**1** Answer: **D**
Topic: mole concept

Solution:
$C_nH_{2n+2}$ + ((3n+1)/2)$O_2$ → n$CO_2$ + (n+1)$H_2O$
Residual gas, V = $CO_2$ and unreacted $O_2$ at rtp.

For 10 $cm^3$ $CH_4$
⇒ $CO_2$ = 10 $cm^3$
⇒ $O_2$ unreacted = 70 – 20 = 50 $cm^3$
⇒ V = 60 $cm^3$
Only option D starts with 60 $cm^3$.

**2** Answer: **A**
Topic: Mole Concept

Solution:
Ammonium cyanate → $CO(NH_2)_2$
Ammonium, $NH_4^+$
To balance the atoms and charge:
Cyanate should have 1 C, 1N, 1O;
overall –1 charge. ⇒ Hence, $CNO^-$.

**3** Answer: **D**
Topic: Energetics

Solution:
A×: $O_2$ is a covalent molecule.
B×: Atomising $O_2$ requires breaking strong O=O bond.
C: Irrelevant to explain existence of oxides.
D: Refer to Born–Haber cycle. Lattice enthalpy is highly exothermic and it counterbalances the endothermic process including 1st electron affinity.

**4** Answer: **D**
Topic: Energetics

Solution:
$C(s) + O_2(g) \rightarrow CO_2(g)$ (1) $\Delta H_c^\theta$ (C(graphite))
$CO_2(g) \rightarrow CO(g) + ½O_2(g)$ (2) $-\Delta H_c^\theta$ (CO)

(1) + (2) = (3)
$C(s) + ½O_2(g) \rightarrow CO(g)$ (3) $\Rightarrow \Delta H_f^\theta$ (CO)

**5** Answer: **B**
Topic: Electrochem

Solution:
Analysis: Ni oxidised, cation reduced.
From data booklet, $E_{ox}{}^\theta{}_{Ni^{2+}/Ni}$ = – 0.25 V
$E^\theta{}_{Co^{2+}/Co}$ = – 0.28 V
$E^\theta{}_{Fe^{3+}/Fe^{2+}}$ = + 0.77 V
$E^\theta{}_{Mn^{2+}/Mn}$ = – 1.18 V
$E^\theta{}_{V^{2+}/V}$ = – 1.20 V
$E^\theta{}_{cell}$ is >0 in reaction with $Fe^{3+}$.

**6** Answer: **A**
Topic: Kinetics, Ionic Eqm

Solution:
pH 3 ⇒ $[H^+] = 10^{-3}$ mol $dm^{-3}$
pH 1 ⇒ $[H^+] = 10^{-1}$ mol $dm^{-3}$
Given, reaction is 1st order wrt $[H^+]$,
ratio of rate = 0.001/0.1 = 0.1

**7** Answer: **C**
Topic: Ionic Eqm

Solution:
When iodide is added to $Hg^{2+}$, mass of ppt ($HgI_2$) increases as volume of iodide increases. As more iodide is added, mass of precipitate decreases due to formation of soluble complex, $HgI_4^{2-}$. Decrease in [iodide] due to formation of complex in (2) causes eqm in (1) to shift left to produce more iodide. Hence ppt dissolves. [Concept is similar to $PbI_2$ dissolving in excess KI.]

$Hg^{2+} + 2I^- \rightleftharpoons HgI_2$ (1)
$HgI_2 + 2I^- \rightarrow HgI_4^{2-}$ (2)

**8** Answer: **C**
Topic: Group II

Solution:
Decomposition of group II nitrate forms an oxide. Hence only A and C are possible answers: BaO is formed. However, question states that an unreactive gas is produced with heat evolved, $N_2$ (high bond energy released N≡N) is the gas and not NO. Also, NO is rapidly oxidised by air to produce $NO_2$, hence unlikely to be the product in this reaction.

**9** Answer: **D**
Topic: Periodic Table

Solution:
A×: Atomic size decreases across period ⇒ N > O > F
B, C×: Ionic radius across isoelectronic series decreases across period
⇒ $N^{3-} > O^{2-} > F^-$
⇒ $Na^+ > Mg^{2+} > Al^{3+}$ (ionic radius in Data Booklet)
D: Na+, Ne and $F^-$ are isoelectronic (10 electrons) but nuclear charge is highest for Na+, followed by Ne than F– (refer to proton no.). Hence, electrostatic attraction for the valence electrons decreases from $Na^+$ to Ne to $F^-$.
⇒ size: $Na^+ > Ne > F^-$

**10** Answer: **C**
Topic: Periodic Table

Solution:
**Y** is phosphorus, **X** is silicon, **Z** is sulfur.
Sulfur has lower 1st IE than phosphorus due to inter–electron repulsion in $3p^4$ configuration.
In terms of melting point: $P_4 < S_8 <$ Si
Si is giant molecular compound.
$P_4$ and $S_8$ has weak intermolecular vdw forces of attraction and $S_8$ has larger no. of electrons hence stronger intermolecular vdw forces than $P_4$.

**11** Answer: **C**
Topic: Periodic Table
Solution:
Property 1: $SiO_2$ is insoluble in water while $SO_2/SO_3$ forms $H_2SO_3/H_2SO_4$.
Property 2: Si, [Ne] $3s^2$ $3p^2$; S [Ne] $3s^2$ $3p^4$

**12** Answer: **D**
Topic: Periodic Table

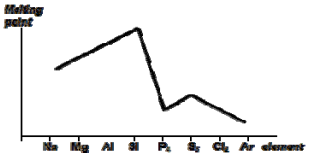
Solution:
Oxides and chlorides of phosphorus form acidic solutions.
$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$ (pH = 1–2)
$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$
$PCl_5(l) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

**13** Answer: **A**
Topic: Periodic Table/Chem. Bonding

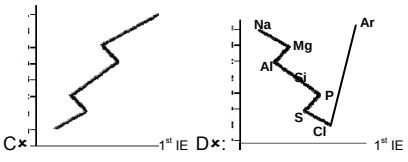
Solution:
Al in $AlCl_3$ has only 6 electrons, hence can accept lone pair from $Cl^-$ ion via dative bond to form $AlCl_4^-$, achieving octet configuration.

**14** Answer: **A**
Topic: Periodic Table

Solution:
A: mass number increases from Na to Ar. ($A_r$ – atomic no. ≈ mass no.)




B×:




C× D×:

**15** Answer: **A**
Topic: Group II

Solution:
A: $Li_2CO_3 \rightarrow Li_2O + CO_2$.
B×: Oxide not nitrate is formed.
C×: Li reacts vigorously with $O_2$.
D×: Like Mg, Li reacts slowly with cold water.

**16** Answer: **B**
Topic: Group II

Solution:
2nd IE decreases down the group due to decreasing ENC.
A, C, D: Incorrect. Reactivity increases down the group. Solubility of group II hydroxides increases and thermal stability increases.

**17** Answer: **A**
Topic: Group II

Solution:
Formation of soluble complex with thiosulfate enables AgCl to dissolve (concept similar to AgCl soluble in $NH_3$).
B, C, D: Incorrect. This is not a redox reaction. Oxidation no. of $Ag^+$ (+1) remains the same before and after.

**18** Answer: **B**
Topic: Transition Elements

Solution:
$NH_3$ is produced to form alkaline solution.
Grey–green ppt is $Fe(OH)_2$.

**19** Answer: **A**
Topic: Organic Chem

Solution:
Ethanoic acid is soluble in water but not ethyl ethanoate. It reacts with aqueous NaOH but not ethanol.

**20** Answer: **A**
Topic: Organic Chem.

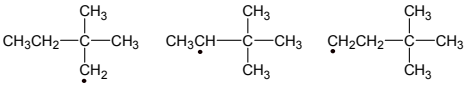
Solution:
A: Alcohols: $C_nH_{2n+2}O$
B: Aldehydes: $C_nH_{2n}O$
C: Carboxylic acids: $C_nH_{2n}O_2$
D: Halogenoalkanes: $C_nH_{2n+1}X$

**21** Answer: **D**
Topic: Arenes

Solution:
Length of C–C bond in benzene is in between that of C–C and C=C bonds in aliphatic compounds due to delocalisation of electrons.
B: Incorrect. Benzene does <u>not</u> conduct electricity unlike graphite with delocalised electrons. In graphite, the $\pi$–electrons are delocalised over the entire plane of C–atoms in a giant molecular structure, while in a benzene molecule, they are only delocalised within the molecule (ring). The delocalised electrons in one benzene molecule cannot '*move*' to another molecule to conduct electricity.

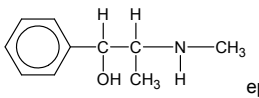
**22** Answer: **C**
Topic: Alkane

Solution:
Three different forms of radical:



**23** Answer: **B**
Topic: Amine, benzene, alcohol

Solution:



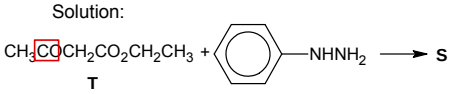
ephedrine

A×: $CH_3COOH$ is neutralised by amine group. $CH_3COCl$ reacts with alcohol to form ester.

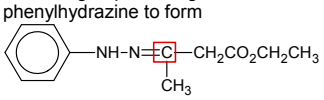
B: amine group in ephedrine can act as nucleophile to substitute –Br in $CH_3Br$. Alcohol and amine do not react with NaOH.
C×: HCl reacts with amine group. $PCl_5$ reacts with alcohol group.
D×: Tollens' reagent does not react since no aldehyde present. $Br_2$ does not react since catalyst is necessary for ES of benzene.

**24** Answer: **D**
Topic: Carbonyl compounds

Solution:

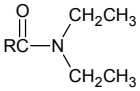



Ketone group undergoes condensation with phenylhydrazine to form




**25** Answer: **B**
Topic: Amides

Solution:




Protonated amine, $(CH_3CH_2)_2NH_2^+$ is least likely to be obtained after <u>*basic*</u> hydrolysis.

**26** Answer: **D**
Topic: Alcohol, acids and derivatives

Solution:
**P** is an alcohol. **Q** is $CH_3CH_2COBr$ and **R** is carboxylic acid which reacts less readily than **Q** to form an ester.

**27** Answer: **B**
Topic: Alcohols

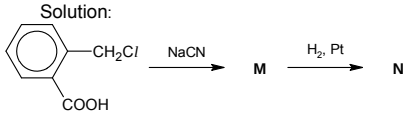
Solution:
A:

True. $\underset{\text{acid}}{(CH_3)_3COH_2^+} \rightleftharpoons \underset{\text{conjugate base}}{(CH_3)_3COH} + H^+$

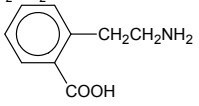
B: Untrue. $H^{\delta+}$–$Cl^{\delta-}$. The alcohol group in $(CH_3)_3COH$ is protonated by HCl in step 1. ⇒ HCl is acting as an (acid) proton donor. The nucleophile in this reaction (step 3) is $Cl^-$.
C: True. Add all three equations up to get the overall eqn.
D: True. From overall eqn, it can be seen that $Cl^-$ nucleophile substitutes –OH group bonded to $C^{\delta+}$.

**28** Answer: **B**
Topic: Carboxylic acid and halogen derivatives

Solution:




Halogenoalkane group $–CH_2Cl$ undergoes nuc. sub to form $–CH_2CN$ in **M**. $H_2$ gas <u>*cannot*</u> reduce –COOH but can reduce –CN to $–CH_2NH_2$ in **N**.




**N**:
Hence, option C and D are incorrect.

**29** Answer: **D**
Topic: Organic cpd synthesis

Solution:

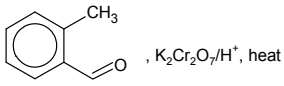
$(CH_3)_2CHCH_2CH_2OH + CH_3COOH \rightleftharpoons CH_3CO_2CH_2CH_2CH(CH_3)_2 + H_2O$

<u>*Sequence of synthesis:*</u>
Distill→$NaHCO_3$→ separating funnel → $Na_2SO_4$

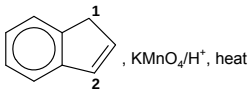
II: distillation separates ester and the excess ethanoic acid and water.
IV: Adding aqueous $NaHCO_3$ to the liquid ester and shaking the mixture removes the any trace of acid.
III: Shaking mixture in a separating funnel separates aqueous and organic layer (ester)
I: adding anhydrous sodium sulfate to the liquid ester removes any remaining trace of water.

**30** Answer: **B**
Topic: Carboxylic acid and derivatives, alkenes, aldehydes.

Solution:




B:
Alkyl side chain <u>*cannot*</u> be oxidised by acidified $K_2Cr_2O_7$ to form –COOH.




A:
The cyclic side–chain is like two alkyl groups and since each of the C (1, 2) has at least one H atom, each of them becomes –COOH upon oxidation.

**31** Answer: **C**
Topic: Atomic structure

Solution:
**1×** K.E.=½ $mv^2$ ⇒ At the same temp and pressure, KE is the <u>*same*</u> (not different) for both gases. So since the molecules have different masses, the heavier $^{37}Cl_2$ will move slower.
**2✓** As a result of different masses, isotopes have <u>*different*</u> physical properties. Pure $^{37}Cl_2$ has higher density, melting and boiling point than $^{35}Cl_2$.
**3✓** $M_r$ = 70 and 74.

**32** Answer: **D**
Topic: Chemical bonding

Solution:
1✓ $CH_3COOH$ is a polar molecule.
2× NaCl is <u>*not*</u> a molecule.
3× $SiO_2$, although polar, does not absorb microwave due to its giant molecular structure.
*[For info: When exposed to microwave (that consists of electric field), simple molecular polar compounds like water are 'free' to align their dipoles to absorb it. In giant molecular polar $SiO_2$, dipoles are fixed in position, unable to align. Hence no absorption.]*

**33** Answer: **C**
Topic: Ionic eqm

Solution:
**1×** $NH_4^+$ is the conjugate acid of $NH_3$. Hence the solution is <u>*acidic*</u>. $NH_4^+ \rightleftharpoons NH_3 + H^+$.
**2✓** $CO_3^{2-}$ is the conjugate base of $HCO_3^-$. Hence the solution is basic.
$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$.
**3✓** $CH_3COO^-$ is the conjugate base of $CH_3COOH$. Hence the solution is basic.
$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$. .

**34** Answer: **A**
Topic: Energetics

Solution:
**1✓** $M^{2+}(g) \rightarrow M(g)$ ⇒ –(sum of 1st and 2nd IE)
$Mg^{2+}$: –2186 kJmol$^{-1}$; $Ca^{2+}$:–1750 kJmol$^{-1}$
**2✓, 3✓** $|\Delta H_{hyd}| \propto \frac{q_+}{r_+}$ and $|\Delta H_{latt}| \propto \frac{q_+q_-}{r_+ + r_-}$
Since $Mg^{2+}$ is smaller than $Ca^{2+}$ it has larger $|\Delta H_{hyd}|$ and $|\Delta H_{latt}|$. Hence more exo hydration and lattice enthalpy (both enthalpies are always exo).

**35** Answer: **C**
Topic: Electrochemistry

Solution:
This is about the electrolytic cell.
**1×** Cu electrode is oxidised and $Cu^{2+}$ is reduced. Hence neither $O_2$ or $H_2$ is produced. This is like the copper–plating process.
**2✓** Bromide is oxidised to produce bromine. ⇒ $E^\theta_{Br_2/Br^-}$ (+1.07V) is less positive than $E^\theta_{O_2/H_2O}$ (+1.23V). Hence preferentially oxidised. Water is reduced to form $H_2$.
**3✓** Water is reduced to form $H_2$ (not $Na^+$ due to less negative $E^\theta_{H_2O/H_2}$ –0.83V); water is oxidised to form $O_2$ (not $SO_4^{2-}$ due to less positive $E^\theta_{O_2/H_2O}$ +1.23V).

**36** Answer: **C**
Topic: Kinetics

Solution:
**1×** trans–isomer is more stable (lower energy level than cis–isomer), hence $\Delta H^\theta_{hydrogenation}$ should be –116 kJ mol$^{-1}$.
**2✓** Since they both form butane, the difference in $\Delta H^\theta$ value represents difference in energy level between cis and trans–isomer.
**3✓** Let fraction amount of trans–isomer be (1–x); cis–isomer be x.
⇒ x(–120) + (1–x)(–116) = –117 ⇒ x = 0.25.

**37** Answer: **C**
Topic: Intro to Organic Chem

Solution:
**1×** π bond is <u>*weaker*</u> than the σ bond due to more less overlap between the two p–orbitals.
**2✓** since the C=C is made of one π and one σ bond, the π bond can be estimated to be (610 – 350) ≈ 260 kJ mol$^{-1}$.
**3✓** C≡C is made of one π bond is <u>*weaker*</u> than the σ bond . Hence using the π bond value of in 2, C≡C bond energy = 610 + 260
= 870 kJ mol$^{-1}$.

**38** Answer: **C**
Topic: Intro to Organic Chem

Solution:
**1×** In the presence of strong acid ($H_2SO_4$), alcohol cannot act as an acid to deprotonate and form $CH_3CH_2O^-$ ion.
**2, 3✓**
In acting as a base in the presence of concentrated acids, alcohols accepts a proton:
$CH_3CH_2OH + H_2SO_4 \rightarrow CH_3CH_2OH_2^+ + HSO_4^-$

**39** Answer: **D**
Topic: Alcohols

Solution:
**1✓** Only primary and secondary alcohols undergoes oxidation due to presence of H atom bonded to C with OH group.
**2×** Steric hindrance plays no part in the oxidation of alcohols.
**3×** Boiling point bears no relevance to oxidation.

**40** Answer: **B**
Topic: Redox and alcohol

Solution:
**1, 2✓** Ethanol is oxidised to ethanal (**L**; positive Tollens' test) and both give positive iodoform test.
**3×** Copper cannot be reduced! It is a metal in the elemental state, with an oxidation state of 0. In this reaction, $O_2$ in air is reduced to form water.

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