M14/4/CHEMI/HP3/ENG/TZ1/XX/M



International Baccalaureate[®] Baccalauréat International Bachillerato Internacional

MARKSCHEME

May 2014

CHEMISTRY

Higher Level

Paper 3

23 pages

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Subject Details: Chemistry HL Paper 3 Markscheme

Mark Allocation

Candidates are required to answer questions from **TWO** of the options $[2 \times 25 \text{ marks}]$. Maximum total = [50 marks].

- 1. A markscheme often has more marking points than the total allows. This is intentional.
- 2. Each marking point has a separate line and the end is shown by means of a semicolon (;).
- **3.** An alternative answer or wording is indicated in the markscheme by a slash (/). Either wording can be accepted.
- 4. Words in brackets () in the markscheme are not necessary to gain the mark.
- 5. Words that are <u>underlined</u> are essential for the mark.
- 6. The order of marking points does not have to be as in the markscheme, unless stated otherwise.
- 7. If the candidate's answer has the same "meaning" or can be clearly interpreted as being of equivalent significance, detail and validity as that in the markscheme then award the mark. Where this point is considered to be particularly relevant in a question it is emphasized by *OWTTE* (or words to that effect).
- 8. Remember that many candidates are writing in a second language. Effective communication is more important than grammatical accuracy.
- 9. Occasionally, a part of a question may require an answer that is required for subsequent marking points. If an error is made in the first marking point then it should be penalized. However, if the incorrect answer is used correctly in subsequent marking points then **follow through** marks should be awarded. When marking, indicate this by adding **ECF** (error carried forward) on the script.
- **10.** Do **not** penalize candidates for errors in units or significant figures, **unless** it is specifically referred to in the markscheme.
- **11.** If a question specifically asks for the name of a substance, do not award a mark for a correct formula unless directed otherwise in the markscheme. Similarly if the formula is specifically asked for, unless directed otherwise in the markscheme do not award a mark for a correct name.
- **12.** If a question asks for an equation for a reaction, a balanced symbol equation is usually expected, do not award a mark for a word equation or an unbalanced equation unless directed otherwise in the markscheme.
- **13.** Ignore missing or incorrect state symbols in an equation unless directed otherwise in the markscheme.

Option A — Modern analytical chemistry

1. (a) *Emission spectrum*: coloured lines and *Absorption spectrum*: black/dark lines;

OR

2.

Emission spectrum: lines and Absorption spectrum: continuous; Allow "Emission spectrum: electrons emit energy as they drop to lower energy levels and Absorption spectrum: electrons absorb energy as they are promoted to higher energy levels" / OWTTE.

(b)	Type of	Type of atomic or	Region of]
	spectroscopy	molecular process	electromagnetic spectrum	
	¹ HNMR	(change in) nuclear spin;	radio;	
	IR	bond vibrations / stretching and bending of bonds;	infra-red	
	visible/UV / <u>atomic</u> absorption/AA	electronic transitions	visible/UV	

For M4 both visible/UV/atomic absorption/AA for type of spectroscopy and region of EMS required.

to determine the amount/percentage/concentration of the element present; (c)

(a) Amount / mol Element **Simplest ratio** $\frac{68.11}{5.671} = 5.671$ 5 carbon 12 01 $\frac{13.74}{1.01} = 13.60$ hydrogen 12 / OWTTE; $\frac{18.15}{16.00} = 1.134$ 1 oxygen

Accept mass of $C_5 H_{12}O = 88.17$ so % of $C = \left(\frac{60.05}{88.17}\right) \times 100 = 68.11$, % of $H = \left(\frac{12.12}{88.17}\right) \times 100 = 13.75$ and % of $O = \left(\frac{16.00}{88.17}\right) \times 100 = 18.15$.

Allow integer values for atomic masses.

[4]

[1]

[1]

[3]

(b) Mass spectrum:

molecular ion peak at $88/M^+ = 88$ shows molecular formula is $C_5H_{12}O$;

absorption at 73 due to $(M-CH_3)^+$ / X contains a methyl group as peak at M-15 / *OWTTE*;

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absorption at 59 due to $(M-C_2H_5)^+$ / X contains an ethyl group as peak at M–29; Penalise once only if + charge omitted.

Accept that X contains a CHO group due to M-29 but in fact it cannot as there are too many hydrogen atoms in the compound for it to be an aldehyde.

Infrared spectrum:

peak in range at $3200-3600 \text{ cm}^{-1}$ shows it contains an OH group / *OWTTE*; (sharp) peaks just below 3000 cm⁻¹/in range 2850–3100 cm⁻¹ due to C–H absorptions;

lack of peak at approximately 1700 cm^{-1} shows it does not contain C=O; absorption between 1050 and 1410 cm⁻¹ due to C–O;

Allow "due to alcohol" instead of due to C–O.

Accept "absorption between 1050 and 1410 cm^{-1} due to ether or ester" although it cannot be either as there is only one O atom and it has been identified as bonded to H.

fingerprint region specific to compound but needs to be compared with library / *OWTTE*; [3 max]

¹HNMR spectrum:

(12 protons are in) four different chemical environments (in the ratio 1:2:6:3); singlet (with integration trace of 1) due to OH proton; singlet (with integration trace of 6) suggests (two CH₃) groups attached to a carbon atom with no Hs attached to it; quartet (with integration trace of 2) due to CH₂ next to CH₃; triplet (with integration trace of 3) due to CH₃ next to CH₂; [4 max] *Reference must be made to the association of the splitting pattern (singlet, triplet etc.) to the specific carbon fragments.*

(**X** is) 2-methylbutan-2-ol/CH₃CH₂C(CH₃)₂OH; *No ECF throughout 2(b).*

3. (a) $\varepsilon = ((\log_{10} 100/10)/(0.100 \times 4.00 \times 10^{-5}) = 1/4.00 \times 10^{-6} =) 2.50 \times 10^{5};$ dm² mol⁻¹; Accept 2.50 × 10⁴ mol⁻¹ dm³ cm⁻¹ or 2.50 × 10⁷ cm² mol⁻¹. [2]

(b) (colour) depends on (crystal field) energy splitting/size of splitting of d orbitals / OWTTE;
 Reference must be made to d orbitals.
 splitting is different in different oxidation states (of iron) / different number of

electrons in two different oxidation states causes splitting to be different / *OWTTE*;

[2]

4.	(a)	Spot 1: $R_{\rm f} = 0.75$ and Spot 2: $R_{\rm f} = 0.25$;	[1]
	(b)	two amino acids have the same $R_{\rm f}$ value;	[1]
	(c)	change the polarity/make-up of the solvent / use a different solvent; <i>Accept two way (paper) chromatography</i> .	[1]

Option B — Human biochemistry

Penalise missing hydrogens or incorrect bond linkages (eg, NH-C) once only in this option.

5. (a) (i)
$$CH_3(CH_2)_7 CH=CH(CH_2)_7 COOH + I_2 \rightarrow CH_3(CH_2)_7 CHI-CHI(CH_2)_7 COOH$$
; [1]
Allow $C_{17}H_{33}COOH + I_2 \rightarrow C_{17}H_{33}I_2COOH / C_{18}H_{34}O_2 + I_2 \rightarrow C_{18}H_{34}I_2O_2$.

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- (ii) amount of oleic acid = $\left(\frac{1.00}{282.52}\right)^3 \cdot 54 \times 10^{-3} \text{ (mol)} = \text{amount of } I_2 \text{ required};$ volume of 1.00 mol dm⁻³ solution = 3.54 (cm³); [2] Award [2] for correct final answer.
- (b) (i) X: carboxyl; Allow carboxylic acid. Accept fatty acid.

Y: hydroxyl;[2]Allow alcohol/alkanol/hydroxy but not hydroxide.Award [1 max] if X and Y are reversed.

- (ii) consider C=C bonds in chain; Accept unsaturation in chain, but not just double bonds. length of carbon chain; [2] Accept reasons such as close packing, no kink in molecule, stronger van der Waals'/vdW/London/dispersion forces/LDF/intermolecular forces/ instantaneous/temporary induced dipole-induced dipole forces / larger surface area (of contact).
- (c) fewer number of oxygen atoms in fats (compared to carbohydrates of similar molar masses) / fats less oxidized (compared to carbohydrates so more energy given off from oxidation) / OWTTE; Accept converse reasoning.
- (d) *Similarities*:

Award **[1 max]** for one similarity: both unsaturated; Allow both contain C=C/carbon to carbon double bond but not just double bond or COOH/carboxyl group (since acid stated in stem). both have first (carbon to carbon) double bond/C=C on C9; both have *cis*-configuration of (all) C=C (fragments);

Differences:

Award [1 max] for one difference: linoleic acid has $\omega - 6$ (first) C=C and linolenic acid has $\omega - 3$ (first) C=C; linoleic acid has 2 C=C and linolenic acid 3 C=C / linolenic acid has one additional C=C; If either of these last two points are scored award a total of [2] as C=C similarity implied but award [1 max] only for "more unsaturated".

[2]

6. (a) molecule contains polar/OH/hydroxyl/NH/amino/COOH/carboxyl groups / molecule forms hydrogen bonds with water / OWTTE; [1] Accept polar molecule so dissolves in water. Allow class (eg, carboxylic acid, amine etc.) if stated instead of functional groups.

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- (b) (i) xerophthalmia / retinitis pigmentosa/RP; Accept condition such as dry eyes associated with xerophthalmia or condition such as night blindness associated with retinitis pigmentosa.
 - (ii) vitamin A is fat-soluble/water-insoluble / vitamin A can be stored/accumulate in fat cells leading to fatality / excess vitamin A causes hypervitaminosis which can be fatal / OWTTE;
 Do not allow "vitamin A when consumed in large quantities can be poisonous", unless storage/accumulation in fat cells stated.
- (a) thymine (covalently) bonded to deoxyribose/pentose sugar / thymine bonds via a condensation reaction with sugar / N from thymine bonds to C on sugar / thymine joins with pentose sugar;

[1]

[1]

[1]



drawing correctly showing two hydrogen bonds; Do not penalize structural error in bases. Do not penalize if lone pairs are omitted.

Η

Η

[2]

[1]

[4]

- (ii) both have hydrogen bonding;
 C and G have three interactions (and A and T have two) / OWTTE; [2]
 Do not apply ECF here.
- (d) forensic **and** paternity cases; *Allow more specific cases.*

8. (a) aerobic respiration produces more energy / anaerobic respiration produces less energy; glucose undergoes oxidation/oxidized (to pyruvate ions/C₃H₃O₃^{-/}pyruvic acid/ C₃H₄O₃); Accept balanced equation: $C_6H_{12}O_6 + O_2 \rightarrow 2CH_3C(O)COOH/C_3H_4O_3 + 2H_2O$, involving pyruvate ions or pyruvic acid.

> Aerobic respiration: (pyruvate ions/C₃H₃O₃⁻/pyruvic acid/C₃H₄O₃) in presence of oxygen/O₂ oxidized to carbon dioxide/CO₂ and water/H₂O; Accept balanced equation: $2CH_3C(O)COOH/C_3H_4O_3 + 5O_2 \rightarrow 6CO_2 + 4H_2O$, involving pyruvate ions or pyruvic acid.

Anaerobic respiration: lactate ions/C₃H₅O₃⁻/lactic acid/C₃H₆O₃ produced / $C_6H_{12}O_6 \rightarrow 2CH_3CH(OH)COOH/2C_3H_6O_3$ / occurs in absence of oxygen so pyruvate/C₃H₃O₃⁻/pyruvic acid/C₃H₄O₃ not further oxidized;

Penalise incorrectly balanced equations once only.

(b) $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; [1] Ignore state symbols.

Option C — Chemistry in industry and technology

9. (a) chemical (energy) to electrical (energy); [1] (b) Positive electrode (cathode) half-equation: (i) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^- / \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-;$ Negative electrode (anode) half-equation: $2\mathrm{H}_{2} + 4\mathrm{OH}^{-} \rightarrow 4\mathrm{H}_{2}\mathrm{O} + 4\mathrm{e}^{-} \,/\,\mathrm{H}_{2} + 2\mathrm{OH}^{-} \rightarrow 2\mathrm{H}_{2}\mathrm{O} + 2\mathrm{e}^{-} \,/\,$ $\frac{1}{2}$ H₂ + OH⁻ \rightarrow H₂O + e⁻; [2] Award [1 max] if correct half-equations are given but incorrect electrodes. Allow e instead of e^{-} . Penalise use of reversible arrow once only in 9 (b)(i) and 11 (a). (ii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) / \frac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l);$ [1] State symbols required. Allow $H_2O(g)$.

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- (iii) catalyst/electrocatalyst / speeds up reaction but not consumed in reaction itself / provides surface for (initial) decomposition of molecules into atoms;
- (iv) allows flow of ions/H⁺/protons (from anode/negative electrode to cathode/positive electrode) / prevents reactants mixing/moving from one compartment to another / salt bridge / prevents flow of electrons through membrane / OWTTE;
- (v) storage/transport difficulties of gases / potentially explosive/hydrogen is flammable / needs constant supply of fuel / can contain heavy metal(s) / often operated at high temperature / low power to mass ratio / susceptible to poisoning due to impurities in fuel / OWTTE;
 Allow a named gas (hydrogen or oxygen) for storage/transport difficulties.
 Allow problems related to corrosion.
 Accept answers based on ethanol and methanol fuel cells (but needs to be stated) such as difficult to use in cold weather/less clean product (CO₂) formed.

[1]

[1]

(a)	(i)	(LCs are) fluids that exhibit molecular orientation/orderly molecular arrangement and A; Accept LCs show properties of liquids and crystals simultaneously and A.	[1]
	(ii)	<i>I</i> : <u>no</u> , since ionic (so high mp) / lacks long axis; <i>Allow <u>no</u> since it is not a molecule/not rod-shaped</i> .	
		 <i>II:</i> <u>ves</u>, since has long axis present (so limits ability of molecules to pack lowering mp); <i>Allow <u>yes</u> since rod-shaped</i>. has polar functional group / is polar (increasing intermolecular interactions) / (planar/flat) benzene ring present (assists stacking); 	
		 III: no, since lacks long axis; Allow no since non-polar. Allow no since not rod-shaped. Award [1 max] for stating II only will show LC behaviour OR I: No, II: Yes and III: No. Award [2 max] if one correct reason is given for each substance but LC behaviour is either incorrect or not given. Award [3 max] if correct reasons are given for all three substances, but LC behaviour is either incorrect or not given. 	[4]
	(iii)	(free) rotation about carbon-carbon single bonds (hence greater flexibility) so octane molecules not rod-shaped / <i>OWTTE</i> ; <i>Do not allow mark for non-polar (molecule) only.</i>	[1]
(b)	(i)	<i>Thermotropic</i> : pure substances and <i>lyotropic</i> : solutions / <i>thermotropic</i> : show LC behaviour over limited temperature range (between solid and liquid states) and <i>lyotropic</i> : shows LC behaviour at certain concentrations;	[1]
	(ii)	X: yes and Y: no and Z: yes; Award mark if no is stated only for Y or yes is only stated for X and Z.	[1]
(c)	(i)	$\left(\begin{array}{c} 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ $	

Brackets or n not necessary but continuation bonds must be shown. Do not penalise if CO and NH are in cis configuration.

HCl; *Allow correct name for M2.*

10.

[2]

;

- (ii) Kevlar[®] (molecules) have strong covalent bonds (so hard to break); (large number of) hydrogen bonds between C=O and NH groups; CO/NH groups *trans* to each other so orientation maximizes interactions/helps packing/produces more ordered structure / π -bonding/ aromatic stacking interactions between benzene rings in neighbouring strands / *OWTTE*; [2 max]
- (iii) intermolecular forces/hydrogen bonds broken / nitrogen and oxygen atoms become protonated / reverses condensation process / OWTTE;
- **11.** (a) *Positive electrode (anode): Material:* graphite/C / titanium/Ti; *Allow inert metal or any correctly named inert metal (or correct chemical symbol).*

Half-equation: $2\text{Cl}^{-}(\text{aq}) \rightarrow \text{Cl}_{2}(g) + 2e^{-} / \text{Cl}^{-}(\text{aq}) \rightarrow \frac{1}{2}\text{Cl}_{2}(g) + e^{-};$

Allow e instead of e^- throughout (a).

Negative electrode (cathode): Material: (flowing) mercury/Hg; Half-equation: $Na^+(aq) + e^- \rightarrow Na \text{ (amalgam) / } Na^+(aq) + e^- + Hg(l) \rightarrow Na-Hg(l);$ [4] Allow $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ which is the overall equation at cathode (after amalgam reacts with water). Penalize incorrect or missing state symbols once only. Penalise use of reversible arrow once only in 9 (b)(i) and 11 (a).

(b) leakage of mercury is a health concern / mercury poisoning / acrodynia/pink disease / Hunter-Russsell syndrome / Minamata disease / escape of mercury can result in fish dying / toxic mercury passes into food chain / diaphragm cell does not use toxic mercury / OWTTE;
 Allow a specific example of a health-related problem (eg. loss of balance, muscle wastage, paralysis etc.) but association with mercury must be made.

[1]

Option D — Medicines and drugs

12.	(a)	paracetamol blocks transmission of pain at source; Accept paracetamol inhibits prostaglandin release in the brain.	
		codeine blocks (receptor sites in) the brain from receiving pain signals; Accept central nervous system/CNS instead of brain.	[2]
	(b)	codeine contains a hydroxyl group; Allow alcohol/hydroxy but not hydroxide.	
		codeine contains one methoxy group/two ether groups; Allow codeine contains one additional ether group but not codeine contains the ether group.	
		diamorphine contains ester/acetoxy/ethanoate group(s); Names required not functional group formulas. Allow acetyl group.	[3]
	(c)	aspirin may cause ulceration/internal bleeding/allergic reactions/Reye's syndrome / paracetamol (acetaminophen) does not cause ulceration/internal bleeding/allergic reactions/Reye's syndrome; Do not accept general statements such as aspirin has more side effects or paracetamol (acetaminophen) is safer.	[1]
	(d)	prevents (the recurrence of) heart attack/stroke / reduces ability of blood to clot;	[1]
	(e)	codeine/strong analgesic (in Solpadol [®]) is addictive/habit-forming / OWTTE;	[1]
13.	(a)	$Mg(OH)_{2} + 2HCl \rightarrow MgCl_{2} + 2H_{2}O;$ $Al(OH)_{3} + 3HCl \rightarrow AlCl_{3} + 3H_{2}O;$ $CaCO_{3} + 2HCl \rightarrow CaCl_{2} + H_{2}O + CO_{2};$ $Accept H_{2}CO_{3} for H_{2}O and CO_{2}.$	[3]
	(b)	(i) amount of Mg(OH) ₂ = $\left(\frac{0.400}{(24.31 + 32.00 + 2.02)} = \frac{0.400}{58.33}\right) = 6.86 \times 10^{-3} \text{ (mol)}$	
		and amount of Al(OH) ₃ = $\left(\frac{0.306}{(26.92 + 48.00 + 3.03)} = \frac{0.306}{77.95}\right)$ 3.93×10 ⁻³ (mol);	
		amount of HCl reacting $= (2 \times 6.86 \times 10^{-3}) + (3 \times 3.93 \times 10^{-3}) = 2.55 \times 10^{-2}$	
		(mol) so volume of 1.00×10^{-2} HCl = 2.55 (dm ³);	[2]
		No ECF from (a) if formulas of $Mg(OH)_2$ or $Al(OH)_3$ are incorrect. Allow integer values for atomic masses.	

Award [2] for correct final answer.

(ii) amount of
$$CaCO_3 = \left(\frac{1.000}{(40.08 + 12.01 + 48.00)} = \frac{1.000}{100.09} = \right)9.99 \times 10^{-3} \text{ (mol)};$$

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amount of HCl reacting = $(2 \times 9.99 \times 10^{-3}) = 2.00 \times 10^{-2}$ (mol) so volume of 1.00×10^{-2} HCl = 2.00 (dm³); Allow integer values for atomic masses. Award [2] for correct final answer. Penalize incorrect answer based on same units mistake once only in 13 (b) (i) and (ii).

(c) anti-foaming agent / reduces bloating / causes small bubbles (of gas) to coalesce into larger bubbles **and** be released as flatulence;

14. (a) different enantiomers may have different physiological effects / OWTTE; all different enantiomers must be tested for side effects / OWTTE; *Allow reference to specific side-effects for M2.* since drugs can pass from mother to foetus all drugs must be tested for their effect on pregnant women / OWTTE;



[3]

[2]

[2]

[1]



Award [1] for each correct circle.

 (ii) a chiral auxiliary (which is itself optically active/chiral) attaches to nonchiral molecule (to force reaction to follow a certain path); chiral auxiliary is removed (once stereospecific intermediate has been formed to leave desired enantiomer) / OWTTE;

(iii) **EITHER**

doxorubicin contains an amino group (which is basic); *Allow (primary) amine.*

can react with acid/hydrochloric acid (to form acid salt);

OR

doxorubicin contains OH/hydroxyl groups some of which are acidic; can react with sodium hydroxide/NaOH/hydroxide ions/OH⁻ (to form sodium/alkaline salt);

Accept other suitable base such as potassium hydroxide/KOH. Allow "can react with alkali". Award [2] for a correct equation. [2]

Option E — Environmental chemistry

15. (a) Advantages of landfill:

good for dealing with large volumes of waste / land when filled can be used for building purposes / no separation of rubbish/garbage required / cheap / can be expanded easily (where the land is available) / *OWTTE*; *Do not accept "no air pollution"*.

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Disadvantages of landfill:

poisonous/toxic chemicals can be produced / heavy metal (ions) leaching into drinking water supplies/source of underground pollution (soil or water) / often odours occur in immediate environment / non-biodegradable plastics/polymers may not be broken down / unsightly / takes up land (where land is expensive/unavailable) / occupies large area / *OWTTE*;

Do not allow "produces methane/CH4/greenhouse gas" (since given in stem).

Advantages of incineration:

reduces volume of waste (only ash remains) / odour-free (stable) compounds produced / energy source (so can reduce energy cost) / produces slag/ash residues which can be used in building / *OWTTE*; *Do not accept "no land pollution"*.

Disadvantages of incineration:

high construction costs / can form dioxins/toxic/poisonous gases/vapours/ CO/carbon monoxide / needs energy (to run plant) / adds to greenhouse effect (due to carbon dioxide/CO₂ generated) / chlorinated compounds/polymers/plastics can generate hydrochloric acid/HCl resulting in acid rain; *Do not accept the advantage of one being the disadvantage of the other*.

Do not accept general statements without support.

- (b) landfill not recommended since radioactivity can leach/escape/leak (into groundwater) / OWTTE;
 incineration spreads radioactivity / OWTTE;
- (c) (i) swamps/marshes / rice fields/paddies / livestock manure/ruminant from cows/sheep / anaerobic microbial activity in lakes/ponds;
 - (ii) $2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g) / CH_4(g) + 1.5O_2(g) \rightarrow CO(g) + 2H_2O(g);$ [1] State symbols must be included. Allow $H_2O(l)$. Accept any other pollutant, such as methanal: $CH_4(g) + O_2(g) \rightarrow HCHO(g) + H_2O(g)$.

[4]

[2]

16. (a) Step 1: $UV/hf/hv \rightarrow O_2(g) + O_{\bullet}(g);$ $O_{3}(g)$ -UV not needed for mark (since given in question). Step 2: $O_3(g) + O_{\bullet}(g) \rightarrow 2O_2(g);$ [2] Ignore state symbols. Allow O instead of O• if consistent throughout. (b) C₂F₆ still has low reactivity/toxicity/flammability like CFCs; C_2F_6 has (very) strong C–F bond (so stable to UV); C_2F_6 cannot produce chlorine radicals/Cl•/Cl; Do not allow " C_2F_6 contains no chlorine(s)" or general answers such as "does not react with ozone". C_2F_6 has a long lifetime/half-life/ $t_{1/2}$; Allow specific time such as greater than 10,000 years. C_2F_6 also a greenhouse gas/absorbs IR; [3 max] (c) (i) Primary pollutant and source: NO / NO₂ / NO_x and exhaust (from vehicles) / internal combustion engine; Allow correctly named "fumes" oxide (eg, nitrogen monoxide etc). Conditions: Any two of the following for [1]: bowl-shaped / surrounded by hills; lack of wind / no air currents; temperature inversion; [2] (ii) Formation of ozone: $NO_2(g) + UV/hf/hv \rightarrow NO(g) + O(g);$ Condition required for M1. Allow $NO_2(g)$ instead of $NO_2^{\bullet}(g)$ in M1 and M3. Allow NO(g) instead of NO(g). $O_{\bullet}(g) + O_{2}(g) \rightarrow O_{3}(g);$ Termination step showing formation of PANs: $CH_3COOO_{\bullet}(g) + NO_{2} \bullet (g) \rightarrow CH_3COOONO_{2}(g);$ [3] Allow $RCOOO \bullet + NO_2 \bullet (g) \to RCOOONO_2(g)$. Allow representation of radicals without • if consistent throughout. Only penalize inconsistency of radical representations once only in E16. Ignore state symbols.

-17-

(d) Oxygen: correctly drawn Lewis structure and Ozone: correctly drawn Lewis structure:

-18-

Allow any combination of dots, x's or lines to represent electron pairs. Allow representation of two resonance structures for ozone.

oxygen has a higher bond order than ozone and oxygen needs more energy to dissociate / OWTTE; Exact bond orders of 2 for oxygen and 1.5/1 and 2 for ozone may be given for first statement in M2. Do not award M2 if incorrect bond orders are stated for either species.

- $CF_3Cl(+UV/hf/hv) \rightarrow CF_3 \bullet + Cl \bullet;$ (e) $Cl \bullet + O_3 \rightarrow ClO \bullet + O_2;$ $ClO \bullet + O_3 \rightarrow Cl \bullet + 2O_2;$ [2 max] Accept $ClO \bullet + O \bullet \rightarrow O_2 + Cl \bullet$ for M3. Allow representation of radicals without • if consistent throughout. Penalize inconsistency of radical representations once only in E16.
- 17. $(K_{sp} =)[Cu^{2+}(aq)][OH^{-}(aq)]^{2};$ (a) Ignore state symbols.
 - (b) $4.8 \times 10^{-20} = 4x^3$; $(x =)[Cu^{2+}(aq)] = 2.3 \times 10^{-7} (mol dm^{-3});$ Award [2] for final correct answer.

If (b) is attempted any solution should be accepted where the product of the concentrations of $Cu^{2+}(aq)$ and OH (aq) matches the K_{sp} value **OR** if stated that one value unknown, award [2], only if (a) has been answered.

[2]

[2]

Option F — Food chemistry

18. (a)
$$H_2C - O - CO - (CH_2)_6(CH_2CH=CH)_2(CH_2)_4CH_3$$
 $H_2C - O - CO - C_{17}H_{31}$
 $HC - O - CO - (CH_2)_6(CH_2CH=CH)_2(CH_2)_4CH_3$ / $HC - O - CO - C_{17}H_{31}$;
 $H_2C - O - CO - (CH_2)_6(CH_2CH=CH)_2(CH_2)_4CH_3$ $H_2C - O - CO - C_{17}H_{31}$ [1]
Do not accept R for $C_{17}H_{31}$.
Penalize for incorrect bond connectivity.
(b) water/H₂O ; [1]
(c) double bonds cause a "kink" in the hydrocarbon chain / unsaturated hydrocarbon
chains cannot pack so closely together (as saturated);

attractive forces/London/dispersion/van der Waals/vdW/LDF/ /instantaneous/ temporary induced dipole-induced dipole forces between the molecules are weaker / less energy required to overcome the attraction between the molecules; [2]

- (d) addition of hydrogen/H₂ / hydrogenation; heat **and** catalyst/Zn/Cu/Ni/Pd/Pt; [2] Accept any temperature in range $140 - 225 \degree C$.
- (e) Advantages: decreases rate of oxidation / makes it more stable / slows rancidification / has longer shelf life; greater energy released per gram / OWTTE; controls hardness/plasticity/stiffness;
 [2 max]

Disadvantages:

increase risk of heart disease / increase low-density/LDL cholesterol;	
does not contain essential/omega-3/omega-6 fatty acids;	
hydrogenated fats might contain trans-fatty acids;	[2 max]

19.	(a)	antimicrobial agent / delays microbial/bacterial growth/mould / stops	
		fermentation/slows down enzymatic reactions;	[1]
	(b)	fixing colour / inhibits microbial/bacterial growth/mould; Do not allow curing meats.	[1]

20 .	(a)	(i)	carotenoid / carotene / tetraterpene;	[1]
		(ii)	contains extensive conjugation/delocalization (of electrons)/has alternating C-C and C=C (bonds);	[1]
		(iii)	absorbs light in the blue/blue-green/360–500 nm region so transmits the complementary colour/red light; <i>Do not allow "reflects" complementary colour.</i>	[1]
		(iv)	chelation / reduces concentration of (free) metal ions in solution; Allow forms complexes with metal ions / OWTTE. EDTA / salts of EDTA / rosemary / tea / mustard;	[2]
	(b)	(i)	initiation and propagation and termination;	[1]
			Award [2] for three correct equations, [1] for two correct equations: Initiation: $RH \rightarrow R \bullet + H \bullet$	
			Propagation: $R \bullet + O_2 \rightarrow ROO \bullet / ROO \bullet + RH \rightarrow R \bullet + ROOH$	
			<i>Termination:</i> $R \bullet + R \bullet \rightarrow RR / R \bullet + ROO \bullet \rightarrow ROOR / ROO \bullet + ROO \bullet \rightarrow ROOR + O_2 ;;$	[2]
			Allow representation of radicals without • if consistent throughout. Penalize inconsistency of radical representations once only in Option F. Award [1 max] if each correct equation is not linked to a named step OR if linked to an incorrectly named step.	
		(ii)	quench/reacts with (existing) radicals/ROO• / ROO• + AH \rightarrow ROOH + A•; form more stable/less reactive radicals; Allow representation of radicals without • if consistent throughout. Penalize inconsistency of radical representations once only in Option F.	[2]
21.	poter of fo unkn of G risk o as ye loss o susce	ntial ri ods; own c M org of pass of pass of vari of vari	tisk of allergic reactions; isk to health of changing the diet / risk of changing natural nutritional quality consequences of mixing GM DNA with unmodified DNA / unknown effects anisms breeding with unmodified organisms; sing antibiotic resistant genes to harmful organisms; nown effect on food chain; iety of species; ity to "superbugs" / <i>OWTTE</i> ;	
			s controlled by a few companies so farmers lack choice/economically / <i>OWTTE</i> ;	[3 max]

Option G — Further organic chemistry

Penalise missing hydrogens or incorrect bond linkages (eg, NH–C) once only in this option.

22. (a) (i)
$$C_4H_9CHO + HCN \rightarrow C_4H_9CH(OH)CN$$
; [1]
Ignore missing brackets.

(ii) nucleophilic addition; Accept A_N .

(iii)



curly arrow going from lone pair/negative charge on C in NC⁻ to carbonyl C and curly arrow going from double bond to O; Do not allow curly arrow originating on N of NC^{-} . Partial charges not required.

representation of intermediate anion with negative charge on O; Lone pair on O not required.

curly arrow going from lone pair/negative charge on O of intermediate anion to H^+ ;



Award [1] for correct formula of pentan-3-one and [1] for correct equation. Accept condensed formula for 2,4-DNPH.

[2]

[3]

23. (a) ethanal/CH₃CHO and water/H₂O; butan-2-ol/CH₃CH₂CH(OH)CH₃; *Accept 2-butanol. Ignore missing brackets.*

> phosphoric acid/H₃PO₄ and heat; Allow sulfuric acid/H₂SO₄ but not just H^+ . Accept any temperature in the range 100–200°C.

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(b) **EITHER**

magnesium/Mg and dry/ether/inert solvent; propylmagnesium bromide/CH₃CH₂CH₂MgBr; *Accept bromo(propyl)magnesium. Ignore missing brackets.*

carbon dioxide/CO₂ and water/H₂O;

OR

potassium cyanide/KCN/any other inorganic cyanide; *Accept cyanide ions/CN*⁻.

butanenitrile/CH₃CH₂CH₂CN; Accept systematic names such as butyronitrile or propyl cyanide or cyanopropane.

acid (solution)/H⁺(aq)/H₃O⁺(aq) **and** heat/reflux; Accept any temperature in the range 50-300 °C. Do not penalise if (aq) state omitted.

24. (a) non-bonding/lone pair of electrons on the <u>N</u> atom (enables proton/ H^+ acceptance) / *OWTTE*;

(b) diethylamine/ $(C_2H_5)_2NH$;

triethylamine/ $(C_2H_5)_3N$ more hindered / (electron pair on) nitrogen blocked by (three) ethyl/ CH_3CH_2 groups / (three) ethyl/ CH_3CH_2 groups reduce chance of effective collision between triethylamine/ $(C_2H_5)_3N$ and water/ H_2O /proton/ H^+ / *OWTTE*;

Allow for M2 "triethylamine/ $(C_2H_5)_3N$ has limited ability to stabilise itself by hydrogen bonding formation" / OWTTE.

[3]

[3]

[1]

[2]



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curly arrow going from delocalized electrons in benzene to Cl in Cl₂ (and curly arrow going from Cl–Cl bond to AlCl₃);

Allow curly arrow going from delocalized electrons in benzene to Cl^+ for M1. ie, $AlCl_3 + Cl_2 \rightarrow [AlCl_4]^- + Cl^+$

then

$$+ Cl^+$$
 etc.

representation of carbocation with correct formula **and** positive charge on ring; curly arrow going from AlCl₄⁻ to H **and** curly arrow going from CH bond to benzene ring;

Allow other suitable catalysts such as FeCl₃ etc. Allow mechanism with corresponding Kekulé structures. Do not penalize if HCl and/or AlCl₃ missing from products.

(b) methyl group/CH₃ exerts a positive inductive effect/is electron-donating/"pushes electrons";

Do not allow an answer such as methyl group can activate ring.

increases electron density of delocalized π -electrons making electrophiles more readily attracted to aromatic ring / *OWTTE*;

(c) positive charge on carbon atom in intermediate in 2- and 4- positions can be delocalized / stable tertiary carbocation formed from substitution in 2- and 4- positions / OWTTE;
 Allow ortho/o and para/p instead of 2- and 4- positions.

positive charge can be located on carbon atom attached to methyl/CH₃ group which helps to stabilize it / positive inductive effect of methyl/CH₃ group decreases positive charge on tertiary carbocation so stabilizes ion / *OWTTE*; *Accept diagrams that clearly illustrate these points.*

[2]

[3]

[2]