Group A: Quick-reference Answer Key

Q	A	Marks	Q	A	Marks	Q	A	Marks	Q	A	Marks	Q	A	Marks
1	②	1	11	①	2	21	④	1	31	①	1	41	②	2
2	③	1	12	③	4	22	②	2	32	③	1	42	④	4
3	①	1	13	②	4	23	①	2	33	②	1	43	④	4
4	③	1	14	③	4	24	②	2	34	①	1	44	①	4
5	①	1	15	②	4	25	③	2	35	③	1	45	②	4
6	④	1	16	②	1	26	①	2	36	④	1			
7	②	2	17	①	1	27	①	4	37	③	2			
8	④	2	18	①	1	28	②	4	38	④	2			
9	④	2	19	④	1	29	②	4	39	③	2			
10	②	2	20	③	1	30	④	4	40	①	2			

Physical: 15 questions (6 × 1 mark, 5 × 2 marks, 4 × 4 marks), 32 marks total
Organic: 15 questions (6 × 1 mark, 5 × 2 marks, 4 × 4 marks), 32 marks total
Inorganic: 15 questions (6 × 1 mark, 5 × 2 marks, 4 × 4 marks), 32 marks total

Recommended Time: 2 hours 15 minutes.
Approximate Grade Boundaries (marks): A* > 77, A > 68, B > 58, C > 48, D > 39
Coverage is based on the AQA Specification.
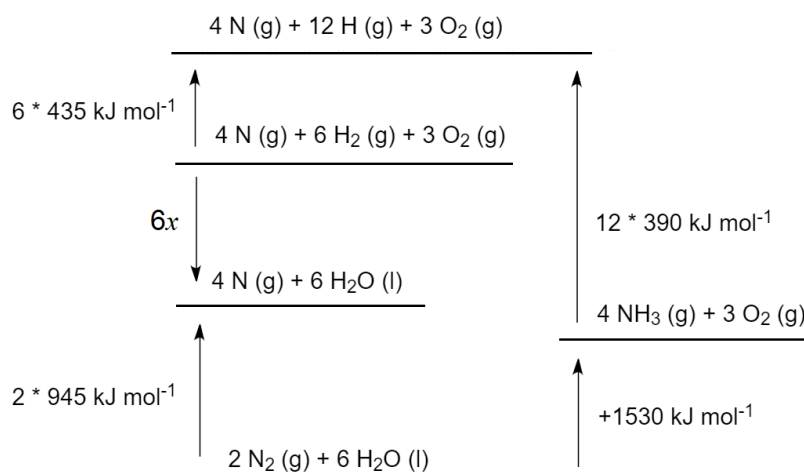
Group A: Worked Solutions

A1.   Answer: ②

[He] $2s^1$ = Li. [He] $2s^2$ $2p^5$ = F. [Ne] $3s^2$ $3p^2$ = Si. [Ne] $3s^2$ $3p^5$ = Cl.
Li is a metal, Si is a metalloid, F and Cl are non-metals.
F is more reactive than Cl due to smaller atomic radius and less shielding (②).

A2.   Answer: ③

Note that we should not break the O=O bond in any calculation as its enthalpy is an additional unknown. Let x be the enthalpy of formation of water.

From Born-Haber cycle algebra,
$1530 = 2 * 945 - 6x + 6 * 435 - 12 * 390 \rightarrow x = -285$ kJ mol^{-1}. (③)

A3.   Answer: ①

We are given that the shown atom is an ion, meaning the number of protons and the number of electrons cannot be equal. We can therefore see that the white circles represent protons (there are 3) while the grey circles represent neutrons (there are 4). Since there are 4 electrons, this is a negative ion, so we are looking for a positive ion i.e. has 1 or 2 electrons. To satisfy the other criteria, it must also have 3 protons and **not** 4 neutrons. Only **B** fits all these conditions. (①)

A4.   Answer: ③

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. First statement does not explain this since Ca^{2+} ions exist on both sides of the equilibrium. (③)

A5.   Answer: ①

Let x be abundance (from 0 = 0% to 1 = 100%) of $^{86}Sr = {}^{87}Sr$. Since all abundances add to 1, the abundance of ^{88}Sr will be 1 - $2x$.
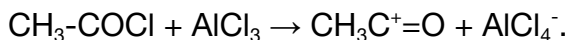$\rightarrow$ 87.7 = $86x + 87x + 88(1 - 2x)$ [definition of atomic mass]
$\rightarrow$ 87.7 = 88 - $3x$
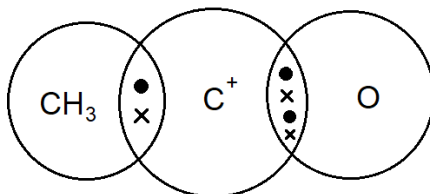$\rightarrow x$ = 0.1 = 10% (①)

A6.   Answer: ④

This is the first step in a Friedel-Crafts acylation reaction:
$CH_3-COCl + AlCl_3 \rightarrow CH_3C^+=O + AlCl_4^-$.
The dot-and-cross structure for this acylium ion is

2 electron domains, 0 lone pairs $\rightarrow$ linear geometry. (④)

A7.   Answer: ②

The hydrogen atoms repel each other due to their surrounding electron density. Therefore, the lowest energy state will be when all hydrogens are as far away from each as possible (staggered conformation), similar to how molecular geometries are determined.
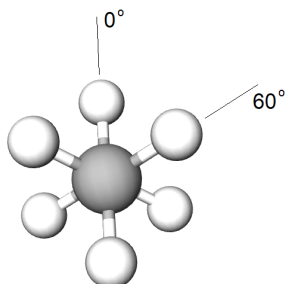
← lowest energy state, viewing along the C-C bond

This occurs when the CH_3 groups are rotated 60° with respect to each other, since in this case the lateral distance between atoms is maximised. The highest energy state will be when all atoms are aligned (eclipsed conformation). (②)

A8.   Answer: ④

Only one of the two bonds made by each Cl is dative covalent, as this arrangement ensures all Be atoms have full octets. The pattern is Be-Cl→Be.

Around the Be atoms, there are 4 electron domains, 0 lone pairs → bond angle is 109.5° → Cl-Be-Cl = 109.5°. Around the Cl atoms, there are 4 electron domains, 2 lone pairs → bond angle is 109.5°, reduced by 2 × 2.5° = 5° due to the lone pairs → Be-Cl-Be = 104.5°. So the difference in bond angle is 5°.

By symmetry, each $BeCl_2$ unit lies in a plane perpendicular to the adjacent units, so the planes are angled at 90° to each other. The 3D structure is:
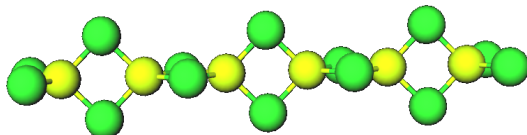
Therefore, none of the statements given are correct. (④)

A9.   Answer: ④

Substituting the given expressions for Ψ' and Ψ'' into the Schrodinger equation,

$$\frac{\Psi}{a_0{}^2} - \frac{2}{r}\frac{\Psi}{a_0} + \frac{2\Psi}{a_0 r} = -\frac{8\pi^2 mE}{h^2}\Psi$$

Divide both sides by Ψ and cancel out the 2nd and 3rd terms,

$$\frac{1}{a_0{}^2} = -\frac{8\pi^2 mE}{h^2}$$

Solve for E:

$$E = -\frac{h^2}{8\pi^2 ma_0{}^2}$$

The mass of a proton is $\frac{1}{6.022 \times 10^{23}} = 1.661 \times 10^{-24}\ g = 1.661 \times 10^{-27}\ kg$.

Therefore $m = \frac{1}{1836} \times 1.661 \times 10^{-27} = 9.045 \times 10^{-31}\ kg$.

So the numerical value of E = -2.193 × 10^{-18} J atom^{-1}.

Converting units with Avogadros, the ionisation energy is 1321 kJ mol^{-1}. (④)

A10.   Answer: ②

Strong acid: completely dissociates into H^+ and conjugate base.

A: yes (strong acid has faster rate of reaction since more H^+)
B: no (same moles of each acid → same volume for neutralisation)
C: yes (strong acid has more free ions to carry current)

→ **A** and **C** only (②)

A11. Answer: ①

Half-equations:

$Zn \rightarrow Zn^{2+} + 2\,e^-$ (oxidation, anode), $Cu^{2+} + 2\,e^- \rightarrow Cu$ (reduction, cathode)

Overall: $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

Useful formulas: Cell emf $= E_{\text{cathode}} - E_{\text{anode}}$; Nernst equation: $E = E^o - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$;

A: in the copper electrode, Cu^{2+} ions are being consumed (lost) so must be replaced by K^+ ions from the salt bridge, so K^+ ions move right.

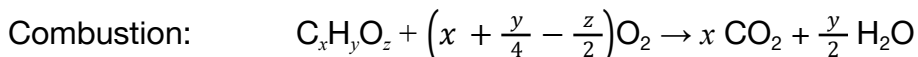**B:** Increasing $[Zn^{2+}]$ would push the anode equilibrium to the left, promoting reduction, increasing E_{anode}, decreasing the overall cell emf

C: Changing temperature will affect the emf since the activation energies for each electrode reaction will be different, producing different rate constants, changing the equilibrium constant, changing the emf.
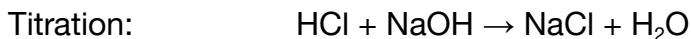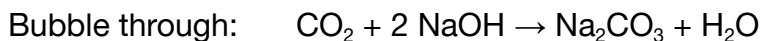
$\rightarrow$ None are correct. (①)

A12. Answer: ③

Let the formula be $C_xH_yO_z$. The balanced reactions are:

Combustion: $C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right)O_2 \rightarrow x\,CO_2 + \frac{y}{2}\,H_2O$

Drying: all H_2O is removed, leaving only CO_2 gas

Bubble through: $CO_2 + 2\,NaOH \rightarrow Na_2CO_3 + H_2O$

Titration: $HCl + NaOH \rightarrow NaCl + H_2O$

Mass of H_2O produced = 0.0931 g $\rightarrow$ moles of H_2O = 0.005172 mol

Titration: 14.7 cm³ NaOH consumed $\rightarrow$ 10.3 cm³ NaOH was reacted with CO_2
$\rightarrow$ moles of NaOH = 0.0103 mol $\rightarrow$ moles of CO_2 = 0.005172 mol
$\rightarrow y = 2x.$

We can set $x = 1$ without loss of generality to simplify the ratio calculations:

Moles of molecule used $= \frac{0.100}{12x + y + 16z} = \frac{0.1}{14 + 16z} = \frac{0.005172}{1}$

Solving for z, we get $z = 0.3334$, which implies that $x : y : z = 1 : 2 : \frac{1}{3}$.

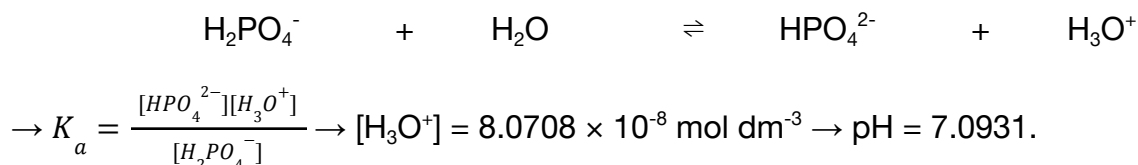Converting to integers: $x = 3$, $y = 6$, $z = 1$ $\rightarrow$ empirical formula is C_3H_6O. (③)

A13. Answer: ②

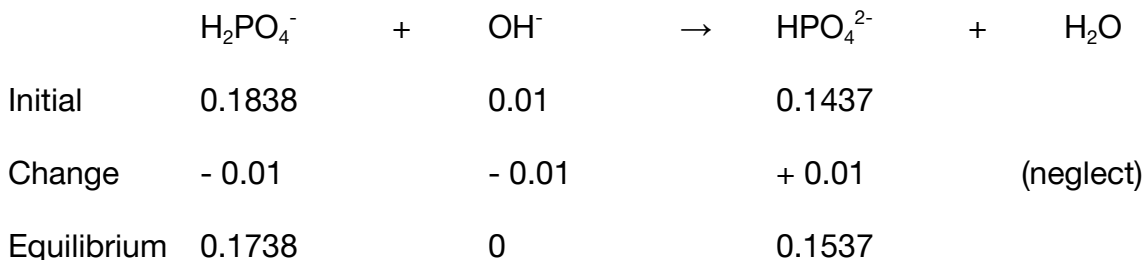Because $H_2PO_4^-$ has one more proton than HPO_4^{2-}, KH_2PO_4 is the weak acid.

Initial moles of $H_2PO_4^- = \dfrac{mass\ of\ KH_2PO_4}{M_r(KH_2PO_4)} = \dfrac{25}{39+2+31+4\times16} = 0.1838$ mol

Initial moles of $HPO_4^{2-} = \dfrac{mass\ of\ K_2HPO_4}{M_r(KHPO_4)} = \dfrac{25}{2\times39+1+31+4\times16} = 0.1437$ mol

Preparing the buffer, we have the acid-conjugate base equilibrium:

$$H_2PO_4^- \quad + \quad H_2O \quad \rightleftharpoons \quad HPO_4^{2-} \quad + \quad H_3O^+$$

$\rightarrow K_a = \dfrac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} \rightarrow [H_3O^+] = 8.0708 \times 10^{-8}$ mol dm^{-3} $\rightarrow$ pH = 7.0931.

On addition of hydroxide, the mole quantities shift to new equilibrium values:

	$H_2PO_4^-$	+	OH^-	$\rightarrow$	HPO_4^{2-}	+	H_2O
Initial	0.1838		0.01		0.1437		
Change	- 0.01		- 0.01		+ 0.01		(neglect)
Equilibrium	0.1738		0		0.1537		

$\rightarrow K_a = \dfrac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} \rightarrow [H_3O^+] = 7.1352 \times 10^{-8}$ mol dm^{-3} $\rightarrow$ pH = 7.1466.

(Alternatively, use the Henderson-Hasselbalch equation:

$$pH = pK_a + log_{10}\left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}\right) = -log_{10}(6.31 \times 10^{-8}) + log_{10}\left(\frac{0.1437}{0.1838}\right) = 7.0931.$$

$$pH_{KOH} = pK_a + log_{10}\left(\frac{[HPO_4^{2-}] + [OH^-]}{[H_2PO_4^-] - [OH^-]}\right) = 7.12 + log_{10}\left(\frac{0.1437 + 0.01}{0.1838 - 0.01}\right) = 7.1466.)$$

So the increase in pH is 7.1466 - 7.0931 = 0.0535 which rounds to 0.05. (②)

A14. **Answer:** ③

The overall reaction is

$$CH_4 \text{ (g)} + 2\,H_2O \text{ (g)} \rightleftharpoons 0\,CO \text{ (g)} + CO_2 \text{ (g)} + 4\,H_2 \text{ (g)}$$

A: $a = 2$, $b = 1$, $c = 4$.

B: the overall equilibrium constant is the product of the two intermediates:

$$K_p = \frac{p_{CO_2}\,(p_{H_2})^4}{p_{CH_4}\,(p_{H_2O})^2} = \frac{p_{CO}\,(p_{H_2})^3}{p_{CH_4}\,p_{H_2O}} \times \frac{p_{H_2}\,p_{CO_2}}{p_{H_2O}\,p_{CO}}$$

$$= K_{p1} \times K_{p2} = 5.80 \times 10^{-5} \times 12 = 6.96 \times 10^{-4}\ \text{Pa}^2$$

C: Overall ΔH° = 206 - 41 = +165 kJ mol^{-1}. Using the given formula, rearrange to $\Delta G^{\circ} = -RT \ln K_p$, so overall ΔG° = +40.679 kJ mol^{-1} → ΔS° = +185 J mol^{-1} K^{-1}.

→ only **B** is true. (③)

A15. Answer: ②

At point **I** and **II**, the ideal gas law gives $V_1 = \dfrac{n_1 R T_1}{P_1}$ and $V_2 = \dfrac{n_2 R T_2}{P_2}$.

Dividing, $\dfrac{V_1}{V_2} = \dfrac{n_1 T_1 P_2}{n_2 T_2 P_1} \rightarrow \dfrac{T_2}{T_1} = \dfrac{n_1 P_2 V_2}{n_2 P_1 V_1}$. Since $\dfrac{V_1}{V_2} = 4$, then $\dfrac{T_2}{T_1} = \dfrac{n_1 P_2}{4 n_2 P_1}$.

Since points **I** and **II** are identical by mass fraction, $\dfrac{n_1}{n_2} = 1$ and so $\dfrac{T_2}{T_1} = \dfrac{P_2}{4 P_1}$.

Let M be the molecular mass of NO_2, with the molecular mass of N_2O_4 being $2M$.
Let the mass fraction of each compound be $m_{N_2O_4}$ and m_{NO_2}.

$$\text{mol } N_2O_4 = n_{N_2O_4} = \frac{\text{mass of } N_2O_4}{2M} = \frac{m_{N_2O_4} w}{2M}; \quad \text{mol } NO_2 = n_{NO_2} = \frac{\text{mass of } NO_2}{M} = \frac{m_{NO_2} w}{M}.$$

The mole fraction of N_2O_4 is then $x_{N_2O_4} = \dfrac{n_{N_2O_4}}{n_{N_2O_4} + n_{NO_2}} = \dfrac{\frac{m_{N_2O_4} w}{2M}}{\frac{m_{N_2O_4} w}{2M} + \frac{m_{NO_2} w}{M}} = \dfrac{m_{N_2O_4}}{m_{N_2O_4} + 2 m_{NO_2}}$.

Since $m_{N_2O_4} + m_{NO_2} = 1$, let $m_{NO_2} = 1 - m_{N_2O_4}$ so that $x_{N_2O_4} = \dfrac{m_{N_2O_4}}{2 - m_{N_2O_4}}$.

Therefore, the mole fractions of N_2O_4 at point **II** and the point **X** at (P_1, T_2) are

Point **II**: $\qquad\qquad x_{N_2O_4} = \dfrac{2/3}{2 - 2/3} = \dfrac{1}{2}, x_{NO_2} = 1 - x_{N_2O_4} = \dfrac{1}{2}$

Point (P_1, T_2): $\qquad x_{N_2O_4} = \dfrac{2/5}{2 - 2/5} = \dfrac{1}{4}, x_{NO_2} = 1 - x_{N_2O_4} = \dfrac{3}{4}$

Using the equilibrium constant at T_2, $\qquad K_p = \dfrac{P_{NO_2}^2}{P_{N_2O_4}} = \dfrac{\left(1 - x_{N_2O_4}\right)^2 P^2}{x_{N_2O_4} P} = \dfrac{\left(1 - x_{N_2O_4}\right)^2}{x_{N_2O_4}} P.$

Equating at each point gives $\dfrac{(1 - 1/2)^2}{1/2} P_2 = \dfrac{(1 - 1/4)^2}{1/4} P_1$ so $\dfrac{P_2}{P_1} = \dfrac{9}{2}$.
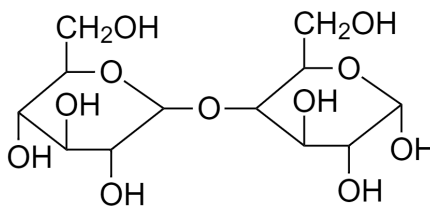
Therefore, $\dfrac{T_2}{T_1} = \dfrac{1}{4} \times \dfrac{9}{2} = \dfrac{9}{8}$. (②)

A16. Answer: ②

The cyclic forms of these sugars are
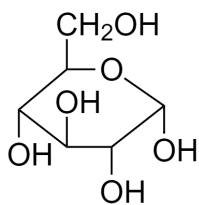
glucose

maltose

Since maltose is a larger molecule than glucose, maltose is more sterically hindered and cannot utilise its -OH groups for hydrogen bonding to the mobile phase as easily. This allows glucose to be attracted to the mobile phase more strongly, giving it a larger R_f. (②)

A17. Answer: ①

The main reactions that could occur are (1,4-DCB = 1,4-dichlorobutane, the starting molecule)
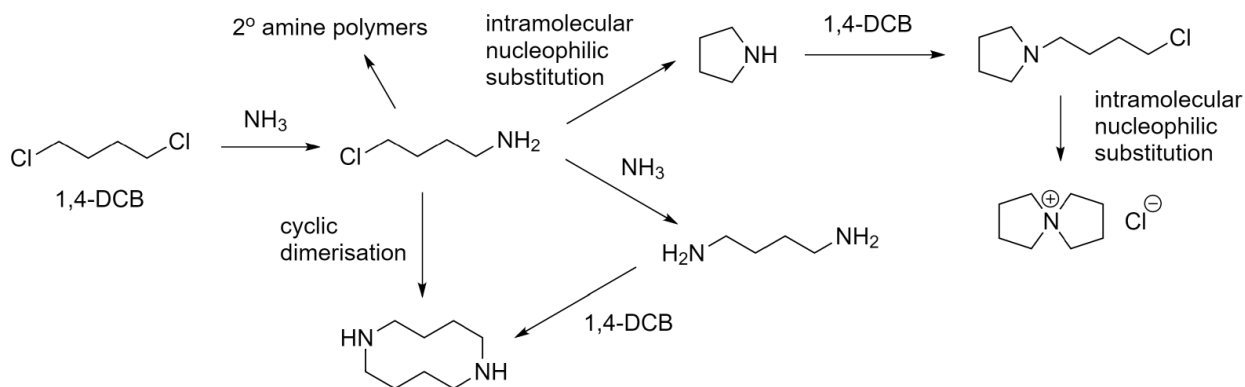
There will be near limitless products due to all the combinations of -NH_2 and -Cl groups on any given pair of molecules, but only 4 shown are possible. (①)

A18. Answer: ①

Since there are two distinct peaks, the carbons cannot be identical, so we can rule out the 1,2-dibromo options. To distinguish between the alkane and the alkene, note that carbons within a C=C bond have peaks at 90-150 ppm, which is far out of the range here. So 1,1-dibromoethane is the only valid option. (①)

A19. Answer: ④

The highest priority group is the -OH alcohol group. The longest carbon chain containing this group is 6 carbons long (hexane), and the number for the -OH group is smallest when numbering right-to-left:
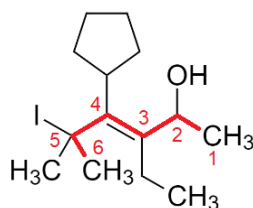
The E/Z for the double bond is assigned by atomic number. Since C, I > C, C, the side containing iodine is prioritised on the left, while since C, O > C, C, the side containing -OH is prioritised on the right. Since these are on opposite sides, the alkene is *trans* and is assigned the letter *E* (*entgegen*).

The substituents are then 3-ethyl, 4-cyclopentyl, 5-methyl, 5-iodo. The suffix will have -3-en-2-ol. Naming alphabetically, we get

(*E*)-4-cyclopentyl-3-ethyl-5-iodo-5-methylhex-3-en-2-ol.

A20. Answer: ③

The fully saturated carboxylic acid has the formula $C_{17}H_{35}COOH$, which can be deduced from the $C_nH_{2n+1}COOH$ homologous formula for carboxylic acids. If the degree of unsaturation (number of double bonds) is k, then the polyunsaturated carboxylic acid has formula $C_{17}H_{35-2k}COOH$.

The reaction with bromine is $C_{17}H_{35-2k}COOH + k\ Br_2 \rightarrow C_{17}H_{35-2k}Br_{2k}COOH$.
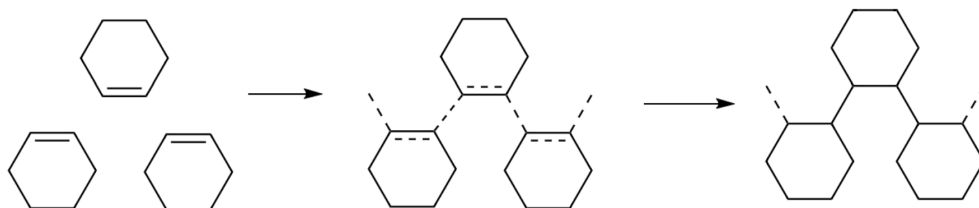
Moles of bromine used $= 0.015 \times 0.2 = 0.003$ mol
Moles of acid used $= 0.001$ mol
$\rightarrow k = 3 \rightarrow$ there are $35 - 2 \times 3 = 29$ hydrogens on the alkyl chain $\rightarrow n = 29$. (③)

A21. Answer: ④

Only cyclohexene gives this polymer. (④)

(not the actual mechanism)

The cyclohexa-1,4-diene will produce a mixture of nonlinear polymers due to the additional double bond left over on the polymer: this would give a very high degree of cross-linking, which we were given is not the case.

A22. Answer: ②

Consider each group of protons in turn:

a is split by **b** into a **doublet** with integration ratio 3. Expected at δ = 0.7 - 1.2 but likely shifted further due to proximity to C=C bond → could be ② or ③.

b is split by **a** and **c** into a **quintet** with integration ratio 1. Expected at δ = 4.5 - 6.0 → closest match is peak ①.

c is split by **b** and **d** into a **quartet** with integration ratio 1. Expected at δ = 4.5 - 6.0 → closest match is peak ①.

d is split by **c** and **e** into a **quintet** with integration ratio 2. Expected at δ = 0.7 - 1.2 but likely shifted further due to proximity to C=C bond → could be peaks ② or ③.

e is split by **d** into a **triplet** with integration 3. Expected at δ = 0.7 - 1.2 → closest match is peak ④.

Peak ③ looks like a doublet more than peak ② so assign **a** to ③ and **d** to ②.

In conclusion, peak ① is a superposition of **b** and **c** (table has incorrect splitting pattern), peak ② is **d** (correct), peak ③ is **a** and peak ④ is **e** (swapped around).

→ row describing peak ② is correct. (②)

A23. Answer: ①

A: Primary and secondary amines all have a hydrogen atom attached to the nitrogen, which will take part in hydrogen bonding with other N atoms in the pure state and with O in water molecules in the aqueous state.

**B:** Tertiary amines have no N-H bonds, so the only hydrogen bonds that can be formed are N…H-O in water.

C: Quaternary ammonium salts are purely ionic in the solid state and form ion-dipole attractions in water.

→ **A** and **B** are true (①).

A24. Answer: ②

Either of the COOH or NH_2 groups in each amino acid can combine with the other group on the other amino acid to form two dipeptides.

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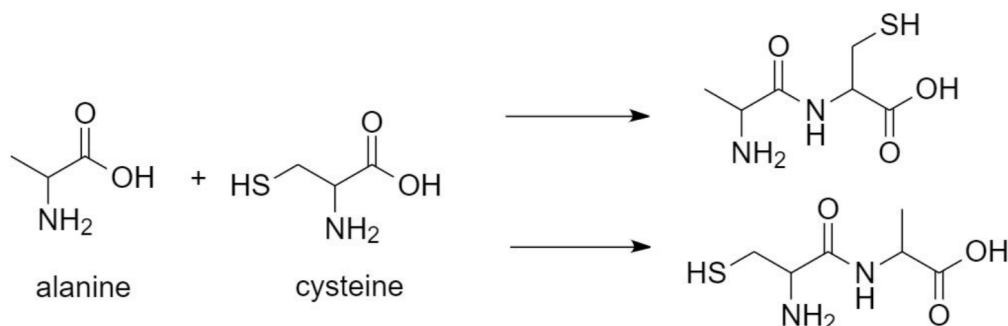
In their aqueous state, the amino acids (and hence the dipeptide) form zwitterions so convert all NH_2 to NH_3^+ and all COOH to COO^- :

$\rightarrow$ $CH_3CH(NH_3^+)CONHCH(CH_2SH)COO^-$ (**A**)
$\rightarrow$ $CH_2(SH)CH(NH_3^+)CONHCH(CH_3)COO^-$ (**C**)
$\rightarrow$ **A** and **C** (②)

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

A25. Answer: ③

4500 base **pairs** $\rightarrow$ 9000 bases $\rightarrow$ 900 A, 900 T
$\rightarrow$ 9000 - 1800 = 7200 are G and C $\rightarrow$ 3600 G, 3600 C.

$\rightarrow$ **B** and **C** are correct $\rightarrow$ 2 correct (③)

A26. Answer: ①

An enzyme's active site has a specific arrangement of functional groups which must all be present in order to carry out its reactions. The acetylation of the -OH group has significantly reduced its nucleophilicity (the ester bond is less polar and has delocalised electrons). (①)

Since the acetyl group is small, it is unlikely to affect the protein folding structure in any way. The aspirin metabolite is a weak acid and its ionisation will have a negligible effect on the pH of the protein environment, simply diffusing away.

A27. Answer: ①

The radical species **X** will place the unpaired electron on the 2° in order to stabilise it by the positive inductive effect (①). Therefore, we have
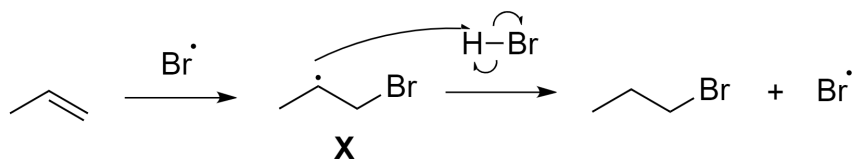
If two molecules of **X** terminate together, the product will be 1,4-dibromo-2,3-dimethylbutane.

The peroxide bond is not polarised, but due to its inherent low bond enthalpy, it easily undergoes homolysis to generate hydroxyl radicals. This is also not disproportionation as both products are identical.

A28. Answer: ②

A: It is true that CO and CO_2 are toxic and have high global warming potential respectively, and they could form as high-temperature oxidation products of the coke. However with regards to the 'poisoned catalyst', this means that the catalyst surface has impurities to reduce its activity, preventing full hydrogenation to ethane. It has nothing to do with biological poisoning.
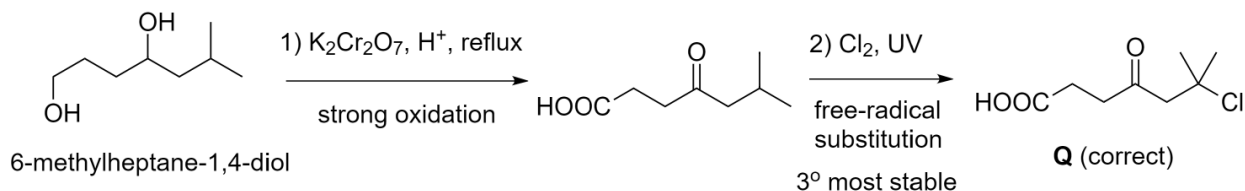
B: For a country without natural resources, the mining of calcium ores and carbon deposits would be very impractical. Instead, it is much more feasible to import crude oil and take advantage of the technological advancements made locally i.e. the robust steam cracker. The comment on its higher efficiency compared to additional separation processes is also correct.

C: The comment on false-carbon-neutrality is valid. GMO yeast strains do not inherently cause a biohazard threat as they are contained and will be isolated from yeast used in other areas. The more important issue is the migrational issues caused by the displacement of local residents from agricultural regions to make space for growing the sugar cane.
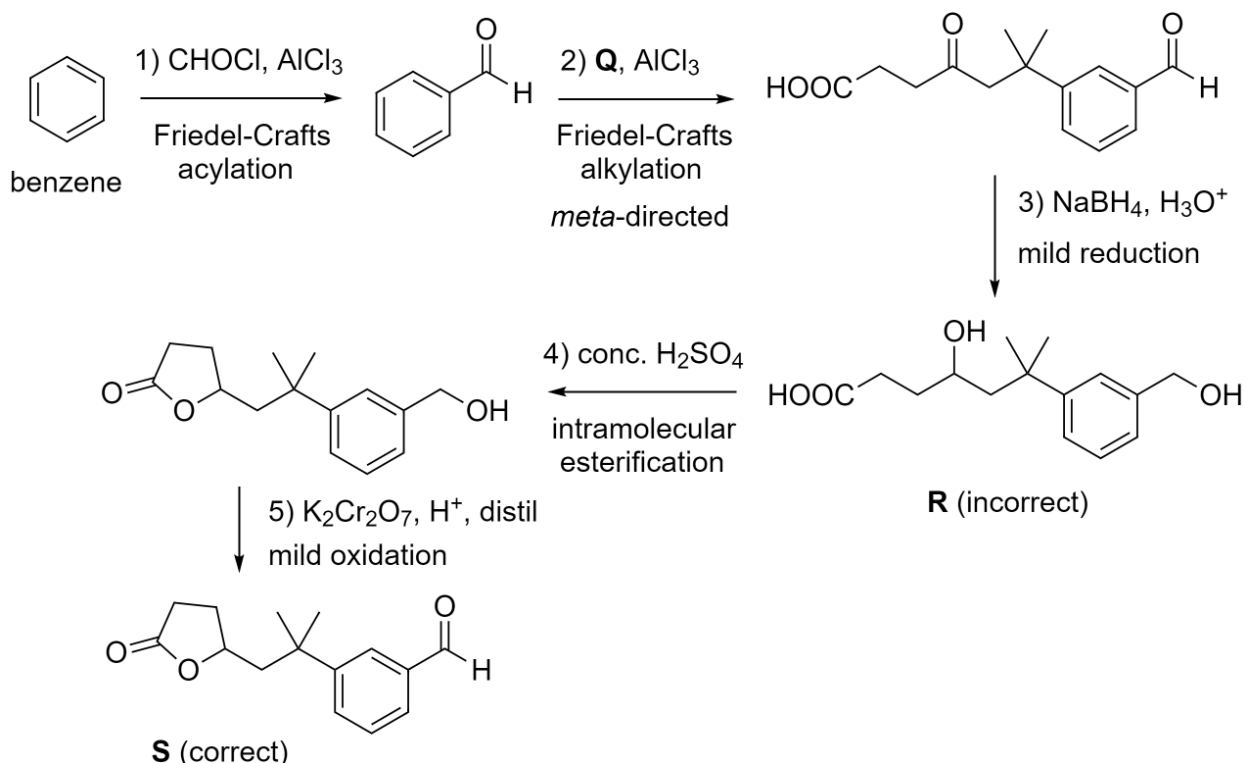
→ only **B** is a completely valid assessment. (②)

A29. Answer: ②

The reactions to form **Q** are:

6-methylheptane-1,4-diol

1) K₂Cr₂O₇, H⁺, reflux — strong oxidation

2) Cl₂, UV — free-radical substitution, 3° most stable

Q (correct)

Then the main synthesis from benzene follows:

benzene

1) CHOCl, AlCl₃ — Friedel-Crafts acylation

2) **Q**, AlCl₃ — Friedel-Crafts alkylation, *meta*-directed

3) NaBH₄, H₃O⁺ — mild reduction

R (incorrect)

4) conc. H₂SO₄ — intramolecular esterification

5) K₂Cr₂O₇, H⁺, distil — mild oxidation

S (correct)

So **Q** and **S** are correct, **R** is incorrect (②). Key features on reaction selectivity:

- In the free-radical substitution with Cl₂ to form **Q**, the 3° position is most likely to hold a free radical due to its stability. It is also most likely to react with the benzene ring due to the stability of its carbocation intermediate.

- The **Q** electrophile is *meta*-directed due to the electron-withdrawing carbonyl group (resonance form of negative inductive effect).

- Step 4 is not alcohol elimination as this requires high temperature - the intramolecular esterification proceeds instead at near room temp.

A30. Answer: ②

The time taken to become optically inactive increases with the activation energy required to attain the transition state, as this is what determines the rate at which the racemic mixture is formed.

Amine **A** is essentially equivalent to the given example of ethylmethylamine but with some bulkier substituents, so there will be somewhat higher steric hindrance to the inversion. This makes it the fastest to racemise (shortest time).

Amines **B** has its nitrogen within a small ring system. In order to invert, the bond angles in the ring would have to change through a cyclopropane-like (aziridine) structure, which is somewhat unstable due to the high ring strain. This makes it slow to racemise.

Amine **C** is tertiary and the nitrogen is fully constrained within three fused rings. The bond angles cannot change much at all and will likely never invert from the given conformation. This makes it the slowest to racemise (longest time).

Therefore the ordering is **C** > **B** > **A**. (②)

A31. Answer: ①

In cold conditions, chlorine and sodium hydroxide gives sodium chloride, sodium chlorate(I) (aka sodium hypochlorite) and water by disproportionation:

Cl_2 (g) + 2 NaOH (aq) $\rightarrow$ NaCl (aq) + NaClO (aq) + H_2O (l) (①)
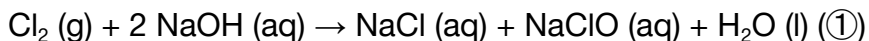
A32. Answer: ③

SiO_2 has lost oxygen to form Si, so SiO_2 has been reduced. The reducing agent must therefore be B, boron. (③)

A33. Answer: ②

The more electropositive a metal atom, the more basic is its oxide. Bi is more electropositive (further from F in group 5) than N so Bi_2O_5 should be more basic than N_2O_5.

The N-N bond is shorter than the P-P bond, and due to the presence of the lone pair on each atom, the lone-pair-bonding-pair repulsion is stronger in N_2H_4 than in P_2H_4, making N-N weaker than P-P. (160 kJ mol^{-1} vs 201 kJ mol^{-1}) (②)

PH_3 is a slightly larger molecule than NH_3, giving PH_3 slightly stronger Van der Waals' forces. However, since N is more electronegative than P, NH_3 can form much stronger hydrogen bonds than PH_3, which gives NH_3 the higher boiling point.

NF_3 is more covalent than BiF_3 as the electronegativities of N and F are more similar than Bi and F.

A34. Answer: ①

CrO_2F_2:   F = -1, O = -2   so Cr = +6.
$K_2Mn_2O_7$:   K = +1, O = -2   so Mn = +6.
$BaTiO_3$:   Ba = +2, O = -2   so Ti = +4.

→ oxidation states are +6, +6, +4. (①)

A35. Answer: ④

$E = \frac{hc}{\lambda}$ → energy per photon = 6.8586 × 10^{-19} J.

Multiplying by Avogadros and converting gives 413 kJ per mole of photons.

One photon breaks one bond, so the bond enthalpy is 413 kJ mol^{-1}. (④)

A36. **Answer:** ③

A heterogeneous catalyst must be in a different state to the reactants.

Heptane is a volatile liquid at stp so will likely be a gas at 400 °C, Pt is a solid metal → heterogeneous.

Propene is a gas, $BiMoO_4$ is ionic so is likely a high-melting point solid → heterogeneous.

Sulfur dioxide and oxygen are both gases and V_2O_5 is a solid → heterogeneous.

→ all three reactions use heterogeneous catalysts. (③)

A37. **Answer:** ③

Ligands work by donating a lone pair of electrons, acting as Lewis bases.

EDTA is a hexadentate ligand, with coordination number 6.

The chelate effect refers to the ease of substitution of monodentate ligands with multidentate ligands, due to the formation of a large number of product molecules, increasing the entropy significantly ($\Delta S > 0$). The enthalpy change is not the driving force here.
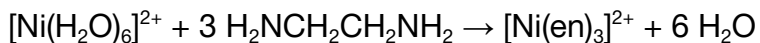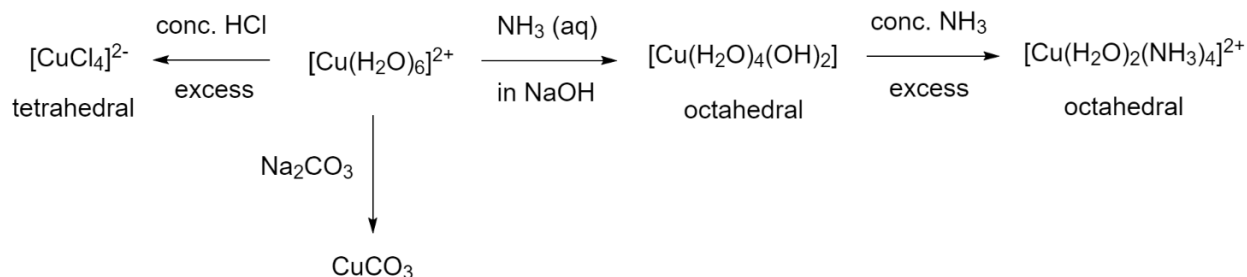
$[Ni(H_2O)_6]^{2+} + 3\ H_2NCH_2CH_2NH_2 \rightarrow [Ni(en)_3]^{2+} + 6\ H_2O$
contains three bidentate ligands and shows optical isomerism:

mirror   (③)
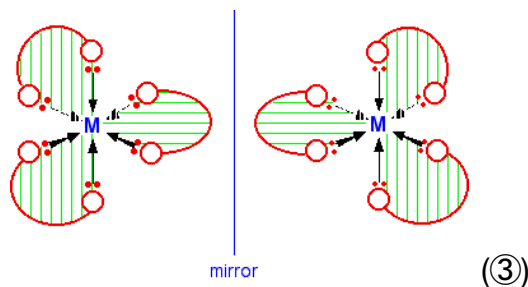
A38. Answer: ④

In the same order as shown in the question, the reactions here are:

$$[CuCl_4]^{2-} \xleftarrow[\text{excess}]{\text{conc. HCl}} [Cu(H_2O)_6]^{2+} \xrightarrow[\text{in NaOH}]{NH_3 \text{ (aq)}} [Cu(H_2O)_4(OH)_2] \xrightarrow[\text{excess}]{\text{conc. } NH_3} [Cu(H_2O)_2(NH_3)_4]^{2+}$$

tetrahedral   octahedral   octahedral

$[Cu(H_2O)_6]^{2+} \xrightarrow{Na_2CO_3} CuCO_3$

Octahedral complexes of the form $[MA_2B_4]$ where A and B are monodentate ligands will always display cis-trans isomerism. (④)

A39. Answer: ③

Cu^{2+} forms pale blue aqueous solutions. $[CuCl_4]^{2-}$ is a yellow-green solution.

The explanation of the difference is due to crystal field theory (**B**). When a Cl^- ion approaches a metal ion, the d orbitals pointing along the bonding directions are put into a higher energy state than those pointing away from the axis, splitting the d shell into two distinct energy levels. This changes the energy level of the d electrons and hence changes the frequency of absorption. (③)

A40. Answer: ①

The nuclear charge of resulting ions does not affect the ionisation process.

Ca^+ : $[Ne]\ 3s^2\ 3p^6\ 4s^1$
K^+ : $[Ne]\ 3s^2\ 3p^6$
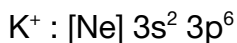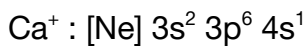
Energy level of 4s is much higher than 3p, so there is significant energy needed to remove $3p^6$ electrons from K^+. (①)

A41. Answer: ②

NH$_3$ and O$_2$ are not absorbed but rather adsorbed: they only interact with the surface of the metal, not the bulk solid. (②)

A42. Answer: ④

If we need 20 times more oxy-haemoglobin than carboxy-haemoglobin, but the CO binds 200 times better than oxygen, then we must have 4000 times more oxygen than CO. The abundance of oxygen in the atmosphere is about 21%, so the abundance of CO must be less than 0.00525% = 52.5 ppm. (④)

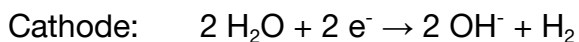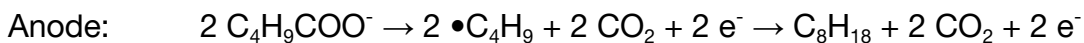**A43. Answer:** ④

The white precipitate forming from a Ca(OH)$_2$ (limewater) solution indicates the presence of CO$_2$ from the anode due to formation of CaCO$_3$.

The squeaky pop with a lighted splint indicates hydrogen from the cathode.

The immiscible liquid layer indicates a non-polar, low-density, hydrophobic substance, and the flammability implies an alkane hydrocarbon. Since butane is a gas at rtp, it cannot be butane: alkanes become liquid from pentane through to around C$_{18}$.

The gasoline-like smell implies octane, which is in fact the correct product, formed by the termination of two butyl free-radicals, which themselves form from decarboxylation of the pentanoate salt: (④)

Anode: 2 C$_4$H$_9$COO$^-$ → 2 •C$_4$H$_9$ + 2 CO$_2$ + 2 e$^-$ → C$_8$H$_{18}$ + 2 CO$_2$ + 2 e$^-$
Cathode: 2 H$_2$O + 2 e$^-$ → 2 OH$^-$ + H$_2$

A44. Answer: ①

When chlorine is dissolved in water, an equilibrium involving HCl and HClO is established. With HCl, we would get 2-chloropropane, but as this is not an option we are looking for the reaction with HClO. This will also take priority over the reaction with Cl_2 since the Cl-Cl bond is nonpolar.

Since O is more electronegative than Cl, Cl acts as the electrophile:

1-chloropropan-2-ol
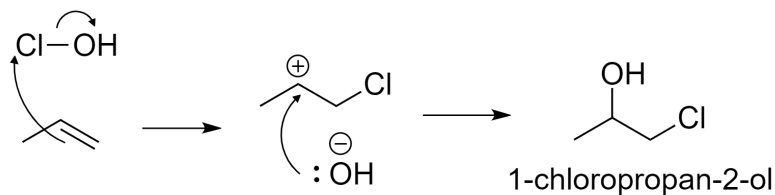
→ major product is $CH_3CH(OH)CH_2Cl$. (①)

A45. Answer: ②

A: Although it is true that fluorine absorbs at a higher frequency than chlorine, the reasoning is not as simple as the one given due to the fact that molecular orbitals are not equivalent to atomic orbitals. It is also incorrect to say that a compound which absorbs outside the visible spectrum would have a colour, which is what is implied here.

B: It is correct that the conjugation and hence increased stability of the porphyrin ring contributes to its colour. This ensures that both haem B and chlorophyll are coloured. Since Mg^{2+} has no d-electrons, which emit characteristically in the visible spectrum, there is no further energy difference here, while in Fe^{2+} there are, giving haem B a different colour to chlorophyll.

→ only **B** is correct. (②)