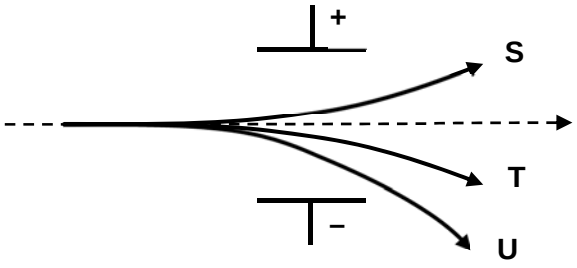
NJC 2018 SH2 H2 Chemistry Paper 1 Solutions:

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

The following are flight paths of charged particles when accelerated in an electric field.



Which correctly identifies **S**, **T** and **U**?

	S	T	U
A	$^{15}O^{+}$	$^{14}C^{+}$	$^{14}N^{+}$
B	$^{15}O^{-}$	$^{15}O^{+}$	$^{28}Si^{+}$
C	$^{14}N^{-}$	$^{28}Si^{2+}$	$^{14}C^{2+}$
D	$^{14}N^{-}$	$^{14}C^{+}$	$^{28}Si^{2+}$

C: Negatively charged ions attracted to positive plate, positive ions to negative plate.

particles	$^{14}N^{-}$	$^{14}C^{2+}$	$^{14}C^{+}$	$^{28}Si^{2+}$
Charge /mass	1/14	2/14 = 1/7	1/14	2/28 = 1/14

Since angle of deflection is charge/mass ratio, **S** and **T** have roughly the same angle of deflection but different polarity, while **U** has almost double the angle of deflection as **T**.

2 In which sequence is the molecules listed in the order of increasing dipole m

A SO_3, CO_2, $AlCl_3$

All non-polar. Dipole moments cancel out due to shape of molecule.

B H_2O, H_2S, HBr

H_2O and H_2S have bent shape. **H_2O is more polar than H_2S** as O is more electronegative than S.

C CF_4, CO, HF

CF_4 is non-polar, dipole moments cancel out due to tetrahedral shape of molecule.
CO and HF are linear. HF is more polar than CO, as electronegativity difference is greater between H and F than between C and O.

D NH_3, HF, $BeCl_2$

NH_3 and HF are polar but $BeCl_2$ is non-polar, dipole moments cancel out due to linear shape of molecule.

3 In which row are the molecules arranged in order of increasing bond angle?

1 CH_4, $AlCl_3$, XeF_2

CH_4 (tetrahedral, 109 degrees)
$AlCl_3$ (trigonal planar, 120 degrees)
XeF_2 (linear, 180 degrees)

2 H_2S, PH_3, NH_3,

H_2S (tetrahedral, 109 degrees)
PH_3 and NH_3 (trigonal pyramidal, around 107 degrees)
NH_3 has a larger bond angle than PH_3 as
1) N is more electronegative than P, N pulls electron density of bond pairs more towards itself, leading to greater bond-pair bond-pair repulsion.
2) N has a smaller lone pair region than P (N is above P in group 15). Lone-pair bond-pair repulsion is smaller, leading to a larger bond angle.

3 NF_3 , NCl_3, SO_3

NF_3 , NCl_3 (trigonal pyramidal, around 107 degrees)
NF_3 has a smaller bond angle than NCl_3. F is more electronegative than N and N is more electronegative than Cl). F pulls electron density of bond pairs more towards itself/ away from central N atom, leading to smaller bond-pair bond-pair repulsion.
SO_3 (trigonal planar, 120 degrees)

A 1, 2 and 3 **B** 1 and 2
C 2 and 3 **D** 1 only

4 Propadiene and propyne both have the same molecular formula, C_3H_4. They exist in equilibrium as shown:

$$H_2C{=}C{=}CH_2 \rightleftharpoons CH_3C{\equiv}CH$$
propadiene propyne

Which bond is present in propadiene but **not** present in propyne?

A a σ bond formed by s – sp overlap

B a π bond formed by p – p overlap

C a σ bond formed by sp – sp^2 overlap

D a σ bond formed by sp^2 – sp^2 overlap

propadiene $H_2C{=}C{=}CH_2$
hybridisation: sp^2 sp sp^2
propyne $CH_3C{\equiv}CH$
hybridisation: sp^3 sp sp

A a σ bond formed by s – sp overlap: in propyne **$CH_3C{\equiv}C{-}H$**, not in propadiene

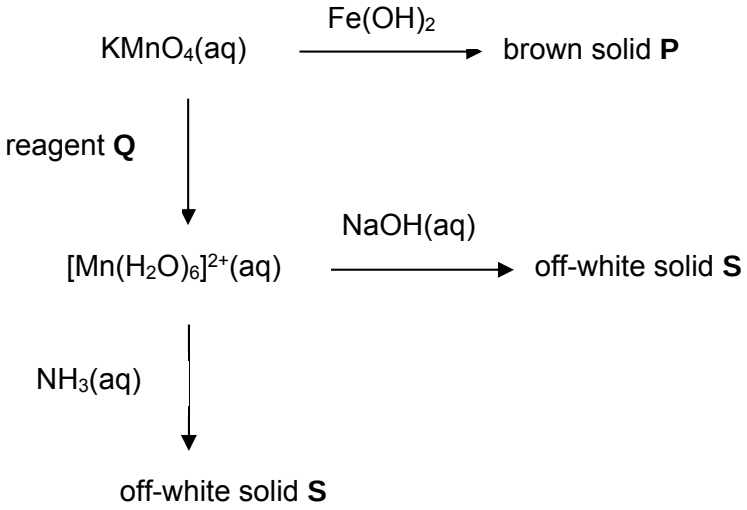
B a π bond formed by p – p overlap: present in both molecules

C a σ bond formed by sp – sp^2 overlap: in propadiene $H_2C{=}C{=}CH_2$, not in propyne

D a σ bond formed by sp^2 – sp^2 overlap :absent in both

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

A reaction scheme regarding manganese compounds is shown below.



Which statements are true?

1 Off-white solid **S** is able to dissolve in excess of $NH_3(aq)$.

2 Manganese in brown solid **P** has an oxidation state of +4.

3 Reagent **Q** can be acidified $[V(H_2O)_6]^{3+}(aq)$.

4 Off white solid **S** turns brown upon standing.

A 1, 2 and 4 **B** 2, 3 and 4

C 2 and 3 **D** All correct

1 off-white solid S is $Mn(OH)_2$. It is insoluble in excess of $NH_3(aq)$. *Check Data Booklet.*

2 Brown solid P is MnO_2. Oxidation state of Mn in MnO_2 is +4. $KMnO_4(aq)$ oxidises $Fe(OH)_2$, itself is reduced to MnO_2.

3 Reagent Q can be acidified $[V(H_2O)_6]^{3+}$ as the $E_{cell} > 0$.

(E_{cell} = (+1.52) + (- 0.34) = +1.18V)

4 off-white solid S turns brown upon standing. *Check Data Booklet.* $Mn(OH)_2$ is further oxidised by air.

6 In which chemical reaction does the transition metal compound or element behave as the described catalyst?

	Reaction	Catalyst
1	Formation of ethanal from ethanol, using acidified potassium dichromate $K_2Cr_2O_7$ is an oxidising agent, not a catalyst.	Homogeneous
2	Formation of oxygen from hydrogen peroxide, using iron(III) hydroxide $Fe(OH)_3$ is a solid catalyst used in the decomposition of hydrogen peroxide, due to the slow rate of reaction.	Heterogeneous
3	Chlorination of benzene, using chlorine and iron(III) chloride $FeCl_3$ is a catalyst as well as a halogen carrier, is regenerated in the last step of the electrophilic substitution.	Homogeneous
4	Removal of air pollutants in exhaust systems of cars, using nickel Nickel is a catalyst in the catalytic converter and is in solid phase, a different phase from the gaseous reactant	Heterogeneous

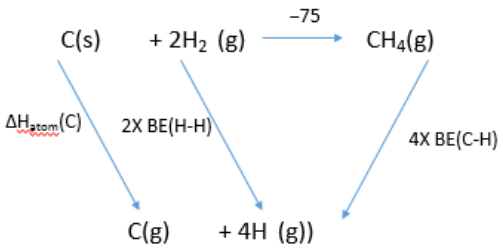
A 1, 2 and 4 **B** 2 and 3

C 3 and 4 **D** 2, 3 and 4

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

Given the following standard enthalpy changes,

	ΔH /kJ mol^{-1}
$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$	−75



a + (2 x436) − (4x 410) = −75

a = +693 kJ mol^{-1}

What is the standard enthalpy change of atomisation of graphite?

A +693 kJ mol^{-1}

B +1129 kJ mol^{-1}

C −2151 kJ mol^{-1}

D −2587 kJ mol^{-1}

8 Ammonia gas and hydrogen chloride gas react to form ammonium chloride as shown in the equation below:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \qquad \Delta H^{\ominus} = -176 \text{ kJ mol}^{-1}$$

The magnitude of standard entropy change of this reaction is 284 J K^{-1} mol^{-1}.

Which statements are correct?

1 $\Delta G^{\ominus} = -261$ kJ mol^{-1}.

No of mol of gas decreases => $\Delta S^{\ominus} = -284$ J K^{-1} mol^{-1}
$\Delta G^{\ominus} = -176 - 298\ (-0.284) = -91.4$ kJ mol^{-1}.

2 The reaction becomes non-spontaneous at temperatures higher than 620 K.

Crossover temperature occurs when $\Delta G^{\ominus} = 0$
$\Delta H^{\ominus} = T\Delta S^{\ominus}$
T = -176000/ -284 = 620K

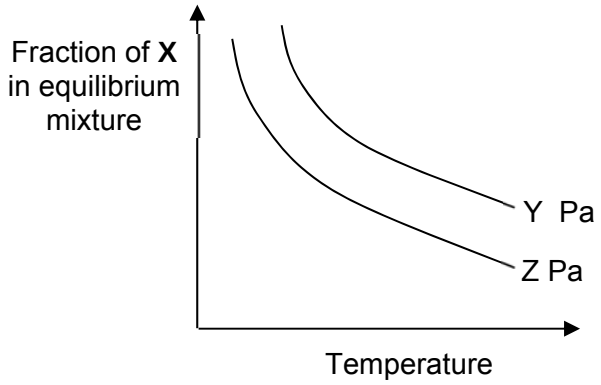
3 There is an increase in order as strong hydrogen bonding between NH_3 and HCl hold the particles in NH_4Cl in fixed positions and close to each other.

NH_4Cl is ionic lattice with strong ionic bonds between NH_4^+ and Cl^-, not strong H bonding between the NH_3 and HCl molecules.

A 1 only **B** 1 and 2 **C** 2 only **D** 2 and 3

9 The graph below shows how the fraction of X, which represents one of the following compounds in the given equilibrium mixture, varies with temperature at pressures of Y Pa and Z Pa.

$$4NH3(g) + 3O2(g) \rightleftharpoons 2N2(g) + 6H2O(g) \qquad \Delta H = -1267 \text{ kJ mol}-1$$



Identify X and the correct relative magnitudes of Y and Z.

	X	Pressure
A	N_2	Z > Y
B	O_2	Y > Z
C	H_2O	Y > Z
D	NH_3	Z > Y

Shape of graph:

(i) As temperature increase, fraction of X decrease.

(ii) As temperature increase, as forward reaction is exothermic, fraction of product should decrease.

Matching (i) and (ii): X should be the product of the reaction => either N_2 or H_2O.

Comparison of the two graphs:

(i) 7 mol of gaseous reactants vs 8 mol of gaseous products => decrease pressure will favour the forward reaction, to partially increase pressure.

(ii) Decrease pressure increase the fraction of X (since X is the product)

Matching (i) and (ii): Fraction of X is higher for Y Pa than Z Pa (Y Pa < Z Pa)

10 One of the key production stages in the Contact Process is the production of sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

The rate constants of the forward and backward reactions are given as k_1 and k_{-1} respectively.

What happens to k_1, k_{-1} and K_c if the temperature of the reaction is increased?

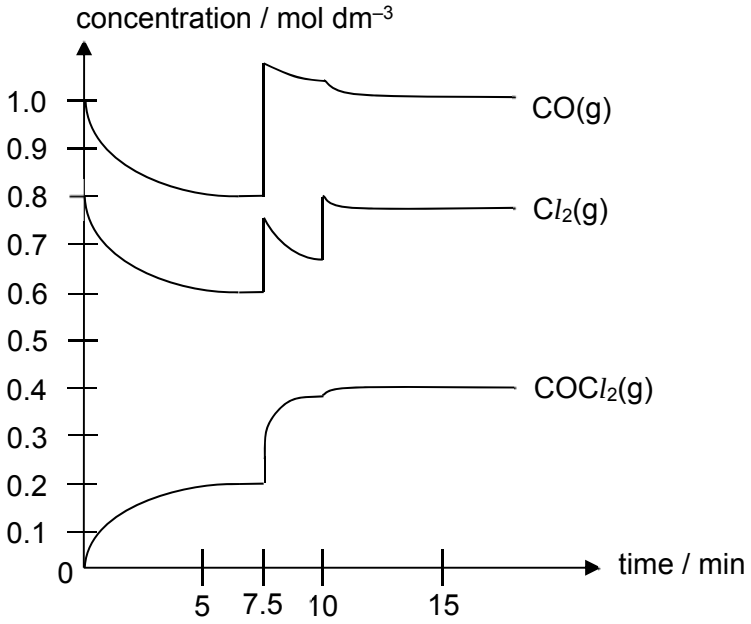
	k_1	k_{-1}	K_c
A	increase	increase	increase
B	increase	decrease	increase
C	decrease	increase	decrease
D	increase	increase	decrease

When temperature increased, no of molecules with energy greater than activation energy increases, frequency of effective collision increased, rate of reaction increases as rate constant increased. k_1 and k_{-1} increase.

As reaction is exothermic, as temperature increase, equilibrium shift backward to partially absorb the excess heat. Hence, K_c decrease as [product]/[reactant] decrease.

11 The reaction between carbon monoxide and chlorine was studied in an experiment by mixing the two gases and changing the reaction conditions inside the reaction vessel at different times during the experiment. The concentrations of the gases in the vessel were followed with time, and the following graph is obtained.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H^{\ominus} = -113.4 \text{ kJ mol}^{-1}$$



Which conclusion deduced from the graph is **incorrect**?

A The rate of forward reaction equals the rate of backward reaction at 7 min.

Correct: At 7 min, the system is in dynamic equilibrium and hence the rate of forward reaction is equal to the rate of backward reaction.

B The change in concentration from 7.5 min to 10 min was produced by an increase in volume at constant temperature.

Incorrect: Increase in volume at constant temperature will cause the concentration to decrease.

C The equilibrium constant, K_c, for the system when determined at 7 min is 0.417 mol^{-1} dm^3.

Correct: Using $K_c = \frac{[COCl_2]}{[CO][Cl_2]}$ and calculate

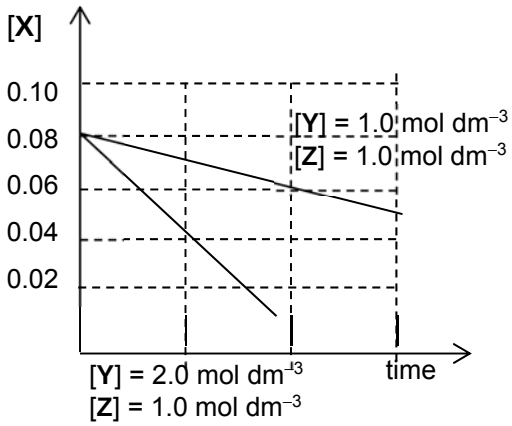
D The change in concentration from 10 min to 15 min was produced by the addition of more chlorine.

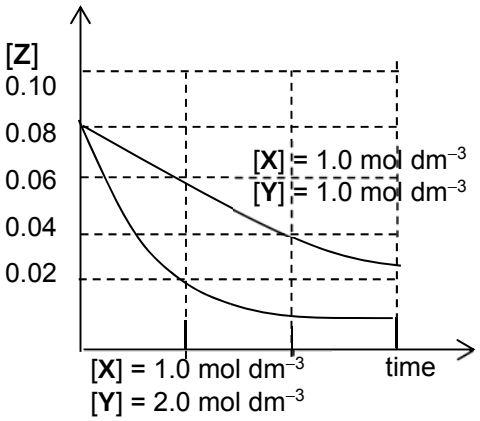
Correct: When chlorine is added, the concentration of chlorine will increase instantaneously as shown in the graph.

12 Substances **X**, **Y** and **Z** react according to the following equation:

$$\mathbf{X}(aq) + 2\mathbf{Y}(aq) + \mathbf{Z}(aq) \rightarrow 2\mathbf{W}(aq) + \mathbf{U}(aq)$$

To find the rate equation for the above reaction, two sets of separate experiments were performed, in which the initial concentrations of each of the reactants **X**, **Y** and **Z** were varied while the other two were kept constant. The results are shown below.





Which rate equations represent the experimental results?

A rate = k[**Y**]^2

B rate = k[**Y**][**Z**]

C rate = k[**Y**]^2[**Z**]

D rate = k[**X**][**Y**][**Z**]

From the [X] versus time graph, a straight line indicates that the rate is constant with respect to any changes in [X]. Therefore order of reaction with respect to X is zero.

From the [Z] versus time graph, a constant half-time is obtained which indicates that the reaction is first order with respect to Z.

From the [Z] versus time graph, the time taken when [Y] is 2.0 mol dm^{-3} is $\frac{1}{4}$ of the time taken when [Y] is 1.0 mol dm^{-3} for [Z] to drop from 0.08 mol dm^{-3} to 0.04 mol dm^{-3} . Therefore order of reaction with respect to Y is 2.

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

The reaction of acidified aqueous potassium iodide with hydrogen peroxide is represented by the following equation.

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

Which statements about the reaction are true?

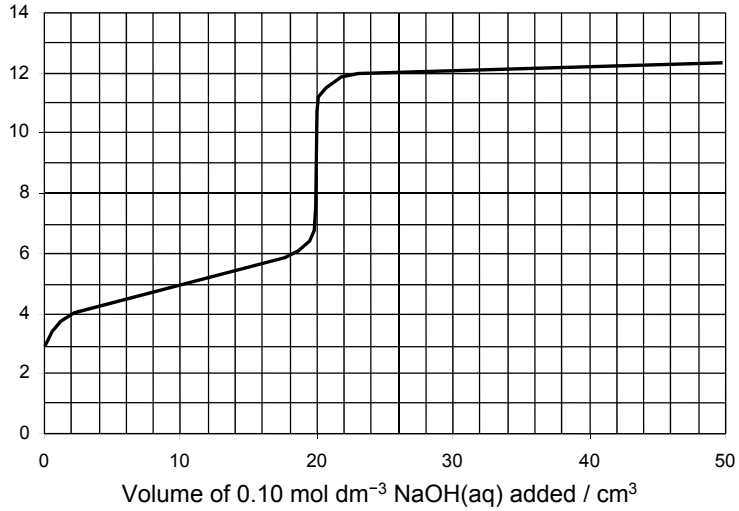
1 E^{θ}_{cell} = +1.23 V.
True: E^{θ}_{cell} = (-0.54) + (+1.77) = +1.23 V

2 E^{θ}_{cell} becomes more negative when $Br_2(aq)$ is added to the anode.
True: $Br_2(aq)$ added will remove I^- causing $E^{\theta}_{oxidation}$ of I^- to be more negative when will cause E^{θ}_{cell} becomes more negative

3 E^{θ}_{cell} becomes more positive when a few drops of $AgNO_3(aq)$ is added to the anode.
False: $AgNO_3(aq)$ added with remove I^- causing $E^{\theta}_{oxidation}$ of I^- to be more negative when will cause E^{θ}_{cell} becomes more negative

A 1 only
B 1 and 2
C 2 and 3
D 1, 2 and 3

14 The titration curve below shows the reaction between a monoprotic acid, **HX**, and aqueous sodium hydroxide.



Given the following data:

Indicator	Colour change (acidic to basic medium)	pH range in which colour change occurs
Methyl red	red to yellow	4.2 – 6.3
Bromothylmol blue	yellow to blue	6.0 – 7.6
Thymolpthalein	colourless to blue	8.3 – 10.5

What statements are correct?

1 Methyl red will indicate an endpoint at a value lower than 20.0 cm^3.

Correct: At a value lower than 20.0 cm^3, the pH is less than 6.5 which coincide with the working range of methyl red.

2 K_a value of HX is 1.0×10^{-5}

Correct: At max buffer capacity, pH= pK_a = 5

$K_a = 1.0 \times 10^{-5}$

3 Buffer at maximum buffer capacity is formed at 25.0 cm^3 since the pH change in that region is relatively constant.

Incorrect: Maximium buffer capacity is formed at 10.0 cm^3 where [HX] = [NaX]

4 Alkaline hydrolysis of salt takes place after the equivalence point accounting for the alkaline pH value of the reaction mixture.

Incorrect: Alkaline hydrolysis of salt takes place **AT** equivalence point accounting for the alkaline pH value of the reaction mixture.

A 1,2 and 3 **B** 2,3 and 4 **C** 1 and 2 **D** 3 and 4

15 Given the following data,

K_a of $CH_3COOH = 1.8 \times 10^{-5}$

Reaction mixture **X**:
25.0 cm^3 of 2.0×10^{-5} mol dm^{-3} CH_3COOH and 25.0 cm^3 water

Reaction mixture **Y**:
25.0 cm^3 of 0.02 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.01 mol dm^{-3} NaOH

Reaction mixture **Z**:
25.0 cm^3 of 0.01 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.02 mol dm^{-3} NaOH

Which is the correct order of pH values of the above reaction mixture?

A **Z > Y > X**

B **Z > X > Y**

C **Y > X > Z**

D X > Y > Z

For reaction mixture X, $[CH_3COOH]_{new} = 0.5 \times 2.0 \times 10^{-5} = 1.0 \times 10^{-5}$ mol dm^{-3}

$[H^+] = \sqrt{(1.0 \times 10^{-5} \times 1.8 \times 10^{-5})} = 1.3416 \times 10^{-5}$ mol dm^{-3}

$pH = -\lg(1.3416 \times 10^{-5}) = 4.87$

For reaction mixture Y,

	CH_3COOH	+	NaOH	→	CH_3COONa	+	H_2O
Initial / mol	0.0005		0.00025		0		-
Change / mol	– 0.00025		– 0.00025		+ 0.00025		-
Final / mol	0.00025		0		0.00025		-

An acidic buffer is formed.

$pH = pK_a$ since $[CH_3COOH]_{new} = [CH_3COONa]_{new}$

$pH = -\lg(1.8 \times 10^{-5}) = 4.74$

For reaction mixture Z,

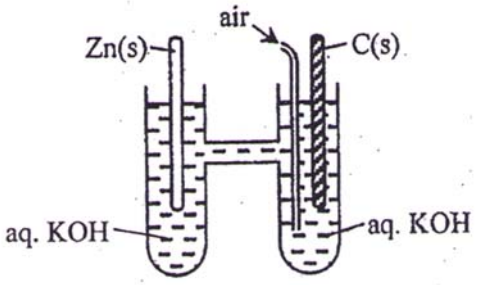
	CH_3COOH	+	NaOH	→	CH_3COONa	+	H_2O
Initial / mol	0.00025		0.0005		0		-
Change / mol	– 0.00025		– 0.00025		+ 0.00025		-
Final / mol	0		0.00025		0.00025		-

Salt hydrolysis is not considered as presence of strong base will suppress the salt's dissociation

$pH = 14 - pOH = 14 + \lg(0.00025 / \frac{25.0+25.0}{1000}) = 11.70$

Answer is B

16 A cell is constructed with zinc and carbon electrodes, each weighing 50 g, partly immersed in aqueous KOH.



When connected in a circuit, some zinc passes into solution as zincate(II) ions, $ZnO_2^{2-}(aq)$. The cell delivers a current of 1.68×10^{-2} A. The zinc electrode is replaced once 60% of it is used up.

What is the time taken, in seconds, before replacement of zinc electrode becomes necessary?

A 2.63×10^6 **B** 4.39×10^6

C 5.27×10^6 **D** 8.78×10^6

Oxidation state of Zn in ZnO_2^{2-} is +2, hence 2 moles of electrons are transferred per mole of Zn.

Amount of Zn used up = $\frac{60}{100} \times \frac{50}{65.4}$ = 0.4587 mol

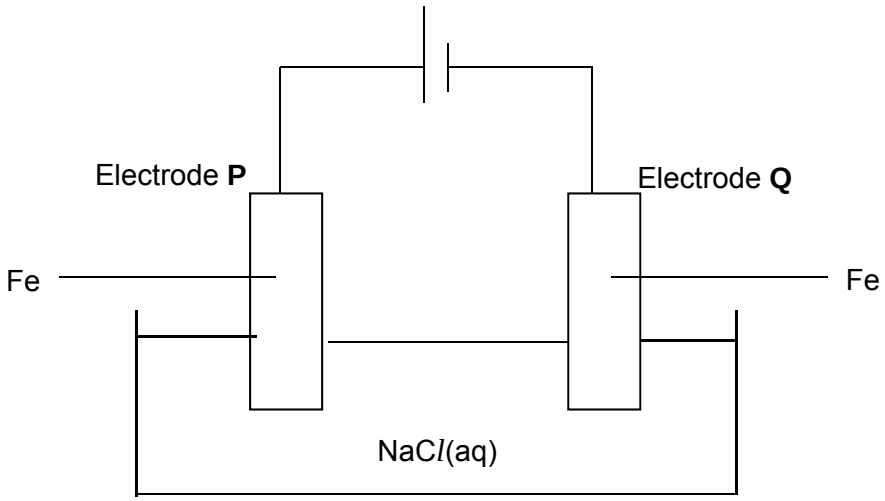
$n_e = 0.4587 \times 2 = 0.9174$ mol and since $Q = It = n_eF$

$(1.68 \times 10^{-2})t = 0.9174 \times 96500$

$= 5.27 \times 10^6$ s

Answer is C

17 An experiment is set up as shown below to study the corrosion of iron.



What will occur at electrodes **P** and **Q**?

	Electrode **P**	Electrode **Q**
A	No corrosion of Fe	Corrosion of Fe ; H_2 gas evolved
B	No corrosion of Fe	Corrosion of Fe ; O_2 gas evolved
C	Corrosion of Fe	No corrosion of Fe ; Na deposited
D	Corrosion of Fe	No corrosion of Fe ; H_2 gas evolved

Electrode P is the positive anode, while electrode Q is the negative cathode

Since oxidation occurs at the anode, while reduction occurs at the cathode,

At the anode:

$Fe \rightleftharpoons Fe^{2+} + 2e^-$ $E^\theta_{ox} = +0.44$ V
$Cl^- \rightleftharpoons Cl_2 + 2e^-$ $E^\theta_{ox} = -1.36$ V
$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ $E^\theta_{ox} = -1.23$ V

Corrosion of Fe will occur at electrode P since first E^θ_{ox} is the most positive

At the cathode:

$Na^+ + e^- \rightleftharpoons Na$ $E^\theta = -2.71$ V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\theta = -0.83$ V

No corrosion of Fe will occur, since Fe cannot be reduced. H_2 gas will be evolved since second E^θ is the most positive

Answer is D

18 *Use of Data Booklet is relevant to this question.*

The calomel electrode was used extensively a reference electrode in the past. However, it has since been replaced by safer options such as the standard hydrogen electrode (S.H.E.).

Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$

When measured with reference to the calomel electrode, a half–cell containing Zn^{2+}/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn^{2+}.

What is the standard electrode potential of the calomel electrode?

A +0.27 V **B** +1.30 V **C** –1.79 V **D** –2.82 V

A change in Gibbs' free energy of +199 kJ per mole of Zn^{2+} being reduced is equivalent to a change in Gibbs' free energy of –199 kJ per mole of Zn being oxidised

$\Delta G^{\theta} = -nFE^{\theta}_{cell}$

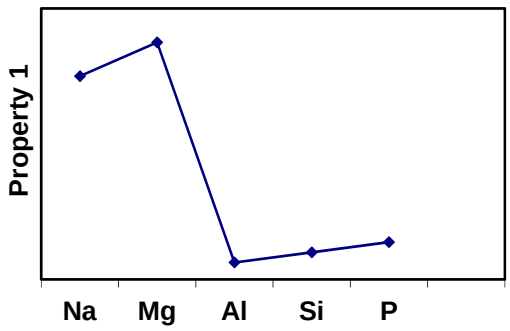
$-199 \times 1000 = -(2)(96500)E^{\theta}_{cell}$

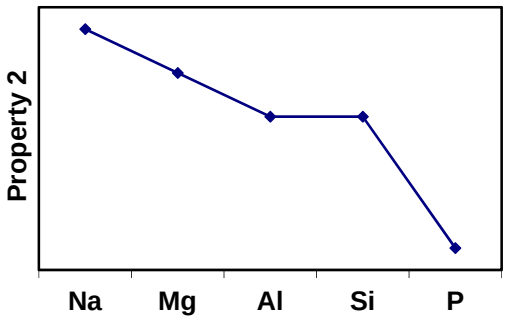
$E^{\theta}_{cell} = +1.03\ V = E^{\theta} + E^{\theta}_{ox\ (Zn\ /\ Zn2+)} = E^{\theta} + 0.76\ V$

$E^{\theta} = +0.27\ V$

Answer is A

19 The graphs below show the variation of two properties of some period 3 elements and/or their compounds.





Which correctly describes properties 1 and 2?

	Property 1	Property 2
A	atomic radius of the elements	electrical conductivity of the elements
B	boiling point of the highest oxidation state chlorides	pH of the oxides when added to water
C	melting point of oxides	first ionisation energies of the elements
D	electrical conductivity of elements	pH of the highest oxidation state chlorides when added to water

For option A Property 1 cannot be atomic radii as it should be a continuous decrease across the period due to increase in nuclear attraction for the outermost electron. This is because of increase in nuclear charge but constant shielding caused by the same number of inner electrons.	Property 2: Electrical conductivity should increase from Mg to Al due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.
For option B Boiling point of chloride compounds decreases from NaCl to $AlCl_3$ as $AlCl_3$ is a simple covalent molecule therefore easier to overcome the intermolecular temporary dipole induced dipole than ionic bonds in giant ionic lattice of NaCl and $MgCl_2$. From $AlCl_3$ to PCl_5, they have the structure of simple covalent molecules with Mr of $AlCl_3$ (133.5) < $SiCl_4$ (170.1) < PCl_5 (208.5). B.pt increases with increasing ease of distortion of the electron cloud of the chloride compound. Hence property1 shows the correct trend in the b.pt of chlorides across period 3 element.	Property 2: **acid base property of oxide** depends on the **nature of bonds present in the oxide** compound. While ionic oxide tends to be basic and covalent oxide is acidic; ionic oxides with significant covalent character will be amphoteric, this is usually observed when cation has high charge/size ratio. **pH of oxides in aqueous medium** not only depends on the nature of the bonds, **solubility** also matters. Na_2O is **basic and fully soluble** in water, therefore pH very high (highly alkaline). Solubility of MgO less than Na_2O but more than Al_2O_3, hence pH of MgO > Al_2O_3. **pH of Al_2O_3 and SiO_2 are both equal to 7 because both are insoluble in water** but Al_2O_3 is an amphoteric oxide while SiO_2 is an acidic oxide. Oxides of P dissolves in water to give phosphoric acid therefore pH is very low. Hence property 2 shows the correct trend for pH of aqueous oxides across period 3.
For option C Melting points of oxides across the period should peak at SiO_2 since it has a very strong giant covalent lattice. Phosphoric oxide is a simple covalent molecule, therefore there should be a drastic drop of m.pt from SiO_2 to P_4O_{10}. Hence property 1 cannot be m.pt of oxides across period 3 elements.	First ionisation energy of elements across period should exhibit a general increasing trend due to increasing nuclear attraction for the most loosely held electron. This is due to increase in nuclear charge but constant shielding effect by the same number of inner shell electrons. Hence property 2 cannot be first ionisation energy.
For option D Electrical conductivity should increase from Na to Mg to Al due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero	For chlorides across period 3 element, they are all soluble in aqueous medium. For chlorides that dissociates into ions in aq medium, cation hydrolysis gives rise to acidic solution. Extent of cation hydrolysis increases with charge/size ratio of the cation. Hence $AlCl_3$ (aq) more acidic than $MgCl_2$(aq) while NaCl is neutral (pH =7)

electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.	On the other hand, covalent chlorides react with water to form HCl therefore the pH value should be low for both $SiCl_4$ and PCl_5. Hence graph of property 2 do not agree with the pH trend of aqueous chlorides across the period.

20 What mass of sodium ethanedioate, $Na_2C_2O_4$, should be added to 250 cm^3 of a 2.2×10^{-3} mol dm^{-3} solution of calcium nitrate before a precipitate is formed?
[K_{sp} of $CaC_2O_4 = 2.27 \times 10^{-9}$ mol^2 dm^{-6}]

In order for precipitate to take place, ionic product > Ksp.
Expression for ionic product and K_{sp} is the same.

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

Magnitude of Ionic product = K_{sp} when solution is saturated with $Na_2C_2O_4$.

$$\left(\frac{mass}{(23.0 \times 2 + 24.0 + 64.0)} \times \frac{1000}{250}\right)(2.2 \times 10^{-3}) = 2.27 \times 10^{-9}$$

Min mass of $Na_2C_2O_4 = 3.46 \times 10^{-5}$ g

A 3.5×10^{-5} g
B 1.0×10^{-6} g
C 2.5×10^{-7} g
D 2.3×10^{-9} g

21 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which statements about benzylamine is correct?

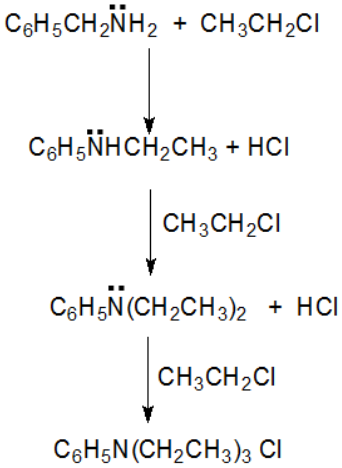
A It can be formed by the reduction of $C_6H_5CH_2CN$.
B It reacts with CH_3CO_2H to form $C_6H_5CH_2NHCOCH_3$.
C It is formed by the reaction between $C_6H_5NO_2$ and tin in concentrated HC*l* followed by NaOH.
D It reacts with excess CH_3CH_2Cl under heat to form the compound, $C_{13}H_{22}NCl$.

Option A: reduction of $C_6H_5CH_2CN$ gives $C_6H_5CH_2CH_2NH_2$ with 1 C more than $C_6H_5CH_2NH_2$. Hence it is not the correct answer.

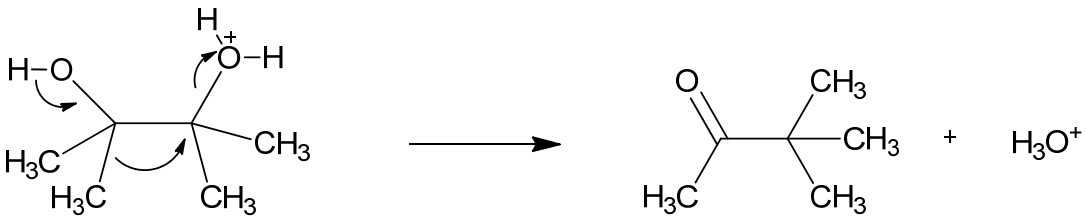
Option B: N in $C_6H_5CH_2NH_2$ uses its lone pair to accept H^+ from CH_3COOH (acid base reaction instead of nucleophilic acyl substitution (condensation)). Hence $(CH_3COO^-)(C_6H_5CH_2NH_3)^+$ is formed instead of $C_6H_5CH_2NHCOCH_3$.

Option C: $C_6H_5NO_2$ will be reduced to $C_6H_5NH_2$ which is isolated as $C_6H_5NH_3Cl$ due to acidic medium. $C_6H_5NO_2$ has 1 less C than $C_6H_5CH_2NH_2$ after reduction, hence not the answer.

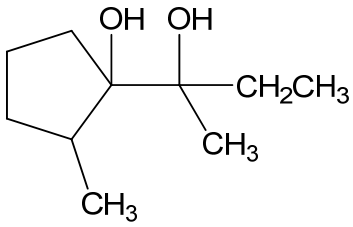
Option D: Correct answer. A quaternary ammonium salt is formed when $C_6H_5CH_2NH_2$ reacts with excess CH_3CH_2Cl.



22 When a 1,2–diol is treated with a dilute acid, the protonated diol undergoes the following pinacol rearrangement.

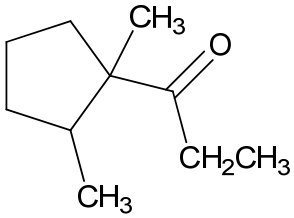


Which structure is **not** formed when diol **Z** undergoes pinacol rearrangement?

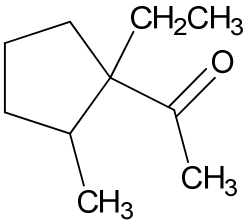


diol **Z**

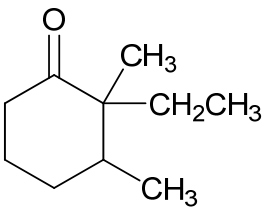
A



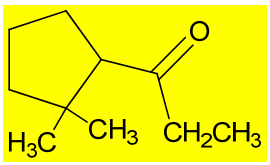
B

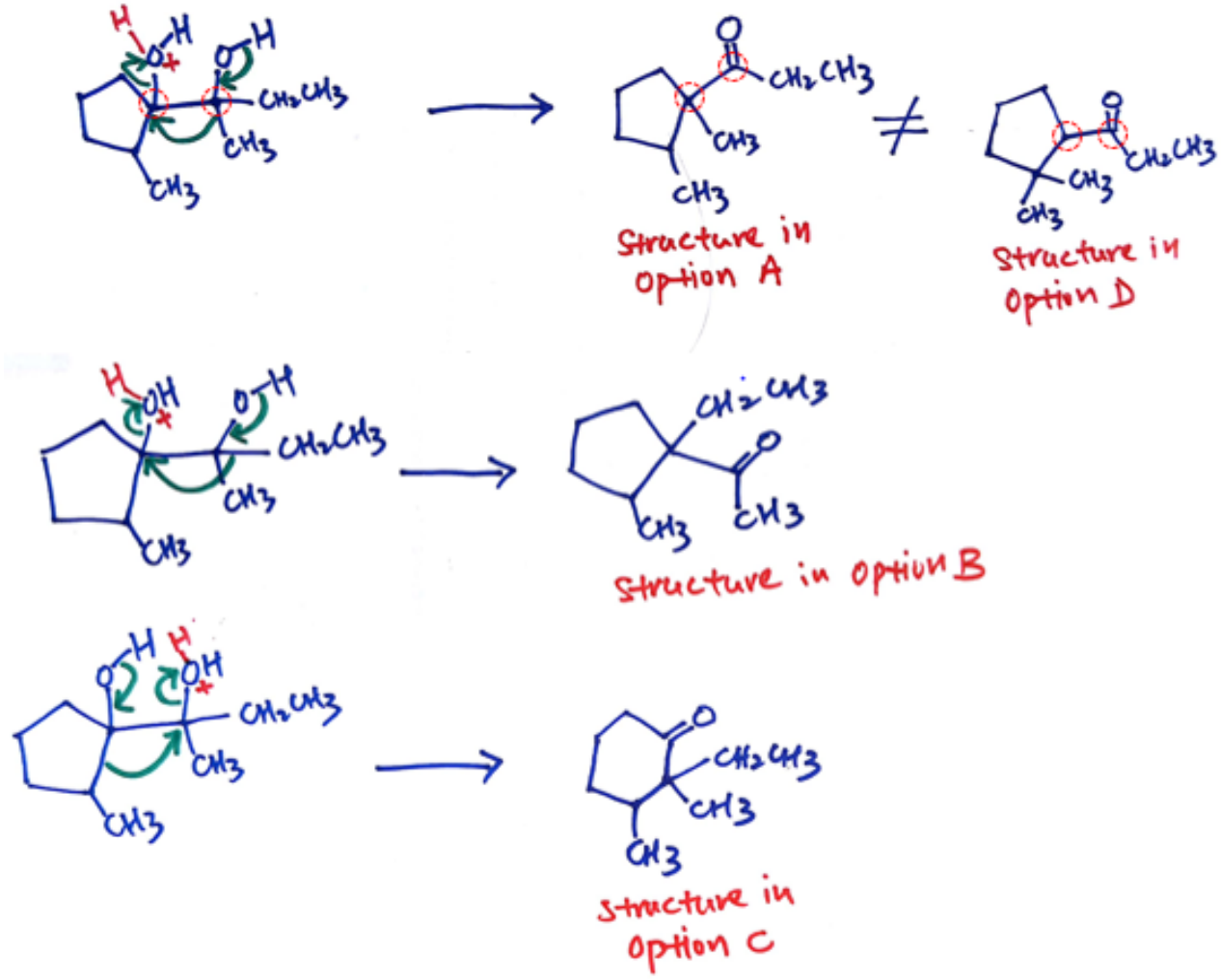


C

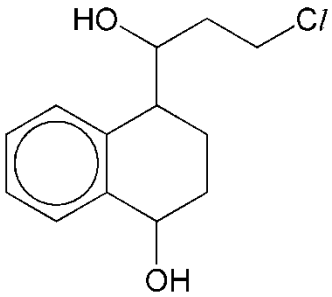


D





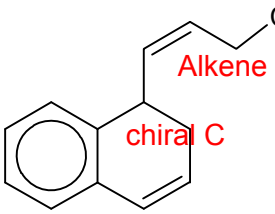
23 What is the total number of possible stereoisomers exhibited by the products when the following compound reacts with excess concentrated H_2SO_4?



A 2 **B** 4 **C** 6 **D** 8

The molecule undergoes elimination of H_2O with excess concentrated H_2SO_4 to give alkene.

The product is



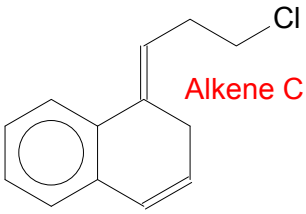
Alkene C that can exhibit cis-trans isomerism

chiral C

Using the formula,

No of stereoisomers = 2^{n+m} where n = no of chiral C and m= no of alkene C that can exhibit cis-trans isomerism, this alkene has 2^{1+1} = 4 isomers.

Another possible products of elimination:



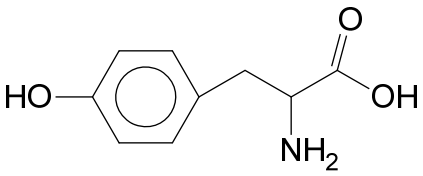
Alkene C that can exhibit cis-trans isomerism

No of stereoisomers: 2^1=2 isomers

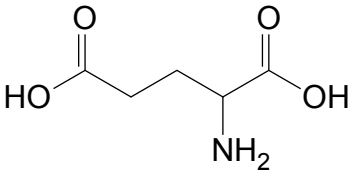
Total no of stereoisomers = 2^2 + 2 = 6

24 Electrophoresis is a technique of separating and identifying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species move towards the anode.

With a buffer at pH 4, which statement is true?



Tyrosine (pI = 5.7)



Glutamic acid (pI = 3.2)

A Both species move towards the anode

B Both species move towards the cathode.

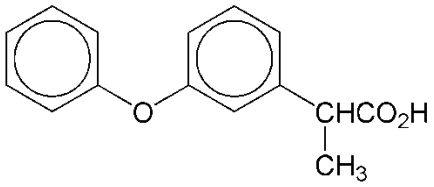
C Tyrosine moves towards the anode, glutamic acid moves towards the cathode.

D Tyrosine moves towards the cathode, glutamic acid moves towards the anode.

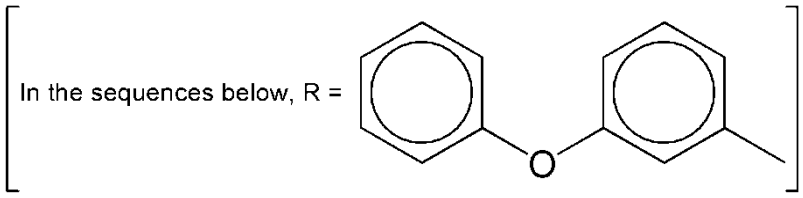
Since pH < pI of Tyrosine, the $–NH_2$ grp will get protonated => Overall positively charged, hence move towards cathode.

Since pH > pI of Glutamic acid, both the –COOH grps will get deprotonated => Overall negatively charged, hence move towards anode. Answer is (D).

25 *Fenoprofen* is an anti-arthritic agent.



Which of the following could be part of a reaction sequence for synthesising *Fenoprofen*?



A $RCHBrCH_3 \xrightarrow[heat]{NaCN(ethanolic)} Intermediate \xrightarrow[heat]{H^+(aq)} Fenoprofen$

B $RCH(CH_3)_2 \xrightarrow[heat]{KMnO_4,\ OH^-(aq)} Intermediate \xrightarrow{H^+(aq)} Fenoprofen$

C $RCHOCOCH_3$ (CH3 branch) $\xrightarrow[warm]{I_2,\ OH^-(aq)} Intermediate \xrightarrow{H^+(aq)} Fenoprofen$

D $RCH(OH)CH_3 \xrightarrow[heat]{KMnO_4,\ OH^-(aq)} Intermediate \xrightarrow{H^+(aq)} Fenoprofen$

For option (A), the halogenoalkane $RCHBrCH_3$ undergoes nucleophilic substitution when heated with ethanolic NaCN, forming $RCH(CN)CH_3$ as the intermediate, which then undergoes acidic hydrolysis of the –CN group to form –COOH.

For option (B), $RCH(CH_3)_2$ does not undergo oxidation when heated with alkaline $KMnO_4$.

For option (C), $RCHO(CH_3)COCH_3$ has methyl carbonyl which is part of the ester functional grp, hence does not undergo iodoform reaction when warmed with alkaline iodine.

For option (D), secondary alcohol $RCH(OH)CH_3$ undergoes oxidation to form ketone intermediate, $RCOCH_3$, which does not react with H^+.

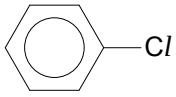
26 Chlorofluorocarbons (CFCs) are commonly used as aerosols, propellants and refrigerants. However in the stratosphere, CFCs can damage the ozone layer through a radical chain reaction.

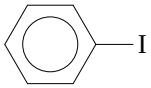
In which sequence are the following compounds listed in increasing order of their ability to destroy ozone?

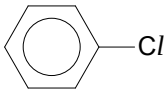
A	$CHClFCClF_2$	<	CCl_2FCCl_2F	<	$CHClF_2$
B	CCl_2FCCl_2F	<	$CHClF_2$	<	$CHClFCClF_2$
C	$CHClF_2$	<	CCl_2FCCl_2F	<	$CHClFCClF_2$
D	$CHClF_2$	<	$CHClFCClF_2$	<	CCl_2FCCl_2F

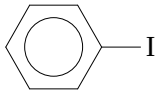
C-F bond is much stronger than C-Cl, it does not break easily to form F radicals => does not damage ozone layer.
All four options (A), (B), (C) and (D) comprise of molecules containing C-F and C-Cl bonds. The molecule with more C-Cl bonds will have higher ability to destroy ozone due to more Cl radicals it is able to produce. Hence, answer is (D).

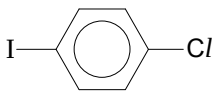
27 Which is the product formed when benzene reacts with iodine chloride, ICl in the presence of a suitable catalyst?

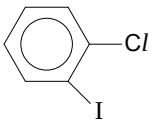
A 

B 

C a mixture of 

and 

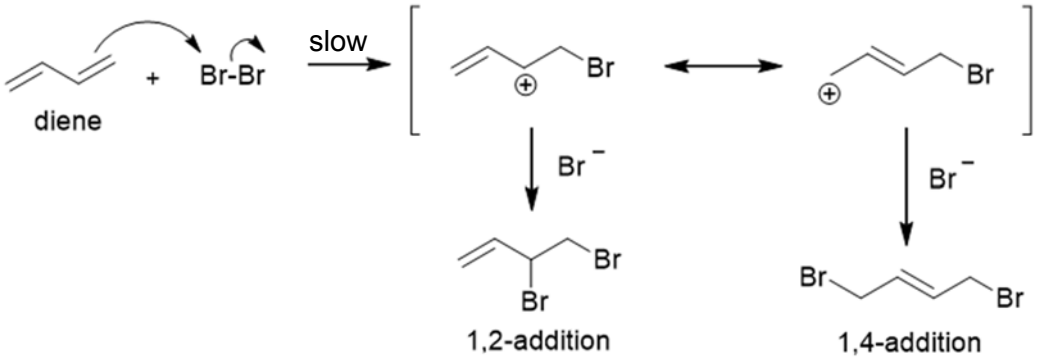
D a mixture of 

and 

Answer:

Cl is more electronegative than I, hence only I^+ electrophile forms for reaction.
$AlCl_3 + ICl \rightarrow AlCl_4^- + I^+$
Hence only 1 electrophilic substitution product is possible.

28 When a conjugated diene undergoes electrophilic addition with Br_2, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.



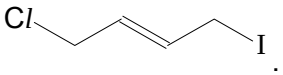
Which statement is **not** correct?

A The overall rate law is second order.

B The carbocation intermediates are resonance stabilised.

C The 1,2–addition product formed when HC*l* is used is 

.

D The 1,4–addition product formed when IC*l* is used is 

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Answer:

A is correct.

Step 1 can be determined to be the slow step as bond breaking occurs. 1 mole of diene and 1 mole of bromine are involved and hence the overall order is 2.

B is correct.

The presence of the pi bond stabilises the positive charge on the cations.

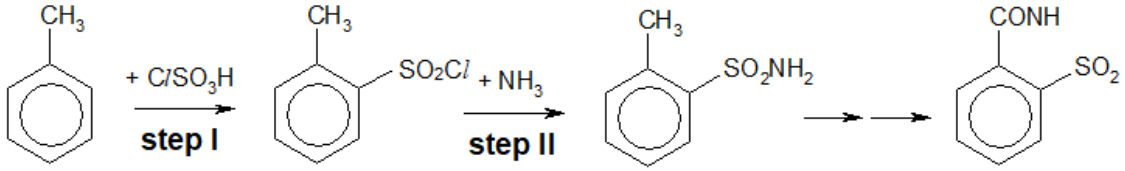
C is incorrect.

For the 1,2-addition product, the positive charge is on the 2nd carbon and hence C*l* should be on the 2nd carbon instead.

D is correct.

C*l* is more electronegative than I, hence in step 1, the I which is δ+ will function as the electrophile and C*l* $^-$ is generated which then attacks the carbocation.

29 Saccharin is an artificial sweetening agent used in some soft drinks and is manufactured from methylbenzene through a four-step synthesis. Part of the reaction scheme is shown below.



What type of reaction do steps **I** and **II** illustrate?

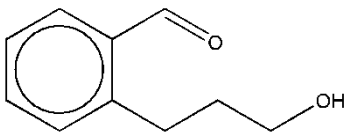
	Step I	Step II
A	Electrophilic addition	Nucleophilic addition
B	Electrophilic substitution	Nucleophilic substitution
C	Nucleophilic addition	Elimination
D	Electrophilic substitution	Neutralisation

Answer:
Step 1: Benzene ring is electron rich: Electrophilic Substitution
Step 2: S is δ+ due to the electronegative atoms attached to it; -C*l* replaced by -NH_2 : Nucleophilic Substitution

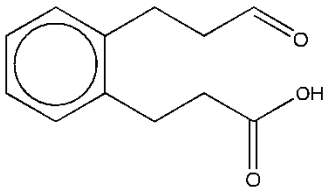
30 Compound **X** gives a positive result when treated with $[Ag(NH_3)_2]^+$ and PCl_5 respectively but a negative result when treated with alkaline Cu(II) complex.

What could **X** be?

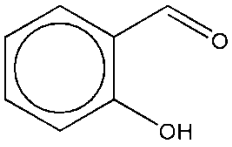
A



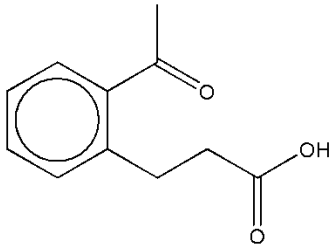
B



C



D



Reacts with $[Ag(NH_3)_2]^+$ (Tollen's)	Aldehyde
Reacts with PCl_5	-OH which can undergo substitution present (not phenol)
No reaction with alkaline Cu(II) complex (Fehlings)	Aromatic aldehyde

END of PAPER

1	C	11	B	21	D
2	C	12	C	22	D
3	A	13	B	23	C
4	C	14	C	24	D
5	B	15	B	25	A
6	D	16	C	26	D
7	A	17	D	27	B
8	C	18	A	28	C
9	A	19	B	29	B
10	D	20	A	30	A