2022 RI H2 Chemistry Prelim Paper 1 – Suggested Solutions

Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Answer	C	C	A	A	A	B	B	B	D	B	A	A	D	D	C

Question	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Answer	C	D	B	A	B	D	C	C	D	C	D	B	B	A	D

MCQ worked solutions

Q1 **(Ans: C)**

Option **A** is incorrect.
$(NH_4)_2Fe(SO_4)_2$ has 5 ions per formula unit $\Rightarrow$ total number of ions = $5 \times 2 \times 6.02 \times 10^{23}$
$K_2Cr_2O_7$ has 3 ions per formula unit $\Rightarrow$ total number of ions = $3 \times 4 \times 6.02 \times 10^{23}$

Option **B** is incorrect.

Number of NO_2 molecules = $\dfrac{46}{14 + (16 \times 2)} \times 6.02 \times 10^{23}$

Number of N_2 molecules = $\dfrac{14}{14 \times 2} \times 6.02 \times 10^{23}$

Option **C** is correct.
Number of electrons in 1 mol of N_2 = $(7 + 7) \times 6.02 \times 10^{23}$
Number of electrons in 1 mol of CO = $(6 + 8) \times 6.02 \times 10^{23}$

Option **D** is incorrect.
Let V_m be the molar volume of gas. At the same temperature and pressure,
number of atoms in 5 dm^3 of O_2 = $\dfrac{5}{V_m} \times 2 \times 6.02 \times 10^{23}$
number of atoms in 10 dm^3 of Ar = $\dfrac{10}{V_m} \times 6.02 \times 10^{23}$

Q2 **(Ans: C)**

Let a be the fraction of ^{63}Cu and (1 – a) be the fraction of ^{65}Cu in naturally occurring copper.

From the *Data Booklet*, the relative atomic mass of Cu is 63.5.

$63.5 = 63a + 65(1 - a) \Rightarrow a = 0.75$

Hence, in the sample of bronze,

$$\frac{\text{\% composition of } ^{63}\text{Cu}}{\text{\% composition of } ^{65}\text{Cu}} = \frac{d}{88 - d} = \frac{0.75}{0.25}$$

d = $\underline{66}$

Q3 (Ans: A)

	$^{30}Si^{4+}$	$^{31}P^{3-}$	$^{32}S^{2-}$
Number of electrons	10	18	18
Number of neutrons	16	16	16
Number of protons	14	15	16

Statement 1 is correct. The ions have the same number of neutrons.

Statement 2 is incorrect. As the ions have different number of electrons, their electronic configurations are different.

Statement 3 is incorrect. The ionic radii increase in the order $^{30}Si^{4+} < {}^{32}S^{2-} < {}^{31}P^{3-}$.

The valence electrons of $^{30}Si^{4+}$ are found in the n=2 shell while the valence electrons of $^{31}P^{3-}$ and $^{32}S^{2-}$ are found in the n=3 shell. Hence the ionic radius of $^{30}Si^{4+}$ is smaller than that of $^{31}P^{3-}$ and $^{32}S^{2-}$.

Since $^{31}P^{3-}$ and $^{32}S^{2-}$ are isoelectronic with the same electronic configuration, their valence electrons experience the same shielding effect. However, nuclear charge of $^{31}P^{3-}$ is smaller than that of $^{32}S^{2-}$. Hence, the effective nuclear charge of $^{31}P^{3-}$ is smaller than that of $^{32}S^{2-}$, and therefore $^{31}P^{3-}$ has a larger ionic radius than $^{32}S^{2-}$.

Q4 (Ans: A)

Angle of deflection $\alpha \frac{\text{charge}}{\text{mass}}$

ions	$^{7}Li^{2-}$	$^{15}O^{2+}$	$^{15}N^{4-}$	$^{11}C^{3+}$
$\frac{\text{charge}}{\text{mass}}$	0.286	0.133	0.267	0.273

Q ($^{11}C^{3+}$) should be a cation as it is attracted to the negatively charged plate, and its charge/mass ratio should be between that of the two anions P ($^{7}Li^{2-}$) and R ($^{15}N^{4-}$).

Q5 (Ans: A)

Indium is a Group 13 element with 3 valence electrons. Hence, there should be a large jump between the third and fourth IE as the fourth electron is removed from an inner electronic shell. Hence, option **A** is correct.

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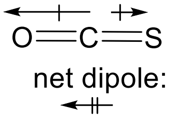
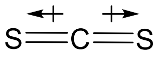
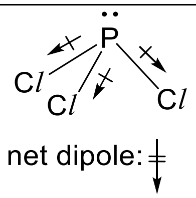
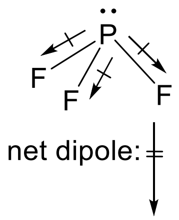
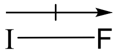
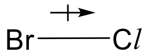
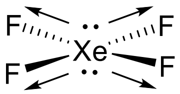
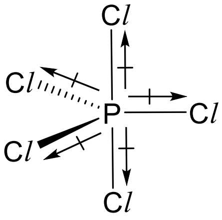
Q6 **(Ans: B)**

	G	H	Remarks
A	 net dipole:	 no net dipole	G has a greater net dipole than H.
B	 net dipole:	 net dipole:	P-F bond is more polar than P-C*l* bond. G has a <u>smaller</u> net dipole than H.
C			I-F bond is more polar than Br-C*l* bond. G has a greater net dipole than H.
D	 no net dipole	 no net dipole	Both G and H do not have a net dipole.

Q7 **(Ans: B)**

Statement 1 is correct. Since compounds M and N have the same electron cloud size, the strength of their intermolecular instantaneous dipole-induced dipole interactions is similar. However, the hydrogen bonds present between molecules of M are stronger than the permanent dipole-permanent dipole interactions between molecules of N. Hence, M would have a higher boiling point and lower volatility than N.

Statement 2 is correct. Compounds M and N are constitutional isomers as both have the same molecular formula $C_5H_{10}O$ but different structural formula.

Statement 3 is incorrect. M has 16 σ bonds whereas N has 15 σ bonds. (Note: Remember to include the C-H and O-H σ bonds.)

Q8 **(Ans: B)**

For ionic compounds, the extent of polarisation/distortion of the electron cloud of the anion and hence the degree of covalent character increases with:
- higher polarising power of the cation
- higher polarisability of the anion

Compared to Ca^{2+}, Mg^{2+} has a smaller ionic radius and hence a higher charge density and polarising power. Mg^{2+} is able to distort the electron cloud of the anion to a greater extent.

Compared to O^{2-}, S^{2-} has a larger and more polarisable electron cloud.

Hence, MgS has the greatest covalent character.

Q9 (Ans: D)

After mixing at constant temperature
Applying $p_1V_1 = p_2V_2$ (since n and T are constant),

(20 kPa)(1 m^3) = (p_{He})(3 m^3)
p_{He} upon mixing = 6.67 kPa

(10 kPa)(2 m^3) = (p_{Ne})(3 m^3)
p_{Ne} upon mixing = 6.67 kPa

From the calculations,
$p_{He} = p_{Ne}$ upon mixing

Total pressure upon mixing = 6.67 + 6.67 = 13.3 kPa

After decreasing temperature

- Total pressure will decrease below 13.3 kPa since $p \propto T$ (at constant V and n)
  $\Rightarrow$ options **A** and **B** are incorrect.
- p_{He} will still be equal to p_{Ne} as the number of moles of each gas remains the same
  $\Rightarrow$ option **C** is incorrect.

Q10 (Ans: B)

Element **D** is silicon as it has the highest melting point. Since the elements are consecutively arranged, **B** is sodium.

Q11 (Ans: A)

Option **A** is correct. The solubility of silver halides in aqueous ammonia decreases down the group (due to decreasing K_{sp} values). Since silver iodide is insoluble in aqueous ammonia, silver astatide is expected to be also insoluble in aqueous ammonia.

Option **B** is incorrect. The melting and boiling points of halogens increase down the group. Since iodine is a solid, astatine is expected to be also a solid at room temperature and pressure.

Option **C** is incorrect. H-X bond energy decreases down the group due to decreasing effectiveness of the valence orbital overlap. Hence the bond energy of HAt is expected to be smaller than that of HI.

Option **D** is incorrect. Oxidising power of halogens decreases down the group. Hence, a halogen can oxidise a halide below (but not above) it. Bromine is expected to be able to oxidise sodium astatide to give astatine.

Q12 (Ans: A)

$\Delta H_r^\ominus = \Sigma n\Delta H_c^\ominus \text{(reactants)} - \Sigma m\Delta H_c^\ominus \text{(products)}$

$= -3268 + 3(-286) - (-3754) = \underline{-372 \text{ kJ mol}^{-1}}$

Q13 (Ans: D)

Option **A** is incorrect. The standard enthalpy change of atomisation of chlorine is the energy absorbed when <u>1 mole of gaseous C*l* atoms</u> is formed from $Cl_2(g)$ under standard conditions. The correct equation should be

$$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$$

Option **B** is incorrect. The standard enthalpy change of combustion of a substance is the energy released when 1 mole of the substance is <u>completely burnt in excess oxygen</u> under standard conditions. The correct equation should be

$$H_2S(g) + \frac{3}{2}O_2(g) \longrightarrow H_2O(g) + SO_2(g)$$

Note: H_2 cannot be the end product of a combustion reaction as it can be combusted to give H_2O.

Option **C** is incorrect. The standard enthalpy change of formation of a substance is the energy change when 1 mole of the pure substance in a specified state is formed from its <u>constituent elements in their standard states</u> under standard conditions. The correct equation should be

$$H_2(g) + 2O_2(g) + S(s) \longrightarrow H_2SO_4(l)$$

Note: The elements, hydrogen and oxygen, do not exist in the monoatomic form under standard conditions (i.e. 1 bar and 298 K).

Option **D** is correct. The standard enthalpy change of solution of a substance is the energy change when 1 mole of the substance (ionic compound) is completely dissolved in a solvent to form an infinitely dilute solution (containing aqueous ions) under standard conditions.

Q14 (Ans: D)

Comparing the first and third experiments,
When [R] × 3 while keeping [S] constant, initial rate × 3 $\Rightarrow$ rate α [R].
Hence, order of reaction with respect to R is 1.

Comparing the first and second experiments,
When [R] × 2 and [S] × 2, initial rate × 8.
Since the order of reaction with respect to R is 1, rate α $[S]^2$.
Hence, order of reaction with respect to S is 2.

The rate equation is: rate = $k[R][S]^2$

Using data from the first experiment,
$k = 5.10 \times 10^{-4} \div (0.015 \times 0.010^2) = \underline{340}$ $mol^{-2}\ dm^6\ s^{-1}$

Q15 (Ans: C)

Statement 1	Correct. As there are no addition of any reactant or product to the system, the mole ratio of NH_3 : CO_2 should always stay the same at 2 : 1 (following the stoichiometric ratio of the balanced equation). Since p α n, P_{NH_3} : P_{CO_2} is also 2 : 1 at t_2.
Statement 2	Incorrect. Since the temperature at t_1 is higher than that at t_2, the rate of the forward (and backward) reaction at t_1 is greater than that at t_2. (Recall that at higher temperatures, a greater proportion of the reactant molecules have energy greater than or equal to the activation energy for reaction. Hence, the frequency of effective collisions increases resulting in an increase in rate of reaction.)
Statement 3	Incorrect. By Le Chatelier's Principle, a decrease in temperature will favour the backward exothermic reaction and a decrease in volume (or increase in total pressure) will favour the backward reaction which reduces the number of gas particles. Hence at t_2, the degree of decomposition of NH_2COONH_4 is smaller than that at t_1.
Statement 4	Correct. Decreasing the volume of the vessel will cause the total pressure (and partial pressures of NH_3 and CO_2) to increase. By Le Chatelier's Principle, the equilibrium position will shift left to reduce the number of gas particles and the partial pressures of NH_3 and CO_2 will decrease. Since the equilibrium constant (K_p = $(P_{NH_3})^2(P_{CO_2})$) remains unchanged (as temperature is constant) and the P_{NH_3} : P_{CO_2} stays the same at 2 : 1, the equilibrium partial pressures of NH_3 and CO_2 at t_2 will be the same as that at t_1.

Q16 (Ans: C)

SO_3 and SO_2 are found in both reactions 1 and 2. For the forward reaction of reaction 2 to proceed, SO_3 must first be formed from reaction 1.

Since the mole ratio of SO_3 and SO_2 is 1 : 1 in reaction 1, let x atm be the initial partial pressures of SO_3 and SO_2 for reaction 2.

	$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g)$	+	$O_2(g)$
initial pressure / atm	x		x		0
change in pressure / atm	–2(0.0275)		+2(0.0275)		+0.0275
eqm pressure / atm	x – 2(0.0275)		x + 2(0.0275)		0.0275

Since total pressure at equilibrium is 0.836 atm,

$P_{SO_3} + P_{SO_2} + P_{O_2} = 0.836$ atm

x – 2(0.0275) + x + 2(0.0275) + 0.0275 = 0.836
x = 0.40425

P_{SO_3} = 0.40425 – 2(0.0275) = 0.34925 atm
P_{SO_2} = 0.40425 + 2(0.0275) = 0.45925 atm

$$K_2 = \frac{(P_{SO_2})^2(P_{O_2})}{(P_{SO_3})^2} = \frac{(0.45925)^2(0.0275)}{(0.34925)^2} = \underline{0.0476\text{ atm}}$$

Q17 (Ans: D)

Option **A**	Incorrect. The correct pH of the buffer solution is: $\text{pH} = \text{p}K_\text{a} + \lg \dfrac{[\text{lactate}]}{[\text{lactic acid}]} = -\lg(1.4 \times 10^{-4}) + \lg \dfrac{0.5}{1.5} = 3.38$
Option **B**	Incorrect. Upon dilution with some water, the pH of the buffer solution should remain the same as the amount of lactic acid and sodium lactate in the buffer solution remains unchanged (although their concentrations decrease). $\text{pH} = \text{p}K_\text{a} + \lg \dfrac{[\text{lactate}]}{[\text{lactic acid}]} = \text{p}K_\text{a} + \lg \dfrac{\text{n(lactate)} \cancel{/ V_\text{buffer}}}{\text{n(lactic acid)} \cancel{/ V_\text{buffer}}} = \text{p}K_\text{a} + \lg \dfrac{\text{n(lactate)}}{\text{n(lactic acid)}}$ *(If the buffer solution is infinitely diluted with water, the $[\text{H}^+]$ in the buffer solution tends towards that of pure water (i.e. 10^{-7} mol dm^{-3}) and pH increases and approaches 7.)* Hence, pH of the buffer solution will not decrease upon dilution with water.
Option **C**	Incorrect. For a given volume, a more diluted buffer solution will have a lower buffering capacity due to smaller amount of the lactic acid and lactate ions to remove any added OH^- and H^+ ions respectively.
Option **D**	Correct. Since the buffer solution has a greater amount of lactic acid (weak acid) than the lactate ions (conjugate base), the buffer solution is more effective in buffering the effect of addition of small amounts of base than acid.

Q18 (Ans: B)

① $\text{Cu}^+(\text{aq}) + \text{C}l^-(\text{aq}) \rightleftharpoons \text{CuC}l(\text{s})$ $K_1 = 8.33 \times 10^5$

② $\text{CuC}l(\text{s}) + \text{C}l^-(\text{aq}) \rightleftharpoons \text{CuC}l_2^-(\text{aq})$ $K_2 = 0.104$

③ $\text{Cu}^+(\text{aq}) + 2\text{C}l^-(\text{aq}) \rightleftharpoons \text{CuC}l_2^-(\text{aq})$ $K_3 = \text{z}$

③ = ① + ②

$$K_3 = \frac{[\text{CuC}l_2^-]}{[\text{Cu}^+][\text{C}l^-]^2} = \frac{1}{[\text{Cu}^+][\text{C}l^-]} \times \frac{[\text{CuC}l_2^-]}{[\text{C}l^-]} = K_1 \times K_2 = 86632 \text{ mol}^{-2} \text{ dm}^6$$

Hence, z = $\underline{8.66 \times 10^4}$

Solubility product, K_sp, of $\text{CuC}l(\text{s}) = [\text{Cu}^+][\text{C}l^-] = \dfrac{1}{K_1} = \dfrac{1}{(8.33 \times 10^5)} = \underline{1.20 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}}$

Q19 (Ans: A)

From the *Data Booklet*: $E^\ominus(Cr_2O_7^{2-}/Cr^{3+}) = +1.33$ V and $E^\ominus(O_2/H_2O_2) = +0.68$ V

For this electrochemical cell, $E_{cell} = E(Cr_2O_7^{2-}/Cr^{3+}) - E(O_2/H_2O_2)$.
Hence, an $\underline{\text{increase in } E(Cr_2O_7^{2-}/Cr^{3+})}$ or a $\underline{\text{decrease in } E(O_2/H_2O_2)}$ will lead to an increase in E_{cell}.

The reduction half-equations of the two half-cells are shown below.
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ ------ (1)
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$ ------ (2)

For option **A**, addition of water to O_2/H_2O_2 half-cell favours the side with more aqueous species so position of equilibrium of (2) shifts left and $\underline{\text{decreases } E(O_2/H_2O_2)}$. Thus, E_{cell} increases.

For option **B**, $E^\ominus_{cell}$ for the reaction between I^- and $Cr_2O_7^{2-} = +1.33 - 0.54 = +0.79$ V
Hence the reaction is spontaneous and the addition of KI(s) to the $Cr_2O_7^{2-}/Cr^{3+}$ half-cell decreases $[Cr_2O_7^{2-}]$ so that position of equilibrium of (1) shifts left and $\underline{\text{decreases } E(Cr_2O_7^{2-}/Cr^{3+})}$. Thus, E_{cell} decreases. (Note: KI(s) is soluble in water and dissolves to form $K^+(aq)$ and $I^-(aq)$.)

For option **C**, 1 atm of O_2 has a higher pressure than 1 bar of O_2. The increase in P_{O_2} shifts position of equilibrium of (2) to the right and $\underline{\text{increases } E(O_2/H_2O_2)}$. Thus, E_{cell} decreases.

For option **D**, using $[Cr^{3+}]$ of 2.0 mol dm^{-3} increases $[Cr^{3+}]$ so that position of equilibrium of (1) shifts left and $\underline{\text{decreases } E(Cr_2O_7^{2-}/Cr^{3+})}$. Thus, E_{cell} decreases.

Q20 (Ans: B)

At **E4**, reduction of Cu^{2+} occurs: $Cu^{2+} + 2e^- \longrightarrow Cu$
$n_{e^-} = 2 \times n_{Cu} = 2 \times 0.635 / 63.5 = 0.02$ mol

Since $Q = n_{e^-} \times F = I \times t$,
$t = (n_{e^-} \times F) / I = (0.02 \times 96500) / 5 = 386$ s $= 6.43$ min $\Rightarrow$ Option **A** is incorrect

As Cu^{2+} is reduced to Cu at **E4**, $[Cu^{2+}]$ decreases and the colour intensity of the solution in cell 2 decreases $\Rightarrow$ Option **D** is incorrect.

At **E2**, H_2O is reduced to H_2: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$
Since OH^- is produced and the electrolyte contains Mg^{2+}, a white precipitate of $Mg(OH)_2$ is formed around **E2** $\Rightarrow$ Option **B** is correct.

At **E1** and **E3**, H_2O is oxidised to O_2 and effervescence is observed. At **E2**, H_2O is reduced to H_2 and effervescence is also observed $\Rightarrow$ Option **C** is incorrect.

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Q21 (Ans: D)

half-cell of V species	VO_2^+/VO^{2+}	VO^{2+}/V^{3+}	V^{3+}/V^{2+}	V^{2+}/V
$E^\ominus$/ V	+1.00	+0.34	−0.26	−1.20

Since the metal is oxidised, $E^\ominus_{cell} = E^\ominus$(species containing V) − $E^\ominus(M^{n+}/M)$

To be thermodynamically feasible, $E^\ominus_{cell} > 0$. Hence, $E^\ominus(M^{n+}/M)$ need to be less positive or more negative than $E^\ominus$(species containing V).

As the resultant solution is violet, the final vanadium-containing species is V^{2+}.

Thus, $E^\ominus(M^{n+}/M)$ must be <u>more negative than −0.26 V but less negative than −1.20</u> so that the metal will not further reduce V^{2+} to V.

half-cell of M^{n+}/M	Mg^{2+}/Mg	Ag^+/Ag	Sn^{2+}/Sn	Zn^{2+}/Zn
$E^\ominus$/ V	−2.38	+0.80	−0.14	−0.76

Since $E^\ominus(Zn^{2+}/Zn)$ is more negative than −0.26 V but less negative than −1.20 V, Zn reduces VO_2^+ to VO^{2+} then to V^{3+} and finally to V^{2+} ⇒ option **D** is correct.

Q22 (Ans: C)

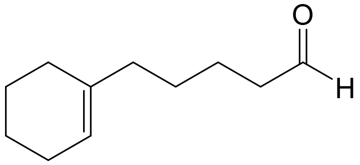
Statement 1 is incorrect. Since **S2** consists of $[CrY_6]^{3+}$ and absorbs orange-red light strongly, $[CrY_6]^{3+}$(aq) cannot be orange in colour as the colour observed is complement of the colour absorbed.

Statement 2 is correct. In **S3**, $[X]_{initial}$ and $[Y]_{initial}$ are reduced by half compared to **S1** and **S2**. The concentration of $[CrY_6]^{3+}$ formed is greater than $[CrX_6]^{3+}$, as can seen by the absorbance peak of $[CrY_6]^{3+}$ being reduced to a smaller extent in **S3**. Hence, ***Y*** forms the complex with Cr^{3+} more readily and ***Y*** forms stronger bond with Cr^{3+}.

Statement 3 is correct. Compared to $[CrY_6]^{3+}$, the absorbance peak of $[CrX_6]^{3+}$ is at a shorter wavelength with higher energy. Hence, d-orbital splitting is larger in $[CrX_6]^{3+}$.

Q23 (Ans: C)

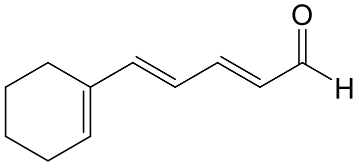
An example of a 11 carbon-containing compound with an aldehyde group, a cyclohexene ring and a straight chain is shown below.



($C_{11}H_{18}O$)

Since compound A ($C_{11}H_{14}O$) has 4 fewer H atoms than the above structure, compound A must have two more C=C bonds ⇒ total of 2 + 2 = 4 double bonds.

A possible structure of compound A:



With 4 double bonds in the structure, there should be <u>4 π bonds</u>.

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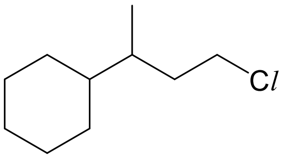
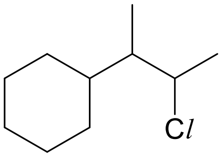
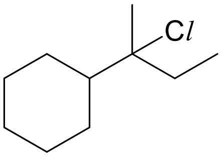
Q24 (Ans: D)

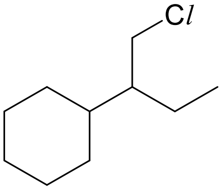
Statement 1 is correct. The initiation step involves the homolytic fission of the C*l*-C*l* bond. The propagation steps can involve the homolytic fission of C-H and C*l*-C*l* bonds.

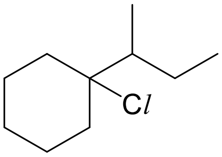
Statement 2 is correct. Ignoring stereoisomers, the eight possible mono-chlorinated products are as follows.

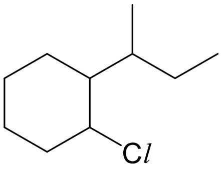


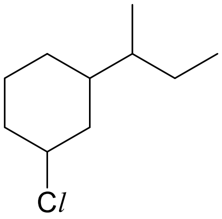


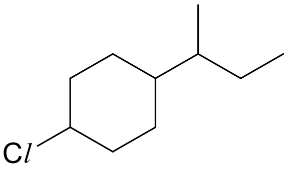




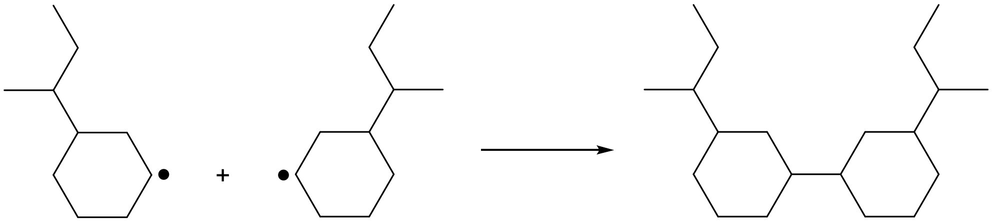








Statement 3 is correct. In the termination step, two alkyl radicals (•$C_{10}H_{19}$) can react together to form the product ($C_{20}H_{38}$) in small quantities. Example:



Q25 (Ans: C)

Cars are fitted with catalytic converters to remove three main pollutants (CO, NO_x and unburnt hydrocarbons) from exhaust gases. The harmful gases are converted into CO_2, N_2 and H_2O.

The following reactions occur in the catalytic converter. Each reaction is a redox reaction.

Reaction	Remarks
$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$	Reaction 1 is correct. • CO is oxidised. • O_2 is reduced.
$2NO(g) + 2CO(g) \longrightarrow 2CO_2(g) + N_2(g)$	• CO is oxidised. • NO is reduced.
$NO_2(g) + 2CO(g) \longrightarrow 2CO_2(g) + \frac{1}{2}N_2(g)$	Reaction 2 is correct. • CO is oxidised. • NO_2 is reduced.
$C_xH_y(g) + (x + \frac{y}{4})O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$	Reaction 3 is correct. • C_xH_y is oxidised. • O_2 is reduced.

Reaction 4 is incorrect as both hydrocarbons and carbon monoxide needs to be oxidised. Hence, they do not react together in the catalytic converter.

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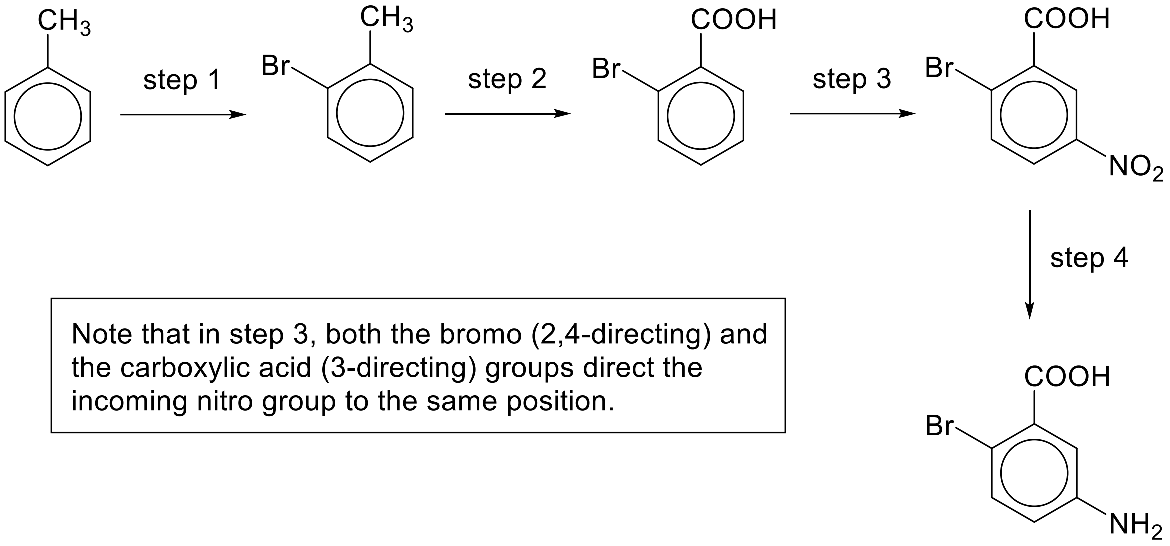
Q26 (Ans: D)

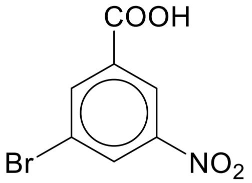
The sequence of reactions that would give the highest yield of compound C is given below.



C

Note that in step 3, both the bromo (2,4-directing) and the carboxylic acid (3-directing) groups direct the incoming nitro group to the same position.

Option **A** is incorrect. The major product,



, formed in step 3 does not lead to the eventual formation of C.

Option **B** is incorrect. In step 4, the amino (2,4-directing) and the carboxylic acid (3-directing) groups do not direct the incoming bromo group to the same position.

Option **C** is incorrect. In step 2, the methyl (2,4-directing) and the bromo (2,4-directing) groups do not direct the incoming nitro group to the same position.

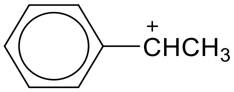
Q27 (Ans: B)

To oxidise the aldehyde group (–CHO) in J to carboxylic acid group (–COOH) in K (without oxidative cleave of the C=C bond), only $K_2Cr_2O_7$ with H_2SO_4 and heating can be used. If J is heated with $KMnO_4$ and H_2SO_4, the C=C bond will undergo oxidative cleavage, in addition to the oxidation of the –CHO to –COOH.

For the reduction of both alkene (C=C) and aldehyde (–CHO) groups in J to $–CH_2CH_2–$ and primary alcohol ($–CH_2OH$) groups respectively in L, only H_2 with Ni and heating can be used. If $NaBH_4$ is used, only –CHO will be reduced to $–CH_2OH$ and the C=C bond will remain unreacted.

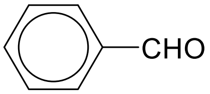
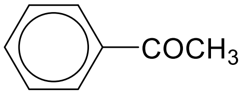
Q28 (Ans: B)

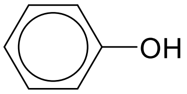
(1-Bromoethyl)benzene reacts with methylamine via <u>nucleophilic substitution</u>. As the rate of the reaction is independent of the concentration of the nucleophile, CH_3NH_2, the reaction proceeds via S_N1 mechanism. The following carbocation will be formed when the C–Br bond breaks in the rate-determining step:

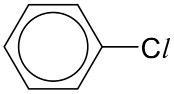
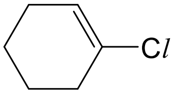


Q29 (Ans: A)

Option **A** is correct. When heated with NaOH, $CH_3CH_2NH_3^+$ will undergo acid-base reaction to form $CH_3CH_2NH_2$ gas which will turn damp red litmus paper blue. For $(CH_3CH_2)_4N^+$, there is no acid-base reaction with NaOH, and no gas will be evolved.

Option **B** is incorrect. Fehling's solution forms brick-red ppt of Cu_2O only with aliphatic aldehyde.  is an aromatic aldehyde and  is a ketone. Hence, both compounds will not form brick-red ppt.

Option **C** is incorrect. Both  and CH_3CH_2OH do not react with aqueous Na_2CO_3 to form CO_2 gas. (Note: Aqueous Na_2CO_3 reacts only with carboxylic acid functional group.)

Option **D** is incorrect. In both  and , the lone pair of electrons in the p orbital of the chlorine is able to delocalise into the benzene ring and C=C bond respectively. As there is partial double bond character in the C–C*l* bond, the bond is strengthened and will not be easily broken to form chloride ions when heated with ethanolic $AgNO_3$. Hence, no AgC*l* (white ppt) will be observed for both compounds.

Q30 (Ans: D)

In options **B** and **C**, the compounds contain the –CH(CH_3)OH group which will give a yellow ppt with hot alkaline aqueous $I_2 \Rightarrow$ Options **B** and **C** are incorrect.

(Note: In option **D**, the –N(CH_3)$COCH_3$ group is an amide which will not form a yellow ppt with hot alkaline aqueous I_2.)

Option **A** is incorrect. The –CN group will be reduced by $LiAlH_4$ in dry ether to form a primary amine (–CH_2NH_2). The product contains the –CH_2NH_2 and –C$(CH_3)_2$OH groups which will react with ethanoyl chloride to form an amide and ester respectively, and hence the product will react with ethanoyl chloride in a 1:2 ratio.

Option **D** is correct. The –N(CH_3)$COCH_3$ group will be reduced by $LiAlH_4$ in dry ether to form a tertiary amine (–N(CH_3)CH_2CH_3) which does not react with ethanoyl chloride. Since only –C$(CH_3)_2$OH group will react with ethanoyl chloride, the product will react with ethanoyl chloride in a 1:1 ratio.

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