CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/01

Paper 1 Multiple Choice

Wednesday 2 September 2015
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and HT group on the Answer Sheet in the spaces provided.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **forty** questions on 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 Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

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.
The use of an approved scientific calculator is expected, where appropriate.

WORKED SOLUTIONS

This document consists of **30** 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*** and record your choice in soft pencil on the ***separate Answer Sheet*** provided.

1 When 20 cm^3 of a gaseous hydrocarbon was completely burnt in 130 cm^3 of oxygen, the volume of gas remaining after the reaction was 100 cm^3. This volume was decreased to 40 cm^3 when the resulting mixture was passed through aqueous sodium hydroxide. All measurements were made at room temperature and pressure.

What is the formula of this hydrocarbon?

A C_2H_2 **B** C_3H_6 **C** C_3H_8 **D** C_4H_{10}

Answer: B

Since temperature and pressure are constant, mol ratio of gas ∝ vol ratio

	$C_xH_y(g)$ +	$(x+\frac{y}{4})O_2(g)$ →	$xCO_2(g)$ +	$\frac{y}{2}H_2O(l)$
Initial vol/ cm^3:	20	130	0	0
Final vol/ cm^3:	0	40	(100-40)	
Vol reacted or formed/ cm^3:	20	(130-40) = 90	60	
	1 vol	4.5 vol	3 vol	

∴ By inspection, x = 3.

$$(3+\frac{y}{4})=\frac{9}{2} \Rightarrow y = 6$$

∴ molecular formula of the hydrocarbon is C_3H_6

2 Consider the following half-equations:

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

What volume of 0.01 mol dm^{-3} potassium manganate(VII) is required to oxidise completely 25.0 cm^3 of an acidified solution of 0.01 mol dm^{-3} FeC_2O_4?

A 10 cm^3 **B** 15 cm^3 **C** 25 cm^3 **D** 42 cm^3

Answer: B

Both Fe^{2+} and $C_2O_4^{2-}$ ions can be oxidised by MnO_4^- ions which is reduced.
Hence, there are two oxidation half-equations to consider:
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ --- 1 and
$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ --- 2
So combine 1+2 first by summing up both half-equations to get:
$Fe^{2+} + C_2O_4^{2-} \rightarrow Fe^{3+} + 2CO_2 + 3e^-$ --- 3

Combine this equation with the reduction half-equation of MnO_4^-
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
To get: **$3MnO_4^- \equiv 5\ FeC_2O_4$**

Amount of FeC_2O_4 = 25/1000 x 0.01 = 2.50×10^{-4} mol
Amount of $KMnO_4$ reacted = $(2.50 \times 10^{-4} / 5) \times 3 = 1.50 \times 10^{-3}$ mol
Vol. of $KMnO_4$ required = $(1.50 \times 10^{-3}) / 0.01 = 1.50 \times 10^{-2}$ dm^3 = 15 cm^3

3 **X** and **Y** are elements with atomic numbers between 6 and 15.

Their first seven ionisation energies in kJ mol^{-1} are shown below.

X	580	1800	2700	11600	14800	18400	23300
Y	1310	3400	5300	7500	11300	13300	71300

Which of the following best describes the compound formed between **X** and **Y**?

A basic
B acidic
C neutral
D amphoteric

Answer: D
Calculate the difference between successive I.E.
For **X**, there is a sharp increase from the 3rd to 4th I.E. This indicates that the 4th electron is removed from an inner electron shell, closer and more tightly bound by the positively-charged nucleus. Thus, there are 3 valence electrons; **X** belongs to Group III, and is *Al*.
Using the same concept, there is a sharp increase from the 6th to 7th I.E. for **Y**. **Y** belongs to Group VI, and is O.
The compound formed from **X** and **Y** has the formula Al_2O_3 which is amphoteric in nature.

Alternatively, you can match the I.E. given to those given in the data booklet to determine the identity of **X** and **Y**.

4 Which pair of compounds fits the following descriptions?

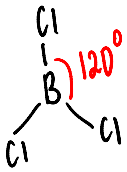
(i) The first compound has a larger bond angle about the central atom than the second compound **and**,
(ii) The second compound is more polar than the first compound.

	first compound	second compound
A	BCl_3	SO_2
B	CF_4	XeF_4
C	HCN	$BeCl_2$
D	PH_3	NH_3

Answer: A

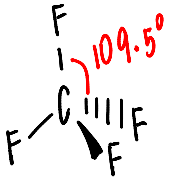
If necessary, draw the dot-and-cross diagrams of the compounds first.

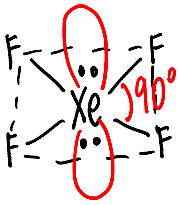
Option A:



SO_2 has a bent shape and a smaller bond angle than 120° due to the presence of the lone pair of electrons. (i) is satisfied.
(ii) is also satisfied as BCl_3 is non-polar while SO_2 has a net dipole moment and is polar.

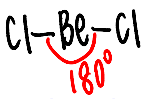
Option B:





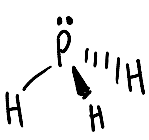
(i) is satisfied but (ii) is not as both are symmetrical and have no net dipole moment and are hence non-polar.

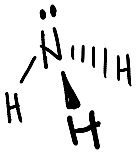
Option C:



(i) is not satisfied. (ii) is not satisfied as HCN is polar while $BeCl_2$ is not.

Option D: The more electronegative the central atom, the greater the repulsion between the bond pairs. N is more electronegative than P and pulls the bonded electron pairs closer to itself. Hence, the bonded electron pairs get closer to each other and repel much more, resulting in a larger bond angle for NH_3 (even though NH_3 and PH_3 are both trigonal pyramidal in shape).





5 Which of the following statements regarding covalent compounds is true?

A Tetrachloromethane is a volatile liquid because the C–C*l* bond can be broken easily.

B $CHCl_3$ has a higher boiling point than CHF_3 because it has more electrons than CHF_3.

C Hydrogen chloride is soluble in water because it can form permanent dipole-permanent dipole forces of attraction with water molecules.

D Each hydrogen bond formed between H_2O molecules is stronger than that formed between HF molecules.

Answer: B

Option A: For a simple covalent molecule like CCl_4, covalent bonds are not broken when a liquid boils/vaporizes. CCl_4 is non-polar and the weak intermolecular van der Waals' forces of attraction are overcome instead.

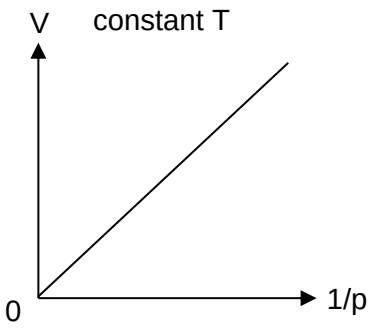
Option B: boiling point ∝ strength of van der Waals' forces ∝ no. of electrons

Option C: HC*l* when dissolved in water undergoes complete dissociation to form H^+ and Cl^- ions which form ion-dipole attractions with water molecules.

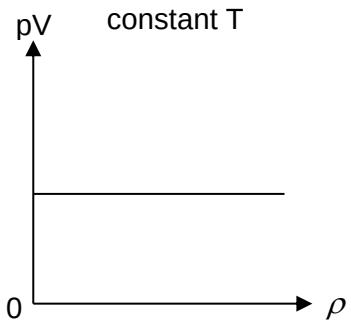
Option D: strength of hydrogen bond ∝ difference in electronegativity of the 2 atoms involved in the hydrogen bonding. O–H bond has a smaller electronegativity difference than H–F bond as O is less electronegative than F. Note: H_2O has a higher boiling point than HF as there are, on average, more hydrogen bonds between H_2O molecules than there are between HF molecules (H_2O has more extensive intermolecular hydrogen bonding than HF).

6 Which of the following diagrams **does not** describe the behaviour of a fixed mass of an ideal gas?
(ρ = density of the gas, T = temperature is measured in K)

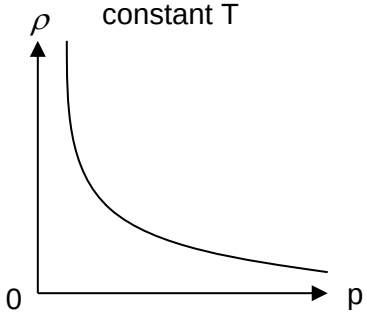
A



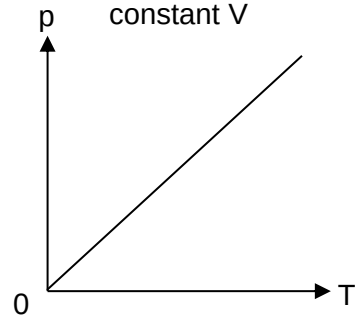
B



C



D



Answer: C

For a given mass of gas, the no. of moles of gas, n, will be constant since *Mr* unchanged.

$$pV = nRT$$

Option A: $V = nRT\left(\frac{1}{P}\right)$

$V = \text{constant} \times \left(\frac{1}{P}\right)$, at constant T for a given mass of gas.

Hence, $V \propto \left(\frac{1}{P}\right)$

Option B: $pV = nRT$

pV = constant, at constant T for given mass of gas, regardless of changes in P, V or ρ

Option C: $pV = nRT = \frac{m}{M_r}RT$

$\rho = \frac{m}{V} = \frac{M_r}{RT}(P) = \text{constant} \times (P)$, at constant T for a given mass of gas.

Hence, $\rho \propto P$ and it should be a Y = mX + C linear graph, passing through origin.

Option D:

$P = \frac{nR}{V}(T)$

$P = \text{constant} \times (T)$, at constant V for a given mass of gas.

Hence, $P \propto T$

7 A nitrogen–hydrogen mixture, initially in the mole ratio of 1:3, reached equilibrium with ammonia when 50 % of the nitrogen had reacted. The total final pressure was *p*.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

What was the partial pressure of ammonia in the equilibrium mixture?

A $\frac{p}{6}$ **B** $\frac{p}{4}$ **C** $\frac{p}{3}$ **D** $\frac{p}{2}$

Answer: C

Let the initial amount of N_2 and H_2 be 1 mol and 3 mol respectively.

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial amount/mol	1		3		-
Change/mol	–(50/100) x 1		–(0.5x3)		+(0.5x2)
Equilibrium amount/mol	0.5		1.5		1.0

At equilibrium, total amount of gas = 0.5 + 1.5 + 1.0 = 3.0 mol

$P_{NH3} = (1.0/3.0) \times p = p/3$ ($p_A = x_A \cdot p_T$) where x is the mole fraction of gas A

8. The heat liberated in the neutralisation given below is -57 kJ mol^{-1}.

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$$

By using this information, what is the most likely value for the heat liberated in the following neutralisation?

$$H_2SO_4\ (aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$

A -57 kJ mol^{-1} **B** -86 kJ mol^{-1} **C** -114 kJ mol^{-1} **D** -228 kJ mol^{-1}

Both neutralisations involve strong acid and strong base. The heat liberated in the neutralization to produce 1 mol of water = - 57 kJ mol^{-1}
The neutralisation between H_2SO_4 and NaOH produces 2 mol of water.
Thus, heat liberated = 2 (-57) = -114 kJ mol^{-1}

9 The value of ionic product K_w, at 35°C is 2.04 x 10^{-14}.

What is correct for pure water at 35 °C?

A pH < 7
B pH = 7
C $[H^+] < [OH^-]$
D $[OH^-] = 1.02 \times 10^{-14}$ mol dm^{-3}

Option A
Since water is neutral, $[H^+] = [OH^-] = (2.04 \times 10^{-14})^{1/2} = 1.43 \times 10^{-7}$ mol dm^{-3}
pH = -log (1.43 x 10^{-7}) = 6.85 <7

10. A solution of 20.0 cm^3 of 0.10 mol dm^{-3} sulfuric acid was titrated with 0.10 mol dm^{-3} ammonia.

Which statement regarding the titration is correct?

A The equivalence point is at pH 7.
B The initial pH of the solution is 1.
C 20.0 cm^3 of ammonia is required for titration for equivalence point to be reached.
D 80.0 cm^3 of ammonia is required for titration for maximum buffer capacity to be reached.

Statement A is incorrect: Since this is a weak base-strong acid titration, the salt obtained is acidic. Thus the equivalence point is less than pH 7.

Statement B is incorrect: Since sulfuric acid is a dibasic acid, the pH of the solution = -lg (0.10 x 2) = 0.700

Statement C is incorrect: since 2 mol of NH_3 is required to neutralize 1 mol H_2SO_4, thus 40 cm^3 of NH_3 is required to reach equivalence point.

Statement D is correct:
Volume required to reach maximum buffer capacity
= 2 x (Volume of NH_3 required for equivalence point)
= 2 x 40
= 80 cm^3

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

Soda is slightly acidic due to the dissolved carbon dioxide.

By considering the relevant $E^{\ominus}$ values, which metal will **not** be dissolved by the soda?

A V
B Ag
C Mg
D Sn

Since soda is acidic, $2H^+ + 2e^- \rightarrow H_2$ $E_{red}^{\ominus}$ = 0.00V
To determine whether metal will not dissolve by soda, $E_{cell}^{\ominus}$ <0. This will indicate the reaction is non-spontaneous.

Equation	$E_{oxi}^{\ominus}$	Overall equation	$E_{cell}^{\ominus}$<0
$V^{2+} + 2e^- \rightarrow V$	-1.20	$V + 2H^+ \rightarrow H_2 + V^{2+}$	+1.20
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Ag + 2H^+ \rightarrow H_2 + Ag^+$	-0.80
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.38	$Mg + 2H^+ \rightarrow H_2 + Mg^{2+}$	+2.38
$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14	$Sn + 2H^+ \rightarrow H_2 + Sn^{2+}$	+0.14

Hence, Ag cannot dissolve in an acidic solution.

12. 15.7 g of the metal gadolinium (Gd) was deposited in electrolysis by a current of 5 A for 96.5 minutes. What is the formula of gadolinium ions?
[A_r of Gd = 157]

A Gd^{+}
B Gd^{2+}
C Gd^{3+}
D Gd^{4+}

Q = It = (5)(60)(96.5) = 28950C
= (28950/96500) F = 0.3F
No. of moles of Gd = 15.7/157 = 0.1

Gd^{n+} + n e^{-} → Gd
Quantity of electricity required to deposit 0.1 mol of Gd = 0.3F
no. of mol of electrons: no. of mol of Gd = 0.3: 0.1
n = 3
Thus, formula of Gd ion is Gd^{3+}.

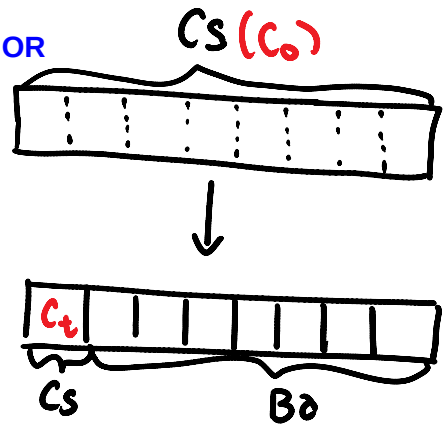
13. Barium is the final product formed by a series of changes in which the rate-determining step is the radioactive decay of caesium-137. This radioactive decay is a first-order reaction with a half-life of 30 years.

How long would it take for a rock sample, originally barium-free, to contain a molar proportion of caesium-137 to barium of 1:7?

A 15 years
B 30 years
C 60 years
D 90 years

Cs: x → ½ x → ¼ x → 1/8 x
Ba: 0 → ½ x → ¾ x → 7/8 x
n = 3 half-lives
Time taken = 30 x 3 = 90 years

OR



Using $\frac{c_t}{c_o} = (\frac{1}{2})^n$

$\frac{1}{1+7} = (\frac{1}{2})^n$

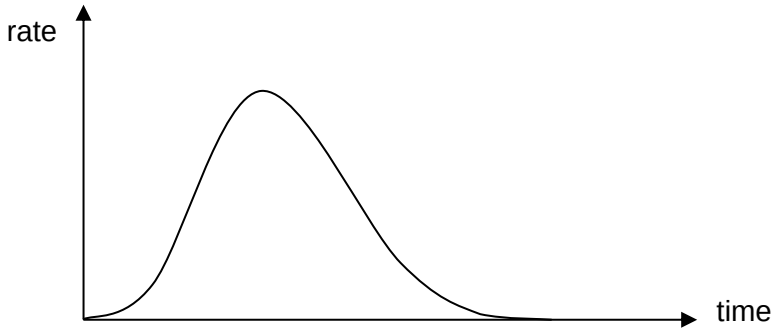
n = 3 half-lives

Time taken = 30 x 3 = 90 years

14. The reaction between chlorite ions, ClO_2^-, and iodide ions, I^-, in acid solution may be represented by the following equation.

$$ClO_2^- + 4I^- + 4\ H^+ \longrightarrow 2I_2 + Cl^- + H_2O$$

The rate-time graph for this reaction is as shown below.

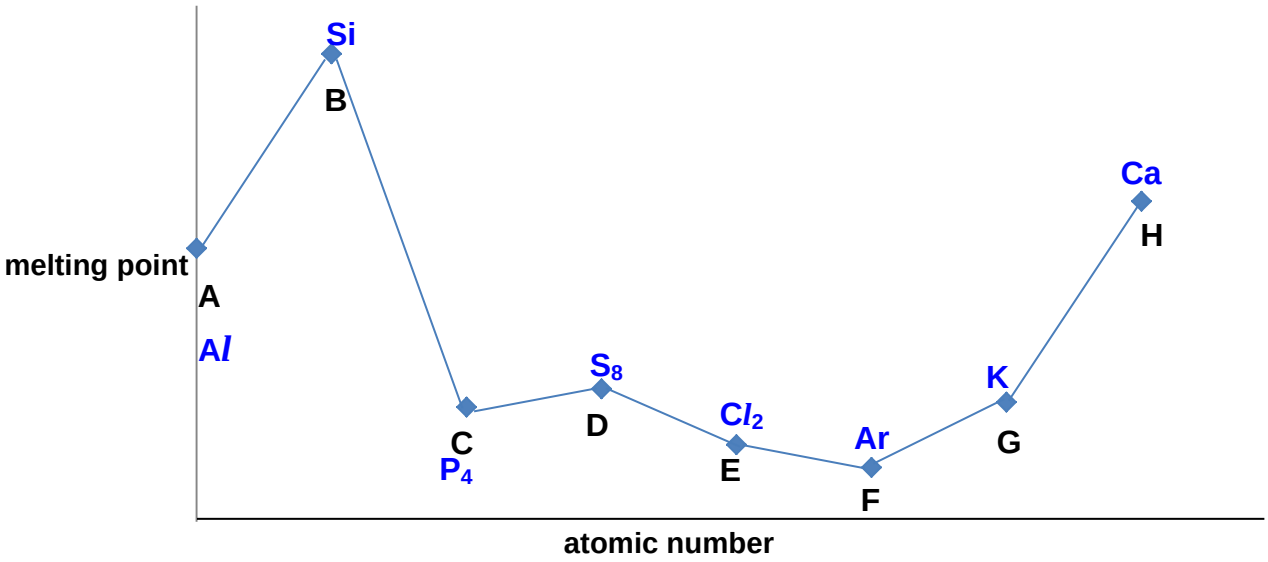


What does the shape of the graph suggest about this reaction?

A The reaction is endothermic.
B The reaction is overall first order.
C The reaction produces its own catalyst.
D The reaction rate is independent of iodide ions.

This is an example of autocatalytic reaction. The rate of reaction is slow at first but increases as the catalyst (product) is produced.

15 The graph below shows the variation in the melting points for eight consecutive elements, **A** - **H**, in the Periodic Table, all with atomic number between 10 and 20.



What can be deduced from the graph?

A The chloride of element **C** fumes in moist air.

PCl_3 and PCl_5 hydrolyse in water to give HCl, which appears as white fumes.

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

B Element **F** exists as a diatomic molecule.

F is a noble gas and exists as monoatomic gas.

C The oxide of element **B** dissolves in water to give an acidic solution.

SiO_2 has a giant covalent structure and is insoluble in water.

D Element **A** has a higher first ionisation energy than the element preceding it.

Al has a lower first ionisation energy than Mg since the electron removed from Al is from a higher energy 3p orbital, as compared to that of Mg which involves 3s orbital. (Note that the exceptions to the trend occur in Groups III and VI.)

16 Which of the following statements about the Group II elements (from Mg to Ba) or its compounds is **incorrect**?

A The ease of thermal decomposition of Group II nitrates decreases down the group.

Ease of thermal decomposition decreases down the group. From Mg^{2+} to Ba^{2+}, the ionic charge remains the same but ionic radius increases. Thus, charge density of the cation decreases down the group. The nitrate ion is less polarised and thermal decomposition occurs less readily.

B The reactivity of the elements with chlorine gas increases down the group.

Group II metals undergo redox reactions with Cl_2. The reducing strength of Group II metals increases down the group. Down the group, the atomic size of atom and shielding effect increases and thus it is easier for the atom to lose two electrons. The reactivity of the metals with Cl_2 would increase down the group. (Recall from Group VII that Cl_2 is an oxidising agent.)

C The melting point of the oxides increases down the group.

Group II oxides are ionic compounds and lattice energy is an indication of the ionic bond strength.

$$\text{Lattice energy} \propto \frac{q^+q^-}{r_+ + r_-}$$

Since ionic radius of the metal cation increases down the group, the lattice energy of the metal oxide becomes less exothermic. The ionic bond strength becomes weaker down the group and thus melting point of the oxides should decrease.

D The volume of gases formed per gram of carbonate decomposed decreases down the group.

$MCO_3 \rightarrow MO + CO_2$

The M_r of the metal carbonate increases down the group. Thus the number of mol per gram of metal carbonate decreases down the group. Amount of CO_2 formed and thus volume of gas formed would decrease.

17 Some properties of two salts, **M** and **N**, are given below.

When salt **M** was mixed with concentrated sulfuric acid, a colourless gas was produced. An aqueous solution of this colourless gas gave a white precipitate with silver nitrate. The precipitate readily dissolved in aqueous ammonia.

Since the precipitate is readily dissolved in aqueous ammonia, precipitate formed is AgC*l*. Thus salt A must contain a C*l*$^-$ ion. The colourless gas evolved is HC*l*.

When salt **N** was heated with concentrated sulfuric acid, two gases were evolved. One gas has a red-brown colour while the other turned acidified potassium dichromate(VI) paper from orange to green.

The red-brown gas is Br_2 and thus salt B must contain Br$^-$. The other gas is SO_2.

$KBr + H_2SO_4 \rightarrow HBr + KHSO_4$

HBr is then oxidised by H_2SO_4:

$2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$

Which of the following are possible identities of salt **H** and **J**?

	salt **M**	salt **N**
A	NaC*l*	KBr
B	NaBr	KI
C	KI	NaBr
D	KC*l*	NaI

18 *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 equation.

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

The reaction can be catalysed by a homogenous catalyst. Given that the standard electrode potential for the following half-equation 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 can be a suitable catalyst for this reaction?

A Cu^{2+}

B Cr^{2+}

C Mn^{2+}

D V^{2+}

Ans: C

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ $\quad E^\theta = +2.01\ V$
$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons [CH(OH)CO_2]_2^{2-} + 2H_2O$ $\quad E^\theta = + 0.56\ V$

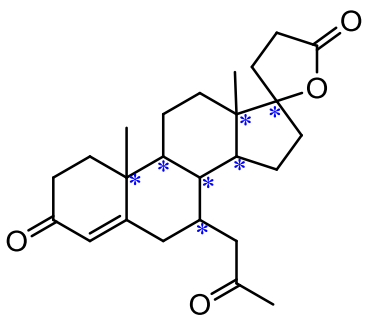
$Cu^{2+} + 2e \rightleftharpoons Cu^+$ $\quad E^\theta = +0.15\ V$
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$ $\quad E^\theta = -0.41\ V$
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$ $\quad E^\theta = +1.49\ V$
$V^{3+} + e \rightleftharpoons V^{2+}$ $\quad E^\theta = -0.26\ V$

Catalyst chosen must have a value between +0.56 V and +2.01 V in order to reduce $S_2O_8^{2-}$ and to oxidize $[CH(OH)CO_2]_2^{2-}$.

Catalysed reaction using Mn^{2+}
$2Mn^{2+} + S_2O_8^{2-} \rightleftharpoons 2Mn^{3+} + 2SO_4^{2-}$
$E^\theta_{cell} = 2.01 - (1.49) = + 0.52V$

$6Mn^{3+} + [CH(OH)CO_2]_2^{2-} + 2H_2O \rightleftharpoons 6Mn^{2+} + 2CO_2 + 2HCO_2^- + 6H^+$
$E^\theta_{cell} = 1.49 - 0.56 = + 0.93\ V$

19 The diagram shows the structure of *Spironolactone*, which is an anti-androgen used in hormone therapy.



How many stereoisomers does *Spironolactone* have?

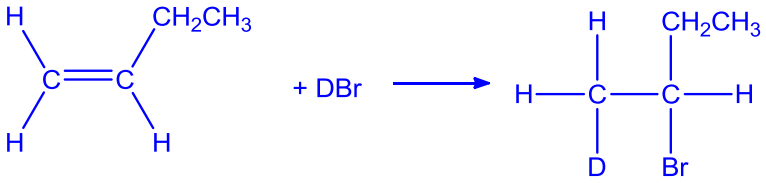
No. of stereoisomers = $2^n = 2^7$

A 2^3 **B** 2^4 **C** 2^6 **D** 2^7

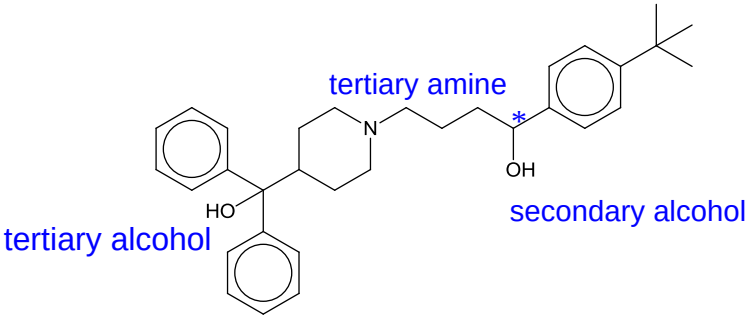
20 What is the major product of the reaction between but-1-ene and gaseous DBr? (D = ^{2}H)

A $CH_3CH_2CH(OD)CH_2Br$ **B** $CH_2DCHBrCH_2CH_3$
C $CH_2BrCHDCH_2CH_3$ **D** $CH_3CHDCH_2CH_2Br$

This reaction is similar to the electrophilic addition reaction with HBr.
Apply Markovnikov's rule.
General guide to get the Markovnikov's product: The electrophile (in this case, δ+ D) will go to the carbon in the C=C with more H directly attached to it.



21 *Terfenadine* (sold under the trade name *Seldane*) alleviates seasickness and asthma in the same way as the older drugs, but it does not cause drowsiness as a side effect.



terfenadine

What deductions about *terfenadine* can be made from this structure?

A It is soluble in aqueous sodium hydroxide.
Alcohols do NOT react with NaOH.

B It is chiral and contains a primary amine group.
There is one chiral carbon but it contains a tertiary amine instead.

C It can be oxidised to form a product which can react with ammoniacal silver nitrate solution.
Secondary alcohols are oxidised to ketones while tertiary alcohols cannot be further oxidised.
Recall that only aldehydes react with Tollens' reagent..

D One mole of *terfenadine* will give out one mole of hydrogen on reaction with two moles of sodium.
1 – OH ≡ ½ H_2 ≡ 1 Na
1 mole of terfenadine contains 2 –OH groups which will react with 2 moles of Na and form 1 mole of H_2 gas.

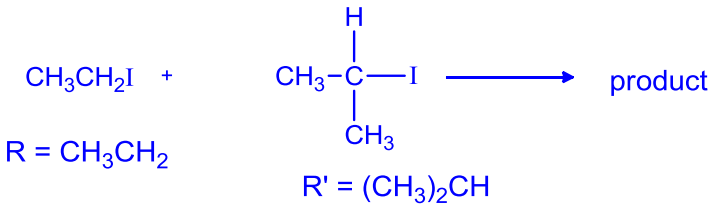
22 An iodoalkane and sodium react when heated under reflux in an inert organic solvent to form an alkane according to the equation:

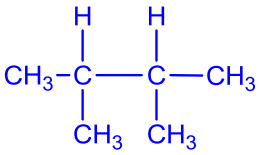
$$2RI + 2Na \longrightarrow R–R + 2NaI$$

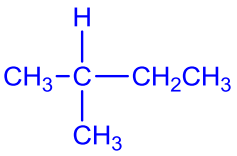
When a mixture of equal number of moles of the two different iodoalkanes, CH_3CH_2I and CH_3CHICH_3, is used, which of the following alkanes will **not** be formed?

A $(CH_3)_2CHCH(CH_3)_2$ **B** $CH_3CH_2CH(CH_3)_2$
C $CH_3CH_2CH_2CH_3$ **D** $CH_3CH_2CH_2CH_2CH_2CH_3$

Pattern recognition question.



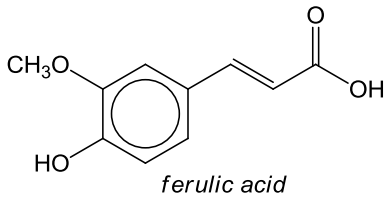
A  R'-R'

B  R'-R

C $CH_3CH_2CH_2CH_3$ R-R

D $CH_3CH_2CH_2CH_2CH_2CH_3$ will NOT be formed

23 *Ferulic acid*, is an antioxidant that is reactive towards free radicals implicated in DNA damage, cancer, and accelerated cell aging.



ferulic acid

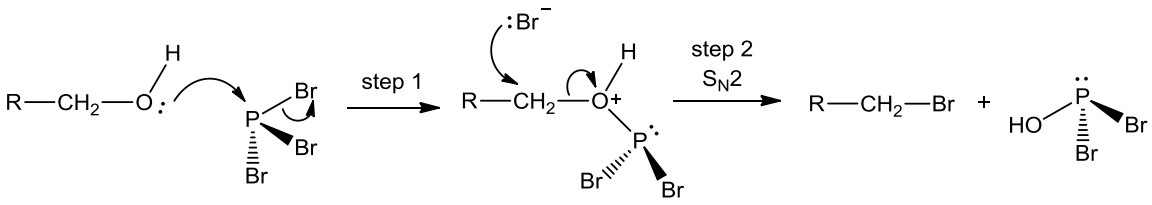
Assuming the CH_3O- group is inert. Which statement about *ferulic acid* is correct?

A One mole of *ferulic acid* reacts with only one mole of bromine.
B An ester is formed when *ferulic acid* is heated with propanoic acid in the presence of concentrated sulfuric acid.
C One mole of *ferulic acid* reacts with only one mole of thionyl chloride.
D *Ferulic acid* reacts with lithium aluminium hydride in dry ether to form a product that does not exhibit geometric isomerism.

Answer: C

A Aside from electrophilic addition of bromine, ferulic acid will also undergo electrophilic substitution with bromine.
B Phenols will not react with carboxylic acids to form esters. Phenyl esters involve the reaction of the phenolic functional group with acyl chlorides.
C Only carboxylic acid reacts with $SOCl_2$. Phenol does not react with $SOCl_2$.
D Lithium aluminium hydride does not react with alkene to form alkane.

24 Bromoalkanes are commonly prepared by reacting either a primary or secondary alcohol with phosphorus tribromide, PBr_3. The reaction usually involves two steps, and the mechanism is shown below:



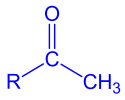
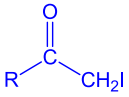
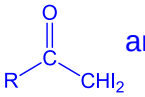
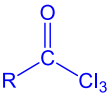
Which of the following statements regarding the reaction shown is correct?

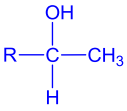
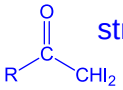
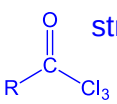
A The rate of reaction for step 1 is independent of the concentration of the alcohol.
B Both step 1 and step 2 involve the formation of a 5-coordinated transition state.
C The reaction can be carried out in aqueous medium.
D The alcohol acts as a nucleophile in step 1.

Answer: D
A The alcohol is involved in the formation of the intermediate species in step 1.
B Only step 2 involves the formation of a 5-coordinated transition state via S_N2.
C PBr_3 will react with water to form H_3PO_3 and HBr.
D The oxygen atom in the alcohol donates a lone pair of electrons to the electron deficient phosphorous atom in PBr_3 to form a dative covalent bond,

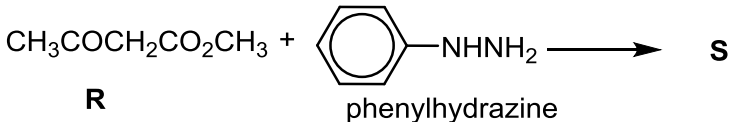
25 Which compound will **not** produce yellow precipitate on warming with alkaline aqueous iodine?

A $CH_3CH_2CH(OH)CH_3$
B $ICH_2COCH_2CH{=}CH_2$
C $CH_3CO_2CHI_2$
D I_3CCOCI_3

Aside from  , aldehydes and ketones with  and  and  will also undergo positive iodoform test as the iodine substitution of the $-CH_3$ group attached to the carbonyl group occurs stepwise.

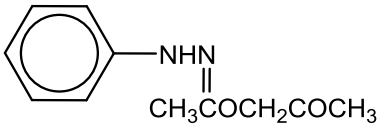
Answer: C
A Alcohols that have  structure give a positive iodoform test.
B  structure is present.
C $CH_3CO_2CHI_2$ is an ester that will not give a positive iodoform test.
D  structure is present.

26 The reaction between compound **R** and phenylhydrazine gives rise to a precursor compound **S**, used in the formation of *Phenazone*, an anti-inflammatory drug.

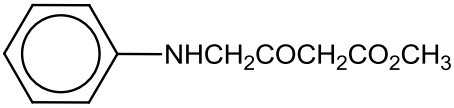


Which of the following is the correct structure of **S**?

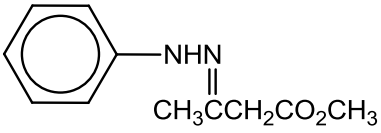
A



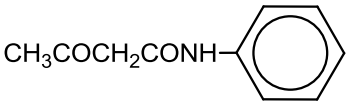
B



C



D



R, which contains the ketone functional group, undergoes condensation reaction with phenylhydrazine, similar to 2,4-DNPH.

Answer: C

A The ester functional group in **R** does not undergo condensation with phenyhydrazine.

B The formation of a 2^{o} amine with loss of NH_3 from the reaction between phenyhydrazine and **R** does not take place.

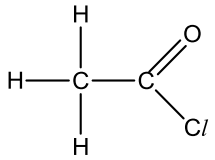
C Condensation takes place between the ketone functional group in **R** with phenylhydrazine.

D The amide shown is not formed from the reaction between **R** and phenylhydrazine.

27 1 g of each of the following compounds was heated with NaOH(aq). After cooling, HNO_3(aq) was added followed by $AgNO_3$(aq).

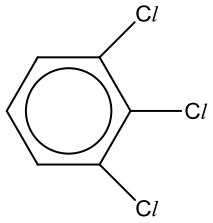
Which compound will produce the largest mass of white precipitate?

A



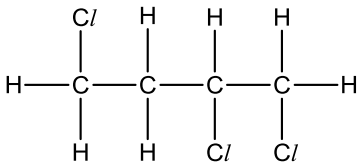
C_2H_3OCl
$M_r = 78.5$

B



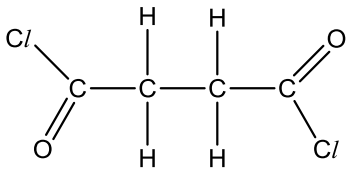
$C_6H_3Cl_3$
$M_r = 181.5$

C



$C_4H_7Cl_3$
$M_r = 161.5$

D



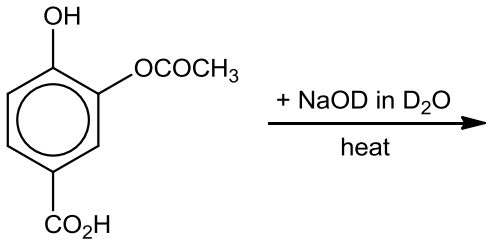
$C_4H_4Cl_2O_2$
$M_r = 155$

Answer: C

Halogenoalkane and acyl chlorides can undergo hydrolysis but not halogenoarenes.

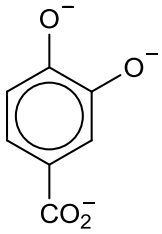
Compound	No. of moles of compound in 1 g	No. of moles of AgCl formed
A	0.0127	0.0127 x 1 = 0.0127
B	0.00550	0 (no hydrolysis due to partial double bond character)
C	0.00619	0.00619 x 3 =0.0185
D	0.00645	0.0645 x 2 =0.0129

28 Deuterium, D, is a heavier isotope of hydrogen. Which of the following shows the correct product when Compound **K** reacts as shown below?

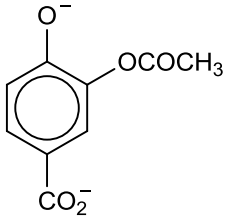


Compound **K**

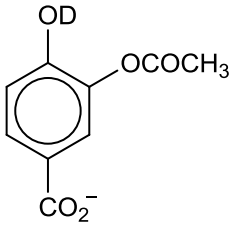
A



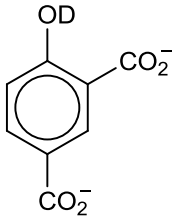
B



C



D



Answer: A

There are 3 functional groups (phenol, ester and carboxylic acid) present in K that can react with NaOD in D_2O under heating.

After reacting with NaOD, -OH in phenol and carboxylic acid loses a proton to give $–O^-$ and $–CO_2^-$ respectively. The ester group ($–OCOCH_3$) attached to the benzene ring is hydrolysed to give $–O^-$ and $CH_3CO_2^-$.

29 Liquid **Q** is sparingly soluble in water but dissolves readily in cold sulfuric acid. 1 mol of **Q** reacts with 3 mol of Br_2(aq).

Which of the following is a possible identity of **Q?**

A $C_6H_5CO_2H$ **B** $C_6H_5NH_2$ **C** $CH_3(CH_2)_5NH_2$ **D** $C_6H_5CH{=}CH_2$

Answer: B

Compound	Solubility in water	Solubility in H_2SO_4	Reaction with Br_2(aq)
$C_6H_5CO_2H$	Soluble as benzoate ion is formed during dissociation	Does not react with H_2SO_4	No reaction
$C_6H_5NH_2$	Sparingly soluble due to formation of H-bonding	Soluble as $C_6H_5NH_3^+$ ions are formed	Reacts with 3 moles of Br_2(aq)
$CH_3(CH_2)_5NH_2$	Sparingly soluble due to formation of H-bonding	Soluble as $CH_3(CH_2)_5NH_3^+$ ions are formed	No reaction
$C_6H_5CH{=}CH_2$	Insoluble	Does not react with H_2SO_4	Reacts with 1 mole of Br_2(aq)

Since only B fits all 3 criteria, B is a possible identity of **Q**.

30 Consider the following compounds below:

I $C_6H_5NH_2$ **II** $CH_3CH_2CONH_2$ **III** $CH_3CH(Cl)NH_2$ **IV** $CH_3CH_2NH_2$

Which of the following shows the correct order of decreasing pK_b values for the above compounds?

A **II, III, IV, I**
B **II, I, III, IV**
C **III, IV, I, II**
D **IV, III, I, II**

Answer: B

The stronger the base, the lower the pK_b value. Basicity depends on the availability of lone pair of electrons on N atom to attract a proton.

IV is the most basic as it has an electron-donating group (CH_3CH_2-) which increases the availability of lone pair of electrons on N atom to attract a proton.

III is a weaker base than **IV** due to the presence of an electron-withdrawing C*l* atom that decreases the availability of lone pair of electrons on N atom to attract a proton.

I is the weakest base as the lone pair of electrons on N can be delocalised into the benzene ring thus making the lone pair of electrons on N atom unavailable to attract a proton.

II is an amide which is neutral so it would have the highest pK_b value.

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

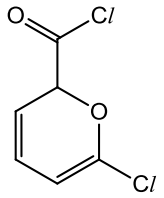
The responses **A** to **D** should be selected on the basis of

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 used as a correct response.

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

Compound **L** (M_r = 179) has the structure as shown:



Which of the following statements about compound **L** are correct?

1 The empirical formula of **L** is C_3H_2ClO.
2 179 g of **L** requires 319.6 g of bromine dissolved in an inert organic solvent for complete reaction.
3 Upon complete reaction with aqueous $AgNO_3$, 358 g of **L** forms 287 g of white precipitate.

Answer: A (1, 2 and 3)

Compound **L** has the molecular formula of $C_6H_4Cl_2O_2$

1: Empirical formula of **L** is C_3H_2ClO. Statement 1 is correct.

2: 179 g of **L** gives 1 mol of **L**. **L** contains 2 C=C therefore 1 mol of **L** will react with 2 mol of Br_2 in CCl_4.
2 mol of Br_2 = 2 (79.9x2) = 319.6 g. Statement 2 is correct.

3: Compound **L** contains 1 acyl chloride and 1 Cl that is directly attached to a C across the C=C, therefore, only the acyl chloride can be hydrolysed to produce Cl^-.
358 g of **L** gives 2 mol of **L**. 2 **L** ≡ $2Cl^-$ (from 2 mol of acyl chloride)
Mass of AgCl produced = 2 (108+35.5) = 287 g Statement 3 is correct.

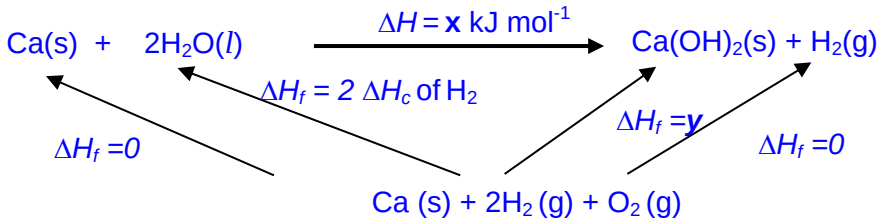
32 The enthalpy change of reaction between calcium and water is measured in the laboratory and found to be **x** kJ mol^{-1}.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g) \qquad \Delta H = \mathbf{x} \text{ kJ mol}^{-1}$$

What other information is needed to calculate the ΔH_f of $Ca(OH)_2(s)$?

1 enthalpy change of combustion of hydrogen
2 lattice energy of calcium hydroxide
3 enthalpy change of atomisation of calcium

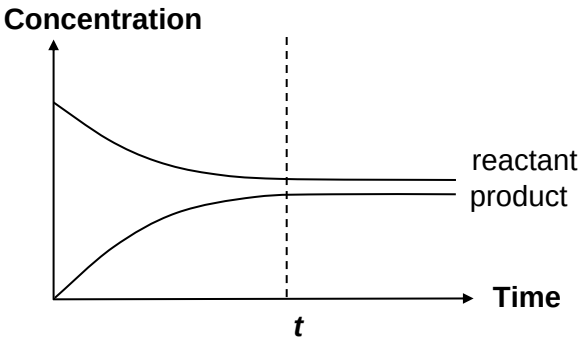
Answer: D (1 only)



1: Equation for combustion of hydrogen : $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$
Enthalpy change of formation of H_2O = 2x(enthalpy change of combustion of hydrogen.) This information is required to find the value for **y** in the energy cycle above.

From the energy cycle above, information **2** and **3** are not required.

33 The following graph is obtained from an experiment.



Which of the following are **not** correct statements about the reaction above?

1 At time ***t***, dynamic equilibrium is achieved.
2 Addition of a catalyst increases the magnitude of ***t***.
3 Upon addition of a catalyst, at time ***t***, the [product] to [reactant] ratio increases.

Answer: C (2 and 3)

At time t, there are no changes to the reactant and product concentrations respectively and the system has reached dynamic equilibrium. Statement 1 is correct.

A catalyst speeds up the reaction rate by providing an alternative reaction pathway with lower activation energy and thus equilibrium is reached faster. Magnitude of t should decrease when catalyst is added. Statement 2 is not correct.

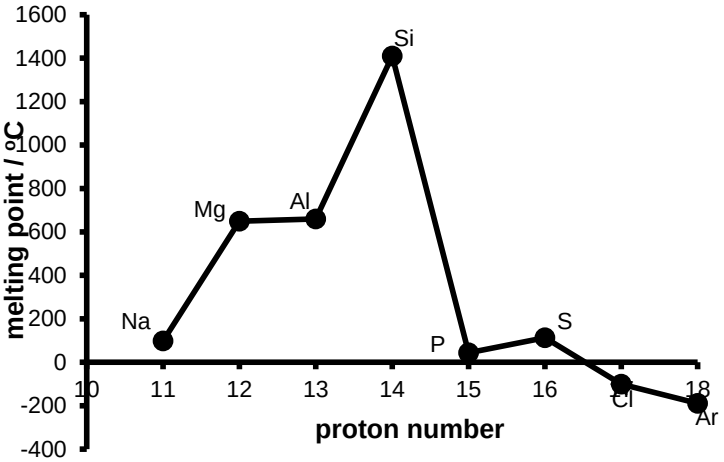
A catalyst has no effect on the position of equilibrium, and so, does not alter the composition of the equilibrium mixture. At time t, the [product] to [reactant] ratio stays the same. Statement 3 is not correct.

34 Which is **not** a trend from left to right across the elements of the third period of the Periodic Table?

1 melting points of the elements decrease steadily
2 compounds of the elements change from ionic to covalent
3 oxides of the elements change from basic to acidic.

Answer: D

Option 1 is correct only; recall melting point trend:



Melting points for Na to Ar

35 During anodising of aluminium, 1 mol dm^{-3} aqueous H_2SO_4 is electrolysed between A*l* anode and graphite cathode, using a constant current for 60 s.

What affects the mass of oxide layer deposited on the A*l* anode?

1 increasing the time taken
2 changing the electrolyte to 1 mol dm^{-3} aqueous HC*l*
3 increasing the concentration of the electrolyte solution

Answer: D

Option 1 is correct.

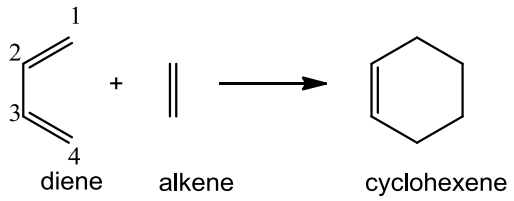
Recall that mass of elements liberated during electrolysis only depends on (i) quantity of electricity (time of passing steady current & magnitude of steady current passed) & (ii) charge on the ion of element.

Option 1: Increasing time will increase the mass of oxide layer deposited on the anode.

Option 2: Changing the anion in the electrolyte from SO_4^{2-} to Cl^- does not change the anode reaction (water is still being oxidised to O_2.)

Option 3: Increasing concentration of the H_2SO_4 (aq) solution will not cause further change in mass of oxide layer deposited.

36 The Diels-Alder reaction is a cycloaddition that occurs between an **"electron-rich"** conjugated diene and **"electron-poor"** alkene, forming a cyclohexene ring.



Which of the following statements about this reaction are correct?

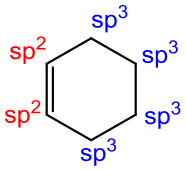
1 During the cycloaddition, carbons 1 and 4 of the diene and the two alkene carbons will change from being sp^2 hybridised to being sp^3 hybridised.

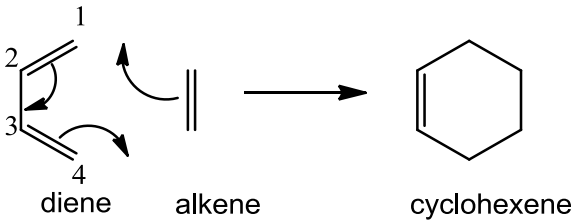
2 The presence of a –CHO substituent on the alkene molecule will increase the rate of the Diels-Alder reaction.

3 The presence of a $–CH_3$ substituent on the diene molecule will increase the rate of the Diels-Alder reaction.

Answer: A

Option 1: Correct;

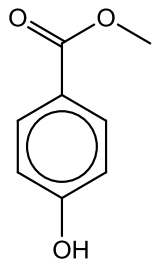




Option 2: Correct; –CHO is an electron-withdrawing substituent which will reduce the electron density of the alkene, causing it to be more "electron-poor", thus increasing the rate of reaction.

Option 3: Correct; the $–CH_3$ substituent is an electron-donating substituent which will increase the electron density of the diene, causing it to be more electron-rich, thus increasing the rate of reaction.

37 *Methylparaben* is an anti-fungal agent that is commonly used in a variety of cosmetic and personal care products.



methylparaben

Which deductions about the reactions of *methylparaben* can be made from its structure?

1 It can decolourise hot acidified $KMnO_4$ solution.
2 It can react with PCl_5 to form steamy fumes.
3 It can react with hydrogen cyanide in the presence of trace amount of NaCN.

Answer: D

Option 1: Correct; ester functional group will first undergo acid hydrolysis to form CH_3OH which in turn undergoes oxidation in presence of $KMnO_4$.

Option 2: Incorrect; methylparaben can only undergo electrophilic substitution but not nucleophilic substitution (due to partial double bond character between C and O atoms of phenolic group).

Option 3: Incorrect; reaction with HCN in presence of NaCN not possible due to absence of carbonyl functional group.

38 Keratin is a fibrous and insoluble protein found in hair, nails and horns of mammals. It comprises mainly of the three amino acids below:

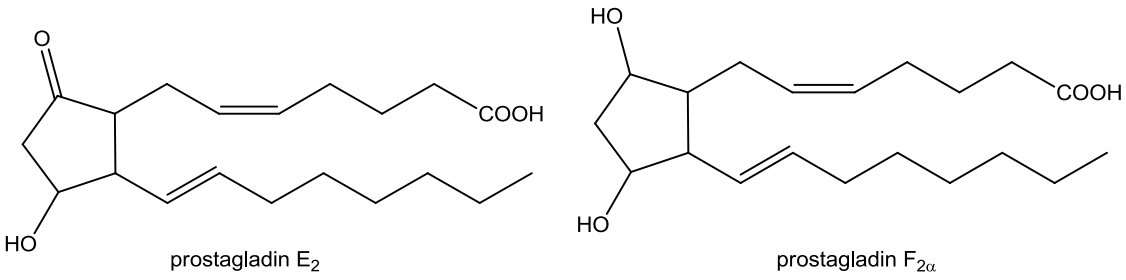
$NH_2CH(CH_2SH)CO_2H$	$NH_2CH(CH_2OH)CO_2H$	$NH_2CH(CH_2CH_2CO_2H)CO_2H$
cysteine	serine	glutamic acid

Based on the above information, what type of bonding would stabilise the tertiary structure of keratin?

1 disulfide bonds
2 hydrogen bonding
3 van der Waals' forces

Answer: B
Options 1 & 2 are correct.
Option 1: Correct; due to presence of $-CH_2SH$
Option 2: Correct; due to presence of $-CH_2OH$
Option 3: Incorrect

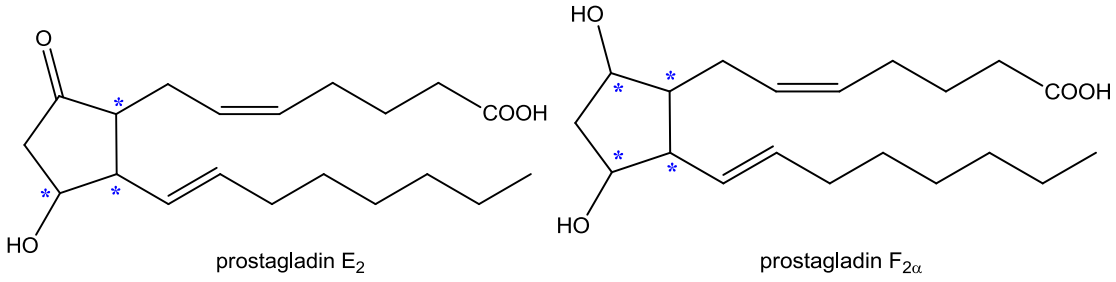
39 The prostaglandins are biomolecules with a wide range of biological effects which include lowering blood pressure and gastric secretion.



Which of the following statements correctly describe the two prostaglandin molecules shown above?

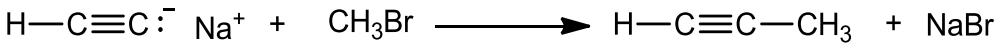
1 Both prostaglandin E_2 and $F_{2\alpha}$ are optically active molecules.
2 Prostagladin E_2 can be converted into prostaglandin $F_{2\alpha}$ by reacting with hydrogen in presence of nickel catalyst.
3 Both prostaglandin molecules will form a silver mirror with Tollens' reagent.

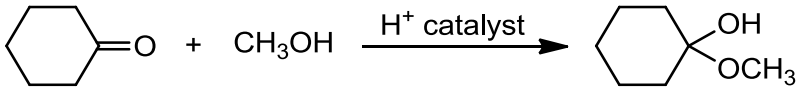
Answer: D
Option 1 is correct only.
Option 1: True; both prostaglandin molecules consist of chiral carbons as highlighted by * below:

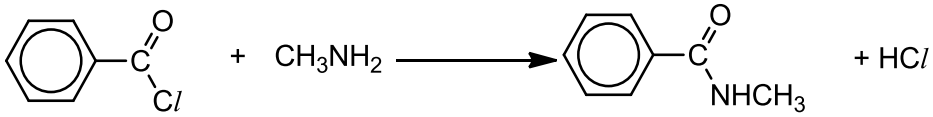


Option 2: False; the alkene functional groups in prostaglandin E_2 will also undergo reduction in presence of H_2/Ni thus prostaglandin $F_{2\alpha}$ will not form.
Option 3: False; both do not contain the aldehyde functional group and thus will not give silver mirror with Tollens' reagent.

40 Which of the following transformations involve a nucleophile?

1 

2 



Answer: A
Options 1, 2 & 3 are all correct.
Option 1: Nucleophilic substitution (S_N2) of CH_3Br; nucleophile: $H\text{-}C{\equiv}C^-$
Option 2: Nucleophilic addition of CH_3OH to ketone; nucleophile: CH_3OH
Option 3: Nucleophilic acyl substitution; nucleophile: CH_3NH_2

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