SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

Candidate Name ☐

Class ☐

CHEMISTRY 9647/01

Preliminary Examination
Paper 1 Multiple Choice

29 August 2014
1 hour

Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, FIN/NRIC number and class on the OMS in the spaces provided.
Shade correctly FIN/NRIC number and your class.
Eg. If your NRIC is S9306660Z, shade **S9306660Z** for the item "index number".

There are **forty** 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 using a **soft pencil** on the separate OMS.

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 question paper.

This document consists of **22** printed pages and **0** 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 The hydrolysis of S_2Cl_2 proceeds by two reactions.

Reaction 1 $S_2Cl_2 + 2H_2O \longrightarrow H_2S + SO_2 + 2HCl$

Reaction 2 $2H_2S + SO_2 \longrightarrow \frac{3}{8}S_8 + 2H_2O$

Which of the following correctly describe the reactions?

A	A weakly acidic solution is formed in Reaction 1.
B	Reverse disproportionation occurs in Reaction 2.
C	The oxidation state of chlorine and oxygen changes in both reactions.
D	The products of Reaction 1 require 2 mol of NaOH for complete neutralisation.

Ans: B

- Strong acid HCl is formed.
- H_2S is oxidised to S_8 while SO_2 is reduced to S_8 (the reverse of disproportionation reaction).
- Oxidation states of chlorine and oxygen remain as –1 and –2 in both reactions.
- $2HCl + 2NaOH \rightarrow 2NaCl + 2H_2O$
  $SO_2 + H_2O \rightarrow H_2SO_3$
  $H_2SO_3 + 2NaOH \rightarrow Na_2SO_3 + 2H_2O$
  Total amount of NaOH required = 4 mol

2 Sodium carbonate peroxyhydrate with the formula $(Na_2CO_3)_x.\ \boldsymbol{y}\ H_2O_2$ is used in eco-friendly cleaning products and as a laboratory source of anhydrous hydrogen peroxide.

When 20.0 cm^3 of 0.100 mol dm^{-3} sodium carbonate peroxyhydrate is titrated with 0.200 mol dm^{-3} acidified $KMnO_4$, it requires 12.0 cm^3 of acidified $KMnO_4$ before the first pink colour appears.

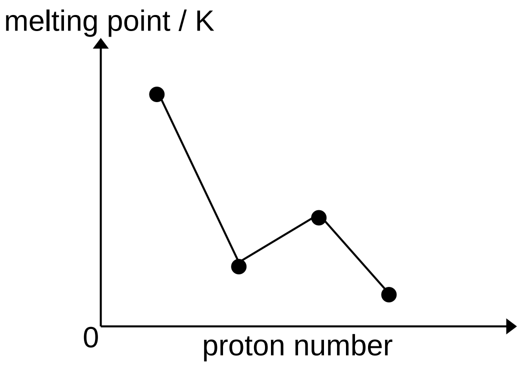
$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

When an identical sample is acidified, it releases 96.0 cm^3 of carbon dioxide at room conditions.

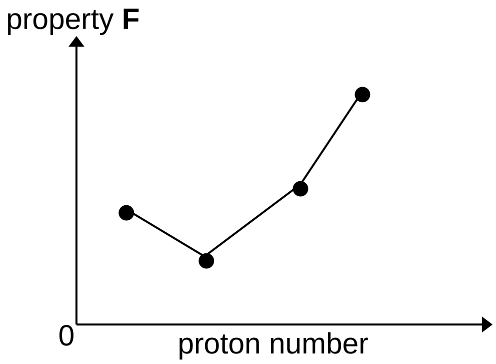
	What is the ratio of ***x:y*** ?	
	A	1 : 3
	B	2 : 3
	C	2 : 1
	D	3 : 1
	Ans: B Amt of MnO_4^- used = 0.002400 mol Amt of H_2O_2 present = 0.002400 / 2 x 5 = 0.006000 mol Amt of sodium carbonate peroxyhydrate = 0.002000 mol y = 0.006 / 0.002 = **<u>3</u>** $Na_2CO_3 + 2H^+ \rightarrow CO_2 + H_2O + 2Na^+$ Amt of CO_2 = 0.096 / 24 = 0.004000 mol x = 0.004 / 0.002 = **<u>2</u>**	

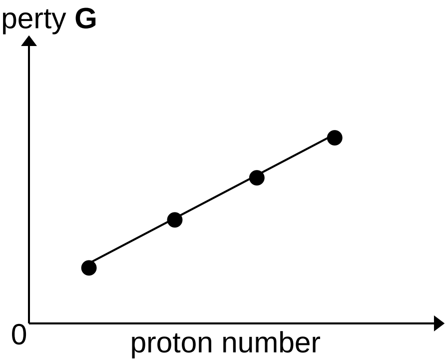
3	The successive ionisation energies, in kJ mol^{-1}, of an element **E** are given below. 578 1820 2750 11600 14800 18400 Which of the following could be the electronic configuration of the outermost shell in **E**?	
	A	ns^2
	B	$ns^2 np^1$
	C	$ns^2 np^2$
	D	$ns^2 np^3$
	Ans: B Largest increase is between the 3rd and 4th IE, hence this is a Group III element. Therefore, the outermost shell electronic configuration is $ns^2\ np^1$	

4 The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.



The sketches below represent another two properties of the elements.





Which of the following represents the properties **F** and **G**?

	property **F**	property **G**
A	third ionisation energy	electronegativity
B	number of valence electrons	boiling point
C	ionic radius	effective nuclear charge
D	electrical conductivity	atomic radius

Ans: A

Based on the melting point data, the four elements are Si (Group IV) (high melting point due to giant molecular structure), P_4 (Group V), S_8 (Group VI) and Cl_2 (Group VII).

Property **F** is 3rd IE as there is an anomaly at Group V:

Si^{2+} → Si^{3+} + e
$3s^2$ $3s^1$

P^{2+} → P^{3+} + e
$3s^2\ 3p^1$ $3s^2$

	Electron from P^{2+} is removed from an outer subshell and hence less energy is required. Property **G** is electronegativity as electronegativity increases across the period.

5	Two identical bulbs at the same temperature contain ideal gases **J** and **K** separately. The density of gas **J** is twice that of gas **K** and the molecular mass of gas **J** is half that of gas **K**. What is the ratio of the pressure of gas **J** to that of gas **K**?	
	A	1 : 2
	B	1 : 1
	C	2 : 1
	D	4 : 1
	Ans: D PV = nRT PM = $\frac{m}{V}$RT P = $\frac{\rho RT}{M}$ $\frac{P_J}{P_K} = \frac{\frac{2\rho_J}{\frac{1}{2}M_K}}{\frac{\rho_J}{M_K}} = \frac{4}{1}$	

6	Which of the following statements about an ideal gas are correct?	
	A	One mole of any ideal gas occupies the same volume under the same conditions of temperature and pressure.
	B	The density of an ideal gas at constant pressure is directly proportional to the temperature.
	C	The volume of a given mass of an ideal gas is doubled when its temperature is raised from 25 °C to 50 °C.
	D	The temperature of a given mass of an ideal gas is doubled when its volume is raised from 0.05 cm^3 to 0.1 dm^3.

Ans: A

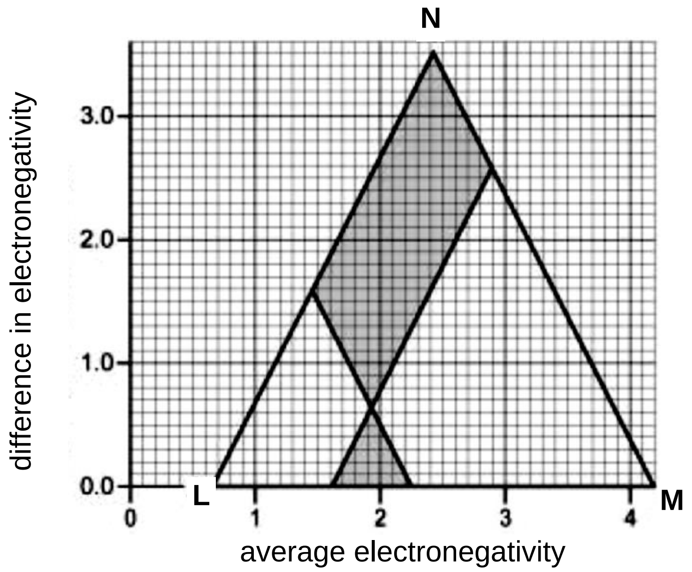
A ✓ PV =nRT

B × $\rho = \dfrac{PM}{RT}$ density is inversely proportional to temperature.

C × Temperature is in kelvin so it is not doubled, thus volume is not doubled also.

D × 0.1 dm^3 is 2000 times of 0.05 cm^3 so temperature should increase by 2000 times.

7 The type of bonding between two elements can be rationalised and even predicted using a van Arkel triangle. The triangle is based on electronegativity values. Difference in electronegativity is plotted along the y–axis and average electronegativity is plotted along the x–axis.



What is the type of bonding present at each of these bonding extremes, labelled **L**, **M** and **N** on the triangle?

	L	M	N
A	covalent	metallic	ionic
B	metallic	covalent	ionic
C	covalent	ionic	metallic
D	ionic	covalent	metallic

Ans: B
Difference in electronegativity is zero for **L** & **M** ⇒ metallic bonding or covalent bonding.
Since metals have low electronegativity ⇒ **L** is metallic bonding.

8 Lead is the final product formed by a series of changes in which the rate–determining stage is the radioactive decay of uranium–238. This radioactive decay is a first–order reaction with a half–life of 4.5 x 10^9 years.

What would be the age of a rock sample, originally lead–free, in which the molar proportion of uranium to lead is now 1:31?

A	2.25 x 10^{10} years
B	2.70 x 10^{10} years
C	3.15 x 10^{10} years
D	3.60 x 10^{10} years

Ans: A

Uranium–238 is reactant; lead is product.

Use formula:
Since Uranium:lead = 1:31
⇒ 1+31 = 32 parts

$$\left(\frac{1}{2}\right)^n = \left(\frac{1}{32}\right) = \left(\frac{1}{2}\right)^5$$ where n = no. of $t_{½}$ = 5

∴ Age = 5 x 4.5 x 10^9 = **2.25 x 10^{10} years**

9 When 0.1 mol of bismuth chloride is added to 2 dm^3 of water, it reacts to form 0.02 mol of white precipitate of bismuth oxychloride and a solution of hydrochloric acid.

The equation for the reaction is as follows:

$$BiCl_3\,(aq) + H_2O\,(l) \rightleftharpoons BiOCl\,(s) + 2HCl\,(aq)$$

What is the correct expression for the equilibrium constant K_c?

A	$\dfrac{(2\ x\ 0.02)^2}{0.08}$
B	$\dfrac{(0.02)(2\ x\ 0.02)^2}{0.08}$
C	$\dfrac{\left(\frac{2\ x\ 0.02}{2}\right)^2}{\frac{0.08}{2}}$
D	$\dfrac{\left(\frac{0.02}{2}\right)\left(\frac{2\ x\ 0.02}{2}\right)^2}{\frac{0.08}{2}}$

Ans: C

	$BiCl_3(aq) + H_2O(l) \rightleftharpoons$		$BiOCl(s) + 2HCl(aq)$	
Initial amt/mol	0.1			0
Change in amt/mol	-0.02		+0.02	+2(0.02)
Final amt/mol	0.08		0.02	2(0.02)

$$K_c = \frac{[HCl]^2}{[BiCl_3]} = \frac{\left(\frac{2 \times 0.02}{2}\right)^2}{\frac{0.08}{2}}$$

10 What is the pH of the resultant solution when 100 cm^3 of 0.10 mol dm^{-3} of aqueous NH_3 and 80 cm^3 of 0.15 mol dm^{-3} aqueous NH_4Cl are mixed at 25 °C? (pK_b of NH_3 = 4.75)

A 9.07 **B** 9.17 **C** 9.32 **D** 9.35

Ans: B

Mixing NH_3 and NH_4Cl produces a basic buffer.

pOH = pK_b + lg $\frac{[salt]}{[base]}$ = 4.75 + lg$(\frac{0.080 \times 0.15}{0.100 \times 0.10})$ = 4.83

pH = 14 – 4.83 = 9.17

11 Instant ‘cold packs’ are often used by athletes to conveniently treat injuries. One type of ‘cold pack’ is composed of powdered ammonium nitrate and water separated by a thin plastic membrane. When the pack is squeezed, the membrane breaks and ammonium nitrate dissolves in water spontaneously.

Which line in the table gives the signs of ΔH, ΔS and ΔG for the overall process?

	ΔH	ΔS	ΔG
A	–	+	–
B	–	–	+
C	+	–	+
D	+	+	–

Ans: D

- As this process is endothermic, ΔH is positive.
- As the reaction occurs readily when solid dissolves in water, the reaction is

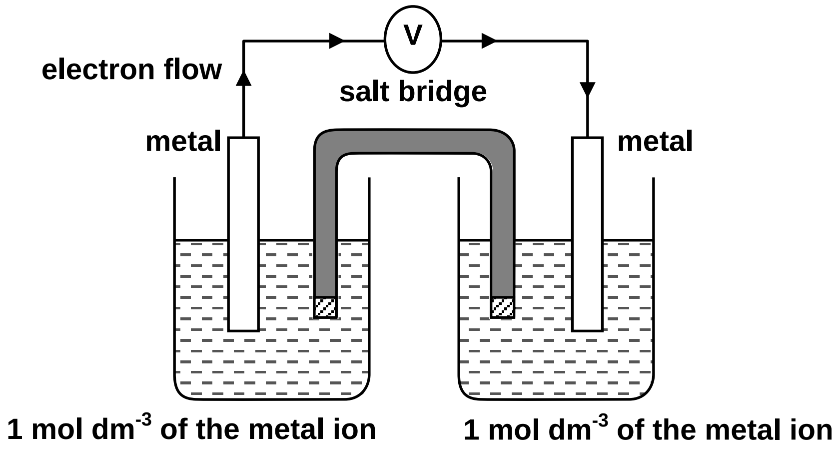
spontaneous. Therefore Δ*G* is negative.

- Δ*G* = Δ*H* - *T*Δ*S*
  (-)   (+)
  Δ*S* must be positive so that the overall Δ*G* is negative.

12 *Use of the Data Booklet is relevant to this question.*

The half-cells for four metals: Mg, **P**, **Q** and **R** were in turn connected in pairs and the potential difference was recorded.

Temperature = 25°C



The results obtained are as shown in the table below.

Positive electrode	Negative electrode	e.m.f /V
P	Mg	+2.10
Q	Mg	+2.72
Mg	**R**	+0.33

Rank the four metals in the order of decreasing reducing power.

A **Q** > **P** > Mg > **R**

B **P** > **Q** > Mg > **R**

C **R** > Mg > **P** > **Q**

D **R** > Mg > **Q** > **P**

Ans: C

Positive electrode (Cathode) → [R]	Negative electrode (Anode) → [O]	e.m.f /V

$E^{\theta}_{cell} = E^{\theta}_{red} - E^{\theta}_{oxid}$

$+2.10 = E^{\theta}_{p} - (-2.38)$

	E^θ_p = -0.28V ; Since -0.28V is less negative than -2.38V, **P** is more easily reduced → less easily oxidised than Mg. Apply the same method for **Q** and **R** to arrive at your answer.

13 **W**, **X**, **Y** and **Z** are four elements in Period 3.

W is a conductor of electricity and does not react with water. **Z** forms a chloride, $\mathbf{Z}Cl_5$ which reacts with water and dissolves in organic solvent. **Y** forms a solid oxide $\mathbf{Y}O_2$. **X**OH is a strong alkali.

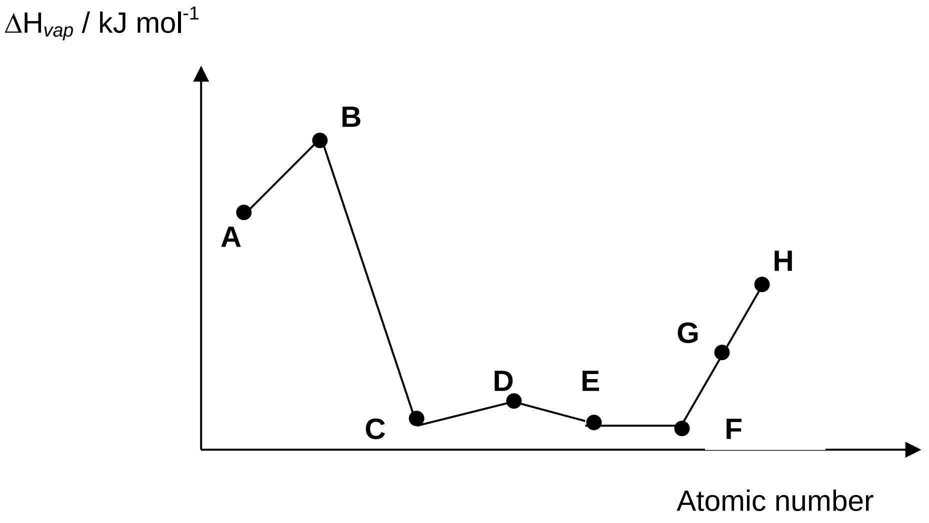
Arrange the above elements in order of increasing proton number.

A	**X**, **W**, **Y**, **Z**
B	**X**, **Y**, **Z**, **W**
C	**W**, **Y**, **X**, **Z**
D	**W**, **X**, **Y**, **Z**

Ans: A

W (can conduct electricity) and **X** (forms strong alkali) are metals.
X is likely to be Na.
W is likely to be Al, as it does not react with water.
Z is likely to be phosphorus, due to PCl_5 formed.
Y is likely to be Si, or Mg due to solid oxide $\mathbf{Y}O_2$.

14 The graph below show the variation in the molar enthalpy change of vapourisation, ΔH_{vap} for 8 consecutive elements in the Periodic Table, all with atomic number ≤ 20.



What can be deduced from the above graph?

	A	Element **A** forms amphoteric oxides.
	B	Element **F** exists as diatomic molecules.
	C	Element **G** forms an oxide which is acidic in aqueous solution.
	D	Element **C** is in the same group as boron in the Periodic Table.
	Ans: A Based on the graph, the sharp dip signifies that **C, D, E** and **F** are simple molecular compounds. **C, D, E** and **F** are likely to be P_4, S_8, Cl_2 and Ar respectively. Hence, **A** and **B** are A*l* and Si respectively.	

15	Radium is the last element in Group II in the Periodic Table. Which of the following is **not** true for radium?	
	A	Its oxide is basic with water.
	B	It is the least reactive element in Group II.
	C	It reacts with water to release hydrogen gas.
	D	Its compounds conduct electricity when molten.
	Ans: **B** Radium is the most reactive element in Group II as the 2 electrons are the most easily removed as the electrons are the furthest away due to the most number of quantum shells. Hence the electrostatic force of attraction between the nucleus and outer electrons is the weakest.	

16	Which of the following factors best explains why magnesium sulfate has a higher solubility than barium sulfate?	
	A	Barium is more electropositive than magnesium.
	B	The charge density of magnesium ions is greater than that of the barium ions.
	C	Magnesium sulfate has numerically larger lattice energy than barium sulfate.
	D	The hydration of barium ions is more exothermic than that of magnesium ions.
	Ans: B L.E. α $\left\|\frac{q^+q^-}{r^+r^-}\right\|$ Statement **A** is true but does not explain why magnesium sulfate is more	

soluble. In fact, it shows that magnesium sulfate is highly insoluble due to its strong lattice structure.

Charge density α $\frac{charge}{size}$

Statement **B** is true as the cationic size of Mg^{2+} is smaller than Ba^{2+} hence charge density of Mg^{2+} is greater than that of Ba^{2+}. This imply that hydration of Mg^{2+} is more exothermic than Ba^{2+} and hence ΔH_{sol} of $MgSO_4$ will be more negative than ΔH_{sol} of $BaSO_4$. Therefore, MgSO4 is more soluble than barium sulphate.

$$\Delta H_{sol} = \Delta H_{hyd} - L.E$$

Statement **C** is true but does not explain why magnesium sulphate is more soluble.

Statement **D** is not true. Hydration of Mg^{2+} is more exothermic than Ba^{2+} due to the smaller cationic radius of Mg^{2+}.

$$\Delta H_{hyd} \;\alpha\; \left|\frac{q^+}{r^+}\right|$$

17 Concentrated sulfuric acid reacts differently with each of the sodium halides, NaC*l*, NaBr and NaI due to their differing chemical properties.

Which of the following statements about their respective reactions is **not** true?

A	Sodium halides may act as reducing agents.
B	White fumes are produced in the reactions involving sodium bromide and sodium iodide only.
C	Redox reaction occurred with concentrated sulfuric acid only for sodium bromide and sodium iodide.
D	There is a difference in the extent of the reduction of the sulfuric acid when the reactions of bromide and iodide with concentrated sulfuric acid are compared.

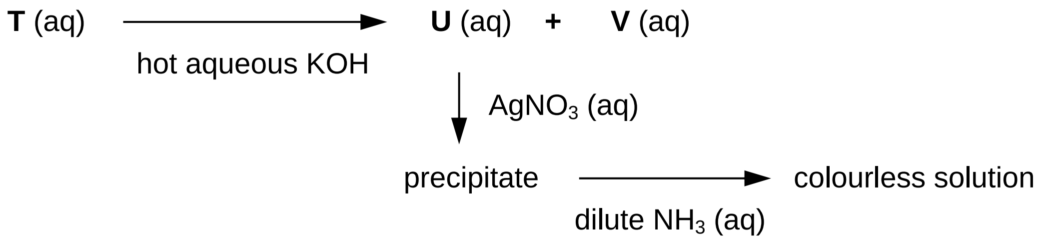
Ans: B

A is true. NaX may act as reducing agent. Reducing power decreases down the group from NaC*l* to NaBr to NaI.

Thus, C and D are true.

B is not true, as white fumes of HC*l* is also produced when NaC*l* reacts with concentrated sulfuric acid.

18 Consider the following reaction route.



What could solutions **T**, **U** and **V** be?

	T	U	V
A	Cl_2	KC*l*	KC*l*O
B	Cl_2	KC*l*	$KClO_3$
C	Br_2	KBr	KBrO
D	Br_2	KBr	$KBrO_3$

Ans: B

Since the precipitate may dissolve in dilute NH_3 (aq) eventually, **T** is Cl_2.
Since hot aqueous KOH is used, **V** is $KClO_3$.

19 *Use of the Data Booklet is relevant to this question.*

Peroxodisulfate(VI), $S_2O_8^{2-}$, is capable of oxidising the tartrate ion, $[CH(OH)CO_2]_2^{2-}$ to carbon dioxide and methanoate as shown in the following reaction.

$$[CH(OH)CO_2]_2^{2-} + 3S_2O_8^{2-} + 2H_2O \longrightarrow 2CO_2 + 2HCO_2^{-} + 6H^{+} + 6SO_4^{2-}$$

The reaction can be catalysed by a homogenous catalyst. Given that the electrode potential for the tartrate ion is

$$2CO_2 + 2HCO_2^{-} + 6H^{+} + 6e \rightleftharpoons [CH(OH)CO_2]_2^{2-} + 2H_2O \qquad E^{\theta} = +0.56\ V$$

Which metal ion is **not** a suitable catalyst for this reaction?

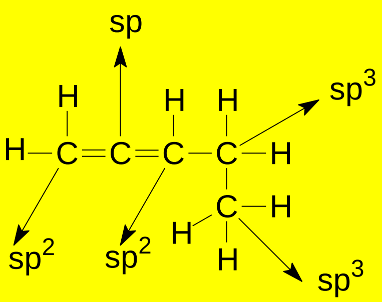
A	Co^{3+}
B	Fe^{3+}
C	Mn^{2+}
D	V^{2+}

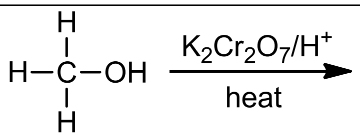
Ans: D

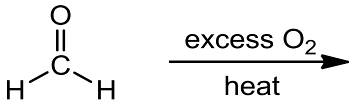
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ $E^o = +2.01\ V$

$Co^{3+} + e \rightleftharpoons Co^{2+}$ $E^o = +1.82\ V$
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^o = +0.77\ V$
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$ $E^o = +1.49\ V$
$V^{3+} + e \rightleftharpoons V^{2+}$ $E^o = -0.26\ V$

	Catalyst chosen must have a value between +0.56 V and +2.10 V in order to reduce $S_2O_8^{2-}$ and to oxidize $[CH(OH)CO_2]_2^{2-}$. Hence V^{2+} cannot be used.

20	Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals. Which bond is **not** present in $CH_2=C=CHCH_2CH_3$?	
	A	π bond formed by $sp - sp^2$ overlap
	B	σ bond formed by $sp^3 - sp^2$ overlap
	C	σ bond formed by $s - sp^3$ overlap
	D	σ bond formed by $sp^3 - sp^3$ overlap
	Ans: A  π bond is formed via sideway overlap of unhybridised p orbitals → Option A is incorrect In option C: 1s orbital refers to 1s orbital of H.	

21	In which reaction will the oxidation number of carbon show the smallest change?	
	A	$CH_3CH(OH)CH_3 \xrightarrow[\text{heat}]{MnO_4^- / H^+}$ *Note: refer to the C atom bonded to the –OH group*
	B	 $H-\overset{H}{\underset{H}{C}}-OH \xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+}$

	C	
	D	$CH_2{=}CH_2 \xrightarrow[\text{heat}]{H_2,\ Ni}$

Ans: D

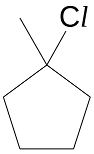
Option A: changes from 0 in RCH(OH)R to +2 (RCOR) → +2

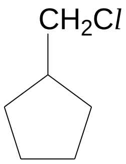
Option B: changes from -2 (CH_3OH) to +2 (HCOOH) → +4

Option C: changes from 0 (HCHO) to +4 (CO_2) →+4

Option D: changes from -2 ($CH_2{=}CH_2$) to -3 (CH_3CH_3) →-1

22 Methylcyclopentane can react with chlorine via free radical substitution to produce a mixture of four monochlorinated products, two of which are shown below.



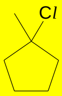
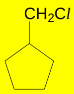
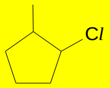
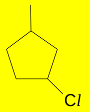


For methylcyclopentane, the order of reactivity of tertiary and primary hydrogen atoms follows a 5 : 1 ratio.

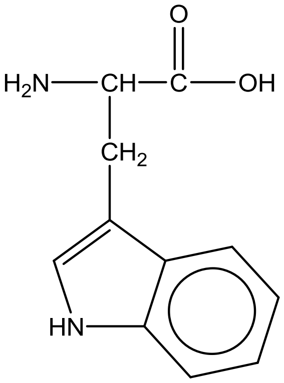
What is the likely ratio of tertiary RC*l* : primary RC*l* formed?

	A	1 : 15
	B	1 : 3
	C	3 : 5
	D	5 : 3

Answer: D

 tertiary RC*l*	 primary RC*l*	 &  Other 2 products are secondary RC*l*
1 H each with reactivity of 5 = **5**	3 H each with reactivity of 1 = **3**	

23 Tryptophan is an amino acid and is essential to the human diet. It also serves as a biological precursor to some chemicals associated with the nervous system of the human body. It has an isoelectric point of 5.89.



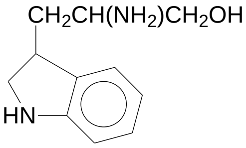
Tryptophan

What of the following statements is **not** true about tryptophan?

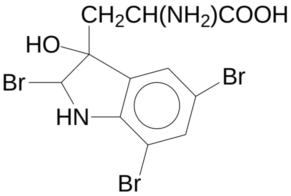
A There are a total of 2 stereoisomers present.

B It has a positive charge when placed in a solution at pH 3.

C It reacts with lithium aluminium hydride to form:



D It reacts with aqueous bromine to form:



Ans: C

C is not true as alkenes are reduced by hydrogen only, not lithium aluminium hydride.

A is true as Cis-trans isomerism is not observed for C=C on cyclic rings. 1 chiral carbon hence 2 optical isomers are possible.

B is true as since pH < pI, Tryptophan becomes protonated in an acidic medium.

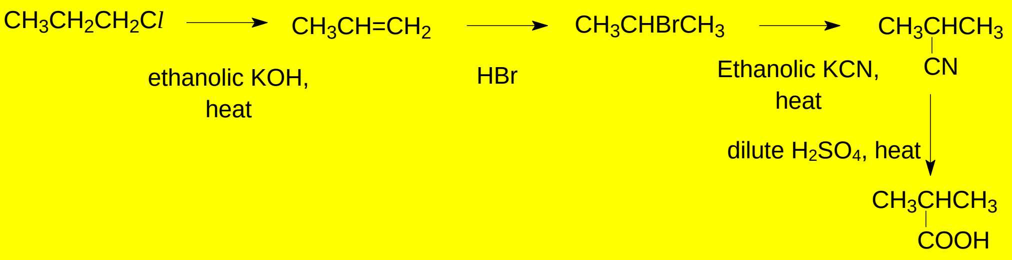
D is true as the alkene reacts via electrophilic addition and the aromatic amin reacts via electrophilic substitution.

24 2–methylpropanoic acid can be synthesised from 1–chloropropane through a series of reactions.

Which set of reagents, used in sequential order, would be the most suitable for this synthesis?

A	ethanolic KCN, dilute HC*l*
B	PC*l*$_5$, acidified KMnO$_4$
C	aqueous KOH, HC*l*, ethanolic KCN, dilute HC*l*
D	ethanolic KOH, HBr, ethanolic KCN, dilute H$_2$SO$_4$

Ans: D



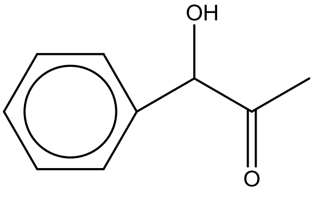
$$CH_3CH_2CH_2Cl \xrightarrow[\text{heat}]{\text{ethanolic KOH,}} CH_3CH{=}CH_2 \xrightarrow[]{\text{HBr}} CH_3CHBrCH_3 \xrightarrow[\text{heat}]{\text{Ethanolic KCN,}} CH_3\underset{CN}{C}HCH_3 \xrightarrow{\text{dilute } H_2SO_4\text{, heat}} CH_3\underset{COOH}{C}HCH_3$$

25 Compound **J** exhibits the following characteristics:

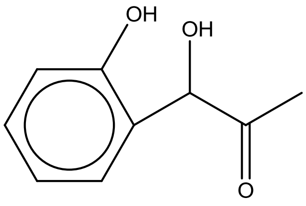
- 1 mol of **J** reacts with excess sodium metal to form 1 mol of hydrogen gas.
- Yellow precipitate is formed when **J** reacts with aqueous alkaline iodine.
- Orange precipitate is formed when **J** reacts with 2,4-DNPH, but no reaction with alkaline silver diammine solution.
- **J** rotates plane-polarised light.

Which of the following could compound **J** be?

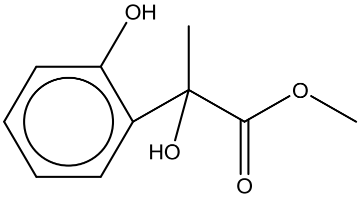
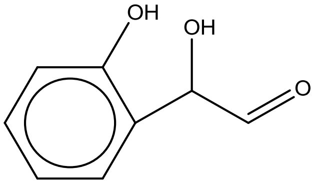
A

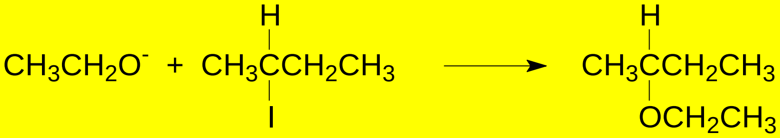


C



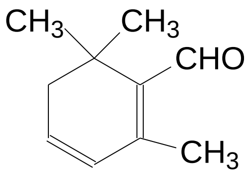
B

	 **D** 
	Ans: C - Option **A** is wrong because 1 mole of J reacts with Na metal to form 1 mol H_2 (g) infers that there are 2 –OH groups. - Options **B** and **D** are wrong because yellow ppt with alkaline aq iodine infers positive iodoform test hence CH_3CO or $CH_3CH(OH)$ must be present. - Option **C** is reconfirmed as it has a chiral centre to rotate plane polarised light.

26	Ethanol reacts explosively with sodium metal to form a salt, sodium ethoxide. What is the product of the reaction between 2-iodobutane and sodium ethoxide?	
	A	$CH_3CH{=}CHCH_3$
	B	$(CH_3)_2CHCH_2OCH_2CH_3$
	C	$CH_3CH_2CH(OCH_3)CH_2CH_3$
	D	$CH_3CH_2CH(CH_3)OCH_2CH_3$
	Ans: D $CH_3CH_2OH + Na \longrightarrow CH_3CH_2O^-Na^+$  $CH_3CH_2O^- + CH_3\underset{I}{\overset{H}{C}}CH_2CH_3 \longrightarrow CH_3\underset{OCH_2CH_3}{\overset{H}{C}}CH_2CH_3$	

27	Deuterium, D, is the $^{2}_{1}H$ isotope of hydrogen. Which reaction could give an organic compound having deuterium incorporated into the molecule?	
	A	$CH_3CD_2CH(Cl)CH(CH_3)_2 \xrightarrow{\text{NaOD (alc.)}}$
	B	$CH_3CH_2CN \xrightarrow[D_2O]{NaOD}$
	C	$CH(CH_3)_2CH_2OD + DBr \longrightarrow$
	D	$CH_3COCI_3 \xrightarrow[D_2O]{NaOD}$
	Ans: D **A** $CH_3CD_2CH(Cl)CH(CH_3)_2 \longrightarrow CH_3CD_2CH{=}C(CH_3)_2 + CH_3CD{=}CH(CH_3)_2$ **Type of reaction: elimination** Deuterium is NOT incorporated **B** $CH_3CH_2CN \xrightarrow[D_2O]{NaOD} CH3CH_2COO^-$ **Type of reaction: basic hydrolysis** Deuterium is NOT incorporated **C** $CH(CH_3)_2CH_2OD + D\mathbf{Br} \longrightarrow CH(CH_3)_2CH_2\mathbf{Br}$ **Type of reaction: nucleophilic substitution** Deuterium is NOT incorporated **D** $CH_3COCI_3 \longrightarrow CH_3COO^- + CDI_3$ **Type of reaction: oxidation (iodoform)** Deuterium is incorporated Since deuterium is an isotope of hydrogen, the type of reaction that the various organic compounds are the same as when hydrogen is used.	

28 Safranal is a component of the yellow dyestuff saffron.

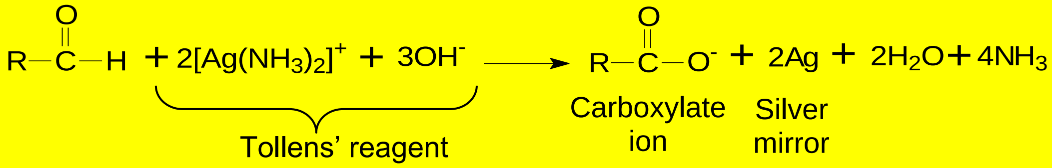


Safranal

What are the products of warming it with Tollens' reagent?

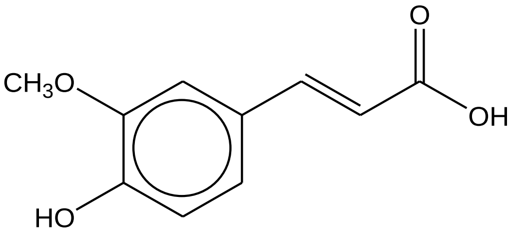
A	a precipitate of silver oxide and a carboxylate salt
B	a silver mirror and a carboxylate salt
C	a silver mirror and a carboxylic acid
D	a silver mirror and an alcohol

Ans: B



$$R-\overset{O}{\overset{\|}{C}}-H + \underbrace{2[Ag(NH_3)_2]^+ + 3OH^-}_{\text{Tollens' reagent}} \longrightarrow \underset{\text{Carboxylate ion}}{R-\overset{O}{\overset{\|}{C}}-O^-} + \underset{\text{Silver mirror}}{2Ag} + 2H_2O + 4NH_3$$

29 Ferulic acid is an abundant phytochemical found in plant cell walls.



Ferulic acid

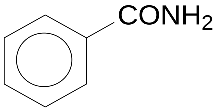
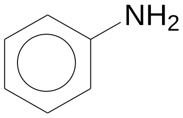
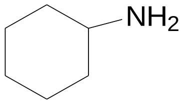
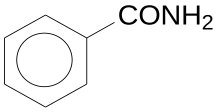
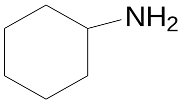
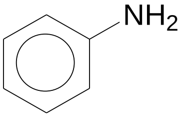
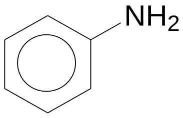
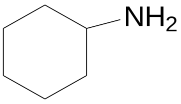
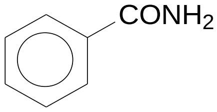
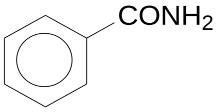
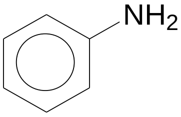
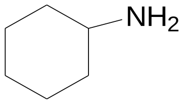
Assume that CH_3O- group is inert. Which statement about ferulic acid is correct?

A	Ferulic acid can only undergo electrophilic addition with aqueous bromine.
B	Ferulic acid forms an ester with ethanoic acid when heated with concentrated sulfuric acid.
C	One mole of ferulic acid can react with only one mole of phosphorous pentachloride.
D	Ferulic acid reacts with lithium aluminium hydride to form a product that

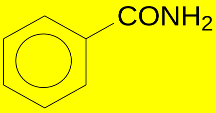
		does not exhibit geometric isomerism.

Ans: C

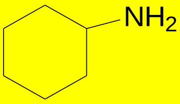
Only the hydroxyl group in the carboxylic acid group in ferulic acid can undergo nucleophilic substitution with phosphorus pentachloride to form an acyl chloride.

30		Which of the following shows the correct order of increasing base strength?			
		Weakest base	→		**Strongest base**
	A			NH_3	
	B				NH_3
	C		NH_3		
	D	NH_3			

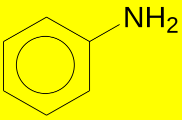
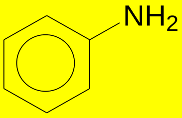
Ans: A



is neutral; it is not basic.



is most basic because of its electron donating group from cyclohexane.

NH_3 is more basic than  because the lone pair of electrons is delocalised into the benzene ring in . This decreases the availability of the lone pair to act as a base.

Section B

For **questions 31 – 40**, one or more of the numbered statements **1** to **3** may be correct. Decide whether each of the statements is or is not correct. The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is to be used as correct response.

31	Which of the following contain more intermolecular hydrogen bonds than ammonia?	
	1	H_2SO_4 (*l*)
	2	CH_3COCH_3 (*l*)
	3	CH_3COOH (*l*)
	Ans: D (1 only) NH_3 forms 1 H–bond per molecule (3H but limited by only 1 lone pair of electrons per molecule) **1** ✓ H_2SO_4 (*l*): 2H and 8 lone pairs ⇒ <u>**2 H–bond**</u> per molecule **2** × CH_3COCH_3 (*l*): no intermolecular H-bonds present **3** × CH_3COOH (*l*): 1H and 4 lone pairs of both O atom ⇒ <u>**1 H–bond**</u> per molecule	

32	Consider the following mechanism. $\mathbf{L} + \mathbf{M} \rightleftharpoons \mathbf{N}$ fast $\mathbf{L} + \mathbf{N} \longrightarrow \mathbf{P} + \mathbf{Q}$ slow $\mathbf{N} + \mathbf{Q} \longrightarrow \mathbf{M} + \mathbf{P}$ fast What can be deduced from the mechanism?	
	1	The unit for rate constant, *k*, in the rate equation is $mol^{-1}\,dm^3\,s^{-1}$.
	2	The overall equation is $2\mathbf{L} + \mathbf{N} \longrightarrow 2\mathbf{P}$.
	3	**M** is a catalyst and **Q** is an intermediate.

Ans: C (2 and 3 only)

1 × Rate equation derived from the slow step is rate = k[L][N].

However, since N is an intermediate, it cannot appear in the rate equation.

From step 1,

$$K_c = \frac{[N]}{[L][M]}$$

$$[N] = K_c[L][M]$$

$rate = k'[L]^2[M]$, where k' is kK_c

Thus, unit for k is $mol^{-2}\ dm^6\ s^{-1}$.

2 ✓ The overall equation can be derived by adding up all the 3 equations and cancelling the species that appears on the left and right side of the equations.

3 ✓ M is a catalyst as it is used in first reaction and is regenerated in third reaction. Q is an intermediate as it is produced in second reaction but used up in third reaction.

33	Which of the following statements are **false**?	
	1	When an inert gas is added at constant volume to an equilibrium mixture, the equilibrium position of the system will not shift.
	2	The magnitude of the equilibrium constant informs us of the relative proportion of products to reactants, providing us information on the reaction rate.
	3	When a change in conditions is introduced to an equilibrium system, both the concentration of reactants and products, as well as the equilibrium constant changes.

Ans: C (2 and 3 only)

1 When an inert gas is added at constant volume to an equilibrium mixture, the equilibrium position of the system will not shift. This is because the inert gas added increases the total pressure of the system, but does not change the partial pressures of the reacting gases.

2 The magnitude of the equilibrium constant informs us of the relative proportion of products to reactants, providing us information on the extent of reaction.

3 When a change in conditions is introduced to an equilibrium system, only the concentration of reactants and products changes.

34 Equal amounts of two organic compounds, **R** and **S**, were added to water and the pH values of both solutions were determined. It was found that the pH of the aqueous solution of **R** is higher.

Which pairs of compounds could be **R** and **S**?

	R	**S**
1	CH_3CH_2OH	CH_3CO_2H
2	$CH_3CH_2NH_2$	$C_6H_5NH_2$
3	$C_6H_5O^-Na^+$	$C_6H_5CO_2^-Na^+$

Ans: A (**1**, **2** and **3**)

1 R is an alcohol, S is a carboxylic acid. S is more acidic so it has a lower pH than R.

2 R is an amine, S is a phenylamine. S is less basic than R because the lone pair of electrons from N in $C_6H_5NH_2$ is delocalised into the benzene right. So R has a higher pH.

3 R is a phenoxide, S is a carboxylate. R is a stronger conjugate base than S because R is from a weaker acid. So R has a higher pH.

35 Iron (III) oxide can be reduced by hydrogen gas to form iron and water.

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2\ Fe(s) + 3H_2O\ (g) \qquad \Delta H^{\theta} = +96\ kJ\ mol^{-1}$$

The table below shows the ΔS^{θ} of the reactants and the products of the reaction.

	Fe_2O_3	**H_2**	**Fe**	**H_2O**
S^{θ} /kJ mol^{-1} K^{-1}	0.090	0.131	0.027	0.189

Which of the following conclusions can be made?

1	The rate of reaction can only be increased by increasing the temperature of the system.
2	The ΔS^{θ} is +0.138 kJ mol^{-1} K^{-1}.
3	The reaction is not spontaneous.

Ans: C

1 The rate of reaction can also be increased by increasing the surface area of iron (III) oxide.
2 $\Delta S = 2(0.027) + 3(0.189) - 0.090 - 3(0.131) = +0.138\ kJ\ mol^{-1}\ K^{-1}$
3 $\Delta G = +96 - (273+50)(0.138) = +51.4\ kJ\ mol^{-1}$ (reaction is not spontaneous)

36 During electrolysis of an aqueous solution of rhodium sulfate, 1.00 mol of rhodium ions was discharged at the cathode. This required 2.90 x 10^5 C of electricity.

Which of the following conclusions can be drawn from the information above?

1 Effervescence will be observed at the anode.

2 The magnitude of the charge on the rhodium ions is three times the charge of an electron.

3 Rhodium is a transition element.

Ans: B (1 and 2 only)

1 SO_4^{2-} and H_2O will be present around the anode. As H_2O is preferentially discharged, oxygen gas is formed, resulting in effervescence.

2 Q = nF
2.90 x 10^5 = n(96500)
n = 3.01 (2 is true)

3 is true with reference to the Periodic Table, but it is not a conclusion from the observations.

37 The hexa-aquairon (III) ion hydrolyses as shown.

$$[Fe(H_2O)_6]^{3+} (aq) + H_2O (l) \rightleftharpoons [Fe(H_2O)_5OH]^{2+} (aq) + H_3O^+ (aq)$$

Which statements are correct?

1 The corresponding iron (II) ion, $[Fe(H_2O)_6]^{2+}$ is less likely to undergo hydrolysis.

2 The iron undergoes a change in oxidation state.

3 This hydrolysis is favoured by low pH values.

Ans: D (1 only)

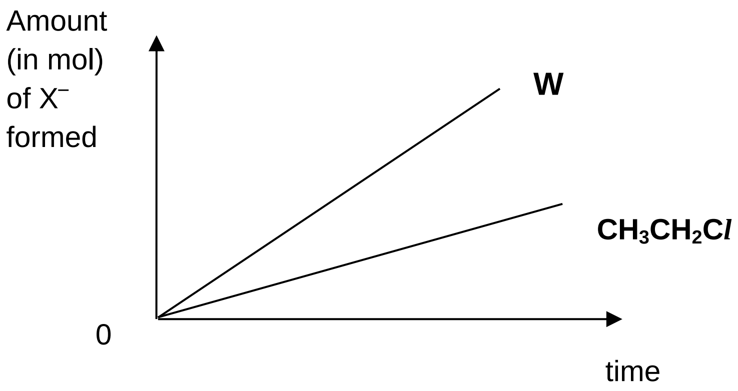
1 is correct. $[Fe(H_2O)_6]^{2+}$ is less polarising than $[Fe(H_2O)_6]^{3+}$ due to its lower charge density. Hence it is less likely to undergo hydrolysis.

2 is not correct. Oxidation state in $[Fe(H_2O)_5OH]^{2+}$ is also +3.

3 is not correct. At low pH, concentration of $[H_3O^+]$ is high. By LCP, equilibrium position will shift to the **left** to reduce $[H_3O^+]$ which does not favour hydrolysis.

38 Halogen-containing organic compounds can be hydrolysed under suitable conditions to produce the corresponding halide ions, X^-.

A student investigated the amount of Cl^- produced by hydrolysing CH_3CH_2Cl and another halogen-containing compound, **W**. In a given time the amount of X^- formed was greater with **W** than with CH_3CH_2Cl.



Which compound could be **W**?

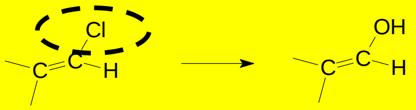
1	$CH_3CHClCH{=}CHCl$
2	CH_3CH_2COCl
3	$ClCH_2CH_2Cl$

Ans: C (2 and 3 only)

With reference to the diagram, the amount of X^- formed from **W** was at any point in time greater than CH_3CH_2Cl.

- **W** must be able to undergo hydrolysis **<u>more rapidly than CH_3CH_2Cl.</u>**

- **Option 1:**



Nucleophilic substitution cannot take place as the p-orbital of the chlorine atom overlaps with the π electrons of the C=C double bond in $CH_3CHClCH{=}CHCl$.
This strengthens the C–Cl bond in $CH_3CHClCH{=}CHCl$, hence making the chlorine atom unreactive.
Hence, this compound undergoes hydrolysis at about the same speed as CH_3CH_2Cl because of the other chlorine atom on carbon-3.

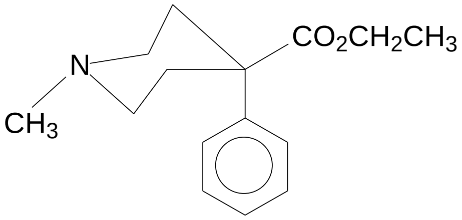
- **Option 2:**

<u>Acyl chloride</u> undergoes **<u>nucleophilic substitution more readily</u>** than alkyl chlorides due to the relatively larger δ+ charge developed in the carbonyl C atom as a result of electronegative O and Cl atoms. Hence, rate of forming X^- is higher.

- **Option 3:**

<u>Each mole</u> of $ClCH_2CH_2Cl$ contains **<u>2 moles of Cl</u>.** Hence, this compound undergoes hydrolysis at about twice the speed as CH_3CH_2Cl.

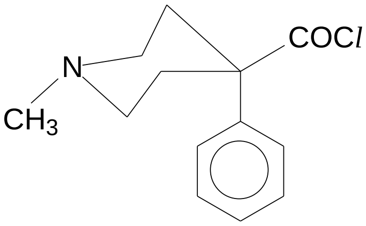
39 Pethidine is a narcotic analgesic drug, used as a substitute for morphine in the treatment of acute severe pain.



Pethidine

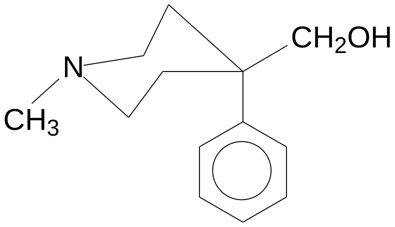
Which pairs of compounds would produce pethidine when reacted together?

1



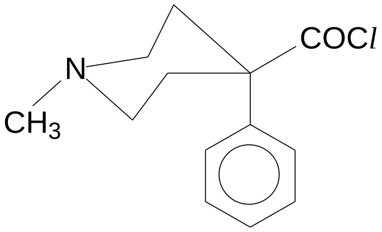
+ CH_3CH_2OH

2



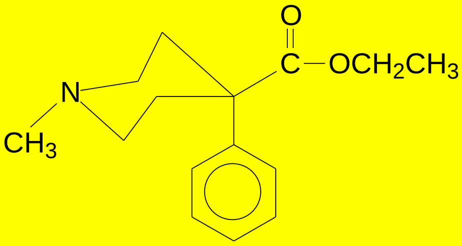
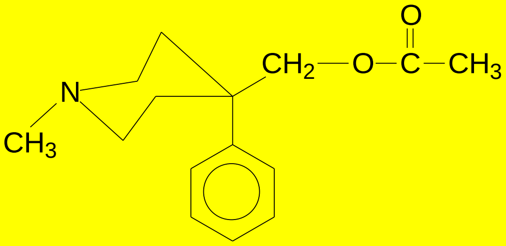
+ CH_3CO_2H

3



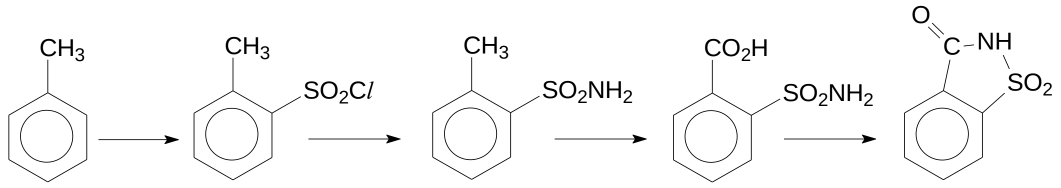
+ CH_3CO_2H

Ans: D (1 only)

Option	**Product formed**
1	 **pethidine**
2	

		A different ester is produced.
	3	No product. Acyl chloride do not react with carboxylic acid to form ester

40 Saccharin is an artificial sweetening agent. It can be synthesised from methylbenzene through a series of reactions as shown.



saccharin

What types of reactions are involved in the series of reactions?

1	Condensation
2	Electrophilic substitution
3	Nucleophilic substitution

Answer: **A**

Step 1: electrophilic substitution
Step 2: nucleophilic substitution
Step 3: oxidation
Step 4: condensation

END OF PAPER