N14/4/CHEMI/HP3/ENG/TZ0/XX/M

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MARKSCHEME

November 2014

CHEMISTRY

Higher Level

Paper 3

26 pages

Subject Details: Chemistry HL Paper 3 Markscheme

Mark Allocation

Candidates are required to answer questions from **TWO** of the options **[2 x 25 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

Penalize missing hydrogens or incorrect bond linkages (eg, CO–H_2C) once only in this option.

1. (a) (i) molar/molecular mass/$M = 74$ (g mol^{-1}) / relative molecular mass/$M_r = 74$;
peak with highest *m/z* (ignoring any peak attributable to ^{13}C) / found from parent/molecular ion peak;
Allow mass for m/z.

OR

compound has methyl/CH_3;
m/z = 15 due to CH_3^+;

OR

compound has propyl/C_3H_7/isopropyl/$CH(CH_3)_2$/acetyl/CH_3CO;
m/z = 43 due to $C_3H_7^+$/$CH(CH_3)_2^+$/CH_3CO^+;

OR

compound has acetoxy/CH_3COO;
m/z = 59 due to CH_3COO^+; ***[2]***

Fragment must contain + sign in relevant marks above.
Penalize missing charges where relevant once only in (a)(i) and (ii).

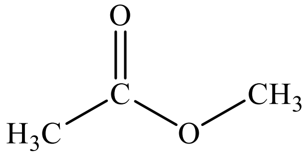
(ii) loss of CH_3-O / loss of radical with *m/z* = 31 / formation of $C_2H_3O^+$/$C_3H_7^+$/$CH(CH_3)_2^+$; ***[1]***
Penalize missing charges where relevant once only in (a)(i) and (ii).

(b) (i) *Present:* carbonyl/C=O;
Do not accept aldehyde / ketone.
Accept ester/alkanoate only if m/z = 59 given in (a)(i).

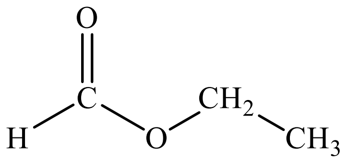
Absent: carbon-carbon double bond/C=C/alkene; ***[2]***

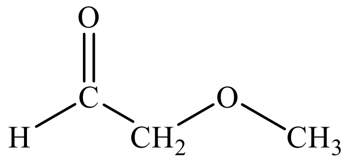
(ii) no (broad) absorption at $2500-3300$ (cm^{-1});
no O–H bond; ***[2]***
*Award **[1 max]** for just stating "absorption at 1050-1410 (cm^{-1}) / C-O bond present of alcohol/ester/ether".*
Do not accept just "C-O bond present".
Accept "peak" for absorption.

(iii) *Any two structures from:*

 / CH_3COOCH_3 ;

Do not penalize CH_3-C connectivity here.

 / $HCOOCH_2CH_3$;

 / $HCOCH_2OCH_3$;

[2 max]

(c) *Award **[1]** for each 3 correct answers.*
*Award **[5]** for 13–14 correct answers.*

Compound	Number of peaks	Chemical shift range	Area	Splitting pattern
Propanoic acid	3	0.9 – 1.0	3	triplet
		2.0 – 2.5	2	quartet
		9.0 – 13.0	1	singlet
Compound I	**1**;	**2.2 – 2.7**;	**1 / 6**;	**singlet**;
Compound II	**3**;	**0.9 – 1.0**;	**3**;	**triplet**;
		2.2 – 2.7;	**2**;	**quartet**; *Accept quintuplet, doublet of quartet, multiplet / OWTTE.*
		9.4 – 10.0;	**1**;	**singlet**; *Accept triplet.*

[5]

*If more than one peak indicated for Compound I, then no "points". Begin marking at Compound II and **[3 max]**.*

2. (a) atomic absorption / AA; ***[1]***

(b) calibrate using known standards / construct a standard calibration curve;
measure absorption from (water) sample; ***[2]***
Accept answers that correctly describe the technique, such as "involves light specific to the wavelength absorbed by copper ions" and "measures the amount of light absorbed by the sample" etc.

(c) (i) ligands cause splitting of d-orbitals;
colour depends on movement of electrons between d-orbitals;
(four of the) water ligands replaced by ammonia;
splitting of orbitals depends on the ligand present;
ammonia ligands increase the splitting of the d-orbitals / cause a greater splitting than water ligands / ammonia higher than water in spectrochemical series;
Accept "Ammonia affects splitting of d-orbitals".
spectrum moves to the blue end / absorbs a higher frequency/shorter wavelength; ***[4 max]***

(ii) oxidation state/number of the metal/charge on metal ion/charge density; ***[1]***
Accept "metal ion involved / geometry of the complex ion / coordination number of ligands of metal ion".

3. (a) different components have different attractions/affinities/bond strengths/solubilities for two phases / *OWTTE*;

components strongly absorbed/adsorbed by stationary phase move less / components weakly absorbed/adsorbed by stationary phase move more / components not very soluble in mobile phase move less / components very soluble in mobile phase move more / *OWTTE*; ***[2]***

(b) (nature of) solvent (used) / (type of) paper / temperature / pH; ***[1]***

Option B — Human biochemistry

Penalize missing hydrogens or incorrect bond linkages (eg, CO–HN) once only in this option.

4. (a) mass (in g) of I_2/iodine reacting with 100 g of fat/oil/substance/lipid; ***[1]***
Allow "grams of I_2" instead of "mass (in g) of I_2".
Allow amount/number of mol of I_2 reacting with 1 mol of fat/oil/substance/lipid.
Do not accept mass number for mass.

(b) $\left(\frac{3.02}{302}=\right)0.0100\,(\text{mol})$ acid;
$\left(\frac{12.7}{254}=\right)0.0500\,(\text{mol})\ I_2$;
$\left(\frac{0.0500}{0.0100}=\right)5$ (carbon-carbon double bonds); ***[3]***
*Award **[1 max]** for 5 if no working shown.*

5. *Similarities:*
*Award **[3 max]** for any three similarities of:*
both contain 18 carbons/same number of carbons;
both unsaturated/contain C=C/carbon-carbon double bonds;
Do not allow just double bond.

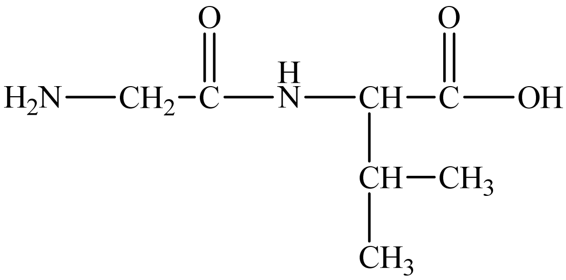
both contain carboxyl/COOH/CO_2H;
Allow "both carboxylic acids".

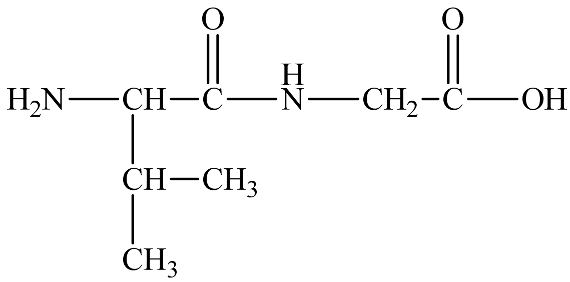
both have first (carbon to carbon) double bond/C=C on C9;
both have *cis*-configuration of (all) C=C (fragments);

Differences:
*Award **[1 max]** for any one difference of:*
linoleic acid (omega-6) contains 2 C=C **and** linolenic acid (omega-3) contains 3 C=C / linolenic acid has one more C=C;
Allow linolenic acid more unsaturated.

closest C=C on linoleic acid is on sixth carbon from methyl end **and** closest C=C on linolenic acid is on third carbon from methyl end / *OWTTE*; ***[4 max]***
*Accept linoleic acid is omega-6/ω-6 **and** linolenic acid is omega-3/ω-3.*
Award similarity mark M2 automatically as long as either difference mark is scored.

6. (a) (i)

 ;

 ;

[2]

Accept condensed structural formulas.
Accept C_3H_7 for CH_3CHCH_3.

(ii) H_2O/water; ***[1]***

(b) add hydrochloric acid/HCl to separate individual amino acids;
Accept strong acid/concentrated H^+ or restriction enzymes but not sulfuric acid/H_2SO_4.

*Award **[4 max]** for any four of:*
mixture/amino acids spotted/placed on gel/PAGE/polyacrylamide/paper;
gel placed in buffer/solution of known pH;
voltage/potential difference applied;
Accept "applied electric field / positive and negative electrodes connected / anode and cathode connected" but not current.

amino acids move differently depending on size and charge/isoelectric point/pH of buffer / amino acids move to oppositely charged electrodes;
Accept any suitable diagram.

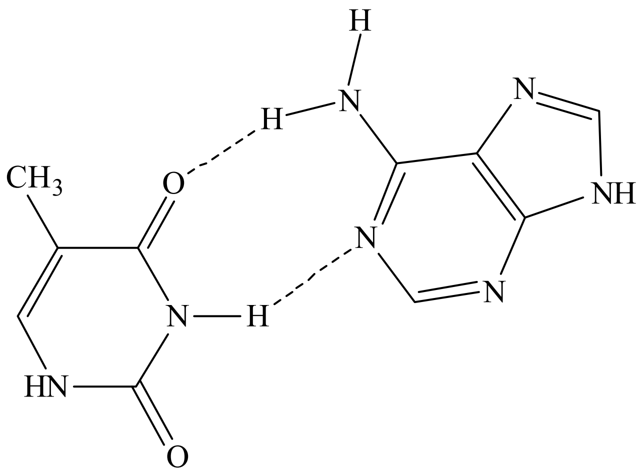
develop with ninhydrin/(organic) dye / detect by UV (light)/staining/fluorescence;
Accept any suitable development method.

measure distances moved / compare with known samples / measure isoelectric points; ***[5 max]***

7. (a) coded information lies in sequence of <u>bases</u> / *OWTTE*;
each sequence of three (bases) represents one amino acid/triplet code;
allows for up to 64 permutations/codons;
represents 20 naturally occurring amino acids;
(sequence of 3-base codes) gives amino acid sequence/primary structure of protein; ***[3 max]***

(b) hydrogen bond; ***[1]***

(c)



selecting correct base pair, A/adenine;
A–T with 2 H-bonds connections;
Allow even if the two bonds are in the wrong place.
correct placement of H–bonds; ***[3]***

8. *Award **[2]** for three correct, **[1]** for two correct.*
enzymes are proteins/polypeptides;
activity depends on 3D/tertiary and quaternary structure;
specificity of action / lock and key/induced fit hypothesis / *OWTTE*;
catalyses/speeds up rate of reaction/lowers activation energy (of reaction pathway) / are regenerated;
pH dependent;
temperature dependent;
has an active site;
can be inhibited; ***[2 max]***

Option C — Chemistry in industry and technology

9. (a) (i) lowers operating temperature of cell;
improves conductivity of the melt; ***[1 max]***
Accept "lowers the melting point (of aluminium oxide)".
Accept "uses less energy".

(ii) *Positive electrode (anode):*
$2O^{2-} \rightarrow O_2(g) + 4e^- \,/\, O^{2-} \rightarrow \frac{1}{2}O_2(g) + 2e^- \,/\, 2O^{2-} - 4e^- \rightarrow O_2(g) \,/$
$O^{2-} - 2e^- \rightarrow \frac{1}{2}O_2(g)$;
Allow $C(s) + 2O^{2-} \rightarrow CO_2(g) + 4e^-$.

Negative electrode (cathode):
$Al^{3+} + 3e^- \rightarrow Al(l)$; ***[2]***

Accept e instead of e^-.
Ignore state symbols.
*If correct equations shown at wrong electrodes, award **[1 max]**.*

(iii) the carbon anode oxidises / burns in/reacts with the oxygen (to produce CO_2); ***[1]***

(b) (i) harder/stronger (than pure aluminium); ***[1]***

(ii) *Award **[1]** for any two of:*
good conductor of electricity;
resists corrosion;
Do not allow rusting.

low density;
Do not allow lighter/light mass/light weight.

ductile; ***[1 max]***
Do not allow malleable.

(c) leakage of mercury is a health concern / formation of toxic organo-mercury compounds;
Specific health concerns might include acrodynia (pink disease) / Hunter-Russell syndrome / Minamata disease / kidney failure / damage to brain/central nervous system/CNS / health hazard associated with mercury contaminated fish / OWTTE.

asbestos in the diaphragm cell causes cancer;
Accept "asbestos in the diaphragm cell causes health problem".

sodium hydroxide in waste effluent changes pH of water/soil; ***[2 max]***
Accept "ozone layer depletion by chlorine in solvents and CFCs".
Accept "carcinogenic chlorinated organic compounds".

Accept other specific environmental impacts such as greenhouse gases from electricity generation.

10.

Catalyst	Mechanism	Disadvantage
Fe^{2+} (aq)	oxidized (by the OA) and subsequently reduced (by the RA) / undergoes redox reaction / changes oxidation state/number;	difficult to separate from reaction mixture;
Fe (s)	reactants are <u>adsorbed</u> onto surface (where reaction takes place) / reaction occurs on surface / weakens reactant bonds;	only effective on surface / must be finely divided; *Allow "must be cleaned/refreshed / OWTTE".*

[4]

Accept "prone to poisoning" as a disadvantage for either catalyst but not both.

11. ***[3 max]***
semiconductors / made of silicon;
(n-type) doped with Group 5 element/As/Sb/P (to provide extra electrons);
(p-type) doped with Group 3 element/B/Ga/Al/In (to create electron holes);
n-type in contact with p-type;
anti-reflective coating;

[2 max]
sunlight gives electrons energy to move from p-type to n-type;
flow <u>through external circuit</u> from n-type to p-type; ***[4 max]***

12. (a) fluids that have physical properties dependent on molecular orientation/orderly molecular arrangement; ***[1]***
Allow "fluids that exhibit molecular orientation/orderly molecular arrangement".
Allow "(LCs) show properties of liquids and crystals simultaneously".

(b) thermal agitation disrupts directional order of liquid crystal / *OWTTE*;
rotation of plane polarized light disrupted / crystals no longer have ability to affect light in same way / *OWTTE*; ***[2]***

(c) *Bullet-proof jackets:*
strong hydrogen bonding between chains;

Liquid crystal:
rigid (polar) rod-shaped molecule / lyotropic liquid crystal behaviour in (conc. sulphuric acid) solution; ***[2]***

13. (a) (research/technology development at) 1–100 nm (range);

*Award **[1 max]** for any one of:*
creates/uses structures with novel properties (because of their small size) / *OWTTE*;
builds on ability to control/manipulate at atomic scale / *OWTTE*; ***[2]***

(b) explosive / small size/large surface area means very fast reactions at possibly dangerous levels;
unknown health effects / immune system/allergy concerns;
industry not concerned about impact of product;
lack of public awareness about dangers;
nanoparticle waste products may require new methods of disposal;
nanoweapons more difficult to detect than conventional weapons (resulting in weapons of mass destruction);
possible toxicity (of small airborne particles); ***[2 max]***
Do not allow "just may cause environmental destruction" / OWTTE.
Accept other valid concerns.
Accept OWTTE throughout.

Option D — Medicines and drugs

14. (a) *Advantages:*
*Award **[1 max]** for any two of:*
strong pain relief/strong analgesic
sedation / *OWTTE*
treatment of diarrhoea
relieve coughing

Disadvantages:
*Award **[1 max]** for any two of:*
addiction
tolerance
dependence
constipation ***[2 max]***
depresses respiratory drive
Accept "criminals/drug addicts might get access to strong analgesics intended for medical use" / OWTTE.

*Award **[1 max]** if one advantage **and** one disadvantage are given.*

(b) molecule of diamorphine is less polar / polar hydroxyl/OH (groups) in morphine are replaced with less polar/non-polar groups in heroin / diamorphine contains two ester groups;
diamorphine is more fat/lipid soluble / OWTTE;
diamorphine more rapidly absorbed into the brain / (less polar molecules such as) diamorphine crosses the blood-brain barrier faster/more easily / diamorphine is more soluble in non-polar environment of the CNS/central nervous system than morphine / *OWTTE*; ***[2 max]***

15. *One similarity:*
*Award **[1 max]** for any one of:*
both contain halogens;
both contain phenyl (groups);
Allow benzene/aromatic ring or aromatic/aryl groups/fragments for phenyl but not benzene or arene alone.
Do not allow "both have chloro groups" as a similarity.

One difference:
*Award **[1 max]** for any one of:*
fluoxetine hydrochloride has a (substituted) ammonium (diazepam does not);
diazepam contains an amido (group) (fluoxetine hydrochloride does not);
Allow amide for amido.

fluoxetine hydrochloride is ionic (diazepam is not);
Allow salt instead of ionic.

diazepam has a chloro (group) / fluoxetine hydrochloride has a chloride (ion/anion);
fluoxetine hydrochloride has an ether (group) (diazepam does not);
diazepam contains an imino (group) (fluoxetine hydrochloride does not);
Allow imine/ketimine for imino.

fluoxetine hydrochloride contains a trifluoromethylphenyl (group) (diazepam does not); ***[2 max]***
Allow trifluoromethyl for trifluoromethylphenyl (group).
Accept any other correct comparison.

16. (a) (tertiary) amino; ***[1]***
Allow amine.

(b) *Award **[1]** for any two of:*
anxiety/restlessness;
irritability;
sleeplessness/insomnia;
increase in urine output/diuretic;
dehydration;
nausea;
headaches;
increase heart rate/tachycardia / increase blood pressure/tension;
increase metabolic rate;
trembling/shaking; ***[1 max]***
Do not accept stimulant.
Do not accept decrease in appetite.

17. (a) isolated/purified/concentrated penicillin;
Accept extracted penicillin.

first successful animal (mice) test / harmless to mice;
first person tested responded favourably / *OWTTE*; ***[2 max]***
Do not allow just "tested on humans" but accept "tested successfully on humans" / OWTTE.
Do not allow large-scale production (since attributed to Moyer and Rousseau, not Florey and Chain);

(b) penicillins interfere with (enzymes involved with) development of cell wall/(cross-link) structure of bacteria;
(due to damage) cells absorb water (by osmosis) **and** burst / *OWTTE*;
modifying side-chain overcomes resistance (by bacteria) / *OWTTE*; ***[3]***

(c) beta lactam ring has strained structure/(four-membered ring with) 90° bond angles on the carbon and nitrogen atoms;
atoms should have larger bond angles based on VSEPR theory / *OWTTE*;
ring stress increases chemical reactivity and opens;
open ring reacts/bonds with enzyme/penicillinase to prevent formation of bacteria cell walls (prevents cross-linking of peptides); ***[3 max]***

18. (a) bacteria are a single cell / viruses are not cellular;
bacteria have cell walls/nuclei / viruses have no nucleus/cell wall;
bacteria larger than viruses / viruses smaller than bacteria;
viruses need host cell to reproduce / viruses take over another cell;
bacteria are organisms/living / bacteria metabolise/can grow/feed/excrete / viruses are not living / viruses do not metabolise/grow/feed/excrete ; ***[2 max]***
Allow "bacteria have both DNA and RNA / viruses have either RNA or DNA only (but not both)".

(b) alter cell's genetic material;
block enzyme activity within host cell;
(changes cell membrane so that it) inhibits virus entry/bonding to cell;
prevents virus from leaving cell (after reproduction);
becomes part of DNA of virus / alters virus / blocks enzyme (polymerase) which builds DNA;
prevents virus from using cell to multiply/reproduce/replicate / prevents virus from using cell's metabolism; ***[2 max]***

(c) HIV retrovirus attacks immune system / binds to white blood cells/T-cells;
virus has ability to mutate;
virus makes people vulnerable to other infections;
metabolism of virus is linked closely to metabolism of the (host) cell / *OWTTE*;
antiretroviral agents are expensive / availability dependent on wealth of community/nation / lack of education/knowledge;
(social) "stigma" of diagnosis leads to not getting treatment / *OWTTE*; ***[3 max]***

19. (NMR/X-ray crystallography/molecular modelling software develop) 3D structure (of target enzymes/proteins);
design molecules to fit enzyme/protein active sites based on structure;
predict how changes to the molecule will affect the shape of the active site; ***[2 max]***

Option E — Environmental chemistry

20. (a) *Natural:* electrical storms/lightning / bacterial decomposition;
Anthropogenic: high temperature combustion in cars/planes/industrial furnaces; ***[2]***

(b) acid deposition / acid rain / nitrous acid / nitric acid;
(photochemical) smog / PANs/peroxyacyl nitrates / ozone; ***[1 max]***
Accept chemical formulas.

(c) catalytic converters / control of fuel-to-air ratio / lean burn engine / use of alternative energy sources / reduce energy consumption / reduce use of gas/petrol engines; ***[1]***
Allow "recirculation of exhaust gases/EGR (lowering operating temperature)".

21. (a) incoming solar radiation is short wavelength/high frequency/higher energy/UV;
(re-)radiated/emitted (by the Earth's surface) as long wavelength/low frequency/low energy/IR radiation;
energy absorbed by (bonds in) greenhouse gases / molecules vibrate when IR radiation absorbed;
energy (re-)radiated/(re-)emitted as IR radiation some of which returns back to Earth; ***[3 max]***
Do not accept reflected, bounced or trapped.

(b) CH_4 / methane;
decomposition of organic matter / livestock/ruminant/cows/sheep / manure / swamps/marshes / rice paddies / oil/gas field / anaerobic microbial activity in lakes/ponds / composting;

OR

N_2O / nitrogen(I) oxide/dinitrogen monoxide/nitrous oxide;
bacterial decomposition/action / combustion/burning of biomass / artificial/nitrogeneous/synthetic fertilizers;

OR

CFCs / chlorofluorocarbons;
solvents / production of polymers / refrigerants / foaming agents / propellants/aerosols / air conditioning units;

OR

SF_6 / sulfur hexafluoride;
electronics industry / high voltage/electrical switches / circuit breakers / electrical generators / insulator used in electrical industrial applications/gas-insulated substations / production of magnesium / *OWTTE*; ***[2]***

Accept any other correct answers such as "nitrogen trifluoride/NF_3 used in electronics industry / manufacture of semi-conductors/computer chips/circuits / (thin-film) solar/photovoltaic cells / solar panels / LCD televisions / chemical lasers" OR "trifluoromethyl sulfur pentafluoride/SF_5CF_3 formed (as by-product from SF_6) in high-voltage equipment / by-product of fluorochemical manufacture".
M2 can only be scored if M1 correct.

22. (a) O_2 double bond **and** O_3 bond order 1.5/between single and double bond;
O_2 stronger/shorter / O_3 weaker/longer bond;
O_2 absorbs shorter λ (242 nm) / O_3 absorbs longer λ (330 nm); ***[3]***

(b) *Initiation*

$$CCl_2F_2(g) \xrightarrow{\text{UV (light)}/hv/hf} \bullet CClF_2(g) + Cl\bullet(g)\ ;$$

Propagation

$$Cl\bullet(g) + O_3(g) \rightarrow ClO\bullet(g) + O_2(g)\ ;$$
$$ClO\bullet(g) + O\bullet(g) \rightarrow O_2(g) + Cl\bullet(g)\ ;$$

Accept for 2nd propagation step
$$ClO\bullet(g) + O_3(g) \rightarrow Cl\bullet(g) + 2O_2(g)\ .$$ ***[3]***

Allow representation of the radical without • if consistent throughout the mechanism.
Allow UV light to be represented above the arrow or mentioned in accompanying description as words.
Ignore state symbols.
Names of processes (initiation and propagation) not required.

23. *Multi-stage distillation:* ***[2 max]***
boil/evaporate and condense water (to remove impurities);
under reduced pressure;
heat released during condensation is used to heat untreated water / *OWTTE*;

Disadvantage: ***[1]***
expensive/requires significant amounts of energy / corrosion of equipment;
Disadvantage must be based on correct process.

Osmosis: ***[2 max]***
high pressure/greater than osmotic pressure/greater than 70 atm pressure required;
Allow "greater than 30 atm pressure".

through semi-permeable membranes / *OWTTE*;
water moves from high to low salt concentration;

Disadvantage: ***[1]***
membranes are sensitive/expensive / require careful maintenance / pre-treatment of water needed / cannot be turned off (to preserve membranes); ***[6]***
Disadvantage must be based on correct process.

24. (a) $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$

correct reactants;
correct products;
correct balancing; ***[3]***
M3 can only be scored if M1 and M2 correct.

(b) *Disadvantage*:
reduces the availability of nitrogen for plant nutrition / plants take in nitrates but not ammonium salts; ***[1]***

Option F — Food chemistry

25. (a)

Nutrient		Food source
carbohydrates	**and**	bread / cereals / grains / pasta / fruit / vegetables / (table) sugar;
proteins	**and**	meat / fish / eggs / dairy products / nuts / seeds / grains / beans / mushrooms / tofu/soy;
vitamins	**and**	fruit / vegetables / meat / fish / eggs / dairy products;

[2 max]

*Award **[1 max]** for two correct nutrients.*
Accept vegetables for proteins.
Do not accept "fortified food/vitamin supplements" as a food source for vitamins.
Accept other valid food sources for each nutrient.

(b) (i) ester; ***[1]***

(ii) water/H_2O; ***[1]***

(c) (i) (fatty acids in) oils are unsaturated/contain (many) C=C /carbon-carbon double bonds / (fatty acids in) fats are (mostly) saturated/contain no/few/fewer (than oils) C=C /carbon-carbon double bonds; ***[1]***

(ii) C=C bonds degrade/oxidize more rapidly / oils become rancid more rapidly / fats are more stable;

*Award **[1 max]** for any two of:*
auto-oxidation;
Allow oxidative rancidity.
Do not accept "reaction with oxygen" (name required).

photo-oxidation;
Do not accept light.

microbial rancidity;
hydrolysis; ***[2]***
Allow hydrolytic rancidity.
Do not accept "addition of water" (name required).
Do not accept "hydrogenation" (since not a degradation reaction).

26. (a) (i) length of time before food is considered unsuitable for sale/use/consumption / length of time that food maintains its expected quality;
owing to changes in taste/flavour/smell/odour/texture/appearance/colour; ***[2]***
Do not give credit for answers of the type "the food is no longer safe to eat".

(ii) water content;
loss of nutrients / browning / rancidity / microbial spoilage / loss of texture;

OR

pH change;
Do not allow chemical change.

off flavours / colour changes / browning / loss of nutrients;

OR

light;
rancidity / vitamin loss / fading of natural colours;

OR

temperature;
changes rate of other types of spoilage;

OR

contact with air/oxygen;
increases rate of reactions involving oxygen / browning; ***[2]***

M2 can only be scored if M1 correct.

(b) (i) light/UV; ***[1]***
Accept metal catalysis.

(ii) *Propagation:*
$R\bullet(g) + O_2(g) \rightarrow ROO\bullet(g)$;
$ROO\bullet(g) + RH(g) \rightarrow R\bullet(g) + ROOH(g)$;

Termination: ***[1 max]***
$R\bullet(g) + R\bullet(g) \rightarrow RR(g)$;
$R\bullet(g) + ROO\bullet(g) \rightarrow ROOR(g)$;
$ROO\bullet(g) + ROO\bullet(g) \rightarrow ROOR(g) + O_2(g)$; ***[3 max]***

Accept ECF for incorrect radicals in termination step from propagation step.
Ignore incorrect propagation and termination steps.
Allow representation of the radical without • if consistent throughout the mechanism.
Ignore state symbols.

(c) remove free radicals (from propagation step);
form less reactive free radicals;
act as electron donors/reducing agents;
reduce concentration of oxygen;
reduce availability/chelate of transition metal ions;
prevents reaction with peroxides/production of radicals; ***[2 max]***

27. (a) (i) heme initially present as oxymyoglobin/MbO_2/myoglobin/Mb;
in both, iron is Fe^{2+};
auto-oxidation causes $Fe^{2+} \rightarrow Fe^{3+}$ / formation of MMb/metmyoglobin;
Fe^{3+} causes discolouration / Fe^{3+} causes brown-red colour; ***[3 max]***

(ii) store free of oxygen/air / vacuum pack;
pack in carbon dioxide/CO_2/nitrogen/N_2/inert gas;
freezing / refrigeration;
Allow keep in a cold place.
place in low gas permeability packaging/film/plastic/polymer; ***[1 max]***

(b) *Similarities* ***[2 max]***:
both have central metal ion;
Accept "metal" for "metal ion" as structure in Data Booklet is incorrect.

both have a metal ion held by (dative) bonds from four nitrogen atoms;
both have (extensive) C=C/conjugation;
both contain porphins / both involve a porphyrin ring structure;

Differences ***[2 max]***:
one has Fe ion, the other Mg ion;
heme B has acid groups **and** chlorophyll a has ester groups;
chlorophyll a has a long hydrocarbon chain;
chlorophyll a has an asymmetric centre; ***[4 max]***

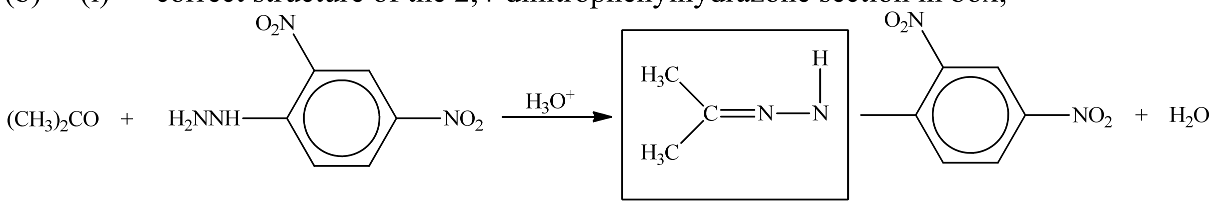
Option G — Further organic chemistry

Penalize missing hydrogens or incorrect bond linkages (eg, C–H_3C) once only in this option.

28. (a) (i) alcohols < phenols < carboxylic acids; ***[1]***
Accept correct order involving named compounds ie,
(propanol < phenol < propanoic acid).

(ii) halogens make them more acidic;
halogens are electron withdrawing;
Accept halogens (can be) electronegative.
reduces charge on/stabilizes anion formed / weakens O–H bond / makes it easier to lose H^+ ion; ***[3]***
Accept decreases pK_a.
Accept causes anion to be weaker base.

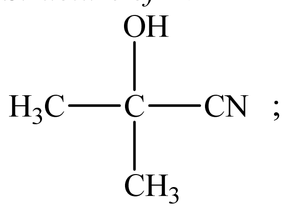
(b) (i) correct structure of the 2,4-dinitrophenylhydrazone section in box;



[1]

(ii) yellow/orange <u>solid/precipitate</u>; ***[1]***

(c) (i) *Structure of **A**:*

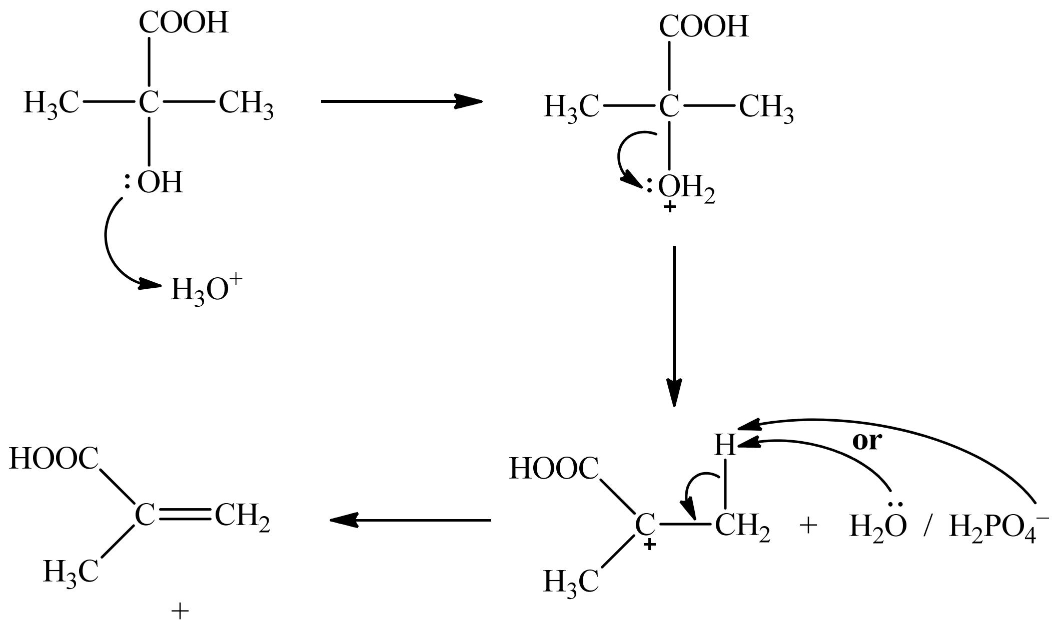


M2 and M3 can only be scored if M1 correct.

*Reagent to form **A**:*
cyanide ion/CN^- / hydrogen cyanide/HCN / sodium cyanide/NaCN / potassium cyanide/KCN;
Accept other ionic cyanides.

*Reagent for converting **A** to the final product:*
dilute acid / H^+(aq)/H_3O^+(aq); ***[3]***
Allow identified acid (eg, HCl(aq)).
Answer must refer to aqueous/dilute/H_2O for mark.

(ii)



H_3O^+/H_3PO_4

curly arrow going from lone pair on O to H^+/H_3O^+;
representation of positively charged O intermediate **and** curly arrow showing H_2O leaving;
curly arrow going from lone pair on O of $H_2O/H_2PO_4^-$/negative charge on O of $H_2PO_4^-$ to H **and** curly arrow going from CH bond to C–C^+ to form C=C;
No mark awarded if C^+ is not identified.
formation of organic product $(HOOC)(CH_3)C{=}CH_2$ **and** H_3O^+/H_3PO_4; ***[4]***

(d) one product involves a primary carbocation **and** other a secondary carbocation;
the secondary carbocation is more stable (than the primary carbocation, and hence this produces the major product);
alkyl groups reduce charge on the carbon atom (through an inductive effect); ***[3]***
Positive inductive effect of alkyl group alone is not enough for M3.

29. (a) (i) chlorobenzene < chloromethylbenzene / $C_6H_5Cl < C_6H_5CH_2Cl$; ***[1]***

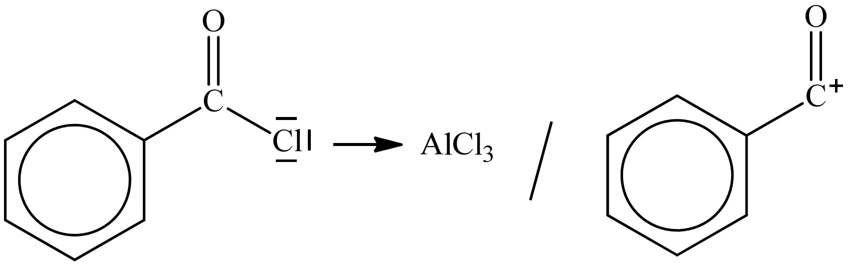
(ii) steric hindrance/repulsion from delocalized electrons prevents attack by the hydroxide ion / *OWTTE*;
lowers partial charge on carbon attached to chlorine atom (because of inductive effect on delocalized electrons) / *OWTTE*;
partial double bonding between chlorine and the ring (through incorporation of lone pair into the delocalized electrons) / interaction between lone pairs on chlorine and delocalized electrons strengthens C–Cl bond (contributing in slow reaction) / *OWTTE*; ***[2 max]***

(b) (i)

Reactant	Reaction type	Class of product
Ethanol	(nucleophilic) addition-elimination;	ester;
Benzene	electrophilic substitution; *Allow acylation.*	ketone;

[4]

(ii) aluminium chloride/$AlCl_3$ / iron(III)/ferric chloride/$FeCl_3$;
Accept aluminium bromide/$AlBr_3$ / iron(III)/ferric bromide/$FeBr_3$.



;

[2]

Accept intermediate structure with Fe.