

Chemistry Solutions (Multiple Choice)

Section A: Fast

1. **Answer:** 18 electrons, 19 protons, 22 neutrons

Working: Element K \rightarrow proton number 19
Mass number 41 \rightarrow neutron number $41 - 19 = 22$
Ion $+1 \rightarrow$ 1 less electron \rightarrow 18 electrons

2. **Answer:** $[\text{Ar}] 3d^9$

Working: $[\text{Cu}] = [\text{Ar}] 4s^1 3d^{10}$ (copper and chromium are exceptions to Aufbau principle)
Electrons are lost from 4s before 3d:
 $\rightarrow [\text{Cu}^{2+}] = [\text{Ar}] 3d^9$

3. **Answer:** 1.8×10^{24}

Working: Moles $= 6 / (14 + 14) = 0.2143$
Molecules $= 0.2143 \times 6.02 \times 10^{23} = 1.29 \times 10^{23}$
Protons $= 7 \times 2 \times 1.29 \times 10^{23} = 1.806 \times 10^{24} = 1.8 \times 10^{24}$ (2 s.f.)

4. **Answer:** $7.76 \times 10^{-2} \text{ mol dm}^{-3}$

Working: Moles $\text{PbCl}_2 = 1.08 / 278.2 = 3.882 \times 10^{-3}$
Mol $\text{Cl}^- = 2 \times 3.882 \times 10^{-3} = 7.764 \times 10^{-3}$
 $[\text{Cl}^-] = (7.764 \times 10^{-3}) / (100 / 1000) = 7.76 \times 10^{-2} \text{ mol dm}^{-3}$

5. **Answer:** butan-2-ol

Working: Butan-2-ol (hydrogen bonding) $>$ butanal (induced dipole forces)
 $>$ 1-fluorobutane (induced dipole forces) $>$ E-but-2-ene (VDW)

6. **Answer:** $(\text{CH}_3)_2\text{CO}$

Working: CCl_4 and CO_2 are symmetrical molecules and so their dipole moments cancel out.
 C_2F_4 is also symmetrical on both sides of the double bond.
Due to the CO bond in CH_3COCH_3 , there is a permanent dipole.

7. **Answer:** $\text{Li (s)} + \frac{1}{2} \text{F}_2 \text{ (g)} \rightarrow \text{LiF (s)}$

Working: Enthalpy of formation: 1 mole of a compound formed in its standard state from its elements in their standard states.

8. **Answer:** $\text{rate} = k [\text{X}] [\text{Y}]$

Working: (1): $\text{rate} = k [\text{W}]^2 [\text{X}]$: false since would be x8.
(2): $\text{rate} = k [\text{W}]^2 [\text{Y}]$: false since also would be x8
(4): $\text{rate} = k [\text{X}] [\text{Z}]$: false since cannot typically include product in rate equation.
By process of elimination, third option is correct.

9. **Answer:** $\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

Working: Third order equation has the form: $\text{rate} = k [\text{reactants}]^3$
 $[k] = [\text{rate}] / [\text{concentration}]^3 = \text{mol dm}^{-3} \text{ s}^{-1} / (\text{mol dm}^{-3})^3$
 $[k] = \text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

10. **Answer:** Low pressure and high temperature

Working: Enthalpy change positive \rightarrow endothermic \rightarrow high temperature shifts equilibrium towards products.
3 gas molecules in products vs 2 in reactants \rightarrow low pressure shifts equilibrium towards products

11. **Answer:** d block

Working: Yttrium (Y): Transition metal, atomic number 39.

12. **Answer:** Cl_2

Working: Oxidising agent \rightarrow accepts electrons \rightarrow most electronegative
Electronegativity of halogens decreases down the group
 \rightarrow most is chlorine

13. **Answer:** sodium chloride, sodium chlorate(I) and water

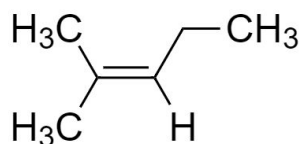
Working: $\text{Cl}_2 + 2 \text{NaOH} \rightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O}$

14. **Answer:** a cream precipitate soluble in concentrated aqueous ammonia

Working: Bromide \rightarrow cream ppt with AgNO_3 (aq)
Solubility in ammonia decreases down the group \rightarrow soluble in conc
 NH_3 (aq) only

15. **Answer:** 2-methylpent-2-ene

Working: Reforming the alkene bond, we get



Longest chain: 5

Starting at bottom left: 2-methylpent-2-ene

16. **Answer:** methyl methanoate

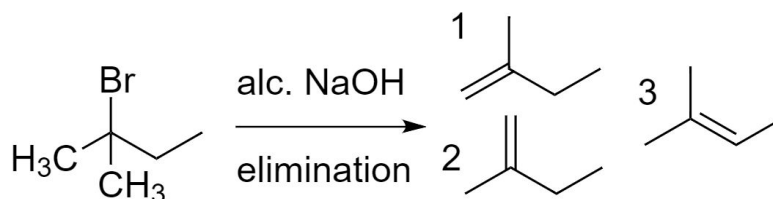
Working: Methanol: $\text{CH}_3\text{OH} = \text{CH}_4\text{O}$ (no match)
Methyl methanoate: $\text{HCOOCH}_3 = \text{C}_2\text{H}_4\text{O} = 2 \text{CH}_2\text{O}$ (match)
Ethane-1,2-diol: $\text{CH}_2\text{OHCH}_2\text{OH} = \text{C}_2\text{H}_6\text{O}_2 = 2 \text{CH}_3\text{O}$ (no match)
Butanal: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} = \text{C}_4\text{H}_8\text{O}$ (no match)

17. **Answer:** 3

Working: 1: electron pair from nucleophile attacks partial positive C (correct)
2: elimination of bromide (correct)
3: $\text{N}^+\text{-H}$ electrons should move to N not H to resolve + charge
4: deprotonation by another ammonia molecule (correct)

18. **Answer:** 2

Working: Ethanolic potassium hydroxide \rightarrow elimination mechanism
Elimination requires a hydrogen to be removed from an adjacent carbon from the halogen carbon:



But the 1 and 2 are the same product \rightarrow 2 alkenes.

19. **Answer:** ethylamine > ammonia > phenylamine

Working: Basicity of amines: $2^\circ > 1^\circ > \text{NH}_3$ (inductive effect)
and $\text{NH}_3 > \text{aromatic}$ (delocalisation) so
ethylamine (1°) > ammonia > phenylamine (aromatic)

20. **Answer:** ClF_4^-

Working: CH_4 , NH_4^+ and AlCl_4^- : tetrahedral (bond angle 109.5°)
 ClF_4^- : 6 pairs (4 b.p., 2 l.p.) \rightarrow square planar $\rightarrow 90^\circ$

21. **Answer:** CH_3OH

Working: HCHO : planar carbonyl group
 CH_3^+ : trigonal planar
 CH_3OH : free rotation of O-H and C is tetrahedral \rightarrow not planar
 C_2H_4 : restricted rotation and trigonal planar

22. **Answer:** Ammonium chloride

Working: $\text{A} + \text{NaOH} \rightarrow \text{NH}_3 + \text{NaCl} + \text{H}_2\text{O}$
A must contain nitrogen and chlorine as it is not on the other side. It also likely contains lots of H since there is only 1 on the left and 5 on the right \rightarrow ammonium.
Likely does not contain O since already has 1:1 reacting ratio.
 \rightarrow ammonium chloride seems reasonable. Check:
 $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NH}_3 + \text{NaCl} + \text{H}_2\text{O} \rightarrow$ simple 1:1 ratio balances.
(This could also be deduced by knowledge of acid-base reactions.)

23. **Answer:** boron

Working: Reducing agent gets oxidised \rightarrow loses e^- / loses H / gains O
Boron (B) gains O to B_2O_3 .

24. **Answer:** 3-bromohexane

Working: Secondary haloalkane: carbon bonded to halogen is bonded to 2 other carbons.

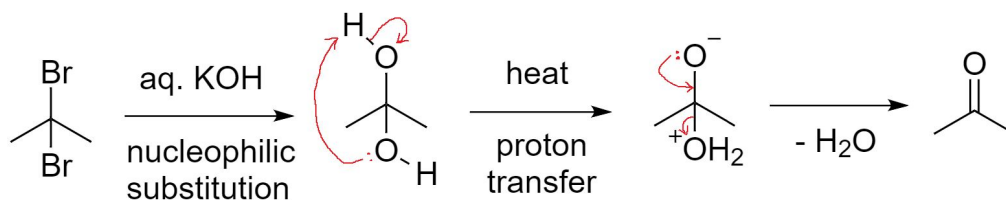
25. **Answer:** -enoic acid

Working: Suffix has the highest priority group.
Priority is carboxylic acid > amide > alcohol etc
So it ends in -oic acid.
However, the longest chain in the molecule contains double
(alkene) bonds → instead of -anoic acid it is -enoic acid.

(Actual full name is:
(E)-6-(2-chloro-5-hydroxycyclohexyl)-4-((ethylamino)methyl)-2-methylundeca-8,10-dienoic acid.)

26. **Answer:** Nucleophilic substitution and dehydration

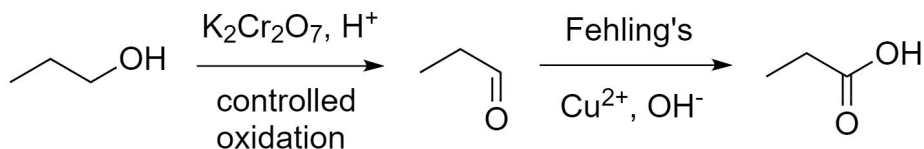
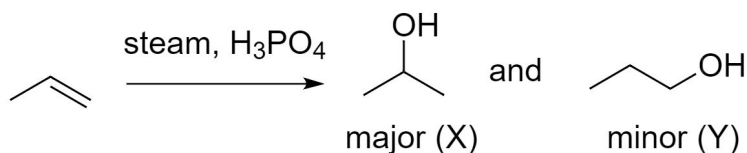
Working: First step is standard nucleophilic substitution (twice; one for each Br) to form propane-2,2-diol. This compound is unstable and can react with itself to transfer a proton (H) and eliminate water.



The loss of a small molecule is condensation; when this molecule is water, it is dehydration.

27. **Answer:** propanal and copper(I) oxide

Working: The reactions are:



(By Markovnikov's rule, primary carbocation is minor.)
(Alkaline CuSO_4 is Fehling's reagent.)

The red precipitate indicates the presence of a transition metal (Cu) ion. Cu^{2+} is blue and Cu^{2+} must have been reduced (since it is an oxidising agent) so the only possible ion is Cu^+ . Cannot be copper(I) dichromate since all chromium was used up (it was limiting in the mild oxidation conditions) so must be oxide (Cu_2O).

28. **Answer:** 1 mole of each electrode metal

Working: Standard conditions are:
Temperature 298 K, 101 kPa for gases, 1 mol dm^{-3} for solutions.

29. **Answer:** **A** and **B** only

Working: α -helices and β -pleated sheets are formed by hydrogen bonds in different geometries. Disulfide bridges are -S-S- bonds.

30. **Answer:** CH_3OCH_3

Working: PCl_5 , C_2H_4 and CO_2 are symmetrical.
In CH_3OCH_3 , the C-O-C bond is non-linear ($\sim 104.5^\circ$) so there is a net dipole moment towards the O-side of the molecule.

31. **Answer:** Calcium sulfide

Working: Most exothermic \rightarrow most stable (strongest ionic bonds).
 LiF : small, singly charged ions.
 LiCl : singly charged ions with covalent character \rightarrow stronger
Magnitude of charge has greater effect than size.
 CaO : doubly charged ions
 CaS : doubly charged ions with covalent character \rightarrow strongest.

32. **Answer:** 1 and 2 only

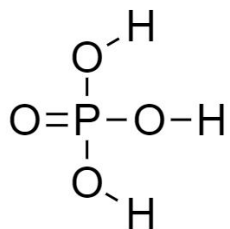
Working: LiAlH_4 is a stronger reducing agent than NaBH_4 .
We know that LiAlH_4 and NaBH_4 both reduce aldehydes/ketones and only LiAlH_4 can reduce carboxylic acids.
Without knowledge of reduction of esters, the answer can be deduced.

33. **Answer:** phosphate

Working: Carbonate: CO_3^{2-} . Phosphate: PO_4^{3-} . Sulfide: S^{2-} .
Hydrogencarbonate: HCO_3^- .

34. **Answer:** 7

Working: The structure of H_3PO_4 is



Each double bond contains one sigma bond and one pi bond.
→ total sigma bonds = 7.

35. **Answer:** $\text{CO}_2 + \text{C} \rightarrow 2 \text{CO}$

Working: Heterogeneous: catalyst in different phase as reactants.
Looking for homogeneous (same phase).
(1) Haber process: catalyst is Fe (iron; solid)
(2) occurs in a catalytic converter of a car: uses Pt / Rh / Pd (solid) catalyst
(4) Contact process: catalyst is V_2O_5 (solid)
By process of elimination, third choice is correct (unfamiliar reaction).

36. **Answer:** H_2

Working: Ligand: must have lone pair(s) of electrons.

37. **Answer:** spontaneous below 66°C

Working: exothermic and negative entropy → feasible at low temperatures

38. **Answer:** fluoride

Working: Enthalpy of hydration: $X^- (g) \rightarrow X^- (aq)$
Most exothermic \rightarrow most stable in solution \rightarrow forms strongest bonds with water molecules.
Fluoride forms strongest ion-dipole forces with partial positive hydrogens.

39. **Answer:** $Li | Li^+ || Li^+, CoO_2 | LiCoO_2 | Pt$

Working: Equations are:
 $Li^+ + CoO_2 + e^- \rightarrow Li^+[CoO_2]^-$ (reduction)
 $Li \rightarrow Li^+ + e^-$ (oxidation)
Combining: $Li + Li^+ + CoO_2 \rightarrow Li^+[CoO_2]^- + Li^+$
Cancelling out Li^+ ,
 $Li + CoO_2 \rightarrow LiCoO_2$
Forming the cell, both solutions must contain Li^+ :
 $Li | Li^+ || CoO_2, Li^+ | LiCoO_2 | Pt$ (since aqueous phases)

40. **Answer:** triethylammonium chloride

Working: This is an ionic compound \rightarrow quaternary ammonium salt.

41. **Answer:** $2n - 1$

Working: When $n = 1$ (simple reaction), 1 molecule of water is lost.
When one of each reactant is added to this product, waters are lost from both ends (total 2 per additional molecule)
 $\rightarrow 2n - 1$ waters. (1, 3, 5 ... etc)

42. **Answer:** Cu^{2+} ions are reduced to Cu^+ ions.

Working: Cu oxidation state before: +2
After positive test result, colour change \rightarrow oxidation state changed to +1 $\rightarrow Cu^{2+}$ was reduced.

43. **Answer:** 4-chlorobutanal, butanoyl chloride

Working: Functional group isomers: same molecular formula, different functional groups.
Cycloalkanes are isomers to alkenes but hexa-2,4-diene is a diene so no match.
Propanoic anhydride and hexanedioic acid contain different numbers of oxygens → no match.
4-chlorobutanal and butanoyl chloride match: it is like a H has swapped place with the Cl.
2-methylpropan-2-ol and butan-2-ol are chain isomers not functional group isomers.

44. **Answer:** gas chromatography

Working: Volatile → easily vaporised → suitable to heat into gas phase and travel through gas chromatography apparatus.

45. **Answer:** 1 only

Working: SiO_2 is an acidic oxide so reacts with bases/basic oxides.
 $\text{SiO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$
 $\text{SiO}_2 + \text{MgO} \rightarrow \text{MgSiO}_3$

46. **Answer:** oxidation/reduction

Working: Acid/base neutralisation: yes since SO_3 is an acidic oxide and NH_3 is a base.
Dative bond formation: yes since N lone pair enters empty S shell.
Ionic: yes since it is an ionic salt product.
Redox: no (S: +6, N: -3) all oxidation states remain constant.

47. **Answer:** a decrease in the bond angle of the species involved.

Working: Lone pair: (NH_3 : yes, C_2H_4 : no)
Oxidation state: (N: -3 , C: -2 \rightarrow -3; hydrogenation is reduction)
Bond angle: (N-H: $109.5^\circ \rightarrow 107^\circ$, C-H : $120^\circ \rightarrow 109.5^\circ$)
Disappearing pi bond: (NH_3 : no, C_2H_4 : yes)

48. **Answer:** HOCCOOH

Working: Hydroxyethanal: HOCH2CHO
Aldehyde \rightarrow carboxylic acid and 1° alcohol \rightarrow carboxylic acid (since excessive/harsh conditions)
 \rightarrow product contains both COOH groups (ethanedioic acid).

49. **Answer:** **C**

Working: When alkenes polymerise, a new C-C bond forms at each end of the alkene bond to the corresponding C-C in the other monomer. So the repeating units can only be 1 carbon away. Only C fully shows this.

50. **Answer:** **1 and 2** only

Working: In the presence of H^+ :
 H^+ reacts with OH^- , shifting the first equilibrium to the right (i.e. dissolving more enamel)
 H^+ reacts with the increased amount of PO_4^{3-} shifting the second equilibrium left, which reduces PO_4^{3-} , further shifting the first equilibrium to the right.
Third statement does not explain this since Ca^{2+} ions exist on both sides of the equilibrium.

51. **Answer:** Br_2O_5

Working: Br : O molar ratio is $1.6/80 : 0.8/16 = 0.02 : 0.05 = 2 : 5 \rightarrow \text{Br}_2\text{O}_5$

52. **Answer:** $1/3$

Working: Average oxidation/charge state of Fe ions in $\text{Fe}_3\text{O}_4 = +8/3$

Let x be mole fraction of Fe ions in 2+ state:

$$2x + 3(1 - x) = 8/3 \rightarrow 6x + 9 - 9x = 8 \rightarrow -3x = -1 \rightarrow x = 1/3$$

53. **Answer:** The N-N σ -bond in N_2H_4 is stronger than the P-P σ -bond in P_2H_4

Working: Bi_2O_5 is more ionic than N_2O_5 (more different electronegativities) so is the more basic (alkaline) oxide.

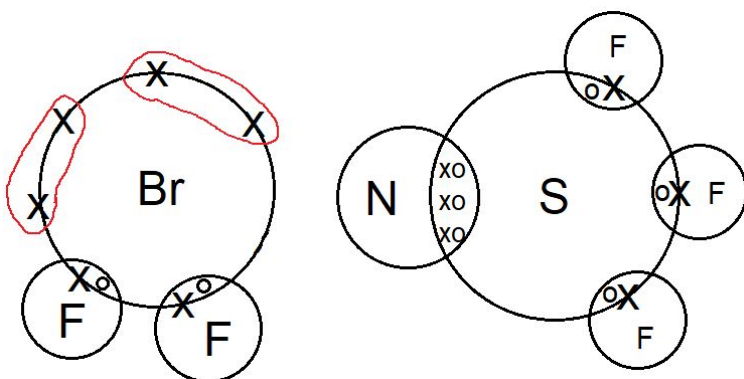
NF_3 is more covalent (less different electronegativities) than BiF_3 .

PH_3 has lower boiling point than NH_3 since NH_3 has strong hydrogen bonding but PH_3 does not (only dipole forces)

N-N bond is weaker than P-P bond since the N atom is smaller than the P atom and so the lone pair-bonding pair repulsion is stronger

54. **Answer:** 2

Working: The dot-and-cross structures are



$$2 \text{ lone pairs in } \text{BrF}_2^+ + 0 \text{ lone pairs in } \text{SNF}_3 = 2 \text{ lone pairs}$$

55. **Answer:** 2 only

Working: Exothermic reactions → temperature of reaction decreases and temperature of surroundings increases (heat is released)
→ entropy of reaction decreases and entropy of surroundings increases.

Endothermic reactions → temperature of reaction increases and temperature of surroundings decreases (heat is absorbed)
→ entropy of reaction increases and entropy of surroundings decreases.

56. **Answer:** [He] 2s² 2p⁵

Working: [He] 2s¹ is a metal
[He] 2s² 2p⁵ and [Ne] 3s² 3p⁵ are more reactive than [Ne] 3s² 3p² since needs only 1 more electron to complete valence shell compared to 3 more
[He] 2s² 2p⁵ is more reactive than [Ne] 3s² 3p⁵ since reactivity increases up group 7 (fluorine > chlorine)

57. **Answer:** NO₃⁻, S₂O₃²⁻, Cr₂O₇²⁻

Working: Correct names of similar ions are:
Nitronium: NO₂⁺, Nitrate: NO₃⁻, Nitride: N³⁻
Sulfate: SO₄²⁻, Thiosulfate: S₂O₃²⁻, Per(oxydi)sulfate: S₂O₈²⁻
Chromate: CrO₄²⁻, Dichromate: Cr₂O₇²⁻, Chromium(III): Cr³⁺

58. **Answer:** ¹⁸F

Working: ¹⁶O: 8 protons, 8 neutrons → no spin
¹⁸F: 9 protons, 9 neutrons → spin
²⁰Ne: 10 protons, 10 neutrons → no spin
²⁴Mg: 12 protons, 12 neutrons → no spin
(Nuclear spin is the property similar to electron spin, which determines whether a nucleus can be used in NMR i.e. ¹H, ¹³C.)

59. **Answer:** the rate constant increases with an increase in temperature. This is due to more collisions whose energy exceeds the activation energy.

Working: $k = A \exp(-E / RT)$.
High $E \rightarrow$ very negative $-E/RT \rightarrow$ small $k \rightarrow$ slow rate
High $T \rightarrow$ small negative $-E/RT \rightarrow$ large k , because more energy in the reactants so more collisions frequently exceed the activation energy.
if E is small, then a change in T produces a smaller change in E/RT than if E was large. So the temperature dependence is weaker.
Preexponential is the rate at which collisions occur, not caring if they have the right energy, but taking into account the reduction in successful collisions due to not being in the right orientation (*steric factor*).

60. **Answer:** (D)

Working: The α means the carbon next to the functional group, so a 2-hydroxyketone (numbering relative to the ketone)
(A) and (B) are aldehydes \rightarrow positive result
(C) is a 2-hydroxyketone \rightarrow false positive result
(D) is a ketone \rightarrow negative result

61. **Answer:** $3 \text{Cu}^{2+} (\text{aq}) + 2 \text{PO}_4^{3-} (\text{aq}) \rightarrow \text{Cu}_3(\text{PO}_4)_2 (\text{s})$

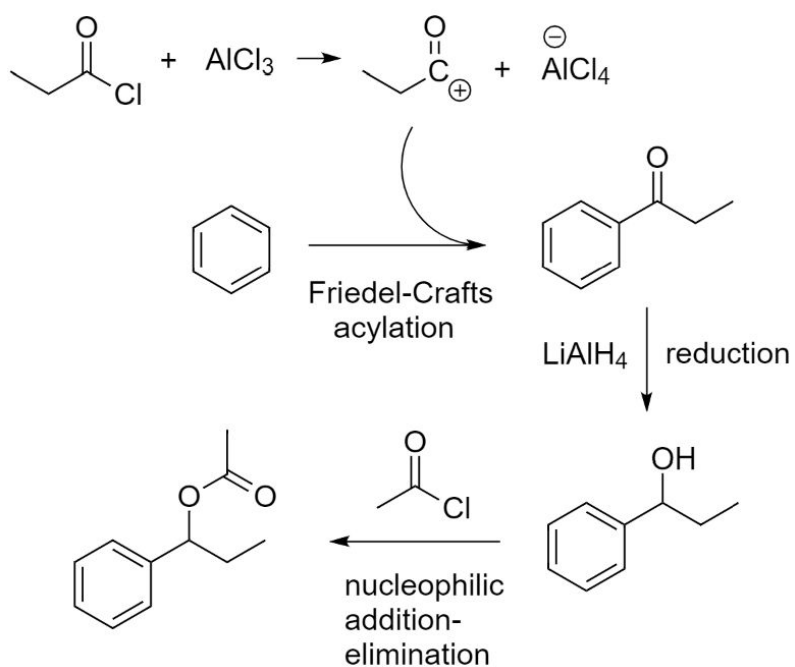
Working: Reaction is
 $3 \text{CuCl}_2 (\text{aq}) + 2 \text{Li}_3\text{PO}_4 (\text{aq}) \rightarrow \text{Cu}_3(\text{PO}_4)_2 (\text{s}) + 6 \text{LiCl} (\text{aq})$
The aqueous species dissociate into ions:
 $3 \text{Cu}^{2+} + 6 \text{Cl}^- + 6 \text{Li}^+ + 2 \text{PO}_4^{3-} \rightarrow \text{Cu}_3(\text{PO}_4)_2 + 6 \text{Li}^+ + 6 \text{Cl}^-$
Cancelling spectator ions (6Li^+ and 6Cl^-),
 $3 \text{Cu}^{2+} (\text{aq}) + 2 \text{PO}_4^{3-} (\text{aq}) \rightarrow \text{Cu}_3(\text{PO}_4)_2 (\text{s})$

62. **Answer:** 10%

Working: Let x be abundance (from 0 = 0% to 1 = 100%) of $^{86}\text{Sr} = ^{87}\text{Sr}$.
→ $87.7 = 86x + 87x + 88(1 - 2x)$ [since all abundances add to 1]
→ $87.7 = 88 - 3x$
→ $x = 0.1 = 10\%$

63. **Answer:** AlCl_4^- and $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$ are formed as intermediates

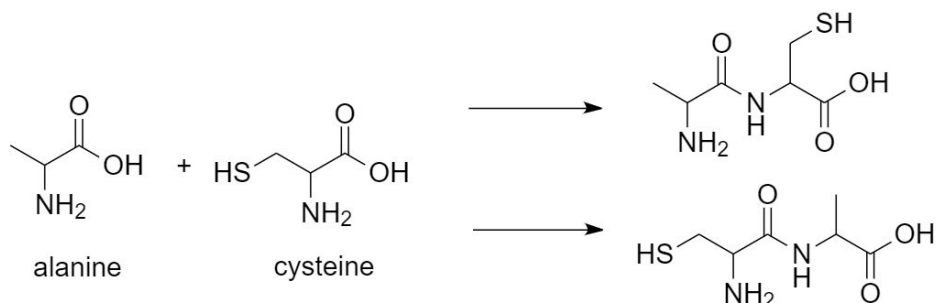
Working: Reactions listed are:



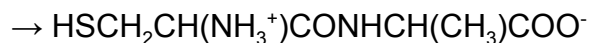
(Intermediates are AlCl_4^- and $\text{CH}_3\text{CH}_2\text{C}^+\text{O}$).

64. **Answer:** 1 and 3

Working: Two products form (ignoring optical isomers) since either the NH_2 on alanine could react with the COOH on cysteine or the other way around. Each group undergoes condensation, eliminating H_2O and forming an amide bond:



In their usual state, the amino acids (and hence the dipeptide) form zwitterions so convert all NH_2 to NH_3^+ and all COOH to COO^- :



(the disulfide **4** is not correct since it does not include alanine.)

65. **Answer:** 13

Working: Adenine and thymine pair with two hydrogen bonds.
Guanine and cytosine pair with three hydrogen bonds.
 $\rightarrow 2 + 3 + 3 + 2 + 3 = 13$

66. **Answer:** 0

Working: Possible reduction routes from nitriles are:
 $\text{R-CN} \rightarrow \text{R-NH}_2$ (notice this requires only one N-C bond)
Or $\text{Ph-CN} \rightarrow \text{Ph-CH}_2\text{NH}_2$ (notice the extra CH_2)
(with H_2 / Pd or LiAlH_4). The 1st, 2nd, 4th and 6th have multiple C-C bonds attached so cannot be formed from a nitrile. The 3rd one could not form a ring from a nitrile alone. The 5th one is reduced from nitrobenzene (not a nitrile).

67. **Answer:** 1 and 3 only

Working: Nylon 6,6 is a six-carbon chain polymer with amide linkages.
So it can be formed by any six-carbon straight chain diamine and dicarboxylic acid/acyl dichloride.

68. **Answer:** absorption of NH_3 and O_2 molecules into the platinum metal

Working: The general stages of heterogeneous catalysis are:
→ diffusion of reactants to catalyst
→ **adsorption** (not absorption - the reactants do not go inside the metal) of the reactants to the surface of the catalyst
→ weak bond formation between reactant(s) and catalyst (usually by donating electron density into the empty d orbitals of the catalyst atoms)
→ products formed, product-catalyst bond(s) broken
→ desorption of products from the catalyst surface

69. **Answer:** The Ca^+ ion has its valence electron in a higher energy orbital than those of the K^+ ion

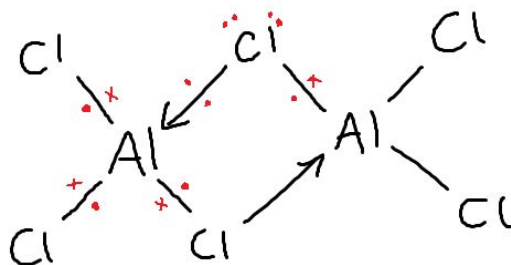
Working: Nuclear charge of resulting ions does not affect ionisation process.
 Ca^+ : $[\text{Ne}] 3s^2 3p^6 4s^1$ K^+ : $[\text{Ne}] 3s^2 3p^6$
Energy level of 4s is much higher than 3p, so there is significant energy needed to remove $3p^6$ electrons from K^+ .

70. **Answer:** The junction at **B** is kept open to allow air inside and further cool the gas

Working: The junction is open to prevent pressure buildup due to increased volume of gas inside the apparatus. Closing it is dangerous and could cause the glass to shatter or explode due to the pressure. (The air does not affect the temperature since after condensation, the liquid will already be near air temperature.)

71. **Answer:** 5°

Working: Aluminium trichloride dimer is Al_2Cl_6 , with dative covalent (coordinate) bonds between a Cl and each Al:



Cl-Al-Cl has Al as central atom: 4 electron pairs, 0 lone pairs
→ tetrahedral around Al → bond angle = 109.5°

Al-Cl-Al has Cl as central atom: 4 electron pairs, 2 lone pairs
→ tetrahedral with distortion → $109.5 - 2(2.5) = 104.5^\circ$
→ difference = 5° .

72. **Answer:** 2 and 3 only

Working: Biodiesel is made by reacting vegetable oils (triglyceride esters) with small primary alcohols such as methanol.

Motor fuels are made by catalytically cracking long-chain alkanes with zeolite.

Soaps are long-chain sodium/potassium salts, formed from base hydrolysis (NaOH / KOH) of long-chain esters such as those in vegetable oils/animal fats.

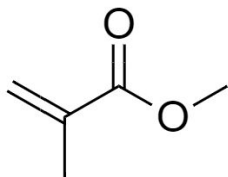
73. **Answer:** 1, 2 and 3

Working: Ethanoyl chloride is less safe (it is corrosive), less easily stored (it is easily hydrolysed to give ethanoic acid and toxic HCl fumes). Ethanoic anhydride on the other hand produces only ethanoic acid (weak acid) and does so with a slower reaction (it is an equilibrium).

Section B: Standard

1. **Answer:** It displays geometrical isomerism.

Working: methyl 2-methylpropenoate:



Geometric (E/Z) isomer: no (double bond has H and H on one side)

Addition polymer: yes (almost all alkenes can)

Reduction: yes (hydrogenation of the double bond and LiAlH_4 on the carbonyl are both possible reduction reactions)

Decolourises bromine: yes (double bond reacts by electrophilic addition to form dibromoalkane)

2. **Answer:** Peaks at $m/z = 70, 72$ and 74 in the ratio 9:6:1

Working: Possible combinations:

$^{35}\text{Cl}-^{35}\text{Cl}$: $m/z = 70$: probability = $\frac{3}{4} * \frac{3}{4} = 9/16$

$^{35}\text{Cl}-^{37}\text{Cl}$: $m/z = 72$: probability = $\frac{3}{4} * \frac{1}{4} = 3/16$

$^{37}\text{Cl}-^{35}\text{Cl}$: $m/z = 72$: probability = $\frac{1}{4} * \frac{3}{4} = 3/16$

$^{37}\text{Cl}-^{37}\text{Cl}$: $m/z = 74$: probability = $\frac{1}{4} * \frac{1}{4} = 1/16$

But $^{35}\text{Cl}-^{37}\text{Cl}$ and $^{37}\text{Cl}-^{35}\text{Cl}$ are the same compound, so 6/16.

Ratios are then $9/16 : 6/16 : 1/16 = 9 : 6 : 1$.

(Could also use binomial distribution.)

3. **Answer:** 34.0 kPa

Working: Moles of oxygen: $n = pV/RT$
 $= 10^5 \times 130 \times 10^{-6} / (298 \times 8.31) = 5.25 \times 10^{-3} \text{ mol}$
Moles of nitrogen = $10^5 \times 40 \times 10^{-6} / (298 \times 8.31) = 1.615 \times 10^{-3} \text{ mol}$
Pressure of mixture: $p = nRT/V$
 $= (5.25 \times 10^{-3} + 1.615 \times 10^{-3}) \times 8.31 \times 298 / (0.5 / 1000)$
 $= 34000 \text{ Pa} = 34.0 \text{ kPa}$

4. **Answer:** A

Working: We know that conjugated systems (double-single-double bonds) are more stable than saturated systems due to resonance. Most exothermic enthalpy of hydrogenation \rightarrow energy of the reactant is highest (least stable) \rightarrow without conjugation. This is the compound without double-single-double bonds.

5. **Answer:** Ethanol is a stronger nucleophile than water.

Working: A haloalkane typically reacts in aqueous conditions by substitution and in alcoholic (ethanolic) conditions by elimination. In elimination, the solvent acts as a base (removes a H) so it makes sense that ethanol would be a stronger base than water.

2nd option is incorrect: O-H bond in ethanol is therefore weaker since it now will be breaking instead of water in elimination.

3rd option is incorrect: the alkoxide ion is irrelevant as it is not formed at any point in the elimination mechanism.

4th option is true but has no relevance to the given information so is an incorrect choice.

6. **Answer:** -273 kJ mol^{-1}

Working: $\text{C}_2\text{H}_6 + 6 \text{ F}_2 \rightarrow \text{C}_2\text{F}_6 + 6 \text{ HF}$
By Hess's law triangle, or by calculation,
 $6 \text{ HF} + (-1344) = (-84) + (-2898) \rightarrow \text{HF} = -273 \text{ kJ mol}^{-1}$.

7. **Answer:** 3

Working: Consider experiments 1 and 2:
Zero order w.r.t. Y and Z is constant \rightarrow 2nd order w.r.t. X.
Consider experiments 2 and 3:
[X] is quartered \rightarrow expect 1/16 rate
But rate is $\frac{1}{8}$ times original \rightarrow double than if zero order w.r.t. Z
[Z] is doubled \rightarrow 1st order w.r.t. Z
 \rightarrow rate = $k [X]^2 [Z]$
 \rightarrow overall order = 3

8. **Answer:** 2.46

Working: Consider changes in moles to each gas:

	CO	+	H ₂ O	\rightarrow	CO ₂	+	H ₂
Initial	4.2		2.0		0		0
Change	-1.60		-1.60		+1.60		+1.60
Equilibrium	2.60		0.40		1.60		1.60

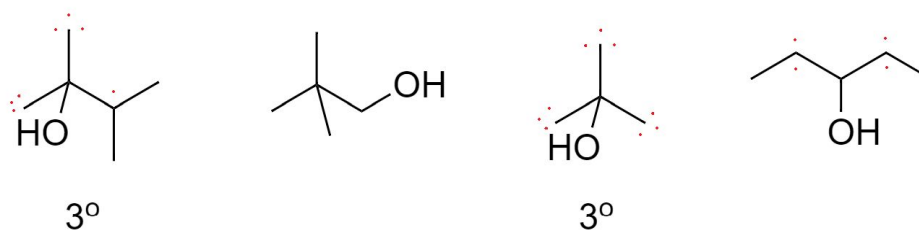
By Raoult's law, moles is proportional to partial pressure, and since 2 molecules on both sides, K_p is independent of total volume.
Then, $K_p = (1.60)(1.60) / (2.60)(0.40) = 2.46$.

9. **Answer:** 2 and 3 only

Working: 1: false (1st IE generally increases across a period)
2: true (electronegativity decreases down a group)
3: true (H-F: hydrogen bonding; H-Cl/Br/I: dipole/VDW)
4: false (ability to reduce increases down group 7)

10. **Answer:** 2,2-dimethylpropan-1-ol

Working:



To be oxidised it must **not** be a tertiary (3°) alcohol.

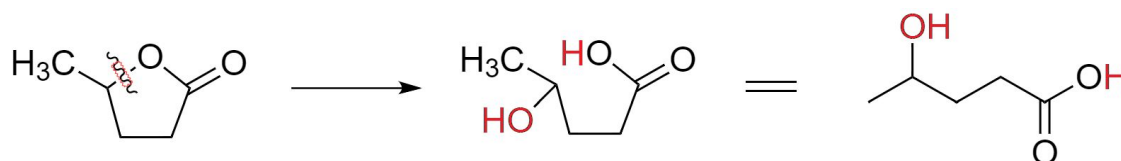
To **not** be dehydrated by H_2SO_4 it must have no hydrogens attached to the adjacent carbon to the OH (shown in red dots)
Only the second option matches both of these.

11. **Answer:** 3-chloropropanal

Working: Nucleophilic substitution: haloalkane
Nucleophilic addition: aldehyde/ketone
Only 3-chloropropanal has both these functional groups.

12. **Answer:** $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{COOH}$

Working: In acid hydrolysis, the O-C bond in the ester breaks and an OH adds to the C (forming OH) and a H adds to the O (forming COOH).



13. **Answer:** B

Working: From Arrhenius, $k = A \exp(-E_a / RT)$ so with respect to T, it is neither constant, proportional nor exponential growth.

14. **Answer:** 1, 2 and 3

Working: 1: true (K_p is dependent on temperature)
2: true (liquid \rightarrow gas is positive entropy change)
3: true (since vaporisation is endothermic, enthalpy of formation of liquid water is more exothermic than gas. So overall enthalpy change becomes more endothermic.)

15. **Answer:** Tests 1 and 3 only

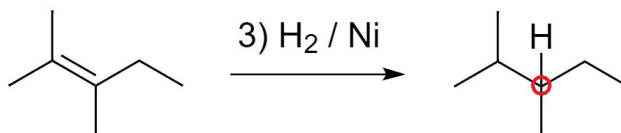
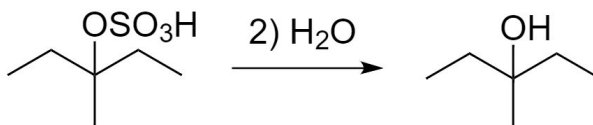
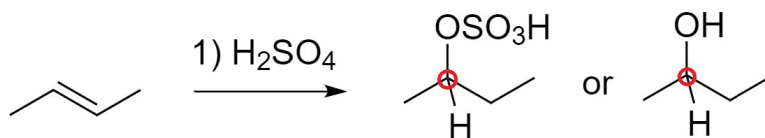
Working: Strong acid: completely dissociates into H^+ and conjugate base.
1: yes (strong acid has faster rate of reaction since more H^+)
2: no (same moles of each acid \rightarrow same volume for neutralisation)
3: yes (strong acid has more free ions to carry current)

16. **Answer:** +6, +6, +4

Working: All are neutral compounds so the overall oxidation state is zero.
 CrO_2F_2 : $O = -2$, $F = -1 \rightarrow Cr = +6$
 $K_2Mn_2O_7$: $K = +1$, $O = -2 \rightarrow 2 Mn = +12 \rightarrow Mn = +6$
 $BaTiO_3$: $Ba = +2$, $O = -3 \rightarrow Ti = +4$

17. **Answer:** 1 and 3 only

Working: The reactions are:

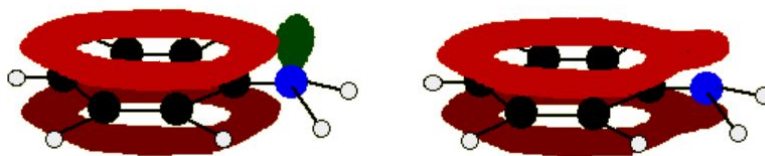


The chiral carbons are circled in red.

(The product of (2) is not chiral since it contains two ethyl groups.)

18. **Answer:** pyridine, lone pair in pyridine **not** delocalised into aromatic ring

Working: Both amines are aromatic, however this does not mean the lone pair will be delocalised in both.
Consider the molecular geometry of phenylamine. At the nitrogen atom, we have a bond angle of about 107° (tetrahedral) and so the lone pair will be pointing almost vertically (close to 90°). This allows the lone p orbital to overlap with the delocalised π system in the ring, making the electrons less available to accept a proton and hence a weaker base.



However in the case of pyridine, we find a bond angle of about 120° (trigonal planar), meaning the lone pair points outwards from the ring, parallel to the delocalised ring. There is almost zero overlap and therefore no inhibition to attract a proton.



19. **Answer:** $\frac{1}{125}r$

Working: Concentration = moles / volume
Since moles is the same (amount is the same), conc is inversely proportional to volume.
Increased by $4V \rightarrow$ new volume = $V + 4V = 5V$
 $V \rightarrow 5V$ means $[A] \rightarrow \frac{1}{5} [A]$
So overall new rate is $k \left(\frac{1}{5} [A]\right)^2 \left(\frac{1}{5} [B]\right) = k \left(\frac{1}{5^2 * 5}\right) [A]^2 [B]$
 $\rightarrow \frac{1}{125}$ times the original rate $\rightarrow = \frac{1}{125} * r$

20. **Answer:** A

Working: Boiling points: stronger IMFs \rightarrow higher bp.
Carboxylic acid > alcohol since twice the amount of hydrogen bonding (also forms a stable dimer so stronger VDW)
Z-isomer has higher boiling point since electronegative Cl and COOH groups are on the same side \rightarrow more polar.

21. **Answer:** When a platinum wire is dipped into a mixture of hexachloroiridate(III) and hexachloroiridate(IV) solutions and connected to the standard hydrogen electrode, doubling the concentration of the solution at the anode decreases the e.m.f. of the cell.

Working: 1st option: Since $0.80 < 0.87$, $[\text{IrCl}_6]^{3-}$ is not strong enough to reduce nitric acid to NO_2 ; the third equilibrium (forming NO) is pushed instead.

2nd option: Both nitric acid electrode potentials are larger than 0.34 so nitric acid can oxidise copper.

3rd option: e.m.f. = reduction E^\ominus - oxidation $E^\ominus = 0.96 - 0.34 = 0.62$.

4th option: Anode: where oxidation occurs (less positive electrode potential). Since SHE has $E^\ominus = 0$ and all others are positive, the SHE is the anode. Increasing $[\text{H}^+]$ shifts the $2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{H}_2$ equilibrium to the right, increasing E^\ominus for the anode. So a positive value minus a positive value is smaller than before \rightarrow e.m.f. decreases.

22. **Answer:** 251 kg

Working: Initial reaction: $\text{P}_4\text{O}_{10} + 6 \text{H}_2\text{O} \rightarrow 4 \text{H}_3\text{PO}_4$.
Using the titration information,

	H_3PO_4	+	3NaOH	\rightarrow	[products]
Moles	0.00353		0.0106		
Conc	0.1413		0.5		
Vol	0.025		0.0212		

Moles of H_3PO_4 in tank = $0.1413 \times 25 \times 1000 = 3533 \text{ mol}$

Moles of P_4O_{10} added = $3533 / 4 = 883.3 \text{ mol}$

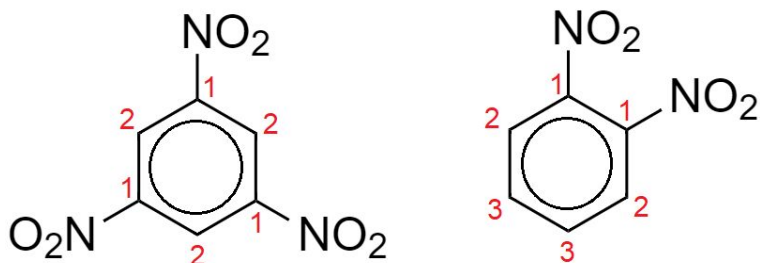
Mass = $883.3 \times (4 \times 31 + 10 \times 16) = 250900 \text{ g} = 251 \text{ kg}$ (3 s.f.)

23. **Answer:** Cl^- will reduce MnO_4^-

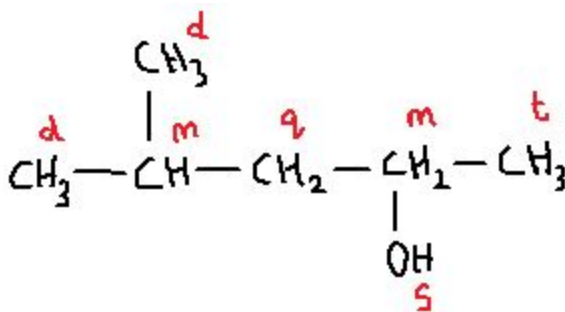
Working: MnO_4^- is a very strong oxidising agent - the very high oxidation state of Mn(+7) makes it 'want' to be reduced easily. Cl^- , although it is a weak reducing agent (halide reducing ability increases down the group) is still strong enough to reduce MnO_4^- - the high oxidising ability of MnO_4^- 'overpowers' it.
Therefore, MnO_4^- is reduced (gets oxidised) by Cl^- .

24. **Answer:** None of the above.

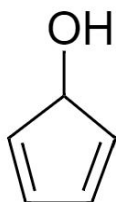
Working: 1st option: false - 1,2-dinitrobenzene has 3 peaks,
1,3,5-trinitrobenzene has 2 peaks.



2nd option: false - the hydrogen in the OH does not split (under normal conditions) so is a singlet.



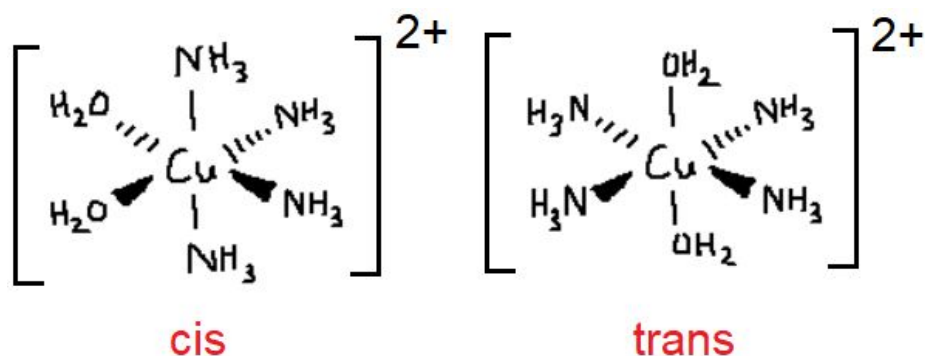
3rd option: false - no resonance with the OH group so no ketone state exists so no absorbance at C=O wavenumbers.



25. **Answer:** The complex ion responsible for the deep blue solution in reaction 2 displays cis-trans isomerism.

Working: Reaction 1: uses small amount of NH_3 (aq) in NaOH, forms $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]$, an octahedral complex.

Reaction 2: uses excess / conc NH_3 , forms $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$, with ligand substitution occurring. Since both are monodentate, the chelate effect does not apply. It is octahedral. It shows cis-trans isomerism:

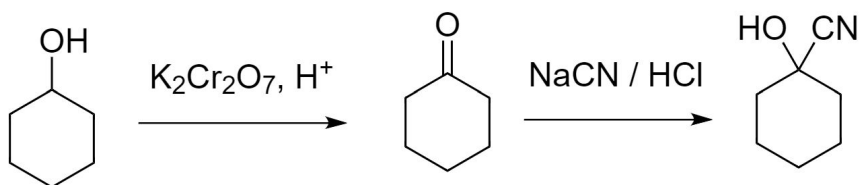


Reaction 3: uses Na_2CO_3 , forms CuCO_3 .

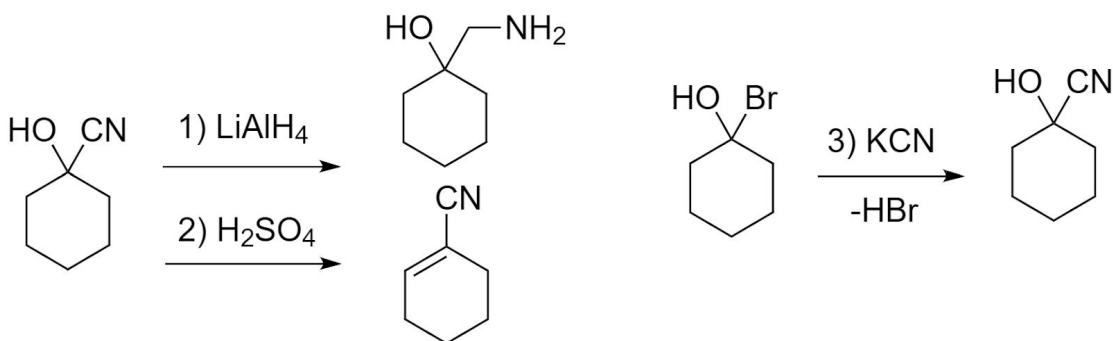
Reaction 4: uses excess / conc HCl, forms $[\text{CuCl}_4]^{2-}$, which is tetrahedral.

26. **Answer:** 2 and 3 only

Working: The reactions to form **X** are



The reactions involving **X** are



(1) is reduction of nitrile to amine, (2) is acid-catalysed elimination, (3) is nucleophilic substitution

27. **Answer:** 1 and 2 only

Working: Primary and secondary amines can form hydrogen bonds both with themselves and with water molecules since they contain N-H bond.

Tertiary amines can form hydrogen bonds only with water molecules due to the $\text{N} \cdots \text{H}-\text{O}$ interaction but has no N-H bond to hydrogen bond with itself.

Quaternary ammonium salt is ionic, so forms ionic bonds in the pure state and ion-dipole forces with water in solution.

Ionic bonds are stronger than ion-dipole forces due to both charges being permanent and full whereas only one is in ion-dipole.

28. **Answer:** Ion-dipole forces in the NaCl solution are stronger than the hydrogen bonds in the pure water.

Working: More energy must be required to break the forces between water molecules in the solution than in pure water. So the $\text{Na}^+ \cdots \text{OH}_2$ bond and/or $\text{Cl}^- \cdots \text{HOH}$ bond must be stronger than the $\text{H}-\text{OH}_2$ bond.

Enthalpy of solution is dependent on enthalpy of hydration and lattice enthalpy, and no comparisons can be made since no other salt solution is given.

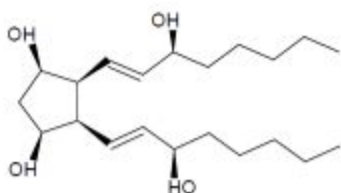
There are more hydrogen bonds in ice than in water, as they are broken when ice melts. So there will be more polarisation of bonds in the solid state than in the liquid state.

29. **Answer:** 126 mg

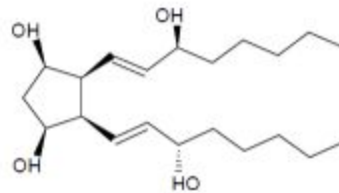
Working: This is not an easy equation to balance but to balance Mn we see that there is a 1 : 1 stoichiometric ratio between MnCl_2 and KMnO_4 , and also in the redox step between MnO_4^- and Mn^{2+} .
Redox: $2 \text{MnO}_4^- + 16 \text{H}^+ + 5 \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$
Working in units of millimoles and mg for simplicity,
mmol ethanedioic acid = $225 / 90 = 2.5$
mmol permanganate = $2/5 * 2.5 = 1$
Mass $\text{MnCl}_2 = 1 * (55 + 71) = 126 \text{ mg}$.

30. **Answer:** 7

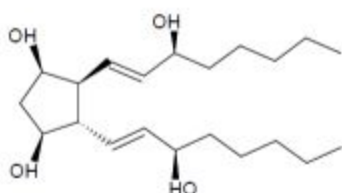
Working: There are three possible things (configuration of OH (hash/wedge), configuration of C-C (hash/wedge), geometry of double bond (E/Z) to change, so a total of $2^3 = 8$ different stereoisomers.



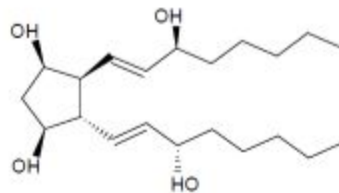
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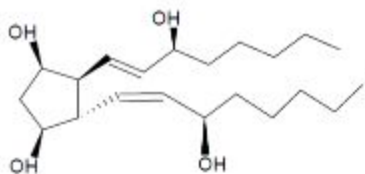
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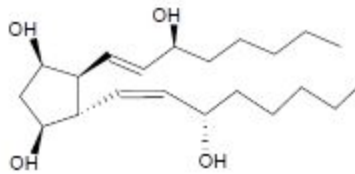
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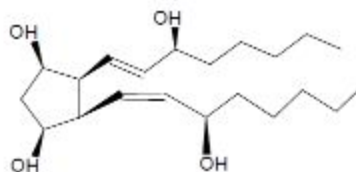
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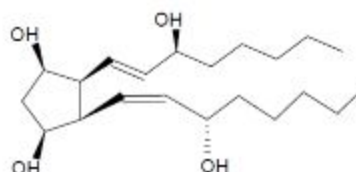
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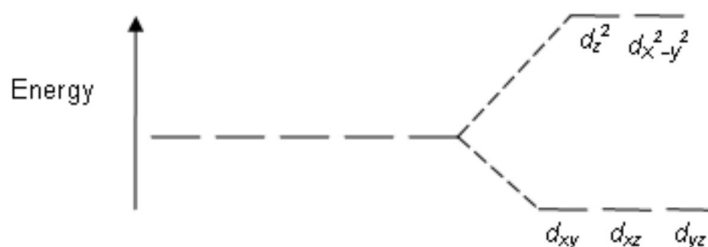
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Only the first one is optically inactive since it is perfectly symmetrical, leaving 7 optically active isomers.

31. **Answer:**

blue	yellow-green	A
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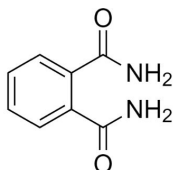
Working: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ aqueous ions are blue. $[\text{CuCl}_4]^{2-}$ is yellow-green.



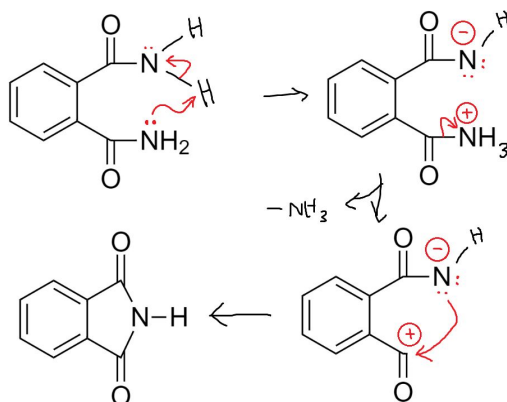
The Cl^- ligand splits the 3d orbital of the Cu^{2+} ion into two levels of different energy. Now the frequency at which light is absorbed has changed, so the colour also changes. (*crystal field theory*)

32. **Answer:**  , alanine, ethanol

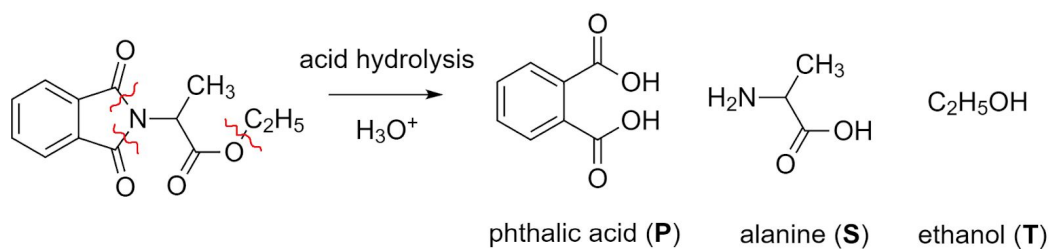
Working: **P** is a (di)carboxylic acid, so adding ammonia gives amide groups in both positions. So **Q** is



On heating, the intramolecular hydrogen bond between the amine groups can cause a proton transfer and eliminate NH_3 :



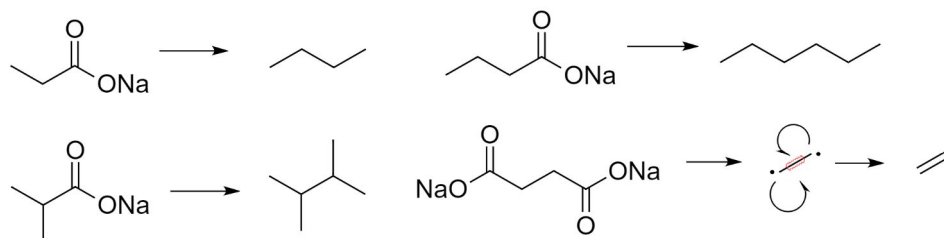
The large product near the end contains both an ester bond and two amide bonds, so it will hydrolysis in three places in H_3O^+ . The reaction is then (red lines show bond breaking location)



(Alanine, the amino acid, is 2-aminopropanoic acid.)

33. **Answer:** sodium butanoate

Working: propanoate will form ethyl radicals which combine to butane.
butanoate will form propyl radicals which combine to hexane.
2-methylpropanoate will form propyl with radical on second carbon which combines to a branched hexane.
In the last case, only one molecule is required. An ethyl diradical will form, with one unpaired electron on each carbon, which can combine (reverse of homolytic fission) to form another bond, giving ethene (and a mixture of other termination products)



More carbons \rightarrow higher boiling point.

Straight chain \rightarrow more surface area \rightarrow more Van der Waals' interactions \rightarrow higher boiling point \rightarrow 2nd option.

34. **Answer:** $\mathbf{A} + \mathbf{C} \rightarrow \mathbf{E} + 4 \text{ NH}_4\text{Cl}$

Working: First step is nucleophilic substitution of one Cl group on **A** with NH_3 , this forms **B**. From here three things could happen:

(1): the NH_2 group on **B** could act as a nucleophile for the Cl group on the **same** molecule, forming cyclic amine **D** (intramolecular reaction), which is $\mathbf{B} \rightarrow \mathbf{D} + \text{HCl}$

(2): the NH_2 group on **B** could act as a nucleophile for the Cl group on a **different** molecule, forming cyclic diamine **E** (intermolecular reaction) which is $2 \mathbf{B} \rightarrow \mathbf{E} + 2 \text{HCl}$

(3): an NH_3 molecule acts as a nucleophile, replacing the other Cl group and forming diamine **C**

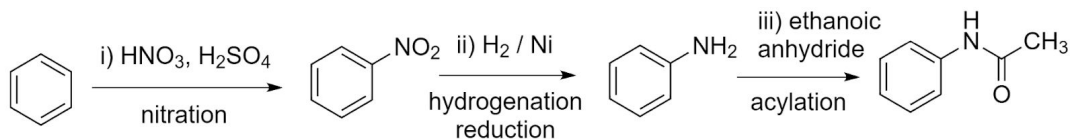
Now if **A** and **C** reacts with each other's groups, forming **E** and either 2 HCl or 2 NH_4Cl (not 4).

(Note: HCl could usually be replaced with any of the amine salts formed in this process, depending on the base strength of the amine, i.e. its ability to remove the proton compared to Cl^- .)

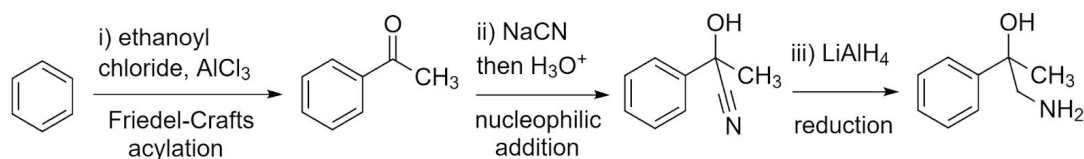
35. **Answer:** 1 only

Working: The name N-phenylethanamide indicates phenyl group attached to N, and ethyl group attached to carbonyl side.

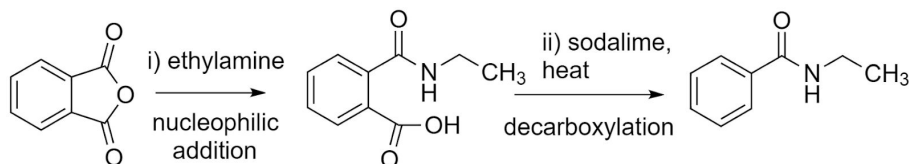
Reactions of scheme 1:



Reactions of scheme 2:



Reactions of scheme 3:



(Product of **3** is not correct - groups are wrong way around.)

36. **Answer:**

rate = $k_3 [\text{H}^+]^c$	$[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$ are large so $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$ are approximately constant
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Working: Since $[\text{H}_2\text{O}_2]$, $[\text{I}^-] \gg [\text{H}^+]$, the change in $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$ is very small compared to the change in $[\text{H}^+]$.
So $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$ can be absorbed into the rate constant and the rate law becomes rate = $k_3 [\text{H}^+]^c$.

37. **Answer:**

$\ln([A])$	- $\ln(\text{time for dark blue to appear in reaction mixture})$
------------	--

Working:

Stage 1 Preparation

1a Measure (suitable/known volumes of) some reagents (ignore quoted values for volume)

1b Measure (known amount of) X / use a colorimeter

1c into separate container(s) – (allow up to two reagents and X measured together into one container); reference to A, B or C added last. NOT if X added last.

Stage 2 Procedure

2a Start clock/timer at the point of mixing (don't allow if only 2 reagents mixed) (allow even if X not added or added last)

2b Time recorded for appearance of blue colour/specific reading on colorimeter/disappearing cross

2c Use of same concentration of B and C / same total volume / same volume/amount of X

2d Same temperature/use water bath

2e Repeat with different concentrations of A (can be implied through different volumes of A and same total volume)

Stage 3 Use of Results

3a $1/\text{time}$ taken is a measure of the rate

3b plot of $1/\text{time}$ against volumes/concentrations of A or plot $\log(1/\text{time})$ vs $\log(\text{volume or concentration of A})$

3c description of interpreting order from shape of $1/\text{time}$ vs volume or concentration graph / gradient of log plot gives order / allow interpretation of time vs concentration graph / ratio between change in concentration and change in rate
(e.g, $2[A] = 2 \times \text{rate}$ so 1st order)

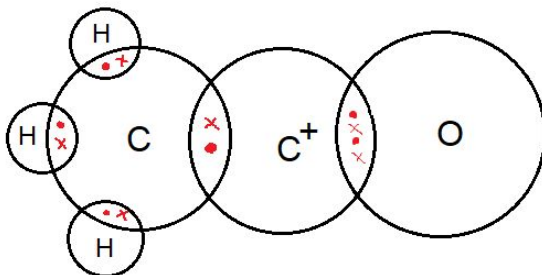
(only log-plots give order through gradient, other form requires 'guessing' from the shape (horizontal line/diagonal line/curve) and assumes an integer order. An alternative approach is using colorimetry and repeated continuous monitoring.)

38. **Answer:** 71.8

Working: Density = $3.162 \text{ g dm}^{-3} = 3162 \text{ g m}^{-3}$
Let V = volume, m = mass and M_r = relative molecular mass of gas
 $\rightarrow m/V = 3162 \rightarrow V = m/3162$
Using ideal gas law, $pV = nRT$
 $pV = nRT \rightarrow p(m/3162) = (m/M_r) * R * T$
Dividing through by m ,
 $\rightarrow p/3162 = R * T / M_r$
 $\rightarrow M_r = 3162 * R * T / p$
 $\rightarrow M_r = 3162 * 8.314 * (50 + 273) / 100\,000$
 $\rightarrow M_r = 84.9$

39. **Answer:** linear

Working: $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{C}^+\text{O} + \text{AlCl}_4^-$



Two electron domains, no lone pairs \rightarrow linear.

40. **Answer:** HI, because the H-I bond is the weakest

Working: The mechanism is electrophilic addition, so the H-X bond needs to break most easily. In H-I, the bond length is long making the proton easily accessible (electrons are far from H and I, since almost completely non-polar). So the H-I bond is very weak.

41. **Answer:** In species **X**, the unpaired electron lies predominantly on the 2° C

Working: Initiation step: $\text{H-O-O-H} \rightarrow \text{H-O}\cdot + \cdot\text{O-H}$
O-O bond breaks homolytically since the bond is nonpolar. It is a very weak bond. No change in oxidation states (O = -1, H = +1).
Propagation steps: the $\text{Br}\cdot$ makes a bond with one p electron in the double bond. This breaks the C=C bond, leaving the other carbon with the electron. Since the Br went to the primary carbon, the radical must be on the secondary carbon.
Possible termination step to form bromoalkane is
 $2 \text{CH}_3\text{C}\cdot\text{HCH}_2\text{Br} \rightarrow 1,4\text{-dibromo-2,3-dimethylbutane}$

42. **Answer:** The O-H bond in CH_2ClCOOH is more polarised than in CH_3COOH

Working: Cl is more electronegative than C, so the Cl pulls electron density (negative inductive effect) towards itself. This spreads out the charge on the COO^- region, stabilising the charge. As a result, the negative charge moves further away from the proton, further polarising the O-H bond and weakening it, making it easier to lose the proton in chloroethanoic acid.

43. **Answer:** none of these

Working: The electrospray solvent must be volatile (so it can easily disperse into an aerosol / fine mist when ejected from the syringe), be a proton donor (so it can protonate the dipeptide to a cation) and not react with the sample.

solvent	volatile?	proton donor?	inert?
water	no	yes	no (hydrolysis of amide linkage)
TMS	yes	no	yes
pentane/hexane	yes	no	yes

None of these meet all three conditions.

Section C: Hard

1. **Answer:** 2

Working: Using the information from the back-titration,

	ethanedioic acid	+	2 OH ⁻	→ [products]
Moles	0.00125		0.0025	
Conc	0.07911		0.1	
Vol	0.0158		0.025	

$$\text{Moles in original} = 0.07911 \times 0.25 = 0.019778$$

$$M_r = (\text{ethanedioic acid}) + n \times (\text{water})$$

$$= (2 + 2 \times 12 + 4 \times 16) + 18n = 90 + 18n$$

$$\text{Moles} = \text{mass} / M_r \rightarrow M_r = \text{mass} / \text{moles}$$

$$\rightarrow 18n + 90 = 2.5 / 0.019778 \rightarrow 18n + 90 = 126.4$$

$$\rightarrow n = 2.022 \rightarrow \text{rounds to 2}$$

(could also predict this result by considering the hydrogen bonding in ethanedioic acid - two places for H's in water to bond, at each COOH)

2. **Answer:** 6

Working: When the triglyceride is hydrogenated, all alkene (C=C) bonds will become alkane (C-C) bonds and as a result two H atoms will be gained each time.

In the top hydrocarbon chain, we have C₁₇H₃₁ - an alkane would have C₁₇H₃₆ (by 2n + 2 homologous series formula). But one hydrogen is lost as the end carbon is bonded to the glycerol part. So the fully saturated chain would have C₁₇H₃₅ - 4 H's are missing, requiring 2 molecules of H₂.

In the middle chain: 2 H missing → 1 molecule of H₂

In the bottom chain: 6 H missing → 3 molecules of H₂

In total, 2 + 1 + 3 = 6 molecules of H₂.

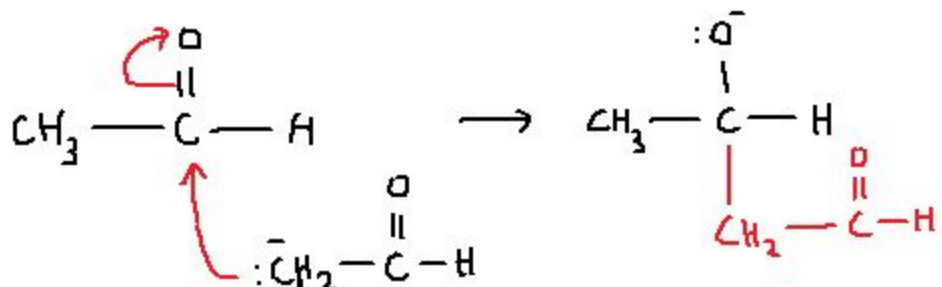
3. **Answer:** A and B only

Working: Check A:

Both ethanal and OH^- appear once in the first step of the mechanism. Since the reaction is first order with respect to both of these, it must be the rate determining step.

Check B:

Yes, as it shows a nucleophile (the $:\text{CH}_2\text{CHO}$) adding to a carbonyl:



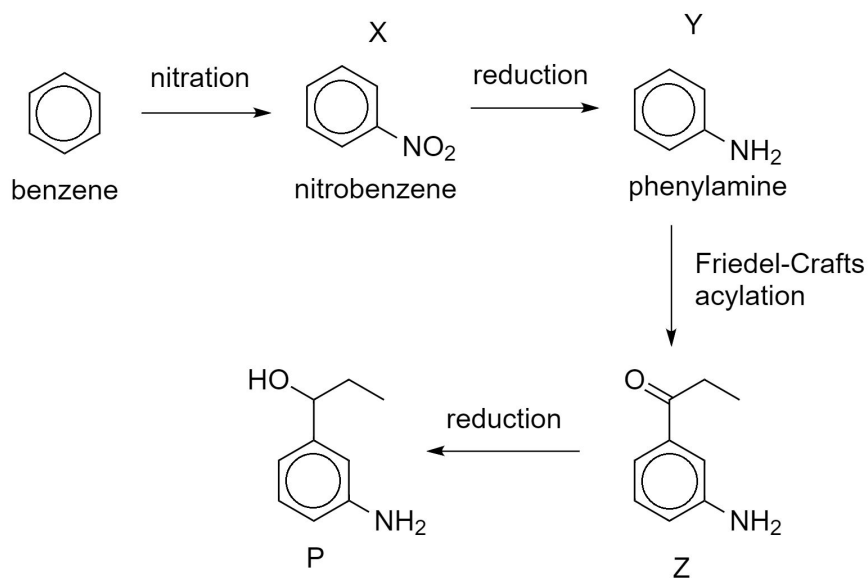
which is the product shown (in a different orientation)

Check C:

Water (H_2O) loses a H to the organic compound and becomes OH^- .
So water acted as an acid.

4. **Answer:** X: nitrobenzene, Y: phenylamine,
Z: 1-(3-aminophenyl)propan-1-one

Working: The likely reactions are



5. **Answer:** 1 only

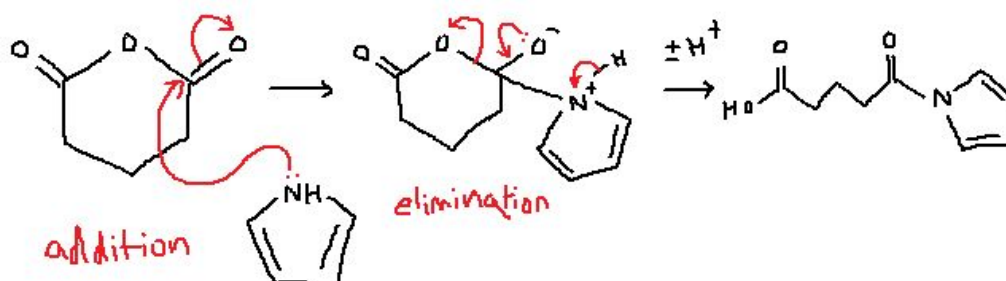
Working: Identifying the functional groups in each compound,

A: acid anhydride

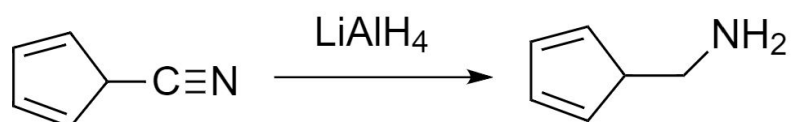
B: 2° amine and (conjugated) alkene

C: ester

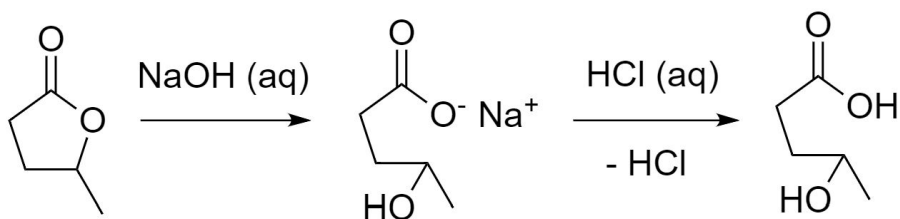
1: yes, since amine has lone pair and can add to the carbonyl:



2: no, the product of this reduction clearly does not match B:



3: no, as the Na^+ is removed by the chloride:



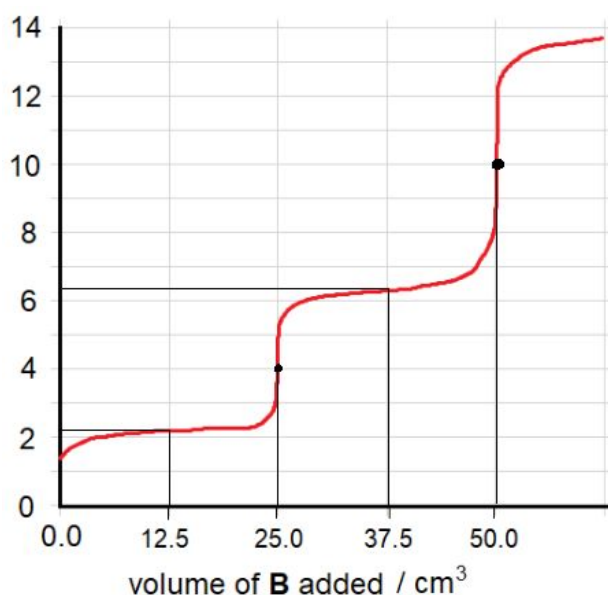
6. **Answer:** 0.066 Pa

Working: Define ξ using the given information. For the reaction we are concerned with,
$$\xi = p(\text{H}_2) / p(\text{H}_2\text{O})$$
Since partial pressure is proportional to mole fraction, in the N_2 gas coming in, we have $p(\text{H}_2\text{O}) = 0.01 * P = 0.01 * 100,000 = 1,000 \text{ Pa}$.
 $\rightarrow \xi = p(\text{H}_2)$ (using units of kPa for partial pressure)
In order for this reaction (the tarnishing of the copper) to **not** happen, it needs to be non-feasible i.e. $\Delta G > 0$.
Gibbs energy change = products - reactants
$$\Delta G^\ominus = -78 - (-178) = +100 \text{ kJ mol}^{-1}$$
Using the given formula, with units of kJ and kPa for simplicity,
$$\Delta G = \Delta G^\ominus + RT \ln \xi \rightarrow \Delta G = 100 + (0.00831)(1250) \ln (p(\text{H}_2))$$
In the limiting case, we put $\Delta G = 0$ and solve for $p(\text{H}_2)$:
$$0 = 100 + 10.3875 \ln p(\text{H}_2)$$
$$\rightarrow p(\text{H}_2) = 6.59 \times 10^{-5} \text{ kPa} = 0.066 \text{ Pa (2 s.f.)}$$

7. **Answer:**

possible identity of H_2A	possible identity of B	initial volume of H_2A / cm^3	pK_a of the anion HA^-
propanedioic acid	sodium hydroxide	25	6.3

Working: From the graph, the pH when base **B** is in excess is about 13.7
 \rightarrow strong base \rightarrow **B** is NaOH.
 It is not totally clear whether H_2A is a strong or weak acid so we need to look at other options in the table.

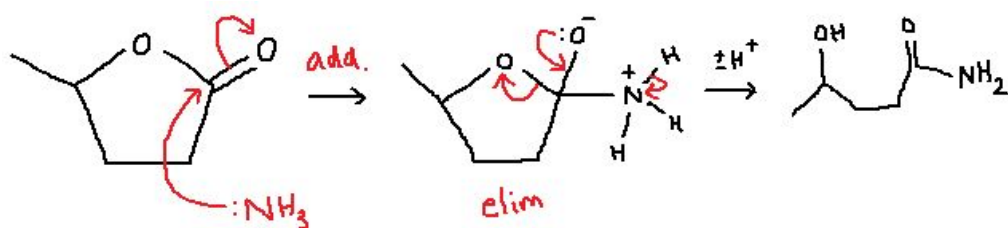


The reaction of H_2A occurs in two steps since it is diprotic.
 First: $\text{H}_2\text{A} + \text{OH}^- \rightarrow \text{HA}^- + \text{H}_2\text{O}$ (equilibrium: $\text{H}_2\text{A} \rightleftharpoons \text{HA}^- + \text{H}^+$)
 Second: $\text{HA}^- + \text{OH}^- \rightarrow \text{A}^{2-} + \text{H}_2\text{O}$ (equilibrium: $\text{HA}^- \rightleftharpoons \text{A}^{2-} + \text{H}^+$)
 Overall: $\text{H}_2\text{A} + 2 \text{OH}^- \rightarrow \text{A}^{2-} + 2 \text{H}_2\text{O}$
 \rightarrow from reacting ratios, we see initial volume of H_2A was 25 cm^3 .
 The desired value of pK_a is for HA^- , not H_2A so we are looking at the second reaction.
 The second reaction takes place only between 25 and 50 cm^3 .
 At the half-equivalence point, $V = 37.5$
 $\rightarrow \text{pK}_a$ of $\text{HA}^- = \text{pH}$ when $[\text{HA}^-] = [\text{A}^{2-}] = 6.3$ (from graph).
 (The first pK_a , that of H_2A , would be 2.2 (from graph).)

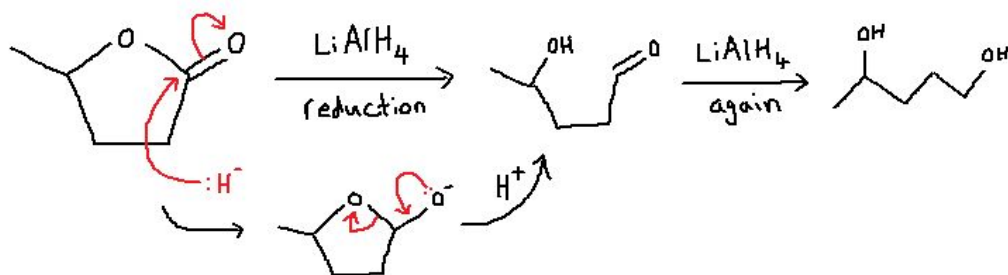
8. **Answer:** A and C only

Working: These reactions are all somewhat unfamiliar but knowledge of mechanisms can be used to how the reaction will occur.

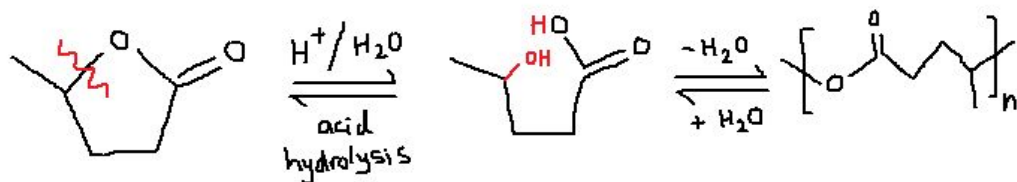
A: yes (nucleophilic addition-elimination)



B: no, the product is pentane-1,4-diol
(nucleophilic addition: reduction twice)

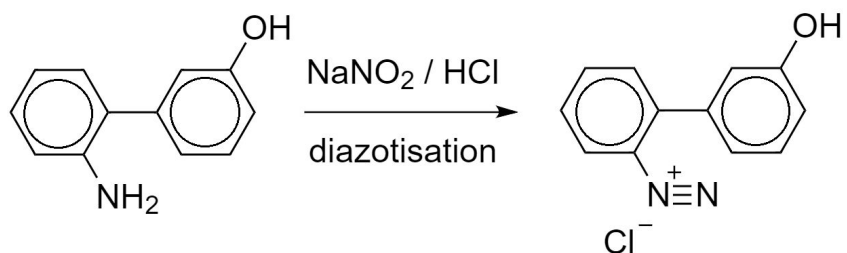


C: yes, after acid hydrolysis of the ester, a compound with both alcohol and carboxylic acid group is formed so can polymerise to form a polyester.

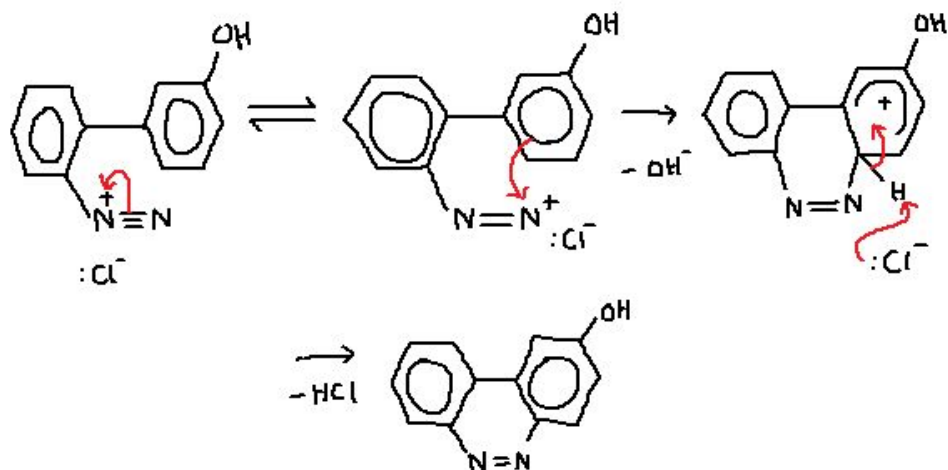


9. **Answer: C**

Working: Using the similar reaction given, the first step will be

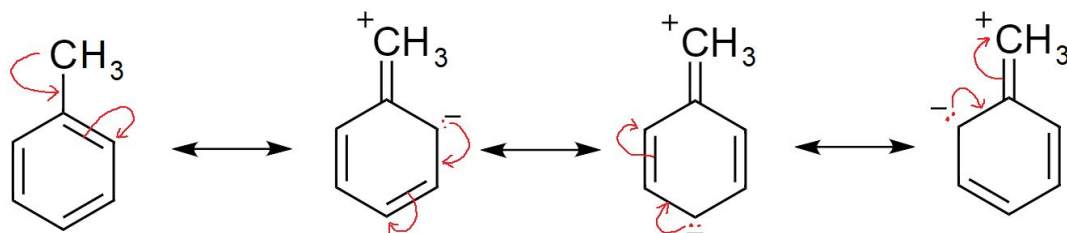


We are now left with OH^- to use. A possible proton transfer (converting OH^- to H_2O and reforming OH^- catalyst later) followed by electrophilic substitution into the other benzene ring gives:



10. **Answer:** A and C

Working: The methyl group is electron releasing, and due to the inductive effect can push electron density away from itself. A simultaneous (resonance) structure forms, which can push the double bond (also an instantaneous process, considering the Kekule structure) around, forming negative charges on every other carbon atom:



Therefore, the 2- and 4- positions gain electron density, while the 3- position has reduced electron density. It is these positions which are now most likely to attack the NO_2^+ electrophile, and so the major products will be the 2-nitro and 4-nitro compounds.

11. **Answer:** 1 and 3 only

Working: Dilution A: since the CH_3COOH is in excess, the final solution will be a buffer of CH_3COOH and CH_3COONa . In this case, we have have that moles of acid = moles of salt (= 0.001 mol) and using $\text{pH} = \text{pK}_a + \log [\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$
 $= \text{pK}_a + \log 1 = \text{pK}_a = \text{constant}$.

For the next two, it will be helpful to derive a new relation. We are looking at changes so we need to find as many constants as possible. Let $\text{A} = \text{CH}_3\text{COO}^-$.

Using $\text{K}_a = [\text{H}^+] [\text{A}^-] / [\text{HA}]$ and $\text{K}_w = [\text{H}^+] [\text{OH}^-]$,
 $\text{K}_a \text{K}_w = [\text{H}^+]^2 [\text{A}^-] [\text{OH}^-] / [\text{HA}]$ and $\text{K}_w / \text{K}_a = [\text{OH}^-] [\text{HA}] / [\text{A}^-]$.
 $\rightarrow [\text{H}^+]^2 = \text{K}_w \text{K}_a ([\text{HA}] / [\text{A}^-] [\text{OH}^-]) \rightarrow [\text{H}^+] \propto 1/\sqrt{[\text{A}^-]}$

Dilution B: there is nothing in excess, the result is 0.002 mol of salt. Before (in 40 cm^3): $[\text{CH}_3\text{COO}^-] = 0.05 \text{ mol dm}^{-3}$.

After (in 80 cm^3): $[\text{CH}_3\text{COO}^-] = 0.025 \text{ mol dm}^{-3}$

Using the derived formula, halving $[\text{A}^-]$ has the effect of multiplying $[\text{H}^+]$ by $\sqrt{2}$.

Dilution C: the numbers are identical, except now we have a basic buffer instead of acidic, so the $[\text{H}^+]$ is replaced by $[\text{OH}^-]$. Using the K_w expression (or by direct logic: $[\text{H}^+]$ is inversely proportional to $[\text{OH}^-]$), $[\text{H}^+]$ will be the reciprocal of the previous result, i.e. $[\text{H}^+]$ is multiplied by $1/\sqrt{2}$.

Dilution D: because the solid is still present, the solution remains saturated and therefore $[\text{OH}^-]$ is constant. Again by K_w this implies $[\text{H}^+]$ is also constant.

12. **Answer:** $\Delta G^\circ = -RT \ln K_c$

Working: Define the rate constants: let k_f be for the forward reaction and k_b for the backward reaction. Using Arrhenius,
 $k_f = A \exp(-E_f / RT)$ and $k_b = A \exp(-E_b / RT)$
Consider the equilibrium constant. Define, using the reaction given,
 $K_c = [C] / [A]^2[B]$

Next, the rates of reaction, using the given orders:

Rate (forward) = $k_f [A]^2[B]$ and Rate (backward) = $k_b [C]$

Since at equilibrium, rate (forward) = rate (backward), so:

$$k_f [A]^2[B] = k_b [C] \rightarrow [C] / [A]^2 [B] = k_f / k_b$$

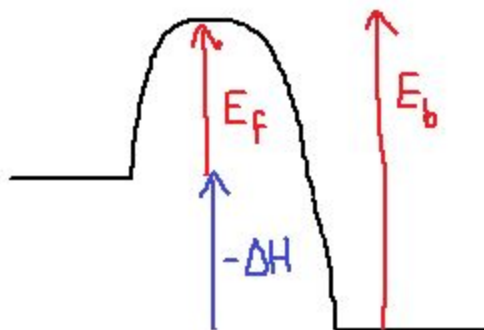
Notice the LHS is K_c , while the RHS can be found with Arrhenius:

$$\rightarrow K_c = (A \exp(-E_f / RT)) / (A \exp(-E_b / RT))$$

Cancelling A (frequency of collisions must be same to maintain constant rate) and dividing exponentials we get

$$K_c = \exp(E_b / RT - E_f / RT) = \exp((E_b - E_f) / RT)$$

Consider the energy profile for this reaction.



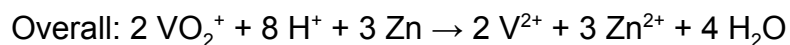
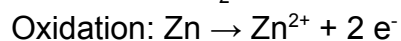
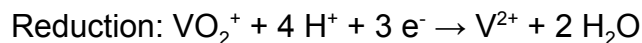
We see that $E_b - E_f = -\Delta H = -\Delta G$ (since entropy changes cancel).

Replacing, $K_c = \exp(-\Delta G / RT)$ and rearranging for ΔG , we find

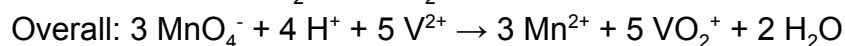
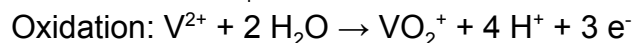
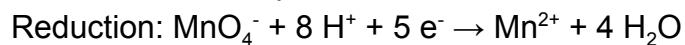
$$\Delta G = -RT \ln K_c.$$

13. **Answer:** The percentage by mass of vanadium in ammonium vanadate(V) is 40.8%

Working: The first half equations are:



The second half equations are:



$$\text{Moles of } \text{MnO}_4^- = 0.02 \times 0.0385 = 0.00077$$

From second half equation, we see a 3:5 reacting ratio, so

$$\text{Moles of } \text{V}^{2+} = 0.001283$$

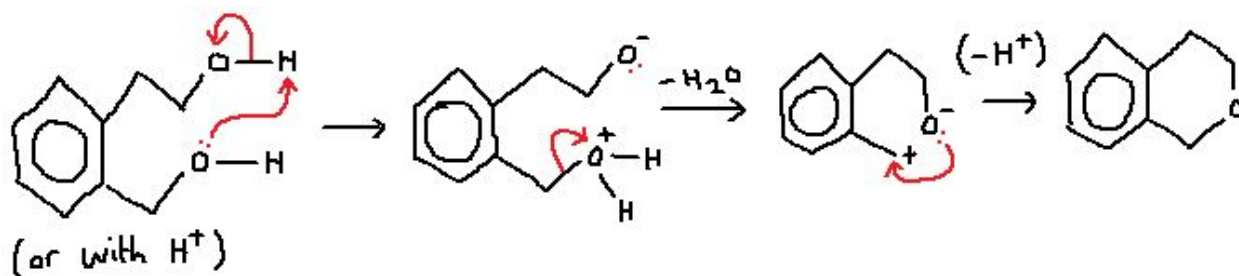
$$\text{Mass of V} = 0.001283 \times 50.9 = 0.06532$$

$$\text{Percentage mass} = 0.06532 / 0.16 = 0.408 = 40.8 \%$$

(Mn^{2+} acts as an indicator but not an autocatalyst in the titration.)

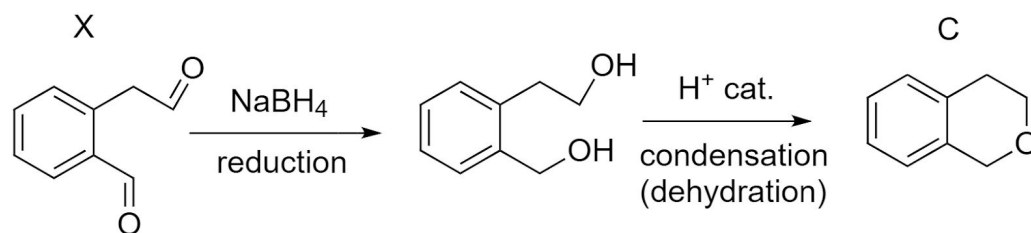
14. **Answer:** All three schemes form the same final major product.

Working: Notice all three schemes end with adding conc acid and nothing else. This implies an elimination mechanism, which we will look at when we have an example. Skipping ahead, the mechanism for that common elimination step can be deduced to be

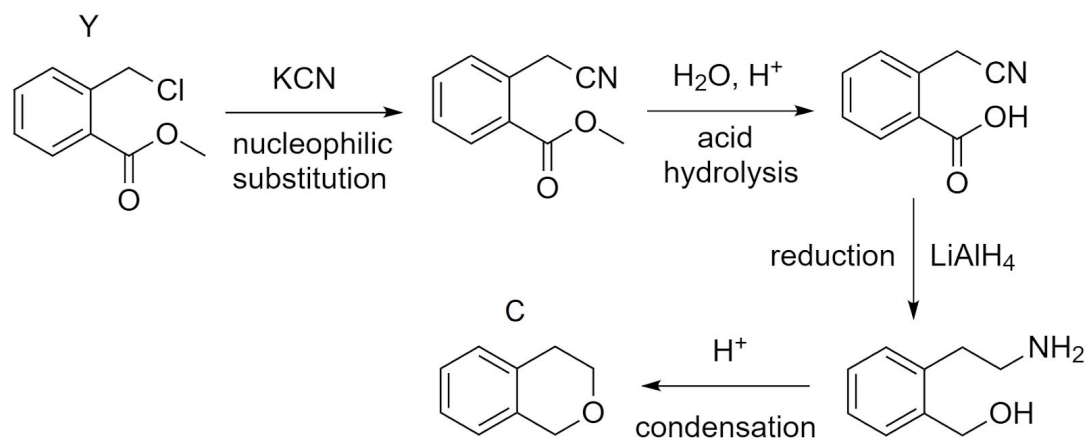


(Notice how H⁺ catalyses this elimination). The same applies if OH is replaced by NH₂, where NH₃ will be lost.

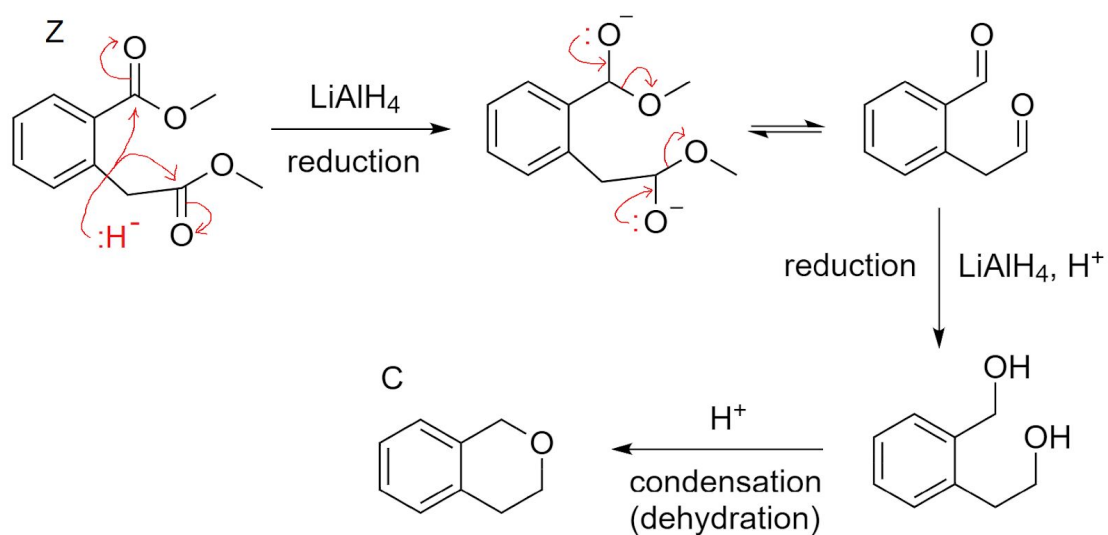
The reactions of Scheme 1 are:



The reactions of Scheme 2 are:



The reactions of Scheme 3 are:



(Some of these reactions are again unfamiliar and need their own mechanisms deducing, but all steps are logical and predictable.)

All three schemes form the same product, C.

15. **Answer:** If the central metal ion was Mg^{2+} instead of Fe^{2+} , the complex would appear colourless.

Working: 1st option: if haem was less conjugated (had less double bonds), then its HOMO-LUMO gap would not be as close so the energy of electron transitions would be larger, from green, to blue/violet regions of the visible spectrum. These would appear their complementary colours, which are orange/yellow \rightarrow true.

2nd option: since when a ligand bonds, the other ligands are unaffected (i.e. the porphyrin ring system does not change), any colour change must be due to the metal ion and not the conjugated system \rightarrow true.

3rd option: although Mg^{2+} would not show the characteristic colour changes due to not being a transition metal, the porphyrin ring system remains conjugated and therefore can still be coloured.
e.g. chlorophyll (green; contains Mg^{2+} in conjugated system)

4th option: F_2 : yellow \rightarrow absorbs violet (high frequency/energy)
 I_2 : purple (violet) \rightarrow absorbs yellow (low frequency/energy).
 \rightarrow HOMO-LUMO transition energy of F_2 is higher than in I_2 .
Alternative reasoning: iodine is a larger atom than fluorine, and orbitals get closer together at higher energy levels
 \rightarrow higher transition energy in F_2 than I_2 .

16. **Answer:** 5%

Working: The boiling point is when the vapour pressure is at atmospheric pressure, since above this the vapour leaves the solution (boils).

From the graphs,

boiling point of X = 360 K, boiling point of Y = 367

ΔT_b of X with NaCl = 362 - 360 = 2

ΔT_b of Y with NaCl = 368 - 367 = 1

$\rightarrow \Delta T_b(X_{NaCl}) = 2 * \Delta T_b(Y_{NaCl})$

Now using the given equation,

$\rightarrow K_X * i_{NaCl} * n_{NaCl} / m_X = 2 * K_Y * i_{NaCl} * n_{NaCl} / m_Y$

Given: $i_{NaCl} = 2$ (since $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$)

and $n_{NaCl} / m_X = n_{NaCl} / m_Y$ (*isomolal*)

$\rightarrow K_X = 2 * K_Y$.

Next, consider the dimerisation of S. This means that when x moles of S monomers dimerise,

	2 S	\rightarrow	S ₂
mole fraction	1		0
	1 - x		x/2

so the number of free ions formed per moles of S is 1 - x/2

i.e. $i_S = 1 - x/2$.

Plugging this back in the equation for given boiling point elevation,

$\rightarrow \Delta T_X = 3 * \Delta T_Y$

$\rightarrow K_X * i_{SX} * n/m = 3 * K_Y * i_{SY} * n/m$

$\rightarrow 2(1 - x_X/2) = 3(1 - x_Y/2)$ (since n/m is constant, and $K_X / K_Y = 2$)

Using the fact that 70% dimerises in Y i.e. $x_Y = 0.70$, we find

$\rightarrow 2(1 - x_X/2) = 3(1 - 0.35)$

$\rightarrow 1 - x_X/2 = 0.975$

$\rightarrow x_X = 0.05$

\rightarrow 5% dimerisation.