the equilibrium constant for the decomposition of calcium carbonate, CaCO₃. He sealed 2.0 g of CaCO₃ in an evacuated 2.0 dm³ metal flask and connected a pressure gauge to the flask. The flask was placed in an oven and heated to a temperature of 800 °C, at which an equilibrium was reached according to the following equation:

$$CaCO_3(s) \implies CaO(s) + CO_2(g)$$

When the equilibrium was established, 1.40×10^{-2} mol of CO₂ was present in the flask.

What is the value of equilibrium constant, K_c, for this reaction at 800 °C?

A 3.27 x 10⁻² **B** 1.63 x 10⁻² **C** 1.40 x 10⁻² **D** 7.00 x 10⁻³

The equilibrium system involves 2 solids and a gas.

Thus $K_c = [CO_2(g)]$ (solids have fixed concentrations / densities) = 1.40 x 10⁻² /2 = **7.00 x 10⁻³ mol dm⁻³** 11 Water dissociates into ions according to the following equilibrium.

 $H_2O(l) = +57 \text{ kJ mol}^{-1} \text{ at } 25 \text{ °C}$

Which statement is not true as temperature rises?

- **A** The pH of water decreases.
- **B** The dissociation constant of water increases.
- **C** The extent of dissociation of water increases.
- **D** The concentration of $H^+(aq)$ is higher than that of $OH^-(aq)$.

As forward reaction is endothermic, increasing T favours forward reaction, i.e. water would dissociate to a greater extent

Thus [H⁺] increases and pH decreases. Thus options **A**, **B** and **C** are true.

From the equilibrium given, $[H^+] = [OH^-]$ is always true as each water molecule dissociates to form 1 H⁺ and 1 OH⁻ ions. Thus option **D** is false.

12 The distribution of the number of molecules with energy *E* is given in the sketch below for two temperatures, T_1 , and a higher temperature T_2 . The letters *P*, *Q*, *R* refer to the separate and differently shaded areas. The activation energy is marked on the energy axis.



Which is the fraction of the molecules with energy larger than the activation energy at T_2 ?



Total area under curve = no of molecules in the sample = P + Q

no of molecules with $E \ge E_a$ at $T_2 = Q + R$ \therefore fraction of molecules with $E \ge E_a$ at $T_2 = \frac{Q + R}{P + Q}$ (option **C**) **13** A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third periods of the Periodic Table. One such pair is beryllium and aluminium, where they share similar chemical properties.

Which is **not** a property of the compounds of beryllium?

- A Beryllium chloride has a high melting point.
- **B** Beryllium chloride can form the dimer Be_2Cl_4 .
- **C** Effervescence is observed when aqueous sodium carbonate is added to beryllium chloride.
- **D** Beryllium oxide reacts with carbon dioxide to form a salt.

Aluminium chloride forms dimers of Al_2Cl_6 and is an essentially simple covalent compound with weak intermolecular van der Waals' interactions. Thus option **A** is **not** a likely property while option **B** is a likely property of beryllium chloride.

Just like Al^{3+} , Be^{2+} has a high charge-density (or $\frac{charge}{size}$ ratio) and would undergo extensive hydrolysis in water to give an acidic solution which readily reacts with sodium carbonate. Thus option **C** is a likely property.

Due to high charge-density of Be^{2+} , BeO is likely to be amphoteric (has both ionic and covalent characters) and would behave as a base to react to acidic carbon dioxide to form a salt. Thus option **D** is true.

14 The graphs below show the variation of two properties of some Period 3 elements and their compounds.



Which of the following correctly describes properties A and B?

	Property A	Property B
Α	enthalpy change of vapourisation of the elements	pH of the oxides when added to water
	Vaporisation refers to changing from liquid state to gaseous state. From Na to A <i>l</i> , enthalpy change should increase as the metallic bond strength increases due to increasing no. of valence electrons. Strong covalent bonds are broken in Si, so enthalpy change should be very high. So, this option is wrong.	Na ₂ O and MgO forms metal hydroxides which are completely and partially soluble in water respectively to give OH ⁻ , so their pH should be 13-14 and 8-9 respectively. So, this option is wrong. Both Al ₂ O ₃ and SiO ₂ are insoluble in water, so the pH should be 7. So, this option is wrong.
В	first ionisation energy of the elements First I.E. should increase from Na to Mg, followed by a small decrease from Mg to A <i>l</i> (anomaly), then increase from A <i>l</i> to P. So, this option is wrong.	enthalpy change of vapourisation of the elements
C	enthalpy change of vapourisation of the chlorides NaCl and MgCl ₂ have giant ionic lattices held by strong ionic bonds. By $ L.E. \propto \frac{q^+q^-}{r^++r^-}$, q^+ increases and r^+ decreases, hence magnitude of lattice energy increases and the ionic bond is stronger in MgCl ₂ than in NaCl. ΔH_{vap} should increase. AlCl ₃ , SiCl ₄ and PCl ₃ (or PCl ₅) have simple covalent molecular structures with weak intermolecular forces. In liquid state, AlCl ₃ exists as Al ₂ Cl ₆ dimer. Al ₂ Cl ₆ , SiCl ₄ and PCl ₅ are non- polar. No. of electrons: 128, 82, 100. The larger the electron cloud, the stronger the td-id, the larger the ΔH_{vap} . Hence, the graph shows the correct trend in ΔH_{vap} .	electrical conductivity of the elements Electrical conductivity increases from Na to AI as the no. of valence electrons which acts as mobile charge carriers increases. Si is a metalloid which behaves as a semi-conductor. P does not conduct electricity due to the absence of delocalised electrons. Hence this option is correct.
D	electrical conductivity of the elements	pH of the chlorides when added to water pH decreases from 7 (NaC <i>l</i> no hydrolysis) to 6.5 (MgC <i>l</i> ₂ , Mg ²⁺ undergoes slight hydrolysis) to 3 (A <i>l</i> ³⁺ has higher charge/size ratio and undergoes greater extent of hydrolysis) to 2 (chlorides of Si and P gives strong acid HC <i>l</i>). So this option is wrong.
elimina	ary Examination 9647/01	/15 [Turn Over

- **15** Which statement about the compounds of Group VII elements is **incorrect**?
 - **A** The oxidising power of halogens decreases down the group.

Correct statement. E_{red}^{e} (+1.36 V, +1.07 V, 0.54 V) decreases down the group, showing that the halogens have a decreasing tendency to be reduced and their oxidising power decreases.

B The K_{sp} value of silver halides decreases down the group.

Correct statement. For AgI, the value of K_{sp} is extremely low, thus the ionic product is greater than K_{sp} regardless of the concentration of NH₃. Hence the precipitate remains insoluble when dilute or concentrated NH₃ is added.

C The magnitude of the lattice energy of silver halides increases down the group.

This statement is incorrect and this is the answer. By $|L.E.| \propto \frac{q^+q^-}{r^++r^-}$, down the group, r⁻ increases whereas the other terms are constant. Magnitude of lattice energy should decrease.

D The magnitude of the hydration energy of gaseous halide ions decreases down the group.

Correct statement. Magnitude of hydration energy $\propto \frac{\text{charge}}{\text{size}}$, hence as r⁻ increases, magnitude of hydration energy decreases.

16 X is a transition metal. In a concentrated aqueous solution of Cl^- , it forms a coloured complex ion, $[\mathbf{X}Cl_4]^{2^-}$. When $[\mathbf{X}Cl_4]^{2^-}$ is reduced to $[\mathbf{X}Cl_2]^-$, the solution turns colourless.

What is the ground state electronic configuration of X?

Α	[Ar] 3d ⁵ 4s ¹	B	[Ar] 3d ¹⁰ 4s ¹
С	$[Ar] 3d^5 4s^2$	D	[Ar] 3d ⁹ 4s ²

Solution turns colourless \Rightarrow no d-d transition took place, electronic configuration of d subshell is either d⁰ or d¹⁰.

In $[\mathbf{X}Cl_4]^{2^-}$, oxidation number of X is +2. In $[\mathbf{X}Cl_2]^-$, oxidation number of X is +1. Since X⁺ is $[Ar]3d^{10}$ (cannot be $3d_0$ because if X⁺ is [Ar], then X is $[Ar]3d^1$, Sc, which is not a transition metal), X is $[Ar]3d^{10}4s^1$. Answer is **B**.

17 Which statement about the following reaction is true?

 $[Fe(CN)_6]^{3-} + 3C_2O_4^{2-} \implies [Fe(C_2O_4)_3]^{3-} + 6CN^- \qquad K_c = 3 \times 10^{-21} \text{ mol}^3 \text{ dm}^{-9}$

A It is a redox reaction.

False. Oxidation number of Fe remains constant at +3.

B $[Fe(CN)_6]^{3-}$ is less stable than $[Fe(C_2O_4)_3]^{3-}$.

False, from the extremely small value of K_c given, equilibrium position lies mainly on the left, showing that $Fe(CN)_6]^{3-}$ is more stable than $[Fe(C_2O_4)_3]^{3-}$.

C The reaction is more feasible at high temperatures.

Since $Fe(CN)_6]^{3-}$ is more stable than $[Fe(C_2O_4)_3]^{3-}$, ΔH is positive. ΔS is positive as the amount of molecules in the aqueous state increases from 4 to 7.

For reaction to be feasible, $\Delta H - T\Delta S < 0$

 $\Delta H < T\Delta S$

Only at high T, T Δ S is more than Δ H, reaction is feasible. Hence, this statement is true.

D The coordination numbers of $[Fe(CN)_6]^{3-}$ and $[Fe(C_2O_4)_3]^{3-}$ are 6 and 3 respectively.

False, 1 $C_2O_4^{2-}$ can form two dative bonds with the central metal ion, hence the no. of dative bonds in each complex is the same and the co-ordination numbers are both 6.

18 Some vegetable oils contain 'trans fats' that are associated with undesirable increases in the amount of cholesterol in the blood.

In the structures below, R₁ and R₂ are different hydrocarbon chains.

Which structure correctly illustrates an optically active 'trans fat'?





cis with one chiral carbon

19 3-Methylhex-2-enoic acid is an unpleasant smelling chemical.

$$CH_3$$

 $|$
 $CH_3CH_2CH_2C = CHCO_2H$

3-methylhex-2-enoic acid

When the compound is treated with cold dilute acidified potassium manganate(VII), how many stereoisomers does the product have?



Temperature determines whether vigorous or mild oxidation of alkenes will occur.

Cold dilute acidified $KMnO_4 \Rightarrow mild$ oxidation of alkene to form diol

Product:

Total number of stereoisomers = 2^{n} (where n is the total no. of C=C exhibiting cis-trans and no. of chiral carbons)

 $2^2 = 4$ (answer is **C**)

20 A reaction profile diagram is shown below.



reaction pathway

Reaction profile shows a two-step reaction. The E_a of the first step is greater, therefore, the slow step is the first step.

Which reaction does not have such a profile?

Α

D

$$CH_3CHO + HCN \xrightarrow{NaCN} CH_3CH(OH)CN$$

Reaction is nucleophilic addition. Two-step reaction with the first step being the rate-determining step.

 $C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$

B Reaction is nucleophilic substitution. C_2H_5Br is a primary halogenalkane, hence it undergoes S_N2 which only has one step. So, this option does **not** have such a profile.

 $(CH_3)_3CBr + NaOH \rightarrow (CH_3)_3COH + NaBr$

C Reaction is nucleophilic substitution. $(CH_3)_3CBr$ is a tertiary halogenalkane, hence it undergoes S_N1 which has two steps with the first step being the rate-determining step.



Reaction is electrophilic addition. Two-step reaction with the first step being the ratedetermining step. 21 A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.



A electrophilic addition **B** nucleophilic addition

С	nucleophilic substitution	D	condensation
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Answer is **D**. Stages 1 and 3 are oxidation whereas stage 2 is nucleophilic addition with CH_3CH_2OH acting as the nucleophile. Stage 2 is not condensation as there is no loss of any molecules.

22 Considering all the structural isomers of alcohols with the molecular formula $C_4H_{10}O$, what is the number of alcohols that will react with each of the following chemicals?

	hot acidified KMnO ₄	alkaline aqueous iodine	Na metal
Α	2	1	3
В	2	2	4
C	3	1	<mark>4</mark>
D	3	2	5

	hot acidified KMnO ₄	alkaline aqueous iodine	Na metal		
	(tertiary alcohols cannot be oxidized)		(all alcohols react with Na)		
Alcohols which will react	ОН ОН	OH	OH OH OH OH		

Answer is **C**.

23 Which reagent reacts with the following organic compound to give **only** one organic product?



Α hot NaOH(aq) В hot acidified potassium dichromate(VI) hydrolyse the ester to give Acid is present. It hydrolyses the ester to give two organic products. The primary two organic products. alcohol fragment undergoes further oxidation to give carboxylic acid C bromine in hexane D NaBH₄ in methanol add Br across C=C No reaction; no product formed. (electrophilic addition) to give only one organic product

Correct.

24 Pentaerythritol is used as an intermediate in the manufacture of paint.



pentaerythritol

Which statement about pentaerythritol is correct?

A It can react with HBr(aq).

False. Alcohol undergoes substitution with HBr(g), not HBr(aq).

B Its empirical and molecular formulae are different.

False. Same empirical and molecular formulae of $C_5H_{12}O_4$.

C It can undergo elimination with hot concentrated sulfuric acid to form an alkene.

False, to undergo elimination, the H and OH must be on adjacent carbons. In pentaerythritol, there is no H on the adjacent carbon of the C-OH.

D One mole of pentaerythritol gives two moles of hydrogen gas on reaction with excess sodium.

True. 4ROH + 4Na \rightarrow 4RONa + 2H₂.

25 When heated with aqueous sodium hydroxide, the rate of hydrolysis of (CH₃)₃CC*l* varies when it is dissolved in different solvents. The reaction follows the mechanism shown below.



The reaction proceeds faster when the carbocation is more stabilised.

Which series of solvents would result in an increasing rate of hydrolysis?

A $CH_3(CH_2)_4CH_3$, CH_3CH_2OH , $(CH_3)_2CO$, H_2O

- $\mathbf{B} \qquad \mathbf{CH}_3(\mathbf{CH}_2)_4\mathbf{CH}_3, (\mathbf{CH}_3)_2\mathbf{CO}, \mathbf{CH}_3\mathbf{CH}_2\mathbf{OH}, \mathbf{H}_2\mathbf{O}$
- $\textbf{C} \qquad H_2O, CH_3CH_2OH, (CH_3)_2CO, CH_3(CH_2)_4CH_3$
- **D** CH₃CH₂OH, H₂O, (CH₃)₂CO, CH₃(CH₂)₄CH₃

The carbocation can be stabilised by the formation of ion-dipole interactions. The more polar the solvent, the more stabilised the carbocation and the faster the reaction. $CH_3(CH_2)_4CH_3$ is non-polar. C=O bond is less polar than O–H bond. H₂O is a more polar solvent than CH_3CH_2OH as H₂O has two very polar O–H bonds. In increasing order of polarity: $CH_3(CH_2)_4CH_3$, $(CH_3)_2CO$, CH_3CH_2OH , H₂O Answer is **B**.

26 Which reagent can be used to distinguish between Y and Z shown below?



This is used to test for halogenoalkanes. C-Cl bond in **Y** has partial double bond character, hence there is no reaction with this reagent.

Reacts with both alcohols and carboxylic acids but not phenols. Hence there is no reaction with **Y** and **Z**.

- С Na₂CO₃(aq) D hot acidified KMnO₄(aq) Gives effervescence of CO₂ Oxidises ethyl side-chain of Z and give off effervescence of CO₂. Does when it reacts with carboxylic acids. Phenol in Z is only not oxidise side-chain in Y as there is weakly acidic and it does not no H on the first carbon attached to react with Na₂CO₃(aq). Hence benzene ring. This option is correct. there is no reaction with Y and Z.
- 27 Metoclopramide is a drug used to treat heartburn caused by gastroesophageal reflux disease (GERD).



metoclopramide

Which statement about metoclopramide is true?

A 1 mole of metoclopramide would react with 3 moles of CH₃COC*l*.

False. Primary and secondary amines and phenylamine would react with CH_3COCl to form amide. Tertiary amine would not react as there is no more H on N to be lost. Amide group would not react with CH_3COCl

B It would decolourise aqueous bromine to form a white precipitate.

True. Metoclopramide contains a phenylamine group and it is able to react with $Br_2(aq)$ to give white precipitate.

C It would dissolve in NaOH(aq) at room temperature.

False, there is no acidic carboxyl or phenol group. The bulky benzene ring also makes the molecule very non-polar and insoluble in aqueous medium.

D It is insoluble in dilute HC*l*.

False, there phenyl amine and tertiary amine can react with HC*l*. When NH_2 is ionized to NH_3^+ , favourable ion-dipole interactions can be formed and the compound dissolves in water.

18

28 Deuterium $\binom{2}{1}D$ is an isotope of hydrogen $\binom{1}{1}H$.

Which reaction would produce an organic product containing deuterium?

19



29 0.10 mol each of the solids CH₃CH₂ONa, CH₃COONa and C₆H₅ONa are dissolved in three separate beakers each containing 1 dm³ of water.

What is the expected trend for the pH of their resultant solutions?

	lowest pH		highest pH
Α	CH ₃ CH ₂ ONa	CH₃COONa	C_6H_5ONa
в	CH ₃ CH ₂ ONa	C_6H_5ONa	CH₃COONa
C	CH₃COONa	<mark>C₀H₅ONa</mark>	CH₃CH₂ONa
D	CH₃COONa	CH ₃ CH ₂ ONa	C ₆ H₅ONa

Ans: C

The following anions are obtained when dissolved in water:

 $CH_3CH_2O^-$, CH_3COO^- and $C_6H_5O^-$

The conjugate bases undergoes salt hydrolysis to give OH^- . Since equimolar salts are dissolved in the same volume of water, then the [OH^-] is directly proportional to the strength of the base.

The strength of the base is determined by the availability of lone pair electron on O⁻ to accept H⁺

In general $A^- + H_2O \implies HA + OH^-$

The more available the lone pair electron on O⁻ is to accept H⁺

 \Rightarrow the stronger the base, hence the higher the pH.

Stability of conjugate base					
CH₃COO [−]	C ₆ H ₅ O [−]	CH ₃ CH ₂ O [−]			
The negative charge is the most dispersed as the negative charge is delocalised O overCO where there are two electron withdrawing O atoms.	This is actually the phenoxide O- ion, . The negative charge is able to delocalise into the pi-electron cloud of the benzene ring.	The negative charge is in fact intensified by the electron donating –CH ₃ group.			

Hence the pH of the salts when dissolved in water also follows a similar trend.

- **30** Polypeptides can be enzymatically hydrolysed to form shorter peptide chains. When a nonapeptide was hydrolysed by enzymes, the following tripeptides were obtained.
 - gly-ala-leu tyr-ser-leu
 - leu-gly-tyr
 - lys-gly-ala
 - ser-leu-gly

What is the sequence of this nonapeptide?

- A gly-ala-leu-gly-ser-tyr-leu-gly-tyr
- B gly-ala-leu-gly-tyr-ser-leu-gly-tyr
- C lys-gly-ala-tyr-ser-leu-gly-tyr-ser
- D lys-gly-ala-leu-gly-tyr-ser-leu-gly

Ans: D

This concept involves primary structure of proteins having a <u>specific sequence</u> of amino acid residues. Sequence of amino acid is read from left to right.

The starting portion of the nonapeptide is derived by looking for the hydrolysed peptide chain containing only one of the amino acid residue (not repeated in any hydrolysed peptide chain).

Clearly, lys only appears once. So start with lys-gly-ala.

Then attach the subsequent hydrolysed peptides by choosing those with the same sequence of letters.

i.e. lys - gly - ala

Thus the sequence of this nonapeptide is:

lys-gly-ala-leu-gly-tyr-ser-leu-gly

31 Alpha particles, ⁴₂ He²⁺, are commonly emitted by larger radioactive nuclei during radioactive decay. The diagram below shows the path of a mixture of a charged species X, ⁷₃ Li⁺ and alpha particles after passing through an electric field.



Which statements are true?

- **1 X** could be electron.
- 2 Plate Y is positive.
- 3 angle of deflection of alpha particles = $\frac{7}{4}$ x angle of deflection of Li⁺

Ans: B

Concepts applied:

- Opposite charges attract, so polarity of plate is determined by which charged species it attracts.
- Size of the angle of deflection, θ , is directly proportional to $\frac{q}{m}$

Where q = magnitude of the charge; m = mass of the species

Since the positively charged alpha and ${}^{7}_{3}\text{Li}^{+}$ are both deflected to plate Z, then Z must be negative.

Thus plate Y must be positive, attracting negatively charged species.

So option 2 is correct.

NJC Preliminary Examination

Since the charge of the electron = -1 (gets attracted to plate Y) and its mass is about $\frac{1}{1840}$ mass of

a proton. Hence $\frac{\theta_X}{\theta_{alpha}} = \frac{\frac{1}{\frac{1}{1840}}}{\frac{2}{4}} \Rightarrow \theta_X$ is 920 times the angle of deflection of the alpha particle.

From the diagram, this seems possible.

Thus Option 1 is correct.

$$\frac{\theta_{alpha}}{\theta_{Li^{+}}} = \frac{\frac{2}{4}}{\frac{1}{7}} = \frac{7}{2} \Rightarrow \theta_{alpha} = \frac{7}{2} \times \theta_{Li^{+}}$$

Thus Option 3 is incorrect.

32 Long-chain alkanes are converted on an industrial scale into alkylsulfates for use as detergents. An example of an alkylsulfate is sodium lauryl sulfate.

$$CH_3(CH_2)_{10}CH_2O \overset{O}{\overset{\parallel}{\overset{\parallel}{\overset{\scriptstyle \parallel}{\overset{\scriptstyle \parallel}}{\overset{\scriptstyle \parallel}{\overset{\scriptstyle \parallel}{\overset{\scriptstyle \scriptstyle \parallel}{\overset{\scriptstyle \scriptstyle }}}}}}}}}}}} O$$

sodium lauryl sulfate

Which properties of sodium lauryl sulfate can be deduced from its structure?

- 1 It exists as a solid at room temperature.
- 2 It is soluble in water.
- **3** It is soluble in oil.

Ans: A

Option 1 is correct as this is an ionic compound, hence the energy at room temperature is insufficient to overcome the strong ionic bonds. It is likely to be a solid at room temperature.

Option 2 is correct as this is a sodium salt and all sodium salts are soluble in water.

Option 3 is correct as the long hydrophobic (non-polar) hydrocarbon chain allows for favourable t.d.-i.d. interactions with oil, which is also non-polar, thus rendering it soluble in oil.

Non-polar hydrocarbon chain.

$$CH_{3}(CH_{2})_{10}CH_{2}O = S ONa$$

33 The diagram below shows the energy profile for the following reaction:

 $2HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4N_2(g)$

energy / kJ mol⁻¹ reactants R products progress of reaction

Which statement can be inferred from the information given above?

1 The reaction is feasible at all temperatures.

2 The enthalpy change for the reverse reaction is Q + R.

3 Adding a catalyst would alter the value of R.

Ans: D

Option 1 is correct since for a reaction to be feasible at ALL temperatures, then

 $\Delta G = \Delta H - T \Delta S < 0$ at all temperatures.

For this to happen, then ΔH must be always < 0 and ΔS always > 0.

From the diagram:

- the energy of products < reactants $\Rightarrow \Delta H$ always < 0;
- From $2HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4N_2(g)$; $\Delta n \text{ gas} = +2 (>0)$

Thus $\Delta G = \Delta H - T \Delta S < 0$ and hence feasible at all temperatures.

Option 2 is incorrect as the enthalpy change (magnitude) should be R only.

<u>Option 3 is incorrect</u> as adding a catalyst should decrease the E_a of the forward reaction (represented by Q) only. ΔH for a catalysed reaction remains the same.



34 Three metals X, Y and Z, are connected in pairs in two electrochemical cells as shown below.

Which statements are true?

- **1 Y** is the strongest reducing agent.
- Ecell is +0.78 V when the two half-cells of Y²⁺(aq)|Y(s) and Z²⁺(aq)|Z(s) are connected together.
- 3 $Y^{2+}(aq)$ can oxidise both X and Z.

Ans: B

Concepts applied

- Oxidation is the loss of electrons and reduction is the gain of electrons.
- $E_{cell} = E_{[R]} E_{[O]}$

Since electrode Y has a negative polarity

 \Rightarrow oxidation takes place at electrode Y; thus reduction takes place at electrode X.

Since first cell on left hand side has $E_{cell} = E_{[R]} - E_{[O]} = E_{(X^{2+}/X)} - E_{(Y^{2+}/Y)} = +0.47 \text{ V}$

 $\Rightarrow E_{(X^{2+}/X)} > E_{(Y^{2+}/Y)}$

Similarly, for the next cell, $E_{cell} = E_{[R]} - E_{[O]} = E_{(Z^{2+}/Z)} - E_{(X^{2+}/X)} = +0.31 \text{ V}$

$$\Rightarrow \mathbf{E}_{(\mathbf{Z}^{2+}/\mathbf{Z})} > \mathbf{E}_{(\mathbf{X}^{2+}/\mathbf{X})}$$

Combining these information together, we know that:

$$E_{(Z^{2+}/Z)} > E_{(X^{2+}/X)} > E_{(Y^{2+}/Y)}$$

0.31 V

Option 1 is correct because the strongest reducing agent

- \Rightarrow metal is most easily oxidised;
- ⇒ least positive reduction potential of the cations
- \Rightarrow **Y** is the strongest reducing agent.

Option 2 is correct because



Vol of gas / cm³

35 A student carried out a kinetics experiment using a freshly cut sodium (of known mass) in a large excess of pure ethanol at room conditions and measured the volume of gas liberated every minute. The graph below shows the results of the experiment.



Which of the following can be deduced from the above information?

- 1 This reaction has a constant half-life.
- **2** 0.123 g of sodium was used in the reaction.
- **3** The order of reaction with respect to ethanol could be analysed by adding water to vary the concentration of ethanol.

Ans: B

Option 1 is correct because from the graph, the half-life can be deduced as follows:

Vol of gas / cm3



<u>Option 2 is correct</u> because from the graph, $V_{\text{final}} = 64 \text{ cm}^3$

Reaction is as follows: $2Na + 2CH_3CH_2OH \rightarrow 2CH_3CH_2ONa + H_2(g)$

 $\eta_{Na}{=}2\times\eta_{H_2}{=}2\times\frac{_{64}}{_{24000}}{=}2.666\times10^{^{-3}}\,\text{mol}$

: mass of Na used = $2.666 \times 10^{-3} \times 23.0 = 0.123 \text{ g} (3 \text{ s.f.})$

<u>**Option 3 is incorrect**</u> because sodium can also react with water to produce $H_2(g)$, thus the rate of reaction will no longer be due to that of ethanol with sodium only.

36 Chlorine reacts with hot concentrated sodium hydroxide according to the equation below.

 $3Cl_2(g) + 6NaOH(aq) \rightarrow NaClO_3(aq) + 5NaCl(aq) + 3H_2O(l)$

Which statements about the above reaction are true?

- **1** Sodium hydroxide acts as a reducing agent.
- 2 Chlorine undergoes disproportionation.
- **3** The oxidation state of the chlorine in one of the products is +5.

Ans: C

Option 1 is incorrect as there is no change in oxidation number in either sodium, oxygen nor hydrogen in NaOH.

<u>**Option 2 is correct**</u> as oxidation number of chlorine in Cl_2 has simultaneously increased from 0 to +5 in NaClO₃ and decreased from 0 to -1 in NaCl.

Option 3 is correct since for ClO_3^- , the O.N. of Cl + 3(-2) = -1 \therefore O.N. of Cl = +5

37 In an organic synthesis, a 62% yield of product is achieved.

Which conversions are consistent with the given information?

- 1 74 g of butan-2-ol ($M_r = 74$) \rightarrow 44.64 g of butanone ($M_r = 72$)
- **2** 72 g of butanone ($M_r = 72$) \rightarrow 45.88 g of butan-2-ol ($M_r = 74$)
- 3 56 g of but-2-ene ($M_r = 56$) \rightarrow 37.20 g of ethanoic acid ($M_r = 60$)

Ans: B

62% yield $\Rightarrow \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = 62\%$

Option 1	Option 2	Option 3		
$CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3$	$CH_3COCH_2CH_3 \to CH_3CH(OH)CH_2CH_3$	$CH_3CH=CHCH_3 \rightarrow 2 CH_3COOH$		
$\frac{74}{74} = 1 \text{ mol}$ $\frac{44.64}{72} = 0.62 \text{ mol}$	$\frac{72}{72} = 1 \text{ mol}$ $\frac{45.88}{74} = 0.62 \text{ mol}$	$\frac{56}{56} = 1 \text{ mol}$ $\frac{37.2}{60} = 0.62 \text{ mol}$		
% yield = $\frac{0.62}{1} \times 100 = 62$ %	% yield = $\frac{0.62}{1} \times 100 = 62$ %	% yield = $\frac{0.62}{2} \times 100 = 31$ %		
correct	correct	Incorrect		

Which of the following can be classified as redox reactions?

38

- 1 CH₃COCH₃ + aqueous alkaline iodine
- **2** $CH_3CH=CH_2 + Br_2$
- $3 \qquad CH_3CH_2NH_2 + CH_3CO_2H$

<u>**Option 1 is correct</u>** since methyl ketones, RCOCH₃, can be oxidized by aq. alkaline iodine to the carboxylate ion, RCOO⁻, with I₂ being reduced from 0 to -1 on Γ .</u>

[recall the tri-iodomenthane test]

 $\mathsf{RCOCH}_3 + \mathsf{3I}_2 + \mathsf{4OH}^- \rightarrow \mathsf{RCOO}^- + \mathsf{CHI}_3 + \mathsf{3I}^- + \mathsf{3H}_2\mathsf{O}$

Option 2 is correct since this is an electrophilic addition reaction where:

 $CH_{3}CH=CH_{2} + Br_{2} \rightarrow CH_{3}CH(Br)CH(Br)CH_{3}$ $_{0}$

O.N. of the C=C carbons have increased from -1 to 0 in the -CH(Br)-. O.N. of bromine in Br₂ has decreased from 0 to -1 in CH₃CH(Br)CH(Br)CH₃.

Option 3 is incorrect as this is an acid-base reaction as follows:

 $CH_3CH_2NH_2 + CH_3CO_2H \rightarrow CH_3CH_2NH_3^+ + CH_3CO_2^-$. No change in oxidation state of the atoms.

39 Use of Data Booklet is relevant to this question.

The following tests were carried out on separate fresh samples of $CrCl_3(aq)$.

Which are the correct observations with the corresponding tests?

- **1** The colour of the solution changes when zinc powder is added.
- 2 When NaOH(aq) is added in excess, followed by $H_2O_2(aq)$ and the mixture heated, an orange solution of $Cr_2O_7^{2-}$ is formed.
- **3** A greyish-green precipitate is obtained when excess NaOH(aq) is added.

Option 1 is correct because from the data booklet:

E[⊕] /V

 $Zn^{2+} + 2e^- \rightleftharpoons Zn - 0.76$

 $Cr^{3+} + e^{-} \implies Cr^{2+} = -0.41$

 $E_{cell}^{\circ} = -0.41 - (-0.76) = +0.35 \text{ V} > 0$ (\therefore feasible), thus green $Cr^{3+}(aq)$ changes colour to $Cr^{2+}(aq)$.

[Note: There is no need to know the colour of $Cr^{2+}(aq)$].

<u>Option 2 is incorrect</u> because when OH^- is added in excess, the complex ion, $[Cr(OH)_6]^{3^-}$ is formed. Even if the reaction is feasible (although no E° data for the reduction of $[Cr(OH)_6]^{3^-}$ is provided in the Data Booklet) and the Chromium in $[Cr(OH)_6]^{3^-}$ can be oxidised from +3 to +6 in dichromate (VI), $Cr_2O_7^{2^-}$, the alkaline medium will cause the $Cr_2O_7^{2^-}$ to exist as $CrO_4^{2^-}$ instead.

<u>**Option 3 is incorrect</u>** because when OH^- is added in <u>excess</u>, the dark green soluble complex ion, $[Cr(OH)_6]^{3-}$ is formed. The greyish-green ppt of $Cr(OH)_3$ is only formed when limited NaOH(aq) is added instead.</u>

40 Which statements regarding the following compound are correct?



- 1 When heated with alkaline KMnO₄, it gives a product that can react with 2,4dinitrophenylhydrazine.
- 2 Upon reacting with hot acidified KMnO₄, the product is optically inactive.
- **3** Benzene can be produced when it is heated with ethanolic KOH.

Ans: A

Option 1 is correct because vigorous oxidation of C=C, nucleophilic substitution of Br to OH and further oxidation of secondary OH to ketones occur.



CO₂K which is a carbonyl compound that can react with

2,4-dinitrophenylhydrazine.

Note: Vigorous oxidation (causing cleavage of C=C) can occur with acidified or alkaline $KMnO_4$, as long as heat is supplied.

Option 2 is correct because vigorous oxidation (causing cleavage of C=C) to occur gives:

which is a meso compound that is optically inactive. Even though there are 2 chiral carbons, there is an internal mirror plane. The two parts of the molecule rotate plane-polarised light in opposite directions and equal magnitude, hence the effects cancel out.

Option 3 is correct because elimination of HBr can occur as follows:



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