HL Paper 2

Magnesium, a reactive metal found in many common minerals, is also an essential nutrient for both plants and animals.

Successive ionization energies of magnesium are given in the table below.

	First	Second	Third
Energy required / kJ mol^{-1}	738	1450	7730

Magnesium metal is mainly used as a component in lightweight alloys, particularly in combination with aluminium and titanium.

Magnesium is usually produced by the electrolysis of molten magnesium chloride.

a. Define the term *first ionization energy*. [2]

b. (i) Explain why the second ionization energy is greater than the first ionization energy. [4]

(ii) Explain why the third ionization energy is much greater than the second ionization energy.

c. Although magnesium is usually found as $\mathrm{Mg^{2+}}$ in its compounds, it is possible to use the Born-Haber cycle to investigate the possibility of $\mathrm{Mg^{+}}$ being able to form stable compounds. [3]

Use the ionization energy data from part (b), along with the other data provided below, to determine the enthalpy change of formation of MgCl(s). Assume that, because $\mathrm{Mg^{+}}$ would be similar in size to $\mathrm{Na^{+}}$, MgCl would have a similar lattice enthalpy to NaCl.

Enthalpy of atomization of Mg $+146\ \mathrm{kJ\ mol^{-1}}$

Bond enthalpy in $\mathrm{Cl_2}$ $+243\ \mathrm{kJ\ mol^{-1}}$

Electron affinity of Cl $+349\ \mathrm{kJ\ mol^{-1}}$

Lattice enthalpy of NaCl $+790\ \mathrm{kJ\ mol^{-1}}$

d. Consider the lattice enthalpies of $\mathrm{MgF_2}$, $\mathrm{MgCl_2}$ and $\mathrm{CaCl_2}$. List these from the most endothermic to the least endothermic and explain your order. [3]

$\text{Most endothermic} \rightarrow \text{Least endothermic}$

e. Magnesium hydroxide, $\mathrm{Mg(OH)_2}$, is only sparingly soluble in water and the equilibrium below exists when excess solid is in contact with a saturated solution. [2]

$$\mathrm{Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^{-}(aq)}$$

Outline how the solubility of magnesium hydroxide will vary with pH.

f. (i) Describe the bonding present in magnesium metal. [4]

(ii) Suggest why magnesium is harder than sodium.

(iii) Outline why alloys are generally less malleable than their component metals.

g. (i) Draw a labelled diagram of a suitable apparatus for the electrolysis. [7]

(ii) State equations for the reactions that take place at the electrodes.

Negative electrode (cathode) reaction:

Positive electrode (anode) reaction:

(iii) When dilute aqueous magnesium chloride is used as the electrolyte, the reactions at both electrodes are different. State equations for the reactions that occur in aqueous solution.

Negative electrode (cathode) reaction:

Positive electrode (anode) reaction:

(iv) Outline why magnesium metal is not produced in the electrolysis of aqueous magnesium chloride.

Markscheme

a. minimum energy required to remove one electron / energy required to remove most loosely bound/outermost electron;

from gaseous/isolated atom;

Accept "gaseous state".

More extensive definitions involving one mole may be given.

b. (i) electrons lost in same orbital/valence shell;

(second) electron/electron (being lost from Mg^{+} is) closer to the nucleus;

(second) electron/electron (being lost from Mg^{+}) not subject to e-e repulsion from others in same level;

Apply OWTTE for all marking points.

*Do **not** accept "less electrons to share the charge" or answers employing this concept.*

(ii) electron in lower energy level / more stable electron shell;

electron closer to nucleus;

less shielding by complete inner shells / increase in effective nuclear charge;

Apply OWTTE for all marking points.

c. $\Delta H_{\mathrm{at}}(\mathrm{Cl}) = \frac{1}{2} \times 243\ (\mathrm{kJ\,mol^{-1}})$;

Correct calculation of atomization enthalpy of Cl.

$\Delta H_{\mathrm{f}} = +146 + \frac{1}{2}243 + 738 + (-349) + (-790)$;

Correct sign and magnitude of all terms.

$= -134\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[3]** for correct final answer.*

Final mark involves correct computation of equation the student has produced.

*Award **[2]** for –12 (bond enthalpy of Cl not halved) or +134 (signs wrong).*

*Award **[1]** for +12 (bond enthalpy of Cl not halved and signs wrong).*

d. MgF_2 –$MgCl_2$ –$CaCl_2$;

F^- smaller (ionic radius) than Cl^- / Cl^- larger (ionic radius) than F^-;

Mg^{2+} smaller (ionic radius) than Ca^{2+} / Ca^{2+} larger (ionic radius) than Mg^{2+};

Accept use of atomic radius rather than ionic radius.

e. more soluble at low pH / less soluble at high pH;

higher pH / OH^- will shift the equilibrium to the left / lower pH / H^+ will (react with OH^- and) shift the equilibrium to the right;

f. (i) <u>lattice/layers/framework</u> of cations/magnesium ions/Mg^{2+};

surrounded by <u>delocalized</u> electrons / in a sea/flux of <u>delocalized</u> electrons;

Accept "mobile" instead of "delocalized".

(ii) Mg has more delocalized electrons (than Na);

Accept "Mg has more valence electrons than Na" / "Mg is Mg^{2+} but Na is only Na^+".

(iii) layers of ions/atoms/particles cannot slide over each other so easily (as different sized ions/atoms/particles) / *OWTTE*;

g.

(i)

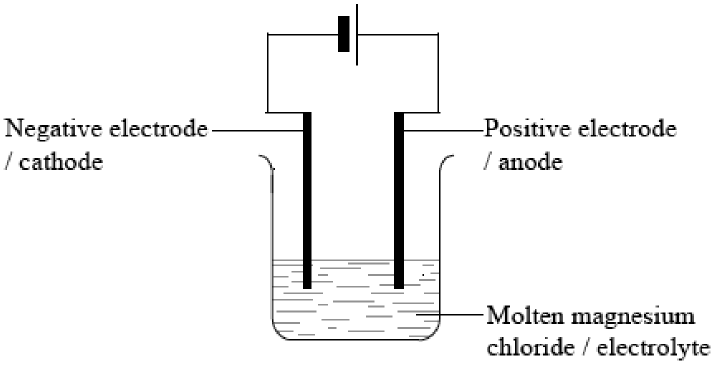

Diagram:

two electrodes connected to a power pack/battery and immersed in an electrolyte;

*Do **not** award mark if salt bridge included in diagram.*

Labelling:

anode/positive electrode, cathode/negative electrode, <u>molten</u> magnesium chloride/$MgCl_2$ (l)/electrolyte correctly labelled;

Check candidates know which end of a battery symbol is which charge.

(ii) *Negative electrode (cathode):* $Mg^{2+}(l) + 2e^- \rightarrow Mg\ (s)$;

Positive electrode (anode):

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

;

Accept $Cl^-(l) \rightarrow \frac{1}{2}Cl_2(g) + e^-$.

Ignore state symbols.

Allow e instead of e⁻.

*If both correct equations are given for the wrong electrodes award **[1 max]**.*

(iii) *Negative electrode* (*cathode):*

$\mathrm{2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)/2H^+(aq) + 2e^- \rightarrow H_2(g)}$;

Accept $4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)/4H^+(aq) + 4e^- \rightarrow 2H_2(g)$ /
$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)/H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$.

Positive electrode (anode):

$\mathrm{2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-/4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-}$;

Accept $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-/2OH^-(aq) \rightarrow \frac{1}{2}O_2(g) + H_2O(l) + 2e^-$.

State symbols not required.

Allow e instead of e⁻.

*If both correct equations are given for the wrong electrodes award **[1 max]**.*

(iv) water/hydrogen ions more easily reduced/better oxidizing agents/have a more positive E^Θ (than magnesium ions);

Accept converse statements for magnesium ions.

Accept "magnesium is very reactive/high in reactivity series" / OWTTE.

Examiners report

a. This was the most popular of the Section B questions, which was surprising because it was often not well answered. Most students were aware of the change involved in ionization, some realised this relates to the most easily lost electron, some that it refers to gas phase changes and a few both. Explanations of the changes in the values of successive ionization energies in terms of the attraction of the nucleus and the repulsion from other electrons were generally weak, however candidates quite often recognised that the third electron lost had to come from a more stable electron energy level. Very few were able to correctly sum the enthalpy terms involved in the Born-Haber cycle, in addition candidates rarely halved the bond enthalpy of chlorine and a significant number appeared not to realise the question referred to MgCl rather than $\mathrm{MgCl_2}$. There were some G2 comments that space should have been left for students to draw a cycle, but this would have implied that such a drawing was required, hence it is better to train students to use additional paper for any background support they may require. Quite a lot of students correctly deduced the order of lattice enthalpy of the group (II) halides, and a number correctly explained this in terms of ionic radii, though many incorrectly invoked electronegativities. Many students could correctly explain the effect of pH on the solubility of $\mathrm{Mg(OH)_2}$, though a significant number attempted to answer the opposite question; how pH would depend on the concentration of dissolved $\mathrm{Mg(OH)_2}$! It was surprising how few students could correctly describe metallic bonding, how it is affected by the number of delocalized electrons per cation and the way it leads to malleability. Alloys are not specifically mentioned in the syllabus but the mark scheme gave credit for answers that indicated the student was aware that malleability is associated with layers of metal atoms/cations sliding over each other. Most students were able to draw appropriately labelled diagrams of electrolysis apparatus, though sometimes the labelling of the polarity of the electrodes did not correspond to the polarity of the battery symbol drawn. Quite a few candidates could quote equations for the reactions occurring the electrodes in both the liquid and aqueous state; both seemed to be equally well answered which was perhaps a little surprisingly. Many could also give good explanations as to why electrolysis of the aqueous solution did not produce magnesium metal, though confusions in terminology (such as hydrogen rather than hydrogen ions being reduced) were not uncommon.

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Buta-1,3-diene can be hydrogenated to produce butane, according to the reaction below.

$$C_4H_6(g) + 2H_2(g) \rightarrow C_4H_{10}(g)$$

a. State the conditions necessary for this reaction. [2]

b. Determine the standard enthalpy change of reaction, ΔH^{Θ}, in $\mathrm{kJ\,mol^{-1}}$, at 298 K for the hydrogenation reaction, using Table 11 of the Data Booklet. [1]

c. Calculate the standard free energy change, ΔG^{Θ}, in $\mathrm{kJ\,mol^{-1}}$, at 298 K for the hydrogenation reaction, using Table 11 of the Data Booklet. [1]

d. (i) Determine the standard entropy change of the reaction, ΔS^{Θ}, at 298 K, in $\mathrm{kJ\,K^{-1}mol^{-1}}$, using your answers from (b) and (c). [8]

(ii) Explain why the standard entropy change for the hydrogenation of buta-1,3-diene has a negative sign.

(iii) Predict whether the hydrogenation reaction becomes more or less spontaneous as the temperature increases.

(iv) Determine the temperature, in K, at which the spontaneity changes.

(v) Determine the standard entropy, S^{Θ}, for hydrogen in $\mathrm{J\,K^{-1}mol^{-1}}$, using Table 11 of the Data Booklet and your answer for (d)(i).

Markscheme

a. heat /warm / 140–225 °C;

Do not accept high temperature.

(finely divided) catalyst / Zn/Cu/Ni/Pd/Pt;

b. $\Delta H^{\Theta} = \Big(\Sigma\Delta H_f^{\Theta}(\text{products}) - \Sigma\Delta H_f^{\Theta}(\text{reactants}) = -127 - (110 + 0) =\Big) - 327\ (\mathrm{kJ\,mol^{-1}})$;

c. $\Delta G^{\Theta} = \Big(\Sigma\Delta G_f^{\Theta}(\text{products}) - \Sigma\Delta G_f^{\Theta}(\text{reactants}) = -16 - (152 + 0) =\Big) - 168\ (\mathrm{kJ\,mol^{-1}})$;

d. (i) $\Delta S^{\Theta} = \left(\frac{\Delta H^{\Theta} - \Delta G^{\Theta}}{T} =\right) \frac{-237-(-168)}{209}$;

$= -0.232\ (\mathrm{kJ\,K^{-1}mol^{-1}})$;

*Award **[2]** for correct final answer.*

*Award **[2]** for –232 J K^{-1} mol^{-1} (units must be given).*

(ii) 3 mol of gaseous reactants and 1 mol of gaseous products / fewer moles of gas in products;

(iii) spontaneity decreases (as temperature increases because $T\Delta S^{\Theta}$ becomes a larger negative value/ΔG^{Θ} becomes positive at higher temperatures);

(iv) $\Delta G^{\Theta} = \Delta H^{\Theta} - T\Delta S^{\Theta} = 0/ - 237 - T(-0.232) = 0$;

$T = 1020\ (K)$;

Remember to allow ECF from 4(d)(i).

(v) $\Delta S^{\Theta} = \Sigma S^{\Theta}(\text{products}) - \Sigma S^{\Theta}(\text{reactants})/ - 232 = 310 - (279 + 2S^{\Theta}(H_2))$;

$S^{\Theta}(H_2) = \frac{1}{2}(310 - 279 + 232) = 132\ \mathrm{J\,K^{-1}mol^{-1}})$;

*Award **[2]** for correct final answer.*

Remember to allow ECF from 4(d)(i).

Examiners report

a. Conditions for the reaction, even though the mark scheme accepted fairly vague answers, were not well known. The calculations of enthalpy, entropy and Gibbs free energy scored well; it was pleasing to note that many realised the importance of conversion of units in part d(v). The link between the changes in temperature and the effect on spontaneity was understood, but many lost credit on part d(ii) for failing to mention the change in the number of gaseous moles. In d(v) most candidates missed the fact that 2 moles of hydrogen were present in the equation.

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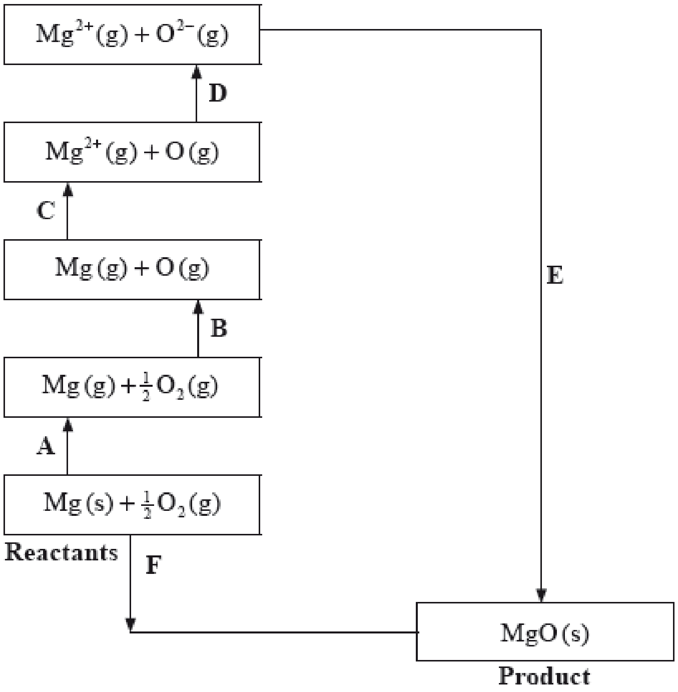
The Born-Haber cycle for MgO under standard conditions is shown below.



The values are shown in the table below.

Process	Enthalpy change / kJ mol^{-1}
A	+150
B	+248
C	+736 + (+1450)
D	−142 + (+844)
E	
F	−602

a.i. Identify the processes represented by **A**, **B** and **D** in the cycle. [3]

a.ii. Define the enthalpy change, **F**. [2]

a.iii Determine the value of the enthalpy change, **E**. [2]

a.iv Define the enthalpy change **C** for the first value. Explain why the second value is significantly larger than the first. [4]

a.v. The inter-ionic distance between the ions in NaF is very similar to that between the ions in MgO. Suggest with a reason, which compound has the higher lattice enthalpy value. [2]

b.i. The standard enthalpy change of three combustion reactions is given below in kJ. [4]

$$\begin{array}{ll} 2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) & \Delta H^\ominus = -3120 \\ 2H_2(g) + O_2(g) \rightarrow 2H_2O(l) & \Delta H^\ominus = -572 \\ C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) & \Delta H^\ominus = -1411 \end{array}$$

Based on the above information, calculate the standard change in enthalpy, $\Delta H^\ominus$, for the following reaction.

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

b.ii Predict, stating a reason, whether the sign of $\Delta S^\ominus$ for the above reaction would be positive or negative. [2]

b.iii Discuss why the above reaction is non-spontaneous at low temperature but becomes spontaneous at high temperatures. [2]

b.iv Using bond enthalpy values, calculate $\Delta H^\ominus$ for the following reaction. [3]

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

b.v. Suggest with a reason, why the values obtained in parts (b) (i) and (b) (iv) are different. [1]

Markscheme

a.i. **A:** sublimation/atomization;

B: atomization/half dissociation enthalpy;

D: (sum of 1st and 2nd) electron affinity;

Do not accept vaporization for A and B.

Accept ΔH_{AT}*· or* ΔH_{EA}*.*

a.ii. enthalpy change when one mole of the compound is formed from its elements (in their standard states);

under standard conditions / 25 °C/298 K **and** 1 atm/$101.3\ \mathrm{kPa}/1.01 \times 105\ \mathrm{Pa}$;

a.iii. $-602 = 150 + 248 + 2186 + 702 + E$;

$-3888\ (\mathrm{kJ\,mol^{-1}})$;

Do not allow 3889 (given in data booklet).

Allow 3888 (i.e no minus sign).

Award ***[2]*** *for the correct final answer.*

a.iv energy required to remove one electron;

from an atom in its gaseous state;

electron removed from a positive ion;

decrease in electron-electron repulsion / increase in nucleus-electron attraction;

a.v. MgO;

double ionic charge / both ions carry +2 and –2 charge/greater charge compared to +1 and –1;

b.i.

$$\left(C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)\right) \quad \Delta H^\Theta = -1560;$$
$$\left(H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)\right) \quad \Delta H^\Theta = +286;$$
$$(2CO_2(g) + 2H_2O(l) \rightarrow C_2H_4(g) + 3O_2(g)) \quad \Delta H^\Theta = +1411;$$
$$(C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)) \quad \Delta H^\Theta = +137\ (\text{kJ});$$

Allow other correct methods.

Award ***[2]*** *for –137.*

Allow ECF for the final marking point.

b.ii. positive;

increase in number of moles of <u>gas</u>;

b.iii. at low temperature, ΔH^Θ is positive **and** ΔG is positive;

at high temperature, factor $T\Delta S^\Theta$ predominates **and** ΔG is negative;

b.iv. Bonds broken (1C–C, 6C–H, or 1C–C, 2C–H) = 2825/1173;

Bonds made (1C=C, 1H–H, 4C–H) = 2700/1048;

+125 (kJ);

Allow 125 but not –125 (kJ) for the final mark.

Award ***[3]*** *for the correct final answer.*

b.v. bond enthalpy values are average values;

Examiners report

a.i. This was the second most popular question and in general candidates demonstrated a good understanding of the Born Haber cycle. Some candidates identified the process A as vaporization instead of atomization.

a.ii. Most candidates correctly stated the definition of enthalpy change of formation although some omitted to specify the standard conditions.

a.iii. The majority of candidates correctly calculated the lattice enthalpy value.

a.iv. The definition of the first ionization energy was stated correctly by most candidates but in a few cases the term gaseous state was missing.

a.v. The compound with higher lattice enthalpy was correctly identified including the reason.

b.i. The majority of candidates manipulated the thermo-chemical equations and calculated the correct answer of +137 kJ although some reversed the sign.

b.ii. [N/A]

b.iii. The explanation for why the reaction was non-spontaneous at low temperature but became spontaneous at high temperature was not always precise and deprived many candidates of at least one mark.

b.iv. The bond enthalpy calculation had the usual mistakes of using the wrong value from the data booklet, bond making minus bond breaking and –125 kJ instead of +125 kJ.

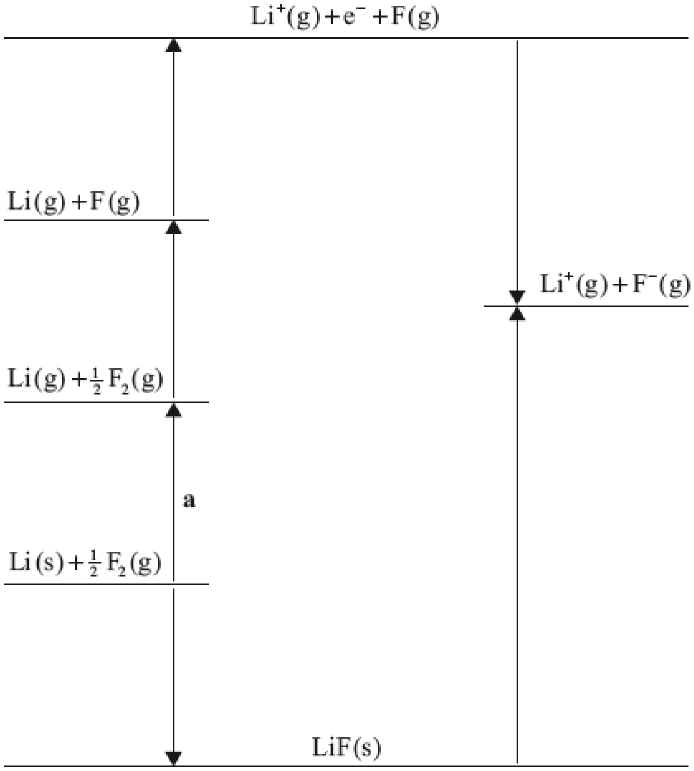
b.v. [N/A]

Lattice enthalpies can be determined experimentally using a Born–Haber cycle and theoretically using calculations based on electrostatic principles.

a. The experimental lattice enthalpies of the chlorides of lithium, LiCl, sodium, NaCl, potassium, KCl, and rubidium, RbCl, are given in Table 13 of the Data Booklet. Explain the trend in the values. [2]

b. Explain why magnesium chloride, $\mathrm{MgCl_2}$, has a much greater lattice enthalpy than sodium chloride, NaCl. [2]

c. (i) Identify the process labelled **a** on the Born–Haber cycle for the determination of the standard enthalpy of formation of lithium fluoride, LiF. [3]



(ii) The enthalpy change for process **a** is $+159\ \mathrm{kJ\ mol^{-1}}$. Calculate the standard enthalpy of formation of lithium fluoride, LiF, using this and other values from the Data Booklet.

Markscheme

a. radius of the metal/positive ion/cation increases;

attraction (between ions) is weaker;

b. higher charge (on cation);

smaller radius (of cation);

c. (i) (standard enthalpy of) atomization/$\Delta H^{\Theta}_{\text{atomization}}$ / (standard enthalpy of) sublimation/$\Delta H^{\Theta}_{\text{sublimation}}$;

(ii) $\text{lattice enthalpy} = +1049\ \text{kJ mol}^{-1}$ (Data Booklet Table 13)
$\text{bond enthalpy F}--\text{F} = +158\ \text{kJ mol}^{-1}$ (Data Booklet Table 10)
$\text{first ionization energy (Li)} = +520\ \text{kJ mol}^{-1}$ (Data Booklet Table 7)
$\Delta H^{\ominus}_{\text{electron affinity}}(\text{F}) = -328\ \text{kJ mol}^{-1}$ (Data Booklet Table 7)
$\Delta H^{\ominus}_{\text{atomization}}\ \text{of Li} = +159\ \text{kJ mol}^{-1}$ (given)

$\Delta H^{\ominus}_{\text{f}} = +159 + \frac{1}{2}(158) + 520 + (-328) - (1049)$;

$= -619\ \text{kJ mol}^{-1}$;

Accept use of theoretical value of lattice enthalpy, +1030 kJ mol^{-1}*:*

$\Delta H^{\ominus}_{\text{f}} = +159 + \frac{1}{2}(158) + 520 + (-328) - (1030)$

= –600 kJ mol^{-1}

Examiners report

a. Many candidates had difficulty correctly explaining the trends in lattice enthalpy values in (a), referring to atomic radii or the attraction between the metal nucleus and valence or bonding electrons, and giving explanations that sounded like descriptions of first ionization energy or covalent bonding.

b. In (b) most candidates scored one mark for stating that the Mg ion has a greater charge than Na ion. Few also mentioned that the size of the Mg ion is less than the Na ion.

c. Most candidates correctly identified sublimation or atomization of Li in (c)(i). Vaporization was the most common error. In (c)(ii), many candidates forgot to divide the bond enthalpy of fluorine by 2. Some had difficulty finding the enthalpy of atomization of fluorine in the Data Booklet, and some obtained all the correct values but did not put the correct signs on the values when using Hess's Law.

Phosphoryl chloride, POCl_3, is a dehydrating agent.

$\text{POCl}_3\ (\text{g})$ decomposes according to the following equation.

$$2\text{POCl}_3(\text{g}) \rightarrow 2\text{PCl}_3(\text{g}) + \text{O}_2(\text{g})$$

POCl_3 can be prepared by the reaction of phosphorus pentachloride, PCl_5, with tetraphosphorus decaoxide, P_4O_{10}.

PCl_3 and Cl^- can act as ligands in transition metal complexes such as $\text{Ni(PCl}_3)_4$ and $[\text{Cr(H}_2\text{O)}_3\text{Cl}_3]$.

a.i. Predict and explain the sign of the entropy change, ΔS, for this reaction. [1]

a.ii. Calculate the standard entropy change for the reaction, $\Delta S^{\ominus}$, in $\text{J K}^{-1}\text{mol}^{-1}$, using the data below. [1]

Substance	$S^{\ominus}$ / J K^{-1} mol^{-1}
$POCl_3$ (g)	325.0
PCl_3 (g)	311.7
O_2 (g)	205.0

a.iii. Define the term *standard enthalpy change of formation*, ΔH_f^Θ. [1]

a.iv. Calculate the standard enthalpy change for the reaction, ΔH^Θ, in kJ mol^{-1}, using the data below. [1]

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$POCl_3$ (g)	–542.2
PCl_3 (g)	–288.1

a.v. Determine the standard free energy change for the reaction, ΔG^Θ, in kJ mol^{-1}, at 298 K. [1]

a.vi. Deduce the temperature, in K, at which the reaction becomes spontaneous. [1]

b.i. Deduce the Lewis (electron dot) structure of $POCl_3$ (with P as the central element) and PCl_3 and predict the shape of each molecule, using the valence shell electron pair repulsion theory (VSEPR). [4]

b.ii. State and explain the Cl–P–Cl bond angle in PCl_3. [3]

c.i. Deduce the Lewis (electron dot) structure of PCl_5. [1]

c.ii. Predict the shape of this molecule, using the valence shell electron pair repulsion theory (VSEPR). [1]

c.iii. Identify all the different bond angles in PCl_5. [1]

c.iv. PCl_3Br_2 has the same molecular shape as PCl_5. Draw the three isomers of PCl_3Br_2 and deduce whether each isomer is polar or non-polar. [3]

d.i. Define the term *ligand*. [2]

d.ii. Explain why the complex $[Cr(H_2O)_3Cl_3]$ is coloured. [3]

Markscheme

a.i. 2 mol (g) going to 3 mol (g)/increase in number of particles, therefore entropy increases/ΔS positive / *OWTTE*;

Accept if numbers of moles of gas are given below the equation.

a.ii. $\left(\Delta S^\Theta = [(2)(311.7) + (205.0)] - (2)(325.0) =\right) (+)178.4\ (\text{J K}^{-1}\text{mol}^{-1})$;

a.iii. heat/enthalpy change/required/absorbed when <u>1 mol</u> of a compound is formed from its elements in their standard states/at 100 kPa/10^5 Pa/1 bar;

Allow 1.01 × 10^5 Pa/101 kPa/1 atm.

Allow under standard conditions or standard temperature and pressure.

Temperatures not required in definition, allow if quoted (for example, 298 K/ 25 °C – most common) but pressure value must be correct if stated.

a.iv. $\left(\Delta H^\Theta = [(2)(-288.1)] - [(2)(-542.2)]\right) =\left.\right) (+)508.2\ (\text{kJ mol}^{-1})$;

a.v. $\left(\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = (508.2) - (298)\left(\frac{178.4}{1000}\right) = \right)$ $(+)455.0\ (\mathrm{kJ\,mol^{-1}})$;

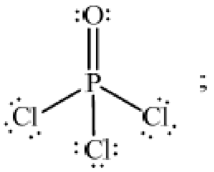
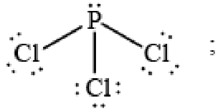
a.vi. $T > \left(\frac{\Delta H^{\ominus}}{\Delta S^{\ominus}} = \frac{508.2}{\left(\frac{178.4}{1000}\right)} = \right)$ $2849\ (\mathrm{K})/2576$ (°C);

Allow temperatures in the range 2848–2855 K.

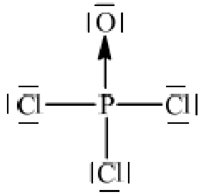
Accept T = 2849(K) .

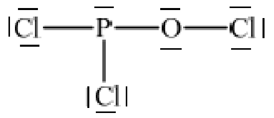
No ECF for temperatures T in the range 0–100 K.

b.i.

<table>
<tr><th></th><th>$POCl_3$</th><th>PCl_3</th></tr>
<tr><td rowspan="2">Lewis (electron dot) Structure</td><td>
;
<i>Accept legitimate alternatives for POCl₃ as shown below*.</i></td><td>
;</td></tr>
<tr><td colspan="2"><i>Allow any combination of dots/crosses or lines to represent electron pairs.
Penalise missing lone pair on P in PCl₃ but penalize missing lone pairs once only on terminal O or Cl atoms.</i></td></tr>
<tr><td rowspan="2">Shape</td><td>tetrahedral;</td><td>trigonal/triangular pyramidal;
<i>Do not allow tetrahedral.</i>
<i>Do not allow just pyramidal.</i></td></tr>
<tr><td colspan="2"><i>Do not allow ECF from Lewis structures with incorrect number of negative charge centres.
Only allow shapes based on legitimate structures below.</i></td></tr>
</table>

**Legitimate alternatives for $POCl_3$:*



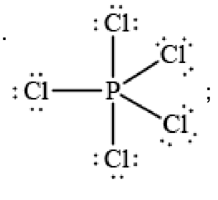


b.ii. allow any bond angle in the range 100° to less than 109° (experimental value is100°);

due to four negative charge centres/four electron pairs/four electron domains (one of which is a lone pair)/tetrahedral arrangement of electron pairs/domains;

extra repulsion due to lone pair electrons / lone pairs occupy more space (than bonding pairs) so Cl–P–Cl bond angle decreases from 109.5° / *OWTTE*;

c.i.



;

Allow any combination of dots/crosses or lines to represent electron pairs.

Do not penalise missing lone pairs on Cl if already penalised in (b)(i).

c.ii. trigonal/triangular bipyramidal;

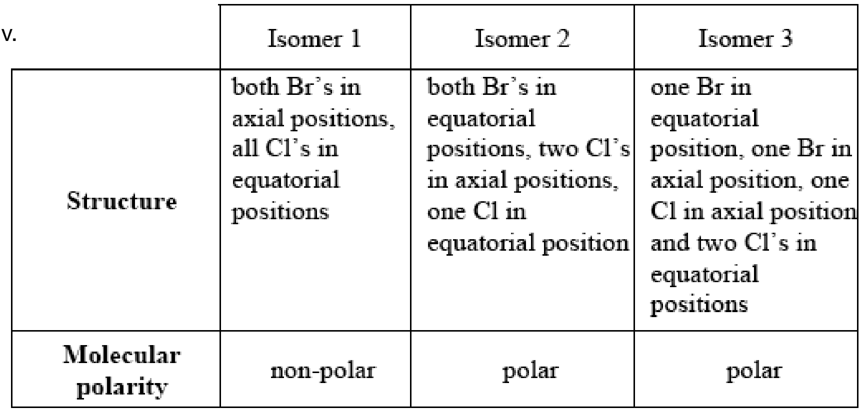
Do not allow ECF from Lewis structures with incorrect number of negative charge centres.

c.iii. 120° **and** 90°/180°;

Ignore other bond angles such as 240° and 360°.

Apply list principle if some correct and incorrect angles given.

c.iv.



	Isomer 1	Isomer 2	Isomer 3
Structure	both Br's in axial positions, all Cl's in equatorial positions	both Br's in equatorial positions, two Cl's in axial positions, one Cl in equatorial position	one Br in equatorial position, one Br in axial position, one Cl in axial position and two Cl's in equatorial positions
Molecular polarity	non-polar	polar	polar

*Award **[1]** for correct structure **and** molecular polarity.*

*Award **[1 max]** for correct representations of all three isomers.*

Lone pairs not required.

d.i. species with lone/non-bonding pair (of electrons);

which bonds to metal ion (in complex) / which forms dative (covalent)/coordinate bond to metal ion (in complex);

d.ii. unpaired electrons in d orbitals / d sub-level partially occupied;

d orbitals split (into two sets of different energies);

frequencies of (visible) light absorbed by electrons moving from lower to higher d levels;

colour due to remaining frequencies / complementary colour transmitted;

Allow wavelength as well as frequency.

Do not accept colour emitted.

Examiners report

a.i. Most candidates were able to calculate the entropy, enthalpy and free energy changes but made mistakes with the correct definition of enthalpy of formation'. Many referred to the gaseous state which suggests some confusion with bond enthalpies. Many were comfortable with writing Lewis structures and shapes of molecules, or some give incomplete explanations, not referring to the number of electron domains for example. Not many students could write a balanced equation for the reaction between PCl_3 and H_2O (A.S. 13.1.2 of the guide). In part (d) even though many knew that a ligand has a lone pair of electrons, they missed the second mark for 'bonding to metal ion'.

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In December 2010, researchers in Sweden announced the synthesis of N,N–dinitronitramide, $\mathrm{N(NO_2)_3}$. They speculated that this compound, more commonly called trinitramide, may have significant potential as an environmentally friendly rocket fuel oxidant.

a. Methanol reacts with trinitramide to form nitrogen, carbon dioxide and water. Deduce the coefficients required to balance the equation for this reaction. [1]

$$\_\_\_\ \mathrm{N(NO_2)_3(g)} + \_\_\_\ \mathrm{CH_3OH(l)} \rightarrow \_\_\_\ \mathrm{N_2(g)} + \_\_\_\ \mathrm{CO_2(g)} + \_\_\_\ \mathrm{H_2O(l)}$$

c. Calculate the enthalpy change, in $\mathrm{kJ\,mol^{-1}}$, when one mole of trinitramide decomposes to its elements, using bond enthalpy data from Table 10 of the Data Booklet. Assume that all the N–O bonds in this molecule have a bond enthalpy of $305\ \mathrm{kJ\,mol^{-1}}$. [3]

d. The entropy change, ΔS, for the decomposition of trinitramide has been estimated as $+700\ \mathrm{J\,K^{-1}mol^{-1}}$. Comment on the sign of ΔS. [2]

e. Using $+700\ \mathrm{J\,K^{-1}mol^{-1}}$ as the value for the entropy change, along with your answer to part (c), calculate ΔG, in $\mathrm{kJ\,mol^{-1}}$, for this reaction at 300 K. (If you did not obtain an answer for part (c), then use the value $-1000\ \mathrm{kJ\,mol^{-1}}$, but this is not the correct value.) [3]

f. Explain how changing the temperature will affect whether or not the decomposition of trinitramide is spontaneous. [2]

g. Outline how the length of the N–N bond in trinitramide compares with the N–N bond in nitrogen gas, $\mathrm{N_2}$. [2]

h. Deduce the N–N–N bond angle in trinitramide and explain your reasoning. [3]

i. Predict, with an explanation, the polarity of the trinitramide molecule. [2]

Markscheme

a. $\underline{(1)}\ \mathrm{N(NO_2)_3(g)} + \underline{\ 2\ }\mathrm{CH_3OH(l)} \rightarrow \underline{\ 2\ }\mathrm{N_2(g)} + \underline{\ 2\ }\mathrm{CO_2(g)} + \underline{\ 4\ }\mathrm{H_2O(l)}$;

c. *bonds broken:* $(6 \times 305) + (3 \times 158) = 1830 + 474 = 2304\ (\mathrm{kJ\,mol^{-1}})$;

bonds made: $(2 \times 945) + (3 \times 498) = 1890 + 1494 = 3384\ (\mathrm{kJ\,mol^{-1}})$;

enthalpy change: $2304 - 3384 = -1080\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[3]** for correct final answer.*

*Award **[2 max]** for +1080 (kJ mol^{-1}).*

Accept –234 kJ mol^{-1} which arise from students assuming that 305 kJ mol^{-1} refers to the strength of a single N–O bond. Students may then take N=O from the data book value (587 kJ mol^{-1}).

bonds broken: (3 × 305) + (3 × 587) + (3 × 158) = 915 + 1761 + 474 = 3150 (kJ mol^{-1})

bonds made: (2 × 945) + (3 × 498) = 1890 + 1494 = 3384(kJ mol^{-1})

enthalpy change: 3150 – 3384 = –234(kJ mol^{-1}).

*Award **[2 max]** for correct calculation of the enthalpy change of reaction for the equation in part (a), which gives –2160 (kJ mol^{-1}).*

*Award **[1]** if the final answer is not –2160 but the candidate has correctly calculated the bonds broken in trinitramide as 2304 (kJ mol^{-1}).*

d. increase in the number of moles of gas;

gases have a greater entropy/degree of randomness (than liquids or solids);

*Award **[1 max]** for answers stating that positive value indicates an increase in disorder/randomness.*

e. $\Delta G = \Delta H - T \times \Delta S$;

$= -1080 - 300 \times \frac{700}{1000}$;

$-1290\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[3]** for correct final answer.*

*Award **[2 max]** for incorrect conversions of units.*

If no answer to part (c), using ΔH = –1000 kJ mol^{-1}, gives –1020 (kJ mol^{-1}).

f. no change in spontaneity / temp has no effect on spontaneity / spontaneous at all temperatures;

ΔG negative at all temperatures / exothermic/ΔH negative **and** involves an increase in entropy/ΔS positive;

g. (N–N bond in) trinitramide is longer/nitrogen (gas) is shorter / 0.145 nm in trinitramide versus 0.110 nm in nitrogen;

trinitramide has single (N–N) bond **and** nitrogen (gas) has triple bond;

h. 106° – 108°;

Accept < 109°.

*Any two for **[2 max]**.*

4 (negative) charge centres/electron pairs/electron domains around central nitrogen;

central nitrogen has a lone/non-bonding pair;

lone/non-bonding pairs repel more than bonding pairs;

molecule will be (trigonal/triangular) pyramidal;

(negative) charge centres/electron pairs/electron domains will be tetrahedrally arranged/orientated/ have tetrahedral geometry;

Do not apply ECF.

i. polar;

net dipole moment present in molecule / unsymmetrical distribution of charge / polar bonds do not cancel out / centre of negatively charged oxygen atoms does not coincide with positively charged nitrogen atom;

Marks may also be awarded for a suitably presented diagram showing net dipole moment.

Do not accept “unsymmetrical molecule”.

Apply ECF from part (h).

Examiners report

a. Most students could insert the coefficients to balance the equation provided and many recognized the benign nature of the products formed. Though the structure of trinitramide was not given this did not seem to hinder students in calculating the required enthalpy change. A worryingly high number of students however used bond enthalpies to calculate the enthalpy change in the part (a) equation rather than the much simpler decomposition asked for, so to allow them to gain some credit, the mark scheme was adjusted. The sections relating to entropy and free energy changes were generally well tackled, as was the comparative lengths of the N-N bonds. Predicting the shape and polarity of the trinitramide molecule often proved more difficult, especially explaining the polarity of the molecule. Explanations of the effect of external pressure on boiling point, in terms of vapour pressure, and of the effect of temperature, in terms of kinetic theory, often lacked clarity.

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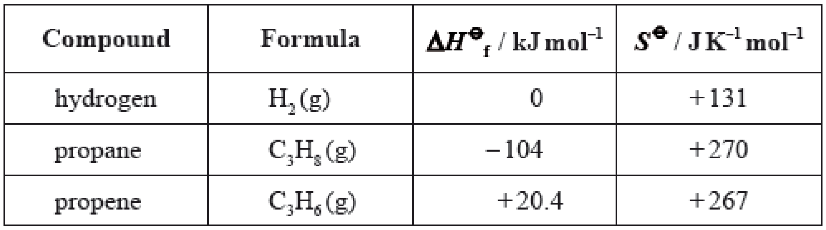
An example of a homogeneous reversible reaction is the reaction between hydrogen and iodine.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$$

Propene can be hydrogenated in the presence of a nickel catalyst to form propane. Use the data below to answer the questions that follow.



Compound	Formula	$\Delta H^{\ominus}_f$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
hydrogen	$H_2(g)$	0	+131
propane	$C_3H_8(g)$	−104	+270
propene	$C_3H_6(g)$	+20.4	+267

a.v.At a temperature just above 700 K it is found that when 1.60 mol of hydrogen and 1.00 mol of iodine are allowed to reach equilibrium in a $4.00\ \mathrm{dm}^3$ flask, the amount of hydrogen iodide formed in the equilibrium mixture is 1.80 mol. Determine the value of the equilibrium constant at this temperature. [4]

b.i.Outline why the value for the standard enthalpy change of formation of hydrogen is zero. [1]

b.ii.Calculate the standard enthalpy change for the hydrogenation of propene. [2]

b.iii.Calculate the standard entropy change for the hydrogenation of propene. [2]

b.iv.Determine the value of ΔG^{Θ} for the hydrogenation of propene at 298 K. [2]

b.v.At 298 K the hydrogenation of propene is a spontaneous process. Determine the temperature above which propane will spontaneously decompose into propene and hydrogen. [2]

Markscheme

a.v.amount of $\mathrm{H_2}$ remaining at equilibrium $= 1.60 - \frac{1.80}{2} = 0.70\ \mathrm{mol}$;

amount of $\mathrm{I_2}$ remaining at equilibrium $= 1.0 - \frac{1.80}{2} = 0.10\ \mathrm{mol}$;

$K_\mathrm{c} = \frac{(1.80/4.0)^2}{(0.70/4.00)\times(0.10/4.00)} / \frac{1.80^2}{0.70\times0.10}$;

$K_\mathrm{c} = \frac{(1.80)^2}{0.70\times0.10} = 46.3$;

*Award **[4]** for correct final answer.*

b.i.by definition $\Delta H_\mathrm{f}^\ominus$ of elements (in their standard states) is zero / no reaction involved / *OWTTE*;

b.ii$\Delta H = -104 - (+20.4)$;

$= -124.4\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[1 max]** for 124.4 (kJ mol^{-1}).*

*Award **[2]** for correct final answer*.

b.iii$\Delta S = 270 - (267 + 131)$;

$= -128\ (\mathrm{J\,K^{-1}mol^{-1}})$;

*Award **[1 max]** for +128 (J K^{-1}mol^{-1}).*

*Award **[2]** for correct final answer*.

b.iv$\Delta G = \Delta H - \mathrm{T}\Delta S = -124.4 - \frac{(-128\times298)}{1000}$;

$= -86.3\ \mathrm{kJ\,mol^{-1}}$;

Units needed for the mark.

*Award **[2]** for correct final answer.*

Allow ECF if only one error in first marking point.

b.v$\Delta G = \Delta H - \mathrm{T}\Delta S = 0 / \Delta H = \mathrm{T}\Delta S$;

$\mathrm{T} = \frac{-124.4}{-128/1000} = 972\ \mathrm{K}/699\ ^\circ\mathrm{C}$;

Only penalize incorrect units for T and inconsistent ΔS value once in (iv) and (v).

Examiners report

a.v.This was the most popularly answered question. Most candidates were able to give a good description of the characteristics of homogenous equilibrium, and apply Le Chatelier‟s Principle to explain the effect of catalysts and changes of temperature and pressure on the position of equilibrium and the equilibrium constant. A good majority were able to calculate the value of K_c although a significant number of candidates incorrectly used the initial rather than the equilibrium concentrations.

b.i.Although most candidates clearly understood the concept of standard *enthalpy change of formation* many were unable to explain why the value for hydrogen is zero. Many responses neglected to mention that $\mathrm{H_2}$ is an element in its standard state.

b.iiMost candidate were able to calculate ΔH and ΔS although some inverted the equation and gave a positive value instead of negative answer or confused the values for propane and propene.

b.iiiThere were some inconsistencies in the use of units and significant figures when calculating ΔG from ΔH and ΔS values although there was a significant improvement in this area compared to previous.

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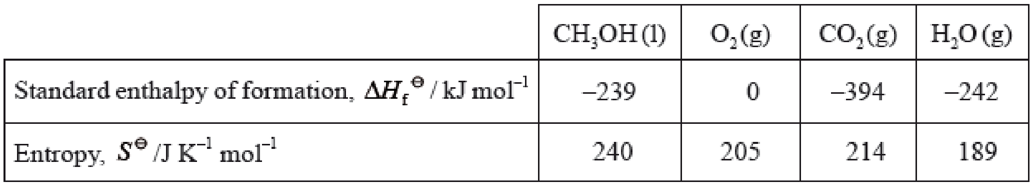
b.v.There were some inconsistencies in the use of units and significant figures when calculating ΔG from ΔH and ΔS values although there was a significant improvement in this area compared to previous. This error resulted in some very strange temperatures for the thermal decomposition of propane to propene.

Methanol is made in large quantities as it is used in the production of polymers and in fuels. The enthalpy of combustion of methanol can be determined theoretically or experimentally.

$$\mathrm{CH_3OH(l)} + 1\frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + \mathrm{2H_2O(g)}$$



	CH_3OH (l)	O_2 (g)	CO_2 (g)	H_2O (g)
Standard enthalpy of formation, $\Delta H_f^{\ominus}$ / kJ mol^{-1}	–239	0	–394	–242
Entropy, $S^{\ominus}$ /J K^{-1} mol^{-1}	240	205	214	189

d. Determine the ΔS^{Θ} for the combustion of methanol. [2]

$$\mathrm{CH_3OH(l)} + 1\frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + \mathrm{2H_2O(g)}$$

e. Using the enthalpy of combustion for methanol from Table 12 of the Data Booklet and the ΔS^{Θ} determined in part (d), calculate the standard free energy change for the combustion of methanol. [3]

f. Explain whether changing the temperature will alter the spontaneity of the reaction. [1]

Markscheme

d. $\Delta S^{\Theta} \left(= \sum S^{\Theta}_{\text{products}} - \sum S^{\Theta}_{\text{reactants}}\right) = 2 \times 189 + 214 - (240 + 1.5 \times 205)$;

$= 44.5\ \mathrm{J\,K^{-1}mol^{-1}}/0.0445\ \mathrm{kJ\,K^{-1}mol^{-1}}$

*Award **[2]** for correct final answer.*

Do not award M2 if M1 incorrect.

e. temperature of 298 K;

$\Delta G^{\Theta}_{c} = (\Delta H^{\Theta}_{c} - T\Delta S^{\Theta}_{c} =) - 726 - 298 \times 44.5 \times 10^{-3}\ (\mathrm{kJ\,mol^{-1}})/$

$= -726\,000 - 298 \times 44.5\ (\mathrm{J\,mol^{-1}})$;

$= -739\ \mathrm{kJ\,mol^{-1}}/ - 7.39 \times 10^{5}\ \mathrm{J\,mol^{-1}}$;

*Award **[3]** for correct final answer.*

f. $\Delta G_c^\ominus$ is always negative **and** temperature won't alter spontaneity of reaction;

Examiners report

d. (d) caused difficulties for candidates with the multiplication factor for the oxygen and the correct units were frequently omitted which caused problems then subsequently in part (e).

e. In (e), problems of units were widespread.

f. (f) usually was well done by the better candidates. One G2 comment also stated that it would have been better if the experimental value would have been closer to the expected value.

Enthalpy changes depend on the number and type of bonds broken and formed.

The table lists the standard enthalpies of formation, $\Delta H_f^\ominus$, for some of the species in the reaction above.

	CH_4 (g)	H_2O (g)	CO (g)	H_2 (g)
$\Delta H_f^\ominus$ / kJ mol^{-1}	−74.0	−242	−111	

Enthalpy changes depend on the number and type of bonds broken and formed.

a. Hydrogen gas can be formed industrially by the reaction of natural gas with steam. [3]

$$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$$

Determine the enthalpy change, Δ*H,* for the reaction, in kJ, using section 11 of the data booklet.

Bond enthalpy for C≡O: 1077 kJ mol^{-1}

b.i. Outline why no value is listed for H_2(g). [1]

b.ii. Determine the value of $\Delta H^\ominus$, in kJ, for the reaction using the values in the table. [1]

c. The table lists standard entropy, $S^\ominus$, values. [1]

	CH_4 (g)	H_2O (g)	CO (g)	H_2 (g)
$S^\ominus$ / J K^{-1}mol^{-1}	+186	+189	+198	+131

Calculate the standard entropy change for the reaction, $\Delta S^\ominus$, in J K^{-1}.

$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$

d. Calculate the standard free energy change, $\Delta G^\ominus$, in kJ, for the reaction at 298 K using your answer to (b)(ii). [1]

e. Determine the temperature, in K, above which the reaction becomes spontaneous. [1]

Markscheme

a. *bonds broken:* 4(C–H) + 2(H–O)/4(414) + 2(463)/2582 «kJ»

bonds made: 3(H–H) + C≡O/3(436) + 1077/2385 «kJ»

ΔH «= $\Sigma BE_{\text{(bonds broken)}} - \Sigma BE_{\text{(bonds made)}}$ = 2582 – 2385» **=** «+» 197 «kJ»

*Award **[3]** for correct final answer.*

*Award **[2 max]** for –197 «kJ».*

[3 marks]

b.i. $\Delta H_{\mathrm{f}}^{\Theta}$ for any element = 0 «by definition»

OR

no energy required to form an element «in its stable form» from itself

[1 mark]

b.ii ΔH^{Θ} « **=** $\sum \Delta H_{\mathrm{f}}^{\Theta}$ (products) – $\sum \Delta H_{\mathrm{f}}^{\Theta}$ (reactants) = –111 + 0 – [–74.0 + (–242)]»

= «+» 205 «kJ»

[1 mark]

c. «$\Delta S^{\Theta} = \Sigma S^{\Theta}_{\text{products}} - \Sigma S^{\Theta}_{\text{reactants}}$ = 198 + 3 × 131 – (186 + 189) =» «+» 216 «J K^{-1}»

[1 mark]

d. «$\Delta G^{\Theta} = \Delta H^{\Theta} - T\Delta S^{\Theta}$ = 205 kJ – 298 K × $\frac{216}{1000}$ kJ K^{-1} =» «+» 141 «kJ»

[1 mark]

e. «$\Delta H^{\Theta} = T\Delta S^{\Theta}$»

«$\mathrm{T} = \frac{\Delta H^{\Theta}}{\Delta S^{\Theta}} = \frac{205000\ \mathrm{J}}{216\ \mathrm{J\ K^{-1}}}$»

«T =» 949 «K»

*Do **not** award a mark for negative value of T.*

[1 mark]

Examiners report

a. [N/A]
b.i. [N/A]
b.ii. [N/A]
c. [N/A]
d. [N/A]
e. [N/A]

To determine the enthalpy change of combustion of methanol, $\mathrm{CH_3OH}$, 0.230 g of methanol was combusted in a spirit burner. The heat released increased the temperature of $50.0\ \mathrm{cm}^3$ of water from 24.5 °C to 45.8 °C.

Methanol can be produced according to the following equation.

$$\mathrm{CO(g) + 2H_2(g) \rightarrow CH_3OH(l)}$$

The manufacture of gaseous methanol from CO and $\mathrm{H_2}$ involves an equilibrium reaction.

$$\mathrm{CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)} \quad \Delta H^\ominus < 0$$

b.i. Calculate the standard enthalpy change of this reaction, using the values of enthalpy of combustion in Table 12 of the Data Booklet. [3]

b.ii. Calculate the standard entropy change for this reaction, $\Delta S^\ominus$, using Table 11 of the Data Booklet and given: [1]

$S^\ominus(\mathrm{CO}) = 198\ \mathrm{J\,K^{-1}mol^{-1}}$ and $S^\ominus(\mathrm{H_2}) = 131\ \mathrm{J\,K^{-1}mol^{-1}}$.

b.iii. Calculate, stating units, the standard free energy change for this reaction, $\Delta G^\ominus$, at 298 K. [2]

b.iv. Predict, with a reason, the effect of an increase in temperature on the spontaneity of this reaction. [3]

c.iii. 1.00 mol of $\mathrm{CH_3OH}$ is placed in a closed container of volume $1.00\ \mathrm{dm^3}$ until equilibrium is reached with CO and $\mathrm{H_2}$. At equilibrium 0.492 mol of $\mathrm{CH_3OH}$ are present. Calculate K_c. [3]

Markscheme

b.i. $\mathrm{CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O} \quad \Delta H_\mathrm{c}^\ominus = -726\ (\mathrm{kJ\,mol^{-1}})$

$\mathrm{CO + \frac{1}{2}O_2 \rightarrow CO_2} \quad \Delta H_\mathrm{c}^\ominus = -283\ (\mathrm{kJ\,mol^{-1}})$

$\mathrm{H_2 + \frac{1}{2}O_2 \rightarrow H_2O} \quad \Delta H_\mathrm{c}^\ominus = -286\ (\mathrm{kJ\,mol^{-1}})$

*Award **[1 max]** for three correct values.*

Mark can be implicit in calculations.

$(\Delta H_\mathrm{R}^\ominus =)\ 2(-286) + (-283) - (-726)$;

$-129\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[3]** for correct final answer.*

*Award **[2 max]** for +129 (kJ mol^{-1}).*

b.ii. $(\Delta S^\ominus = 240 - 198 - 2 \times 131 =)\ -220\ (\mathrm{J\,K^{-1}mol^{-1}})$;

b.iii. $(-129 - 298(-0.220) =)\ -63.4\ \mathrm{kJ\,mol^{-1}}$;

*Award **[1]** for correct numerical answer and **[1]** for correct unit if the conversion has been made from J to kJ for $\Delta S^\ominus$.*

b.iv. not spontaneous at high temperature;

$T\Delta S^\ominus < \Delta H^\ominus$ **and** $\Delta G^\ominus$ positive;

c.iii. $n(\mathrm{CO}) = 0.508\ (\mathrm{mol})$;

$n(\mathrm{H_2}) = 2 \times 0.508\ (\mathrm{mol})$;

$K_\mathrm{c} \left(= \frac{0.492}{0.508 \times (2 \times 0.508)^2}\right) = 0.938$;

Accept answer in range between 0.930 and 0.940.

*Award **[3]** for correct final answer.*

*Award **[2]** for K_c = 1.066 if (c)(ii) is correct.*

Examiners report

b.i. In (i), the most common error was $+129\ \mathrm{kJ\,mol^{-1}}$ but in (ii) the answer was often correct.

b.ii. In (i), the most common error was $+129\ \mathrm{kJ\,mol^{-1}}$ but in (ii) the answer was often correct.

b.iii. Units tended to get muddled in (iii) and many marks were awarded as “error carried forward”.

b.iv. Few were able to explain the ΔH and $T\Delta S$ relationship in detail in (iv).

c.iii. Equilibrium was well understood in general with many candidates gaining one of the two available marks. “Equal rates” was more often given than the constancy of macroscopic properties for the second mark. The K_c expression was given correctly by the vast majority of candidates (including the correct brackets and indices) but many had difficulty with the equilibrium concentrations in (iii).

The changes in equilibrium position were well understood for the most part although if a mark were to be lost it was for not mentioning the number of moles of gas.

Consider the following reaction.

$$2\mathrm{CH_3OH(g)} + \mathrm{H_2(g)} \rightarrow \mathrm{C_2H_6(g)} + 2\mathrm{H_2O(g)}$$

a. The standard enthalpy change of formation for $\mathrm{CH_3OH(g)}$ at 298 K is $-201\ \mathrm{kJ\,mol^{-1}}$ and for $\mathrm{H_2O(g)}$ is $-242\ \mathrm{kJ\,mol^{-1}}$. Using information from Table 11 of the Data Booklet, determine the enthalpy change for this reaction. [2]

b. The standard entropy for $\mathrm{CH_3OH(g)}$ at 298 K is $238\ \mathrm{J\,K^{-1}mol^{-1}}$, for $\mathrm{H_2(g)}$ is $131\ \mathrm{J\,K^{-1}mol^{-1}}$ and for $\mathrm{H_2O(g)}$ is $189\ \mathrm{J\,K^{-1}mol^{-1}}$. Using information from Table 11 of the Data Booklet, determine the entropy change for this reaction. [2]

c. Calculate the standard change in free energy, at 298 K, for the reaction and deduce whether the reaction is spontaneous or non-spontaneous. [3]

Markscheme

a. $\Delta H^{\ominus}_{\mathrm{reaction}} = \Sigma\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{products}) - \Sigma\Delta H^{\ominus}_{\mathrm{f}}(\mathrm{reactants})$

$= [(1)(-85) + (2)(-242)] - [(2)(-201)];$

$= -167\ (\mathrm{kJ/kJ\,mol^{-1}});$

*Award **[1]** for (+)167.*

b. $\Delta S^{\ominus}_{\mathrm{reaction}} = \Sigma S^{\ominus}(\mathrm{products}) - \Sigma S^{\ominus}(\mathrm{reactants})$

$= [(1)(230) + (2)(189)] - [(2)(238) + (1)(131)];$

$= 1\ (\mathrm{J\,K^{-1}/J\,K^{-1}mol^{-1}});$

c. $\Delta G^{\ominus}_{\mathrm{reaction}} = (\Delta H^{\ominus} - T\Delta S^{\ominus}) = (-167) - (298)(0.001);$

*Award **[1]** for correct substitution of values.*

$= -167\ \mathrm{kJ}/-167000\ \mathrm{J};$

Units needed for mark in (c) only.

Accept –167 kJ mol^{-1} or –167000 J mol^{-1}.

spontaneous;

Award marks for final correct answers throughout in each of (a), (b) and (c).

Examiners report

a. In (a) the most common mistakes included: failure to consider the correct amount of moles of products/reactants, incorrect identification of values or wrong use of convention. It also should be noted that the correct units of ΔH^{Θ} here in the answer will be kJ, since n is used in the equation, as explained in previous subject reports.

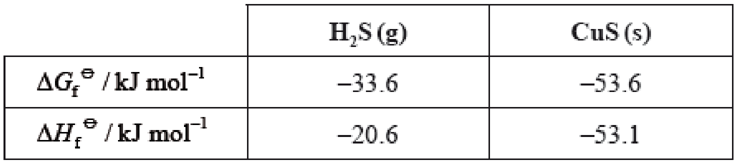
b. Part (b) was another question where the vast majority of candidates scored full marks.

c. Free energy calculations (c) continues to prove problematic for many candidates. Candidates very often lost the first mark due to wrong use of units. ECF allowed them to score the second. In contrast most candidates showed a clear understanding of the relationship between the sign of ΔG^{Θ} and spontaneity.

Consider the reaction:

$$\mathrm{CuS(s) + H_2(g) \rightarrow Cu(s) + H_2S(g)}$$

Given:



	H_2S (g)	CuS (s)
ΔG_f^{Θ} / kJ mol^{-1}	−33.6	−53.6
ΔH_f^{Θ} / kJ mol^{-1}	−20.6	−53.1

a. Deduce and explain the sign of the entropy change for the following reaction. [2]

$$\mathrm{CO(g) + 2H_2(g) \rightarrow CH_3OH(l)}$$

b.i. Suggest why the ΔH_f^{Θ} values for $H_2(g)$ and Cu(s) are not given in the table. [1]

b.ii. Determine the standard enthalpy change at 298 K for the reaction. [1]

b.iii. Determine the standard free energy change at 298 K for the reaction. Deduce whether or not the reaction is spontaneous at this temperature. [2]

b.iv. Determine the standard entropy change at 298 K for the reaction. [1]

b.v. Estimate the temperature, in K, at which the standard change in free energy equals zero. You should assume that the values of the standard enthalpy and entropy changes are not affected by the change in temperature. [1]

Markscheme

a. negative;

liquid more ordered than gaseous phase or *vice-versa / OWTTE*;

b.i. $\Delta H_f^\ominus$ of an element (in its most stable state) is zero (since formation of an element from itself is not a reaction) / *OWTTE*;

Do not allow an answer such as because they are elements.

b.ii $\Delta H^\ominus (= (1)(-20.6) - (1)(-53.1)) = 32.5\ (\text{kJ mol}^{-1})/32500\ (\text{J mol}^{-1})$;

Allow 32.5 (kJ) or 3.25 × 10^4 (J).

b.iii $\Delta G^\ominus (= (1)(-33.6) - (1)(-53.6)) = 20.0\ (\text{kJ mol}^{-1})/20000\ (\text{J mol}^{-1})$;

Allow 20.0 (kJ) or 2.00 × 10^4 (J).

non-spontaneous;

b.iv $\Delta S^\ominus (= (\Delta H^\ominus - \Delta G^\ominus)/T = (32.5 - 20.0)(1000)/298) = 41.9\ (\text{J K}^{-1}\text{mol}^{-1})/$

$4.19 \times 10^{-2}\ (\text{kJ K}^{-1}\text{mol}^{-1})$;

Allow 41.9 (J K^{-1}) or 4.19 × 10–2 (kJ K^{-1}).

b.v $T\ (= \Delta H/\Delta S = (32.5 \times 1000)/(41.9)) = 776\ (\text{K})$;

Examiners report

a. The negative nature of the change gained a mark, but the explanations sometimes lacked clarity and states often were not referred to.

b.i. In (i), often there was no mention of element.

b.ii (ii) to (iv) was often very well done, though as usual some candidates struggled with units.

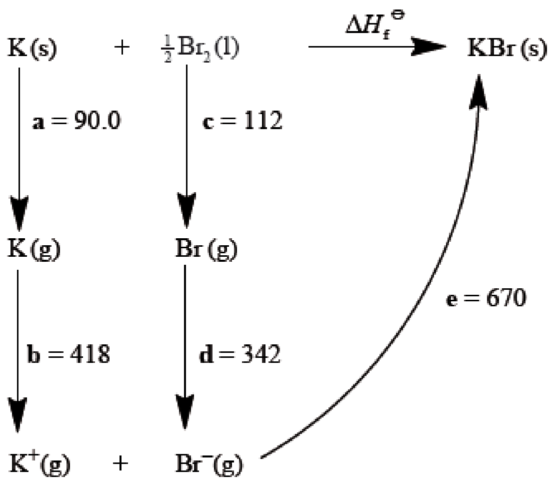
b.iii (ii) to (iv) was often very well done, though as usual some candidates struggled with units.

b.iv (ii) to (iv) was often very well done, though as usual some candidates struggled with units.

b.v. [N/A]

Draw the Lewis structures, state the shape and predict the bond angles for the following species.

Consider the following Born-Haber cycle:



The magnitudes for each of the enthalpy changes (**a** to **e**) are given in kJ mol^{-1} but their signs (+ or –) have been omitted.

a.i. $\mathrm{PCl_3}$ [3]

a.ii. $\mathrm{NH_2^-}$ [3]

a.iii. $\mathrm{XeF_4}$ [3]

b.i. State the names for the enthalpy changes **c** and **d**. [2]

b.ii. Deduce which **two** of the enthalpy changes **a** to **e** have negative signs. [1]

b.iii. Determine the value for the enthalpy of formation of potassium bromide. [2]

b.iv. Explain why the quantitative value for the lattice enthalpy of calcium bromide is larger than the value for the lattice enthalpy of potassium bromide. [2]

c.i. Compare the formation of a sigma (σ) and a pi (π) bond between two carbon atoms in a molecule. [2]

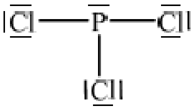
c.ii. Identify how many sigma and pi bonds are present in propene, $\mathrm{C_3H_6}$. [2]

c.iii. Deduce all the bond angles present in propene. [2]

c.iv. Explain how the concept of hybridization can be used to explain the bonding in the triple bond present in propyne. [3]

Markscheme

a.i.



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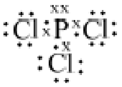
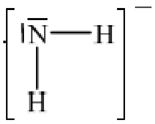


;

trigonal pyramid;

in the range of 100–108°;

a.ii.



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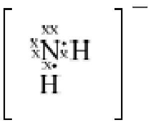


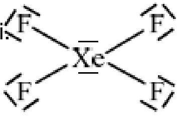
;

Must include minus sign for the mark.

bent/V–shaped;

in the range of 100–106°;

a.iii.



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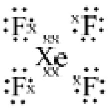

;

square planar;

90°;

Penalize once only if electron pairs are missed off outer atoms.

b.i. **c**: atomization (enthalpy);

d: electron affinity;

b.ii. **d** and **e**;

b.iii. $\Delta H_\mathrm{f} = 90.0 + 418 + 112 + (-342) + (-670)$;

$= - 392{\text{ kJ}}\,{\text{mo}}{{\text{l}}^{ - 1}}$;

b.iv. Ca^{2+} is smaller than K^{+} **and** Ca^{2+} has more charge than K^{+} / Ca^{2+} has a greater charge density;

so the attractive forces between the ions are stronger;

Do not accept 'stronger ionic bonds'

*Award **[1 max]** if reference is made to atoms or molecules instead of ions.*

c.i. sigma bonds are formed by end on/axial overlap of orbitals with electron density between the two atoms/nuclei;

pi bonds are formed by sideways overlap of parallel p orbitals with electron density above **and** below internuclear axis/σ bond;

Accept suitably annotated diagrams

c.ii. 8 sigma/σ ;

1 pi/π ;

c.iii. 109°/109.5°;

120°;

c.iv. sp hybridization;

1 sigma and 2 pi;

sigma bond formed by overlap between the two sp hybrid orbitals (on each of the two carbon atoms) / pi bonds formed by overlap between remaining p orbitals (on each of the two carbon atoms) / diagram showing 2 sp hybrid orbitals and 2 p orbitals;

Examiners report

a.i. This question was the most popular of the Section B questions. Part (a) was generally well answered with many candidates drawing clear Lewis structures and applying their knowledge of VSEPR theory well. Common errors included the omission of lone electron pairs on outer atoms, and the omission of a bracket and charge on the ion. Incorrect angular values were common. Some candidates described shapes and bond angles in terms of the 'parent shape'. Good candidates explained the answers well and scored full marks. Weaker candidates simply wrote two answers; for example, 'tetrahedral bent' and could not be awarded marks.

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b.i. In part (b) many candidates incorrectly identified the process converting liquid bromine molecules to gaseous bromine atoms as vaporization.

b.ii.Deducing the enthalpy changes with negative signs proved challenging for many although, with follow through marks credit was earned for the calculation of the enthalpy of formation of potassium bromide.

b.iii.Some teachers commented on the G2 forms that the energy cycle diagram was strange, however, the stages of the Born-Haber cycle were clearly given and candidates should be familiar with those.

b.iv.Very few candidates could explain why calcium bromide has a larger lattice enthalpy than potassium bromide. Many referred to atoms instead of ions, and tried to answer this in terms of the electronegativity of the metals.

c.i. Part (c) was answered well by some candidates who produced clear and well annotated diagrams as part of their answers. Many candidates however omitted mention of orbitals when trying to describe the formation of sigma and pi bonds or to explain hybridization. There were many diagrams which had no annotations and were difficult to interpret.

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The electron configuration of chromium can be expressed as $[\mathrm{Ar}]4\mathrm{s}^{\mathrm{x}}3\mathrm{d}^{\mathrm{y}}$.

Hydrogen and nitrogen(II) oxide react according to the following equation.

$$2\mathrm{H_2(g)} + 2\mathrm{NO(g)} \rightleftharpoons \mathrm{N_2(g)} + 2\mathrm{H_2O(g)}$$

At time = t seconds, the rate of the reaction is

$$\mathrm{rate} = k[\mathrm{H_2(g)}][\mathrm{NO(g)}]^2$$

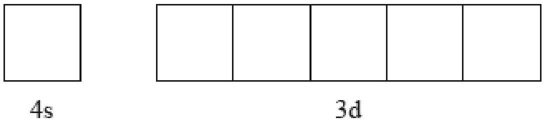
When concentrated hydrochloric acid is added to a solution containing hydrated copper(II) ions, the colour of the solution changes from light blue to green. The equation for the reaction is:

$$[\mathrm{Cu(H_2O)_6}]^{2+}(\mathrm{aq}) + 4\mathrm{Cl^-(aq)} \rightarrow [\mathrm{CuCl_4}]^{2-}(\mathrm{aq}) + 6\mathrm{H_2O(l)}$$

a.i. Explain what the square brackets around argon, [Ar], represent. [1]

a.ii.State the values of x and y. [1]

a.iii. Annotate the diagram below showing the 4s and 3d orbitals for a chromium atom using an arrow, ↿ and ⇂, to represent a spinning electron. [1]



b.i. Explain precisely what the square brackets around nitrogen(II) oxide, [NO(g)], represent in this context. [1]

b.ii. Deduce the units for the rate constant k. [1]

c.i. Explain what the square brackets around the copper containing species represent. [1]

c.ii. Explain why the $[\text{Cu(H}_2\text{O)}_6]^{2+}$ ion is coloured and why the $[\text{CuCl}_4]^{2-}$ ion has a different colour. [2]

d. Some words used in chemistry can have a specific meaning which is different to their meaning in everyday English. [1]

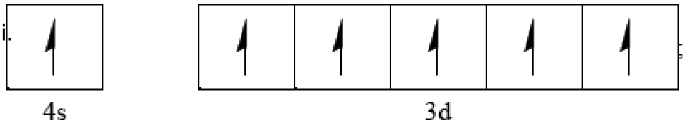
State what the term *spontaneous* means when used in a chemistry context.

Markscheme

a.i. the electron configuration (of argon) / $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6$;

a.ii. $x = 1$ **and** $y = 5$;

a.iii.



Accept all six arrows pointing down rather than up.

b.i. the concentration (of nitrogen(II) oxide);

*Award **[0]** if reference made to equilibrium.*

b.ii. $\text{mol}^{-2}\text{dm}^{6}\text{s}^{-1}/\text{dm}^{6}\text{mol}^{-2}\text{s}^{-1}$;

Accept (mol^{-1} dm^3)2s^{-1}.

c.i. complex (ion) / the charge is delocalized over all that is contained in the brackets;

c.ii. colour is due to energy being absorbed when electrons are promoted within the split d orbitals;

the colour observed is the complementary colour to the energy absorbed / *OWTTE*;

Accept either answer for first mark.

changing the ligand / coordination number / geometry changes the amount the d orbitals are split/energy difference between the d orbitals / *OWTTE*;

d. the reaction gives out (Gibbs Free) energy that can do work;

ΔG for the reaction has a negative value;

a reaction that occurs without adding energy (beyond that required to overcome energy barrier);

Examiners report

a.i. Most candidates were familiar with the use of square brackets to represent noble gas electron configurations and concentrations in rate expressions and it was encouraging to see candidates give a correct orbital diagram with the d electrons unpaired.

a.ii. A significant number of students were unaware of the exceptional nature of the electron configuration for chromium.

a.iii. A significant number of students were unaware of the exceptional nature of the electron configuration for chromium, but were able to gain the mark in (a) (iii) with ecf.

b.i. The understanding of the use of square bracket to represent complex ions was limited.

b.ii. Many candidates omitted the s^{-1} in the units for the rate constant.

c.i. [N/A]

c.ii. (c) (ii) proved to be more challenging with many candidates mixing up sub-shells with orbitals and absorption with emission spectra.

d. Many candidates were familiar with the use of the term *spontaneous* when used in a chemical context.

Hydrazine, N_2H_4, is a valuable rocket fuel.

The equation for the reaction between hydrazine and oxygen is given below.

$$\mathrm{N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)}$$

The reaction between $\mathrm{N_2H_4(aq)}$ and $\mathrm{HCl(aq)}$ can be represented by the following equation.

$$\mathrm{N_2H_4(aq) + 2HCl(aq) \rightarrow N_2H_6^{2+}(aq) + 2Cl^-(aq)}$$

a. (i) Draw the Lewis (electron dot) structure for N_2H_4 showing all valence electrons. [4]

(ii) State and explain the H–N–H bond angle in hydrazine.

b. Hydrazine and ethene, C_2H_4, are hydrides of adjacent elements in the periodic table. The boiling point of hydrazine is much higher than that of ethene. Explain this difference in terms of the intermolecular forces in each compound. [2]

c. (i) The enthalpy change of formation, ΔH_f^Θ, of liquid hydrazine is $50.6\ \mathrm{kJ\ mol^{-1}}$. Use this value, together with data from Table 12 of the Data Booklet, to calculate the enthalpy change for this reaction. [16]

(ii) Use the bond enthalpy values from Table 10 of the Data Booklet to determine the enthalpy change for this reaction.

(iii) Identify the calculation that produces the most accurate value for the enthalpy change for the reaction given and explain your choice.

(iv) Calculate ΔS^Θ for the reaction using the data below and comment on its magnitude.

Substance	$S^\ominus$ / J K^{-1} mol^{-1}
$O_2(g)$	205
$N_2(g)$	191
$H_2O(l)$	69.9
$N_2H_4(l)$	121

(v) Calculate ΔG^Θ for the reaction at 298 K.

(vi) Predict, giving a reason, the spontaneity of the reaction above at both high and low temperatures.

d. The reaction between $\mathrm{N_2H_4(aq)}$ and HCl(aq) can be represented by the following equation. [3]

$$\mathrm{N_2H_4(aq) + 2HCl(aq) \rightarrow N_2H_6^{2+}(aq) + 2Cl^-(aq)}$$

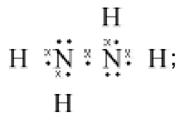
(i) Identify the type of reaction that occurs.

(ii) Predict the value of the H–N–H bond angle in $\mathrm{N_2H_6^{2+}}$.

(iii) Suggest the type of hybridization shown by the nitrogen atoms in $\mathrm{N_2H_6^{2+}}$.

Markscheme

a.

(i) 

Accept x's, dots or lines for electron pairs

(ii) H–N–H $<$ 109 / any angle between 104° and 109°;

due to four centres of electron charge / four electron pairs (one of which is a lone $\mathrm{e^-}$ pair);

extra repulsion due to lone electron pairs;

Do not allow ECF for wrong Lewis structures.

b. weaker van der Waals'/London/dispersion/intermolecular forces in ethene;

stronger (intermolecular) hydrogen bonding in hydrazine;

*If no comparison between strengths then **[1 max]**.*

c. (i) $\Delta H_\mathrm{r}^\Theta = \Sigma\Delta H_\mathrm{f}^\Theta \text{ products} - \Sigma\Delta H_\mathrm{f}^\Theta \text{ reactants};$

Can be implied by working.

$\Delta H_\mathrm{f}^\Theta(\mathrm{H_2O(l)}) = -286\ (\mathrm{kJ});$

$\Delta H_\mathrm{r}^\Theta = 2(-286) - 50.6 = -622.6\ (\mathrm{kJ});$

(ii) bonds broken: 4N–H, N–N, O=O / $+2220\ (\mathrm{kJ\,mol^{-1}})$;

bonds formed: N≡N, 4O-H / $-2801\ (\mathrm{kJ\,mol^{-1}})$;

$-581\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[3]** for correct final answer*.

(iii) value based on ΔH_f more accurate;

ΔH_f accurate for compounds in reaction;

bond energy calculation assumes average bond energies;

(bond energy calculation) only applies to gaseous states / ignores intermolecular bonds;

(iv) $\Delta S^{\Theta} = \Sigma S^{\Theta}\ (\text{products}) - \Sigma S^{\Theta}\ (\text{reactants})$;

Can be implied by working.

$= 191 + (2 \times 69.9) - 205 - 121 = +4.8\ (\text{J K}^{-1}\text{mol}^{-1})$;

small value since number of mol of g on both sides the same;

(v) $\Delta G^{\Theta} = -622.6 - 298(0.0048)$;

$= -624.0\ (\text{kJ mol}^{-1})$;

Allow 623.9 to 624.1.

(vi) all reactions are spontaneous;

ΔG is negative (at high temperatures and low temperatures);

d. (i) acid-base/neutralization;

(ii) 109°/109.5°;

(iii) sp^3;

No ECF if bond angle incorrect in (ii).

Examiners report

a. The Lewis structure for hydrazine proved to be difficult for some in (a). Incorrect answers had double bonds appearing between the two nitrogen atoms or lone pairs missing. Those who could draw the correct structure in (i) gave the correct bond angle, but the explanation was often incomplete. Few mentioned either the four electron domains around the central atom or the extra repulsion of the lone pair.

b. In part (b) most candidates knew that hydrogen bonding was present in hydrazine and Van der Waals" forces in ethene but failed to give a comparison of the relative strength of the intermolecular forces.

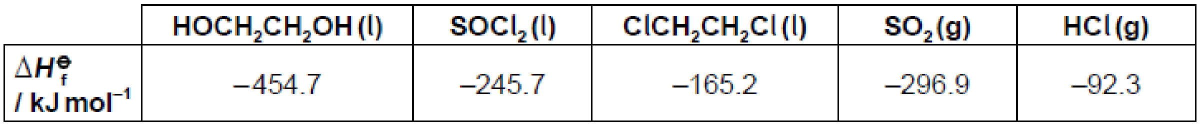
c. Some candidates struggled to calculate the enthalpy changes from enthalpy changes of formation in (c) (i) as they were unable to relate the enthalpy change of combustion of hydrogen to the enthalpy change of formation of water.

d. The bond energy and entropy calculations were more successful with many candidates benefitting from ECF from their incorrect Lewis structures in (a). It was encouraging to see many correct unit conversions for the calculation of ΔG. A number of candidates incorrectly described the combination of hydrazine and hydrochloric acid as a redox reaction, but many were able to identify the bond angle and hybridization in $\mathrm{N_2H_6^{2+}}$.

Ethane-1,2-diol, $HOCH_2CH_2OH$, reacts with thionyl chloride, $SOCl_2$, according to the reaction below.

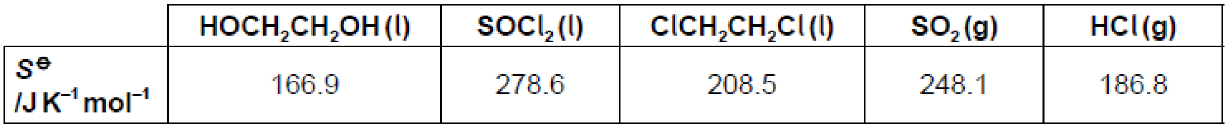
$$HOCH_2CH_2OH\ (l) + 2SOCl_2\ (l) \rightarrow ClCH_2CH_2Cl\ (l) + 2SO_2\ (g) + 2HCl\ (g)$$

a. Calculate the standard enthalpy change for this reaction using the following data. [2]



	$HOCH_2CH_2OH$ (l)	$SOCl_2$ (l)	$ClCH_2CH_2Cl$ (l)	SO_2 (g)	HCl (g)
ΔH_f^{Θ} / kJ mol^{-1}	–454.7	–245.7	–165.2	–296.9	–92.3

b. Calculate the standard entropy change for this reaction using the following data. [1]



	$HOCH_2CH_2OH(l)$	$SOCl_2(l)$	$ClCH_2CH_2Cl(l)$	$SO_2(g)$	$HCl(g)$
$S^{\ominus}$ / $J\ K^{-1}\ mol^{-1}$	166.9	278.6	208.5	248.1	186.8

c. The standard free energy change, ΔG^{θ}, for the above reaction is –103 kJ mol^{-1} at 298 K. [2]

Suggest why ΔG^{θ} has a large negative value considering the sign of ΔH^{θ} in part (a).

Markscheme

a. $\Delta H^{\theta} = [-165.2 + 2(-296.9) + 2(-92.3)] - [-454.7 + 2(-245.7)]$

«ΔH^{θ} = +»2.5 «kJ»

*Award **[2]** for correct final answer.*

*Award **[1]** for –2.5 «kJ».*

*Do **not** accept ECF for M2 if more than one error in M1.*

b. «$\Delta S^{\theta} = [208.5 + 2(248.1) + 2(186.8)] - [166.9 + 2(278.6)]$»

«ΔS^{θ} = +» 354.2 «J K^{-1} mol^{-1}»

c. «3 moles of» liquid to «4 moles of» gas

OR

«large» positive ΔS

OR

«large» increase in entropy

$T\Delta S > \Delta H$ «at the reaction temperature»

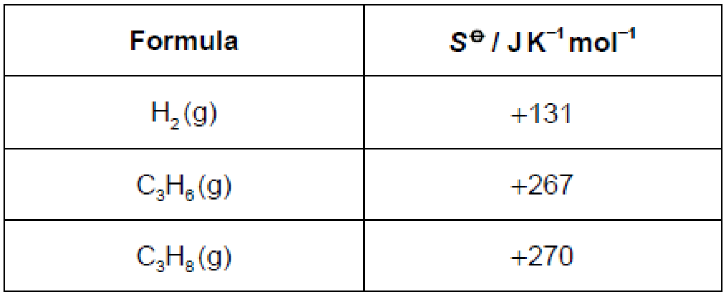
Examiners report

a. [N/A]
b. [N/A]
c. [N/A]

The Bombardier beetle sprays a mixture of hydroquinone and hydrogen peroxide to fight off predators. The reaction equation to produce the spray can be written as:

$C_6H_4(OH)_2(aq) + H_2O_2(aq)$ → $C_6H_4O_2(aq) + 2H_2O(l)$
hydroquinone quinone

b.i. Hydrogenation of propene produces propane. Calculate the standard entropy change, ΔS^{θ}, for the hydrogenation of propene. [2]



Formula	$S^{\ominus}$ / J K^{-1} mol^{-1}
$H_2(g)$	+131
$C_3H_6(g)$	+267
$C_3H_8(g)$	+270

b.ii.The standard enthalpy change, ΔH^{θ}, for the hydrogenation of propene is –124.4 kJ mol^{-1}. Predict the temperature above which the hydrogenation reaction is not spontaneous. [2]

Markscheme

b.i.«ΔS^{θ} =» 270 «J K^{-1} mol^{-1}» – 267 «J K^{-1} mol^{-1}» – 131 «J K^{-1} mol^{-1}»

«ΔS^{θ} =» –128 «J K^{-1} mol^{-1}»

*Award **[2]** for correct final answer.*

[2 marks]

b.ii.«non spontaneous if» $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta} > 0$

OR

$\Delta H^{\theta} > T\Delta S^{\theta}$

«T above» $\frac{-124.4 \ll \text{kJ mol}^{-1} \gg}{-0.128 \ll \text{kJ K}^{-1}\ \text{mol}^{-1} \gg}$ =» 972 «K»

*Award **[2]** for correct final answer.*

Accept 699 °C.

Do not award M2 for any negative T value.

[2 marks]

Examiners report

b.i. [N/A]

b.ii. [N/A]

Millerite, a nickel sulfide mineral, is an important source of nickel. The first step in extracting nickel is to roast the ore in air.

The reaction for the formation of liquid tetracarbonylnickel is shown below:

$$\mathrm{Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(l)}$$

a. Formulate an equation for the oxidation of nickel(II) sulfide to nickel(II) oxide. [1]

b. The nickel obtained from another ore, nickeliferous limonite, is contaminated with iron. Both nickel and iron react with carbon monoxide gas to form gaseous complexes, tetracarbonylnickel, $\mathrm{Ni(CO)_4(g)}$, and pentacarbonyliron, $\mathrm{Fe(CO)_5(g)}$. Suggest why the nickel can be separated from the iron successfully using carbon monoxide. [1]

c.i. Calculate the standard entropy change, ΔS^{θ}, of the reaction, in $\mathrm{J\,K^{-1}}$, using the values given. [2]

	$S^{\ominus}$ / J K^{-1} mol^{-1}
Ni(s)	29.9
CO(g)	197.6
$\mathrm{Ni(CO)_4(l)}$	313.4

c.ii. Calculate a value for ΔH^{θ} in kJ. [1]

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
CO(g)	−110.5
$\mathrm{Ni(CO)_4(l)}$	−633.0

c.iii Use your answers to (c)(i) and (c)(ii), to determine the temperature, in °C, at which the decomposition of liquid tetracarbonylnickel to nickel and carbon monoxide becomes favourable. [3]

(If you did not get answers to (c)(i) and (c)(ii), use $-500\ \mathrm{J\,K^{-1}}$ and $-200\ \mathrm{kJ}$ respectively but these are not the correct answers.)

d. Suggest why experiments involving tetracarbonylnickel are very hazardous. [1]

Markscheme

a. $\mathrm{2NiS(s) + 3O_2(g) \rightarrow 2NiO(s) + 2SO_2(g)}$

[1 mark]

b. formation of «gaseous» pentacarbonyliron is slower

OR

«gaseous» complexes form at different rates

OR

gases have different rates of diffusion «due to difference in masses»

OR

difference in thermal stability of «gaseous» complexes

OR

difference in boiling points of «gaseous» complexes

OR

difference in solubility of «gaseous» complexes

OR

difference in surface affinity «onto solid absorbent»

OR

difference in chemical properties of «gaseous» complexes

Accept any other valid answer.

[1 mark]

c.i. $\sum S^{\theta}_{\mathrm{RHS}} = 313.4 \ll \mathrm{J\,K^{-1}} \gg$

AND

$\sum S^{\theta}_{\mathrm{LHS}} = \ll (4 \times 197.6) + 29.9\ \mathrm{J\,K^{-1}} = \gg 820.3 \ll \mathrm{J\,K^{-1}} \gg$

$\Delta S^{\theta} \ll = \sum S^{\theta}_{\mathrm{RHS}} - \sum S^{\theta}_{\mathrm{LHS}} = 313.4 - 820.3 \gg = -506.9 \ll \mathrm{J\,K^{-1}} \gg$

Award [2] for correct final answer.

[2 marks]

c.ii. $\Delta H^{\theta} \ll = -633.0 - 4 \times (-110.5) \gg = -191 \ll kJ \gg$

[1 mark]

c.iii «when» $\Delta G = 0$ «forward and backward reactions are equally favourable»

«when $\Delta G = 0, \mathrm{T} = \frac{\Delta H}{\Delta S}$», $\mathrm{T} = \ll \frac{191\ \mathrm{kJ}}{0.5069\ \mathrm{kJ\,K^{-1}}} = \gg 377 \ll \mathrm{K} \gg$

«temperature =» 104 «°C»

Award [3] for correct final answer. Use of –500 J K^{-1} and –200 kJ gives 127 °C.

Award [2 max] for T < 104 «°C».

Accept ΔG < 0 and T > 104 «°C».

[3 marks]

d. CO is toxic/poisonous

OR

$Ni(CO)_4$ decomposition deposits nickel in the lungs

OR

tetracarbonylnickel is toxic/poisonous

OR

tetracarbonylnickel is highly flammable «auto-ignition temperature of 60 °C»

[1 mark]

Examiners report

a. [N/A]

b. [N/A]

c.i. [N/A]

[N/A]

c.iii.[N/A]
d. [N/A]

This question is about ethene, C_2H_4, and ethyne, C_2H_2.

a.i. Ethyne, like ethene, undergoes hydrogenation to form ethane. State the conditions required. [2]

a.ii. Outline the formation of polyethene from ethene by drawing three repeating units of the polymer. [1]

b. Ethyne reacts with chlorine in a similar way to ethene. Formulate equations for the following reactions. [2]

One mole of ethyne reacts with one mole of chlorine:

. . . .

. . . .

One mole of benzene reacts with one mole of chlorine:

. . . .

. . . .

c.i. Under certain conditions, ethyne can be converted to benzene. [2]

Determine the standard enthalpy change, $\Delta H^{\ominus}$, for the reaction stated, using section 11 of the data booklet.

$$3C_2H_2(g) \rightarrow C_6H_6(g)$$

c.ii. Determine the standard enthalpy change, $\Delta H^{\ominus}$, for the following similar reaction, using ΔH_f values in section 12 of the data booklet. [2]

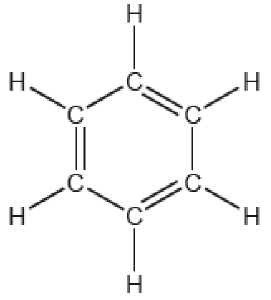
$$3C_2H_2(g) \rightarrow C_6H_6(l)$$

c.iii. Explain, giving two reasons, the difference in the values for (c)(i) and (ii). If you did not obtain answers, use −475 kJ for (i) and −600 kJ for (ii). [2]

c.iv. Calculate the standard entropy change, $\Delta S^{\ominus}$, in $J\ K^{-1}$, for the reaction in (ii) using section 12 of the data booklet. [1]

c.v. Determine, showing your working, the spontaneity of the reaction in (ii) at 25 °C. [3]

d. One possible Lewis structure for benzene is shown. [1]



State one piece of physical evidence that this structure is **incorrect**.

Markscheme

a.i. nickel/Ni «catalyst»

high pressure

OR

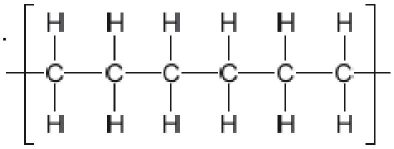
heat

Accept these other catalysts: Pt, Pd, Ir, Rh, Co, Ti.

Accept "high temperature" or a stated temperature such as "150 °C".

[2 marks]

a.ii.



Ignore square brackets and "n".

Connecting line at end of carbons must be shown.

[1 mark]

b. *ethyne:* $C_2H_2 + Cl_2 \rightarrow CHClCHCl$

benzene: $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

Accept "$C_2H_2Cl_2$".

[2 marks]

c.i. $\Delta H^{\ominus}$ = bonds broken – bonds formed

«$\Delta H^{\ominus} = 3(C{\equiv}C) - 6(C\overset{\cdots}{—}C)_{benzene}$ / $3 \times 839 - 6 \times 507$ / $2517 - 3042$ =» –525 «kJ»

*Award **[2]** for correct final answer.*

*Award **[1 max]** for "+525 «kJ»".*

*Award **[1 max]** for:*

«$\Delta H^{\ominus} = 3(C{\equiv}C) - 3(C–C) - 3(C{=}C)$ / $3 \times 839 - 3 \times 346 - 3 \times 614$ / $2517 - 2880$ =» –363 «kJ».

[2 marks]

c.ii $\Delta H^{\ominus} = \Sigma\Delta H_f$ (products) – $\Sigma\Delta H_f$ (reactants)

«$\Delta H^{\ominus}$ = 49 kJ – 3 × 228 kJ =» –635 «kJ»

*Award **[2]** for correct final answer.*

*Award **[1 max]** for "+635 «kJ»".*

[2 marks]

c.iii ΔH_f values are specific to the compound

OR

bond enthalpy values are averages «from many different compounds»

condensation from gas to liquid is exothermic

Accept "benzene is in two different states «one liquid the other gas»" for M2.

[2 marks]

c.iv. «$\Delta S^\ominus$ = 173 – 3 × 201 =» –430 «J K^{-1}»

[1 mark]

c.v. T = «25 + 273 =» 298 «K»

$\Delta G^\ominus$ «= –635 kJ – 298 K × (–0.430 kJ K^{-1})» = –507 kJ

$\Delta G^\ominus$ < 0 ***AND*** spontaneous

$\Delta G^\ominus$ < 0 may be inferred from the calculation.

[3 marks]

d. equal C–C bond «lengths/strengths»

OR

regular hexagon

OR

«all» C–C have bond order of 1.5

OR

«all» C–C intermediate between single and double bonds

Accept "all C–C–C bond angles are equal".

[1 mark]

Examiners report

a.i. [N/A]
a.ii. [N/A]
b. [N/A]
c.i. [N/A]
c.ii. [N/A]
c.iii. [N/A]
c.iv. [N/A]
c.v. [N/A]
d. [N/A]

Vanadium has a number of different oxidation states.

Electrode potentials for the reactions of vanadium and other species are shown below.

$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	−0.26 V
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34 V
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.0 V

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76 V
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13 V
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17 V
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80 V
$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	+1.36 V

a. Determine the oxidation state of vanadium in each of the following species. [2]

V_2O_5:

. . . .

VO^{2+}:

. . . .

b.i. Identify, from the table, a non-vanadium species that can reduce VO^{2+}(aq) to V^{3+}(aq) but no further. [1]

b.ii. Identify, from the table, a non-vanadium species that could convert $VO_2^+(aq)$ to V^{2+}(aq). [1]

c.i. Formulate an equation for the reaction between VO^{2+}(aq) and V^{2+}(aq) in acidic solution to form V^{3+}(aq). [1]

c.ii. Comment on the spontaneity of this reaction by calculating a value for ΔG^{θ} using the data given in (b) and in section 1 of the data booklet. [3]

Markscheme

a. $V_2O_5: \ +5$

$VO^{2+}: \ +4$

*Do **not** penalize incorrect notation twice.*

[2 marks]

b.i. H_2SO_3(aq)

OR

Pb(s)

[1 mark]

b.ii Zn(s)

[1 mark]

c.i. $\mathrm{VO^{2+}(aq) + V^{2+}(aq) + 2H^{+}(aq) \rightarrow 2V^{3+}(aq) + H_2O(l)}$

Accept equilibrium sign.

[1 mark]

c.ii. $E^{\theta} \ll = +0.34\ \mathrm{V} - (-0.26\ \mathrm{V}) \gg = +0.60\ \ll \mathrm{V} \gg$

$\Delta G^{\theta} = \ll -nFE^{\theta} = -9.65 \times 10^{4}\ \mathrm{C\,mol^{-1}} \times 0.60\ \mathrm{J\,C^{-1}} = \gg -57\,900\ \ll \mathrm{J\,mol^{-1}} \gg / -57.9\ \ll \mathrm{kJ\,mol^{-1}} \gg$

spontaneous as ΔG^{θ} is negative

*Do **not** award M3 as a stand-alone answer.*

Accept "spontaneous" for M3 if answer given for M2 is negative.

Accept "spontaneous as E^{θ} is positive" for M3.

[3 marks]

Examiners report

a. [N/A]
b.i. [N/A]
b.ii. [N/A]
c.i. [N/A]
c.ii. [N/A]

The reaction between ethene and steam is used in the industrial production of ethanol.

$$\mathrm{C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)}$$

The enthalpy change of the reaction can be calculated either by using average bond enthalpies or by using standard enthalpies of formation.

a. Determine the enthalpy change of the reaction, in $\mathrm{kJ\,mol^{-1}}$, using the average bond enthalpies in Table 10 of the Data Booklet. [3]

b. (i) Define the term *standard enthalpy change of formation*. [4]

(ii) Determine the enthalpy change of the reaction, in $\mathrm{kJ\,mol^{-1}}$, between ethene and steam using the enthalpy change of formation values given below.

Compound	ΔH_f° / kJ mol^{-1}
$\mathrm{C_2H_5OH(g)}$	–235
$\mathrm{C_2H_4(g)}$	+52
$\mathrm{H_2O(g)}$	–242

c. Comment on which of the values obtained in (a) and (b)(ii) is more accurate, giving a reason. [1]

d. Predict the sign of the entropy change of the reaction, ΔS, giving a reason. [1]

Markscheme

a. (bonds broken) C=C and O–H / 612 + 464 / 1076;

(bonds formed) C–C and C–H and C–O / 347 + 413 + 358 / 1118;

OR

(bonds broken) C=C and two O–H and four C–H / 612 + 4(413) + 2(464) / 3192;

(bonds formed) C–C and five C–H and C–O and O–H / 347 + 5(413) + 358 + 464 / 3234;

Ignore signs (+ and –) in M1 and M2. These two marks are awarded for recognizing the correct bonds.

enthalpy change $= -42\ (\mathrm{kJ})$;

Correct sign is necessary for awarding M3.

*Award **[3]** for the correct final answer.*

Do not penalize candidates using the former Data Booklet bond energy values (348, 412 and 463) (final answer will then be –45(kJ)).

b. (i) heat/enthalpy change when 1 mol of a compound/substance is formed;

from its elements in their standard states/at $100\ \mathrm{kPa}/10^5\ \mathrm{Pa}$;

Allow 1.01 × 10^5 Pa/101 kPa/1 atm as an alternative to 100 kPa/10^5 Pa.

Allow under standard conditions or standard ambient temperature and pressure as an alternative to 100 kPa/10^5 Pa.

Allow "energy needed/absorbed" as an alternative to "heat/enthalpy change".

Temperature is not required in definition, allow if quoted (eg, 298 K / 25 °C).

(ii) $(-235) - (52 - 242) / \Delta H = \Sigma\Delta H_{\mathrm{f}}^{\Theta}(\mathrm{products}) - \Sigma\Delta H_{\mathrm{f}}^{\Theta}(\mathrm{reactants})$;

□–45 (kJ);

*Award **[2]** for the correct final answer.*

*Award **[1]** for +45 or 45.*

c. value in (b)(ii) (is more accurate) as values used in (a) are average values / value in (b)(ii) (is more accurate) as exact bond enthalpy depends on the surroundings of the bond / *OWTTE*;

d. negative **and** fewer number of moles/molecules (of gas);

Examiners report

a. More than half of the candidates identified the correct types and numbers of bonds, and many calculated the enthalpy change of reaction correctly gaining full marks. Common mistakes included reversing the signs of bonds broken and bonds formed, and using incorrect types or numbers of bonds, and arithmetic errors.

b. (i) Less than half of the candidates answered the question correctly. Some were not specific in the definition of the standard enthalpy change of formation, while others had totally incorrect answers such as the formation of the compound from gaseous atoms.

(ii) The majority of candidates calculated the enthalpy change correctly. Some candidates made arithmetic errors.

c. More than half of the candidates referred to bond enthalpies being average values that lead to a less accurate calculated value of the enthalpy change.

d. [N/A]

Tin(II) chloride is a white solid that is commonly used as a reducing agent.

a. (i) State why you would expect tin(II) chloride to have a similar lattice enthalpy to strontium chloride, using section 9 of the data booklet. [4]

(ii) Calculate the molar enthalpy change when strontium chloride is dissolved in water, using sections 18 and 20 of the data booklet.

(iii) Tin(II) chloride reacts with water to precipitate the insoluble basic chloride, Sn(OH)Cl.

$$\mathrm{SnCl_2\,(aq) + H_2O\,(l) \rightleftharpoons Sn\,(OH)Cl\,(s) + H^+\,(aq) + Cl^-\,(aq)}$$

Suggest why tin(II) chloride is usually dissolved in dilute hydrochloric acid.

b. Tin can also exist in the +4 oxidation state. [3]

$$\mathrm{Sn^{4+}\,(aq) + 2e^- \rightleftharpoons Sn^{2+}\,(aq)} \qquad E^\ominus = +0.15\,\mathrm{V}$$

Vanadium can be reduced from an oxidation state of +4 to +3 according to the equation:

$$\mathrm{VO^{2+}\,(aq) + 2H^+\,(aq) + e^- \rightleftharpoons V^{3+}\,(aq) + H_2O\,(l)} \qquad E^\ominus = +0.34\,\mathrm{V}$$

(i) Calculate the cell potential, $E^\ominus$, and the standard free energy, $\Delta G^\ominus$, change for the reaction between the VO^{2+} and Sn^{2+} ions, using sections 1 and 2 of the data booklet.

$E^\ominus$:

$\Delta G^\ominus$:

(ii) Deduce, giving your reason, whether a reaction between Sn^{2+}(aq) and VO^{2+}(aq) would be spontaneous.

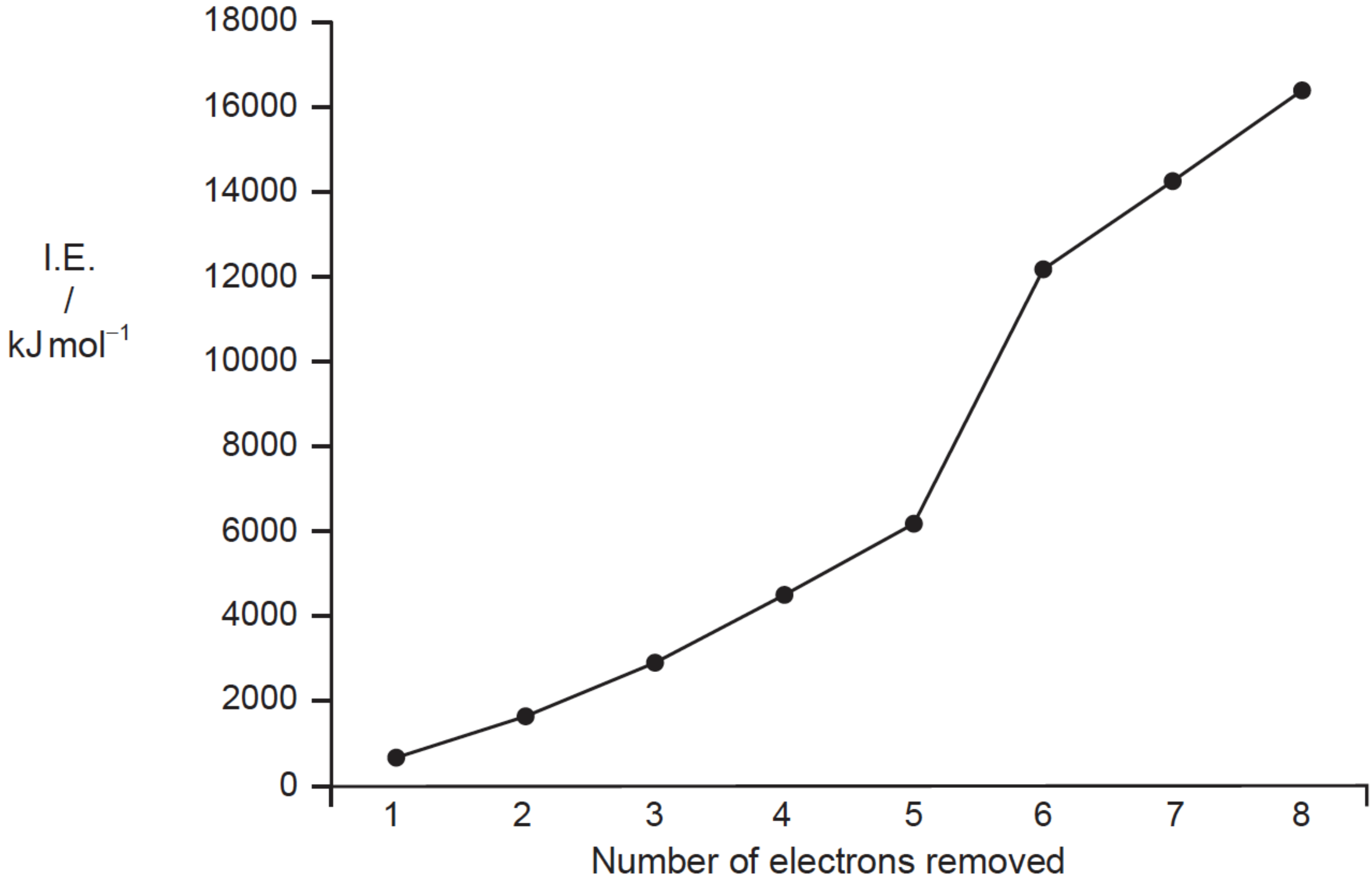
c. Outline, giving the **full** electron configuration of the vanadium atom, what is meant by the term transition metal. [2]

d. In an aqueous solution of vanadium(III) chloride, the vanadium exists as $[V\,(H_2O)_6]^{3+}$, $[VCl\,(H_2O)_5]^{2+}$ or $[VCl_2(H_2O)_4]^+$ depending on the concentration of chloride ions in the solution. [3]

(i) Describe how Cl^- and H_2O bond to the vanadium ion.

(ii) Outline what would happen to the wavelength at which the vanadium complex ions would absorb light as the water molecules are gradually replaced by chloride ions, using section 15 of the data booklet.

e. Eight successive ionisation energies of vanadium are shown in the graph below: [6]



(i) State the sub-levels from which each of the first four electrons are lost.

First: Second: Third: Fourth:

(ii) Outline why there is an increase in ionization energy from electron 3 to electron 5.

(iii) Explain why there is a large increase in the ionization energy between electrons 5 and 6.

(iv) Vanadium is comprised almost entirely of ^{51}V. State the number of neutrons an atom of ^{51}V has in its nucleus.

Markscheme

a. (i)

same charge ***AND*** same/similar ionic radius

(ii)
enthalpy of hydration «= –1483 + 2 (–359)» = –2201 «kJmol^{-1}»
enthalpy of solution «= 2170 – 2201» = –31 «kJmol^{-1}»

*Award **[2]** for correct final answer.*

*Award **[1 max]** for +31 «kJmol^{-1}».*

*Award **[1 max]** for ±4371.*

(iii)
hydrochloric acid shifts equilibrium to left
OR
hydrochloric acid prevents the basic chloride forming/precipitating

*Accept “hydrochloric acid reacts with «basic» chloride” **OR** “hydrochloric acid suppresses salt hydrolysis”.*

b. (i)

$E^\ominus$ «= 0.34 – 0.15» = 0.19«V»

$\Delta GO^\ominus$«= – $nFE^\ominus$ = –2 × 96500 × 0.19» = –36670 / –37000«J» / – 37«kJ»

Accept –18335 «J» or –18 «kJ» as equation not specified.

(ii)

yes ***AND*** $\Delta G^\ominus$ is negative

OR

yes ***AND*** $E^\ominus$ for the cell is positive

OR

yes ***AND*** Sn^{2+} (aq) is a stronger reducing agent than V^{3+}(aq)

OR

yes ***AND*** $E^\ominus$ SN^{4+} (aq) is more negative that $E^\ominus$ or VO^{2+} (aq)

OR

yes ***AND*** VO^{2+} (aq) is a stronger oxidizing agent than Sn^{4+} (aq)

OR

yes ***AND*** $E^\ominus$ for VO^{2+} (aq) is more positive than $E^\ominus$ for SN^{4+} (aq)

*Do **not** accept reference to anti-clockwise rule.*

c. $1s^22s^22p^63s^23p^63d^34s^2$

OR

$1s^22s^22p^63s^23p^64s^23d^3$

incomplete d «sub-» level/orbital/shell «in its compounds/ions»

d. (i)

give/donate a lone/non-bonding electron pair

Accept “through the formation of a dative/ coordinate bond”.

Accept “by acting as Lewis bases”.

Do not accept “act as ligands”.

(ii)
«more chlorido ligands» smaller energy gap between split d-orbitals
OR
Cl^- is lower than H_2O in spectrochemical series
OR
Cl^- is a weaker ligand/has lower charge density

the absorption will move to longer wavelengths

OR

the absorption wavelength will increase

Do not accept answers in terms of change of frequency.

e. (i)

First: 4s ***AND*** *Second:* 4s ***AND*** *Third:* 3d ***AND*** *Fourth:* 3d

*Do **not** apply **ECF** from (c).*

(ii)
«in the same sub-shell and a» decrease in electron-electron repulsion
OR
«in the same sub-shell and» as more electrons removed, the pull of of the nucleus/positive ions holds the remaining electrons more tightly

*Do **not** accept "greater nuclear charge/ effective nuclear charge".*

(iii)
electron 5 is lost from the 3d orbital
OR
electron 5 is lost from the valence shell

electron 6 is lost from a 3p orbital

OR

electron 6 is lost from a «complete» inner shell

3p orbital/complete inner shell experiences a much larger effective nuclear charge
OR
3p orbital/complete inner shell is less well shielded
OR
3p orbital/complete inner shell is nearer the nucleus

*Award **[1 max]** (for M1/M2) (**ECF**) if candidate recognises electrons 5 and 6 are from different levels.*

(iv)
28

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]
d. [N/A]
e. [N/A]

Ethanol has many industrial uses.

a. State an equation for the formation of ethanol from ethene and the necessary reaction conditions. [3]

Equation:

Conditions:

b.i. Define the term *average bond enthalpy*. [2]

b.ii. Ethanol can be used as a fuel. Determine the enthalpy of combustion of ethanol at 298 K, in $\mathrm{kJ\,mol^{-1}}$, using the values in table 10 of the data booklet, assuming all reactants and products are gaseous. [4]

c. Students can also measure the enthalpy of combustion of ethanol in the laboratory using calorimetry. Suggest the major source of systematic error in these procedures. [1]

d. State the equation for the acid-catalysed reaction of ethanol with propanoic acid and state the name of the organic product. [2]

Equation:

Name of the organic product:

e.i. A polyester can be formed when ethane-1,2-diol reacts with benzene-1,4-dicarboxylic acid. [2]

Deduce the structure of the repeating unit and state the other product formed.

Repeating unit:

Other product:

e.ii. State the type of polymerization that occurs. [1]

f.i. The standard enthalpy change of combustion, ΔH_c^Θ, of propanoic acid is $-1527\ \mathrm{kJ\,mol^{-1}}$. Determine the standard enthalpy change of formation of propanoic acid, in $\mathrm{kJ\,mol^{-1}}$, using this information and data from table 12 of the data booklet. [4]

f.ii. Deduce, giving a reason, the sign of the standard entropy change of the system for the formation of propanoic acid from its elements. [2]

g. Identify **three** allotropes of carbon and describe their structures. [4]

Markscheme

a. *Equation:*

$\mathrm{CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH / C_2H_4 + H_2O \rightarrow C_2H_5OH;}$

Conditions:

(concentrated) sulfuric acid/$\mathrm{H_2SO_4}$;

Do not accept dilute sulfuric acid.

Accept phosphoric acid/H_3PO_4 (on pellets of silicon dioxide) (for industrial preparation).

heat / high temperature;

Do not accept warm.

Accept high pressure (for industrial preparation) for M3 only if H_3PO_4 is given for M2.

b.i. energy needed to break (1 mol of) a bond in the gaseous state/phase;

(averaged over) similar compounds;

Do not accept "similar bonds" instead of "similar compounds".

Concept of "similar" is important for M2.

b.ii. $\mathrm{CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O}$;

Bonds broken:

$347 + (5 \times 413) + 358 + 464 + (3 \times 498)/4728\ \mathrm{(kJ)/C–C + 5C–H + C–O + O–H + 3O{=}O}$;

Bonds made:

$(4 \times 746) + (6 \times 464) = 5768\ \mathrm{(kJ)/4C = O + 6O–H}$;

$\Delta H = (4728 - 5768 =) - 1040\ (\mathrm{kJ\,mol^{-1}})$ / bonds broken – bonds formed;

*Award **[4]** for correct final answer.*

*Award **[3]** for (+)1040 ($kJ\ mol^{-1}$).*

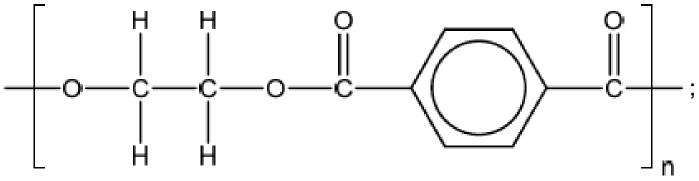
c. heat loss (to the surroundings);

d. $\mathrm{CH_3CH_2OH + CH_3CH_2COOH \rightleftharpoons CH_3CH_2OOCCH2CH_3 + H_2O}$;

ethyl propanoate;

Do not penalize if equilibrium arrow missing.

e.i. *Repeating unit*:



Continuation lines must be shown.

Ignore brackets and n.

Accept condensed formulas such as CH_2 and C_6H_4.

Other product:

$\mathrm{H_2O}$/water;

e.ii. condensation;

f.i. $\mathrm{3C(s) + 3H_2(g) + O_2(g) \rightarrow CH_3CH_2COOH(l)}$;

$\Delta H_f^\Theta = \sum \Delta H_c^\Theta\ \mathrm{(reactants)} - \sum \Delta H_c^\Theta\ \mathrm{(products)}$;

Accept any suitable energy cycle.

$\sum \Delta H_c^\Theta\ \mathrm{(reactants)} = 3 \times (-394) + 3 \times (-286)/ - 2040\ (\mathrm{kJ\,mol^{-1}})$;

$(\Delta H_f^\Theta = [3 \times (-394) + 3 \times (-286)] - (-1527) =) - 513\ (\mathrm{kJ\,mol^{-1}})$;

OR

$\mathrm{CH_3CH_2COOH(l) + 3.5O_2(g) \rightarrow 3CO_2(g) + 3H_2O(g)}$;

$\Delta H_c^\Theta = \sum \Delta H_f^\Theta\ (products) - \sum \Delta H_f^\Theta\ (reactants)$;

$\sum \Delta H_f^\Theta\ \mathrm{(products)} = 3 \times (-394) + 3 \times (-286)/ - 2040\ (\mathrm{kJ\,mol^{-1}})$;

$(\Delta H_f^\Theta = [3 \times (-394) + 3 \times (-286)] - (-1527) =) - 513 \text{ (kJ mol}^{-1})$;

Ignore state symbols.

*Award **[4]** for correct final answer*.

f.ii. negative;

reduction in the number of gaseous molecules;

g. *Allotropes:*

*Any **three** allotropes for **[1]** from:*

diamond

graphite

fullerene

graphene;

Allow (carbon) nanotubes for graphene.

Accept C_{60}/C_{70}/buckminsterfullerene/bucky balls for fullerene.

Structures:

*Any three for **[3]** from:*

Diamond:

tetrahedral arrangement of (carbon) atoms/each carbon bonded to four others / sp^3 **and** 3D/covalent network structure;

Graphite:

each carbon bonded to three others (in a trigonal planar arrangement) / sp^2 **and** 2D / layers of (carbon) atoms;

Fullerene:

each (carbon) atom bonded to three others (in a trigonal arrangement) / sp^2 **and** joined in a ball/cage/sphere/connected hexagons and pentagons;

Accept "trigonal planar" for "each carbon atom bonded to three others" part in M4.

Graphene:

each carbon bonded to three others (in a trigonal arrangement) / sp^2 **and** 2D structure;

Examiners report

a. There was poor understanding of the transformation in (a). When defining the *average bond enthalpy* in (b), the notion of "gaseous" was frequently omitted and very few mentioned the bonds being in similar compounds. In the calculation, many omitted the C–C bond and many did not work from a properly balanced equation which led to disaster. Nearly every candidate attempting this question was able to suggest "heat loss". In (d) the usual errors were made; the name was the wrong way round, water was missing from the equation and wrong products (such as pentanoic acid) were suggested. In (e) (i) the diagrams were poor but water was usually given correctly. Most gave condensation as the type of polymerization. The key to gaining marks in questions such as (f) (i) is to start with a balanced equation, [1 mark], and then set the calculation out correctly and tidily. Part marks cannot be given if the examiner cannot follow what the candidate is doing. Many correctly gave "negative" in (ii) but the explanations lacked clarity. Most gained a mark in (g) for knowing three allotropes but the description of structures was poorly done. The [4] (marks) for this part gives some idea of the amount of detail expected.

b.i. There was poor understanding of the transformation in (a). When defining the *average bond enthalpy* in (b), the notion of “gaseous” was frequently omitted and very few mentioned the bonds being in similar compounds. In the calculation, many omitted the C–C bond and many did not work from a properly balanced equation which led to disaster. Nearly every candidate attempting this question was able to suggest “heat loss”. In (d) the usual errors were made; the name was the wrong way round, water was missing from the equation and wrong products (such as pentanoic acid) were suggested. In (e) (i) the diagrams were poor but water was usually given correctly. Most gave condensation as the type of polymerization. The key to gaining marks in questions such as (f) (i) is to start with a balanced equation, [1 mark], and then set the calculation out correctly and tidily. Part marks cannot be given if the examiner cannot follow what the candidate is doing. Many correctly gave “negative” in (ii) but the explanations lacked clarity. Most gained a mark in (g) for knowing three allotropes but the description of structures was poorly done. The [4] (marks) for this part gives some idea of the amount of detail expected.

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Ethane-1,2-diol, $HOCH_2CH_2OH$, has a wide variety of uses including the removal of ice from aircraft and heat transfer in a solar cell.

b. (i) Calculate ΔH^{θ}, in kJ, for this similar reaction below using ΔH_f^{θ} data from section 12 of the data booklet. ΔH_f^{θ} of $HOCH_2CH_2OH(l)$ is –454.8kJmol^{-1}. [6]

$$2CO\ (g) + 3H_2\ (g) \rightleftharpoons HOCH_2CH_2OH\ (l)$$

(ii) Deduce why the answers to (a)(iii) and (b)(i) differ.

(iii) ΔS^{θ} for the reaction in (b)(i) is –620.1JK^{-1}. Comment on the decrease in entropy.

(iv) Calculate the value of ΔG^{θ}, in kJ, for this reaction at 298 K using your answer to (b)(i). (If you did not obtain an answer to (b)(i), use –244.0 kJ, but this is not the correct value.)

(v) Comment on the statement that the reaction becomes less spontaneous as temperature is increased.

f. Predict the ^{1}HNMR data for ethanedioic acid and ethane-1,2-diol by completing the table. [2]

	Number of signals	**Splitting pattern**
Ethanedioic acid:	....	....
Ethane-1,2-diol:	....	Not required

Markscheme

b. i

«$\Delta H = \Sigma\ \Delta H_f$ products – $\Sigma\Delta H_f$ reactants = –454.8 kJ mol^{-1} – 2(–110.5 kJ mol^{-1}) =» –233.8 «kJ»

ii

in (a)(iii) gas is formed and in (b)(i) liquid is formed

OR

products are in different states

OR

conversion of gas to liquid is exothermic

OR

conversion of liquid to gas is endothermic

OR

enthalpy of vapourisation needs to be taken into account

Accept product is «now» a liquid.
Accept answers referring to bond enthalpies being means/averages.

iii

«ΔS is negative because five mols of» gases becomes «one mol of» liquid

OR

increase in complexity of product «compared to reactants»

OR

product more ordered «than reactants»

Accept "fewer moles of gas" but not "fewer molecules".

iv

$\Delta S = \left(\frac{-620.1}{1000}\right)$ «kJ K^{-1}»

ΔG = –233.8 kJ – (298 K $\left(\frac{-620.1}{1000}\right)$ kJ K^{-1}) = –49.0 «kJ»

*Award **[2]** for correct final answer.*
*Award **[1 max]** for «+»185 × 10^3.*

If –244.0 kJ used, answer is:

ΔG = –244.0 kJ – (298 K $\left(\frac{-620.1}{1000}\right)$ kJ K^{-1}) = –59.2 «kJ»

*Award **[2]** for correct final answer.*

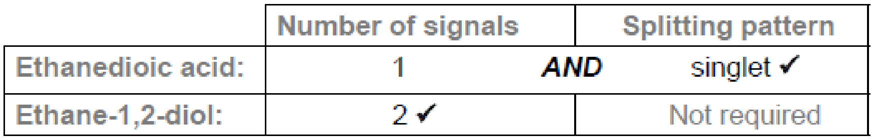
v

increasing T makes ΔG larger/more positive/less negative

OR

–TΔS will increase

f.



	Number of signals	Splitting pattern
Ethanedioic acid:	1 ***AND***	singlet ✓
Ethane-1,2-diol:	2 ✓	Not required

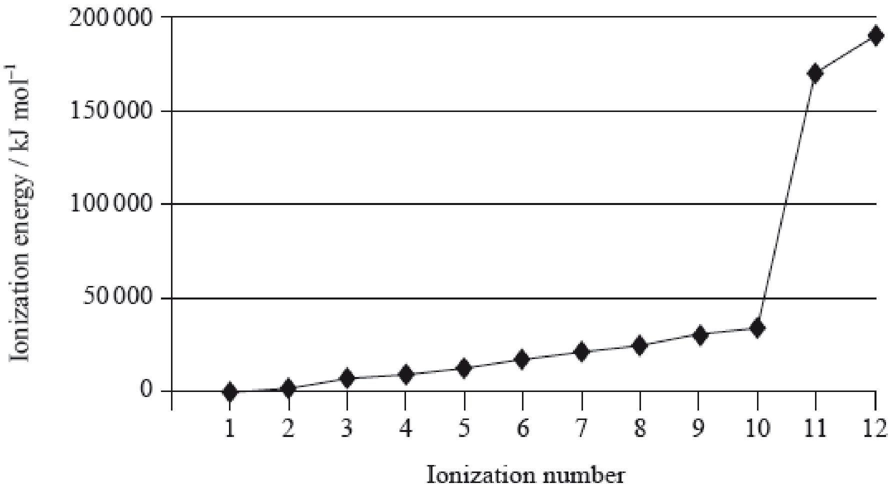
Accept "none/no splitting" for singlet.

Examiners report

b. [N/A]

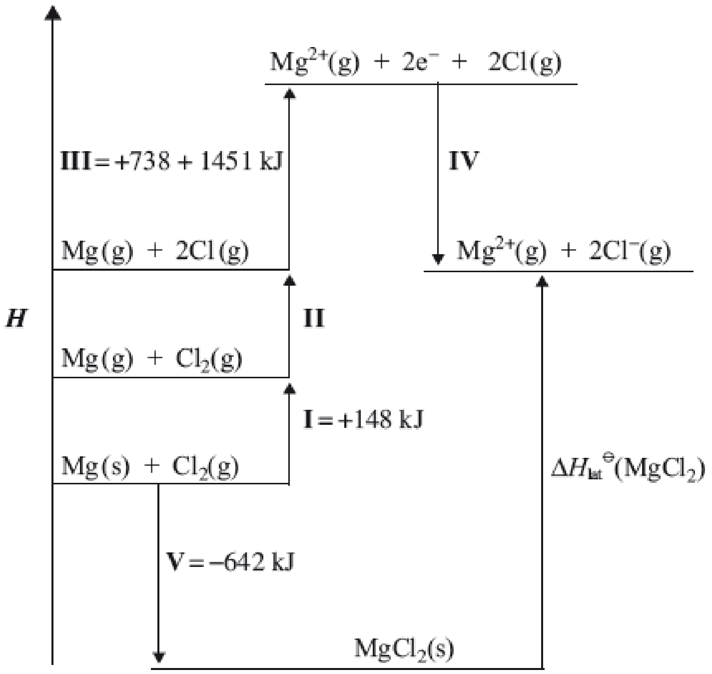
f. [N/A]

Magnesium is the eighth most abundant element in the earth's crust. The successive ionization energies of the element are shown below.



Magnesium can be produced from the electrolysis of molten magnesium chloride, $MgCl_2$.

The lattice enthalpy of magnesium chloride can be calculated from the Born-Haber cycle shown below.



a. (i) Define the term *first ionization energy* and state the equation for the first ionization of magnesium. [8]

(ii) Explain the general increase in successive ionization energies of the element.

(iii) Explain the large increase between the tenth and eleventh ionization energies.

b. (i) Explain how molten magnesium chloride conducts an electric current. [5]

(ii) Identify the electrode where oxidation occurs during electrolysis of molten magnesium chloride and state an equation for the half-reaction.

(iii) Explain why magnesium is not formed during the electrolysis of aqueous magnesium chloride solution.

c. (i) Identify the enthalpy changes labelled by **I** and **V** in the cycle. [10]

(ii) Use the ionization energies given in the cycle above and further data from the Data Booklet to calculate a value for the lattice enthalpy of magnesium chloride.

(iii) The theoretically calculated value for the lattice enthalpy of magnesium chloride is +2326 kJ. Explain the difference between the theoretically calculated value and the experimental value.

(iv) The experimental lattice enthalpy of magnesium oxide is given in Table 13 of the Data Booklet. Explain why magnesium oxide has a higher lattice enthalpy than magnesium chloride.

d. (i) State whether aqueous solutions of magnesium oxide and magnesium chloride are acidic, alkaline or neutral. [2]

(ii) State an equation for the reaction between magnesium oxide and water.

Markscheme

a. (i) energy (per mole) needed to remove one/first/most loosely bound electron from a (neutral) atom;

in the gaseous state;

$\mathrm{Mg(g)} \rightarrow \mathrm{Mg^+(g)} + \mathrm{e^-}$;

Gaseous state symbols needed.

Accept e instead of e⁻.

Only penalize omission of gas phase once in either the second marking point or the third marking point.

(ii) successive electrons (are more difficult to remove because each is) taken from more positively charged ion/ *OWTTE*;

increased electrostatic attraction;

(iii) 10th electron comes from 2nd energy level/$n = 2$ **and** 11th electron comes from 1st first energy level/$n = 1$ / *OWTTE*;

electron in 1st energy level closer to nucleus;

electron in 1st energy level not shielded by inner electrons / exposed to greater effective nuclear charge;

b. (i) contains ions which are free to move (only) in molten state;

$\mathrm{Mg^{2+}}$ move to cathode/negative electrode and $\mathrm{Cl^-}$ move to anode/positive electrode / *OWTTE*;

(ii) anode/positive electrode;

$\mathrm{2Cl^-} \rightarrow \mathrm{Cl_2} + \mathrm{2e^-}/\mathrm{Cl^-} \rightarrow \frac{1}{2}\mathrm{Cl_2} + \mathrm{e^-}$;

Accept e instead of e⁻.

Do not accept $Cl^- \rightarrow Cl + e^-$.

Ignore state symbols.

(iii) magnesium has large negative electrode potential / $E^\ominus$;

reduction of $\mathrm{H_2O/H^+}$ to $\mathrm{H_2}$ has less negative electrode potential;

$\mathrm{Mg^{2+}}$ not readily reduced (in comparison to $\mathrm{H_2O}$);

if formed, magnesium would (immediately) react with water to form $\mathrm{Mg^{2+}}$;

magnesium more reactive than hydrogen;

Do not accept Mg too reactive.

c. (i) *I*:

atomization/sublimation (of Mg) / $\Delta H^\ominus_{\mathrm{atomization}}(\mathrm{Mg})$ / $\Delta H^\ominus_{\mathrm{sublimation}}(\mathrm{Mg})$;

V:

enthalpy change of formation of $(\mathrm{MgCl_2})$ / $\Delta H^\ominus_{\mathrm{formation}}(\mathrm{MgCl_2})$;

(ii) *Energy value for II*:

$+243$;

Energy value for III:

$738 + 1451 = 2189$;

Energy value for IV:

$2(-349)$;

$\Delta H^{\ominus}_{\text{lat}}(\text{MgCl}_2) = 642 + 148 + 243 + 2189 - 2(349) = (-)2524\ (\text{kJ})$;

(iii) theoretical value assumes ionic model;

experimental value greater due to (additional) covalent character;

(iv) oxide greater charge;

oxide smaller radius;

Accept opposite arguments.

d. (i) MgCl_2 (weakly) acidic **and** MgO alkaline;

(ii) $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2$;

Ignore state symbols.

Examiners report

a. In (a) several candidates failed to mention atoms in their definition of first ionization energy and others neglected to state that the gaseous state is involved. Only the strongest students mentioned the electrostatic nature of the attraction between the nucleus and the electrons in explaining trends in ionisation energies. Several candidates lost a mark in explaining the increase between the tenth and eleventh ionisation energies as their arguments were incomplete, with no reference to the change from$n = 2$ energy level to the$n = 1$ level.

b. In (b) many candidates stated that free electrons rather than ions were responsible for the conductivity of magnesium chloride and others did not refer to the movement of both Mg^{2+} and Cl^- ions. The anode was generally identified as the electrode where oxidation occurs but some had difficulties giving the balanced equation for the half reaction. Only the strongest candidates were able to explain why magnesium is not formed during the electrolysis of aqueous solutions.

c. In (c) most candidates were familiar with the enthalpy changes of atomization and formation but some struggled with the Born Haber Cycle. Only the strongest candidates were able to relate differences in experimental and theoretical lattice energies to the covalent character of the solid with a significant number mistakenly giving “heat loss” as the reason for the difference.

d. In (d) many were able to correctly describe the basic nature of magnesium oxide but the acidity of magnesium chloride was less well known. Some gave hydrogen gas as a product in the reaction between magnesium oxide and water.

Carbon monoxide reacts with hydrogen to produce methanol.

$$\text{CO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(l)}$$

Substance	$\Delta H^{\ominus}_{f}$ / kJ mol^{-1}	$\Delta G^{\ominus}_{f}$ / kJ mol^{-1}	$S^{\ominus}$ / J mol^{-1} K^{-1}
CO (g)	– 110.5	– 137.2	+ 197.6
CH_3OH (l)	– 239.0	– 166.0	+ 126.8

a. Calculate the standard enthalpy change, $\Delta H^\ominus$, in $\mathrm{kJ\,mol^{-1}}$, for the reaction. [1]

b. Calculate the standard free energy change, $\Delta G^\ominus$, in $\mathrm{kJ\,mol^{-1}}$, for the reaction [1]

$(\Delta G_\mathrm{f}^\ominus(\mathrm{H_2}) = 0\ \mathrm{kJ\,mol^{-1}})$.

c. Using the values obtained in parts (a) and (b), calculate the standard entropy change, $\Delta S^\ominus$, in $\mathrm{J\ mol^{-1}K^{-1}}$, for the reaction at 298 K. [1]

d. Determine the absolute entropy, $S^\ominus$, in $\mathrm{J\,mol^{-1}K^{-1}}$, for $\mathrm{H_2(g)}$ at 298 K. [2]

Markscheme

a. $(-239.0 - [-110.5] =) - 128.5\ (\mathrm{kJ\,mol^{-1}})$;

b. $(-166.0 - [-137.2] =) - 28.8\ (\mathrm{kJ\,mol^{-1}})$;

c. $\left(\Delta G^\ominus = -28.8 = -128.5 - \left[\frac{298 \times \Delta S^\ominus}{1000}\right]\right)$

$(\Delta S^\ominus =) - 335\ (\mathrm{J\,mol^{-1}K^{-1}})$;

d. $\Delta S^\ominus = \sum S^\ominus_{products} - \sum S^\ominus_{reactants} / -335 = 126.8 - 197.6 - 2S^\ominus_{\mathrm{H_2}}$;

$S^\ominus_{\mathrm{H_2}} = (+)132\ (\mathrm{J\,mol^{-1}K^{-1}})$;

*Award **[2]** for correct final answer.*

*Award **[1 max]** for* $S^\ominus_{\mathrm{H_2}} = (+)264\ (\mathrm{J\,mol^{-1}K^{-1}})$.

Examiners report

a. Most candidates were able to calculate the enthalpy, free energy and entropy changes, although a significant number gave the incorrect units for the latter. The use of the Gibbs free energy equation requires consistency of units since $\Delta H_\mathrm{f}^\circ$ and $\Delta G_\mathrm{f}^\circ$ were given in kJ whereas S° was given in J. This needs reinforcing in class as it tends to be a common error from session to session. The calculation of the absolute entropy of hydrogen proved to be more problematic, with many not taking into account that there are two moles of hydrogen in the reaction.

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Bromomethane was used as a pesticide until it was found to be ozone-depleting.

a. State the equation for the reaction between methane and bromine to form bromomethane. [1]

b.i. Explain, using equations, the complete free-radical mechanism for the reaction of methane with bromine, including necessary reaction conditions. [4]

b.ii. Bromomethane reacts with aqueous sodium hydroxide. State the organic product of this reaction. [1]

c. Explain why the rate of the reaction between iodomethane, CH_3I, and NaOH(aq) is faster than the rate of the reaction between CH_3Br and NaOH(aq). [2]

d.i. Bromine can be produced by the electrolysis of **molten** sodium bromide. [2]

Deduce the half-equation for the reaction at each electrode.

Positive electrode (anode):

Negative electrode (cathode):

d.ii. Predict the products formed at the electrodes during the electrolysis of concentrated **aqueous** sodium bromide. [2]

Positive electrode (anode):

Negative electrode (cathode):

e. Bromine reacts with aqueous sodium iodide. [1]

$$Br_2(aq) + 2NaI(aq) \rightarrow I_2(aq) + 2NaBr(aq)$$

Identify the oxidizing agent in this reaction.

f.i. Define the term *standard electrode potential, E^Θ*. [1]

f.ii. Draw a labelled diagram for the voltaic cell in which the following reaction occurs. [4]

$$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$$

Include in your answer the direction of electron flow and the polarity of the electrodes.

f.iii. A student measures a voltage of 2.65 V in the voltaic cell formed between magnesium and copper half-cells using a digital voltmeter. [2]

State the random uncertainty of this value, in V, and the number of significant figures in the answer.

Random uncertainty:

Significant figures:

f.iv.Outline how the student can reduce the random error in her results. [1]

g. Determine the standard enthalpy change of formation, $\Delta H_{\mathrm{f}}^{\Theta}$, of NaCl(s), in $\mathrm{kJ\,mol^{-1}}$, using a Born-Haber cycle and tables 7, 10 and 13 of the data booklet. The standard enthalpy change of atomization (standard enthalpy change of sublimation), $\Delta H_{\mathrm{at}}^{\Theta}$, of Na(s) is $+108\ \mathrm{kJ\,mol^{-1}}$. [4]

Markscheme

a. $\mathrm{CH_4 + Br_2 \rightarrow CH_3Br + HBr}$;

b.i.*Initiation:*

$\mathrm{Br_2 \xrightarrow{UV/\mathit{hf}/\mathit{hv}} 2Br\bullet}$;

Reference to UV/light or high temperatures must be included.

Propagation:

$\mathrm{Br \bullet + CH_4 \rightarrow CH_3 \bullet + HBr}$;

$\mathrm{CH_3 \bullet + Br_2 \rightarrow CH_3Br + Br\bullet}$;

Termination:

*Award **[1 max]** for any one of:*

$\mathrm{Br \bullet + Br\bullet \rightarrow Br_2}$;

$\mathrm{CH_3 \bullet + Br\bullet \rightarrow CH_3Br}$;

$\mathrm{CH_3 \bullet + CH_3\bullet \rightarrow C_2H_6}$;

Allow representation of radical without • (eg Br, CH_3) if consistent throughout mechanism.

*Award **[3 max]** if initiation, propagation and termination are not stated or are incorrectly labelled for equations.*

b.ii$\mathrm{methanol/CH_3OH}$;

c. C–I bond is weaker than the C–Br bond so more easily broken;

C–I bond is longer than the C–Br bond / I larger than Br so bonding electrons not as tightly held / $\mathrm{I^-}$ is better leaving group than $\mathrm{Br^-}$;

d.i.*Positive electrode (anode):*

$\mathrm{2Br^- \rightarrow Br_2(g) + 2e^- / Br^- \rightarrow \frac{1}{2}Br_2(g) + e^-}$;

Negative electrode (cathode):

$\mathrm{Na^+ + e^- \rightarrow Na(l)}$;

*Award **[1 max]** for correct equations at incorrect electrodes.*

Ignore state symbols.

Accept e *instead of* $\mathrm{e^-}$.

Penalize use of equilibrium signs once only.

d.ii*Positive electrode (anode):*

bromine/$\mathrm{Br_2}$;

Negative electrode (cathode):

hydrogen/$\mathrm{H_2}$;

Allow sodium hydroxide/NaOH/hydroxide/OH^- formation.

e. bromine/$\mathrm{Br_2}$;

Do not accept bromide/Br^-.

f.i. potential of reduction half-reaction under standard conditions measured relative to standard hydrogen electrode/SHE/potential under standard conditions relative to standard hydrogen electrode/SHE;

Instead of standard state allow either solute concentration of $1 mol\, dm^{-3}$ or

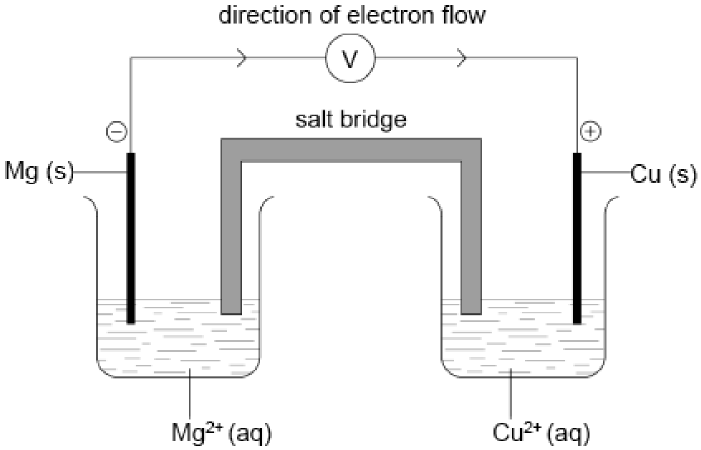
$100 kPa/1.00 \times 10^5 Pa$ for gases.

Allow 1 bar for $100 kPa/1.00 \times 10^5 Pa$.

Allow 1 atm.

Allow voltage instead of potential.

f.ii.



correct diagram including (voltmeter), 4 correct species (state symbols not required) and connecting wires;

No credit if wires to electrodes immersed in the solutions.

Accept ammeter/meter/lamp instead of voltmeter.

labelled salt bridge;

Accept an appropriate salt (name or formula) instead of salt bridge (eg, potassium nitrate).

correctly labelled electrodes as +/cathode **and** –/anode;

flow of electrons from Mg to Cu in external circuit;

f.iii. *Random uncertainty:* (±) 0.01 (V);

Significant figures: 3;

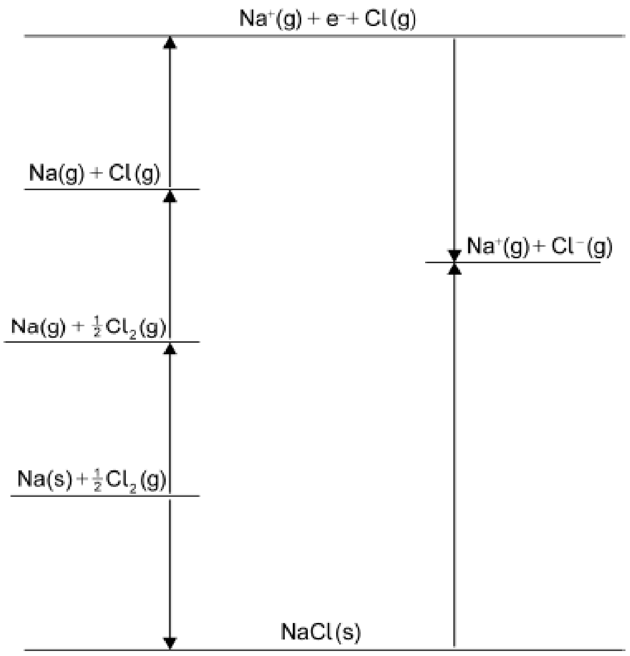
f.iv. repeat readings **and** take an average / use more precise equipment;

g. atomization of chlorine $= \frac{1}{2}$ bond enthalpy / $\frac{1}{2}$ 243 / 121.5 ($\mathrm{kJ\,mol^{-1}}$);

correct values for *ionization* Na ($+496\ \mathrm{kJ\,mol^{-1}}$) **and** *electron affinity* Cl ($-349\ \mathrm{kJ\,mol^{-1}}$) **and** lattice enthalpy of NaCl ($+790\ \mathrm{kJ\,mol^{-1}}$ / $+769\ \mathrm{kJ\,mol^{-1}}$);

Born-Haber energy cycle;

Accept lines or arrows in energy cycle.



$\Delta H_f^\ominus(\mathrm{NaCl(s)}) = -413.5\ /-413\ /-414\ (\mathrm{kJ\,mol^{-1}})$;

Accept $-392.5/-392/-393if+769$ *used for lattice enthalpy.*

*Award **[4]** for correct final answer.*

Examiners report

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Phosgene, $COCl_2$, is usually produced by the reaction between carbon monoxide and chlorine according to the equation:

$$\mathrm{CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)}$$

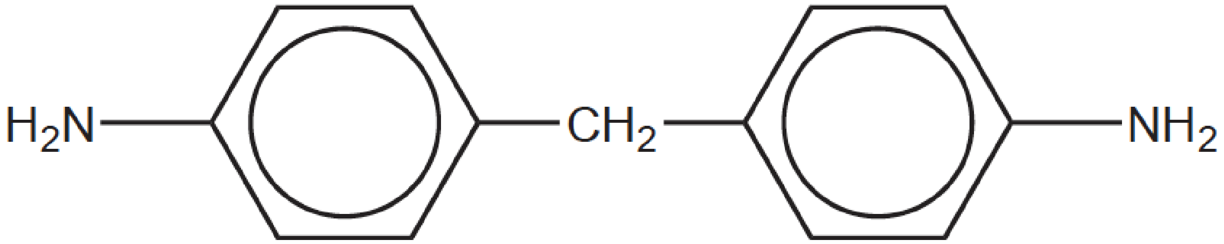
a. (i) Deduce the equilibrium constant expression, K_c, for this reaction. [8]

(ii) At exactly 600°C the value of the equilibrium constant is 0.200. Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the reaction, in kJ, using sections 1 and 2 of the data booklet. State your answer to **three** significant figures.

(iii) The standard enthalpy change of formation of phosgene, $\Delta H_f^{\ominus}$, is –220.1kJmol^{-1}. Determine the standard enthalpy change, $\Delta H^{\ominus}$, for the forward reaction of the equilibrium, in kJ, using section 12 of the data booklet.

(iv) Calculate the standard entropy change, $\Delta S^{\ominus}$, in JK^{-1}, for the forward reaction at 25°C, using your answers to (a) (ii) and (a) (iii). (If you did not obtain an answer to (a) (ii) and/or (a) (iii) use values of +20.0 kJ and –120.0 kJ respectively, although these are not the correct answers.)

b. One important industrial use of phosgene is the production of polyurethanes. Phosgene is reacted with diamine **X**, derived from phenylamine. [8]



X

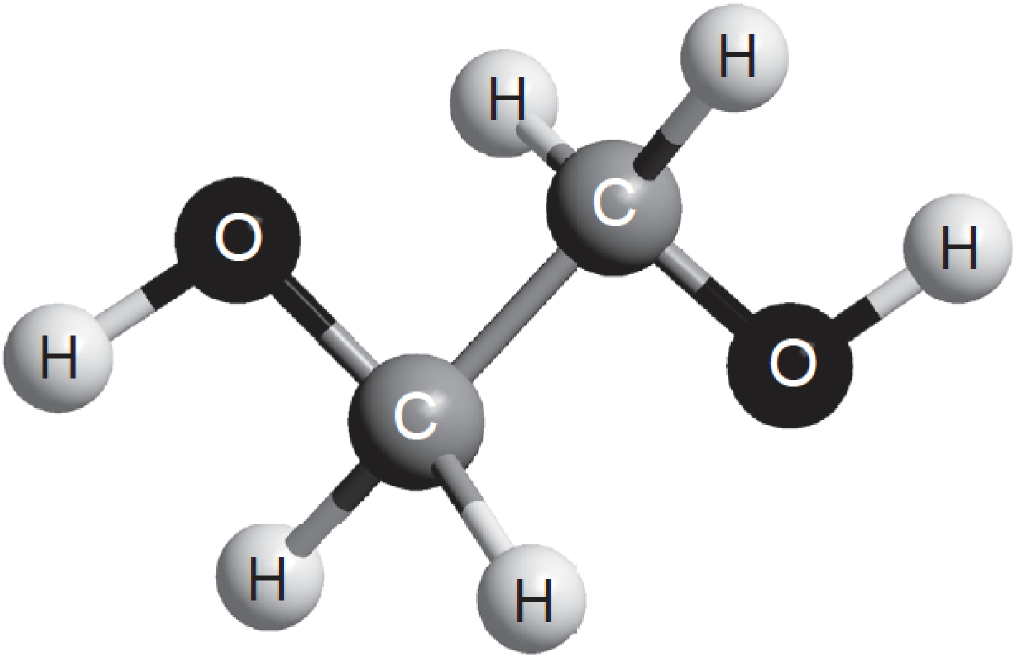
(i) Classify diamine **X** as a primary, secondary or tertiary amine.

(ii) Phenylamine, $C_6H_5NH_2$, is produced by the reduction of nitrobenzene, $C_6H_5NO_2$. Suggest how this conversion can be carried out.

(iii) Nitrobenzene can be obtained by nitrating benzene using a mixture of concentrated nitric and sulfuric acids. Formulate the equation for the equilibrium established when these two acids are mixed.

(iv) Deduce the mechanism for the nitration of benzene, using curly arrows to indicate the movement of electron pairs.

c. The other monomer used in the production of polyurethane is compound **Z** shown below. [5]



(i) State the name, applying IUPAC rules, of compound **Z** and the class of compounds to which it belongs.

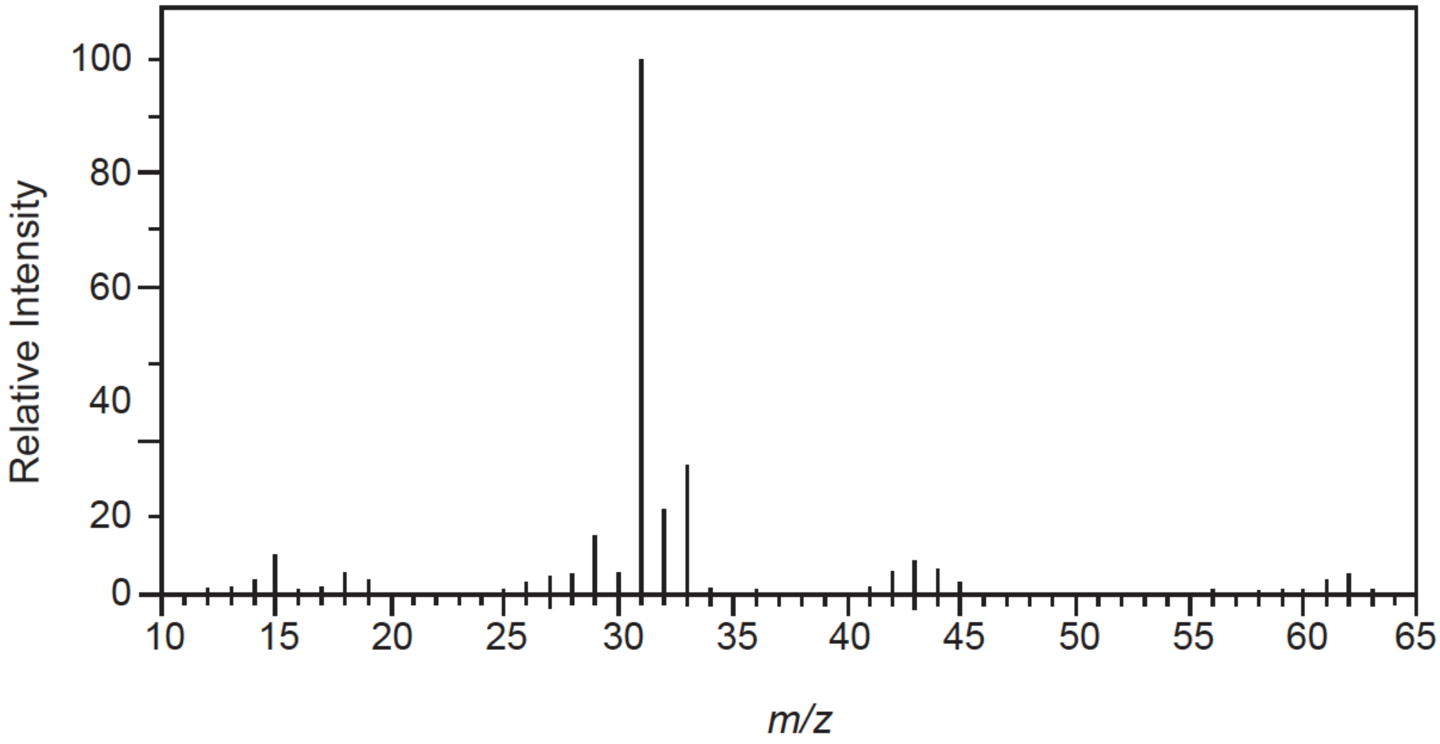
Name:

Class:

(ii) Deduce the number of signals you would expect to find in the ^{1}H NMR spectrum of compound **Z**, giving your reasons.

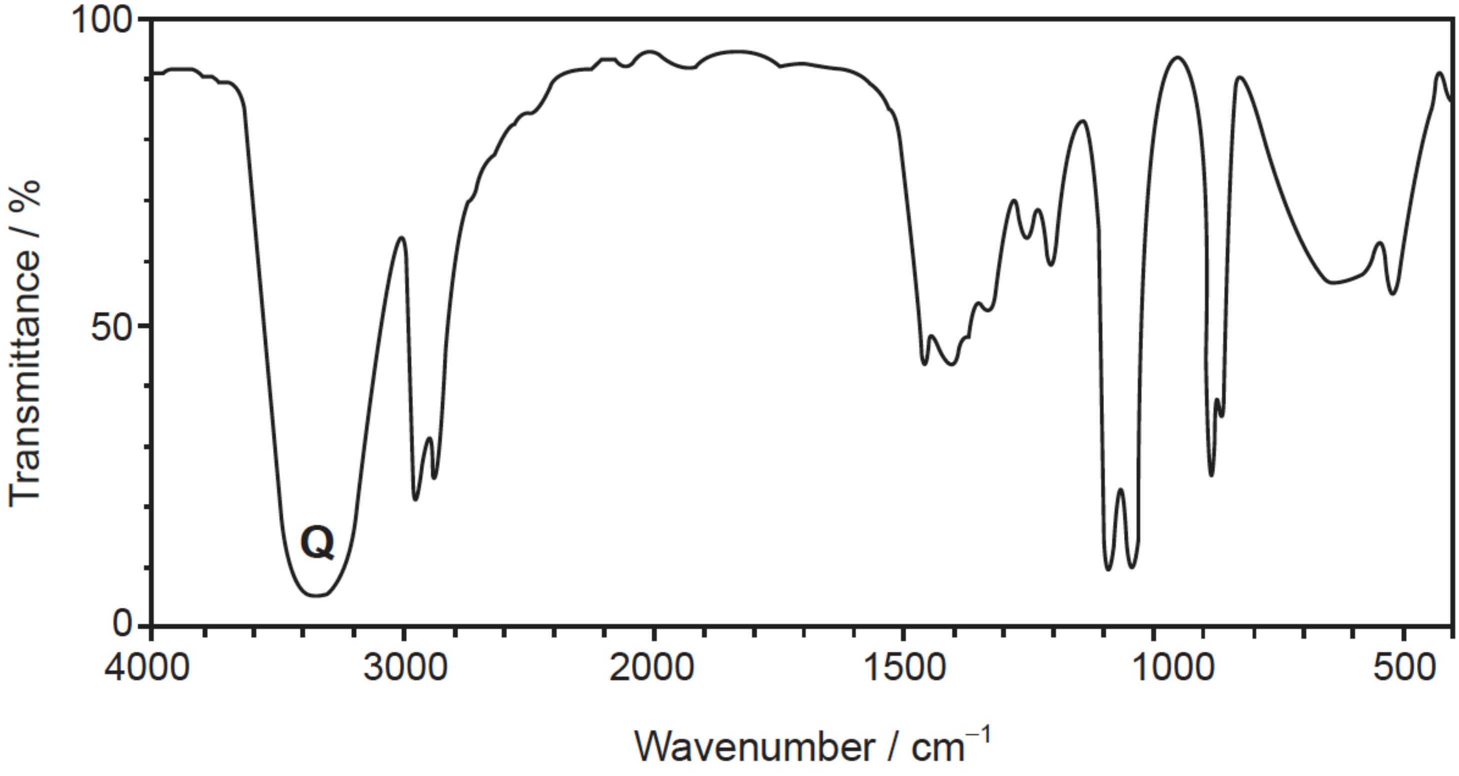
The mass spectrum and infrared (IR) spectrum of compound **Z** are shown below:

Mass spectrum



[Source: http://sdbs.db.aist.go.jp]

IR spectrum



[Source: http://sdbs.db.aist.go.jp]

(iii) Identify the species causing the large peak at *m*/*z*=31 in the mass spectrum.

(iv) Identify the bond that produces the peak labelled **Q** on the IR spectrum, using section 26 of the data booklet.

d. Phenylamine can act as a weak base. Calculate the pH of a 0.0100 mol dm^{-3} solution of phenylamine at 298K using section 21 of the data booklet. [4]

Markscheme

a. (i)

$\ll K_C = \gg \frac{[COCl_2]}{[CO][Cl_2]}$

(ii)
T«= 600 + 273» = 873K

$\Delta G^{\ominus}$ = −8.31 × 873 × ln (0.200)
OR
$\Delta G^{\ominus}$ = « + » 11676 «J»
$\Delta G^{\ominus}$ = « + » 11.7 «kJ»

Accept 11.5 to 12.0.
Award final mark only if correct sig fig.
*Award **[3]** for correct final answer.*

(iii)
$\Delta H^{\ominus}$ = −220.1 − (−110.5)
$\Delta H^{\ominus}$ = −109.6 «kJ»

*Award **[2]** for correct final answer.*
*Award **[1]** for −330.6, or +109.6 «kJ».*

(iv)
$\Delta G^{\ominus}$= −109.6 − (298 × $\Delta S^{\ominus}$) = +11.7 «kJ»
$\Delta S^{\ominus}$«$\frac{(11.7+109.6)\times10^3}{298}$»= −407 «$JK^{-1}$»

*Award **[2]** for correct final answer.*
*Award **[2]** for −470 «JK^{-1}» (result from given values).*
Do not penalize wrong value for T if already done in (a)(ii).
*Award **[1 max]** for −0.407 «kJ K^{-1}».*
*Award **[1 max]** for −138.9 «J K^{-1}».*

b. (i)

primary

(ii)
ALTERNATIVE 1:
«heat with» tin/Sn ***AND*** hydrochloric acid/HCl
aqueous alkali/OH^-(aq)

ALTERNATIVE 2:

hydrogen/H_2

nickel/Ni «catalyst»

Accept specific equations having correct reactants.
*Do **not** accept LiAlH4 or NaBH4.*
Accept Pt or Pd catalyst.

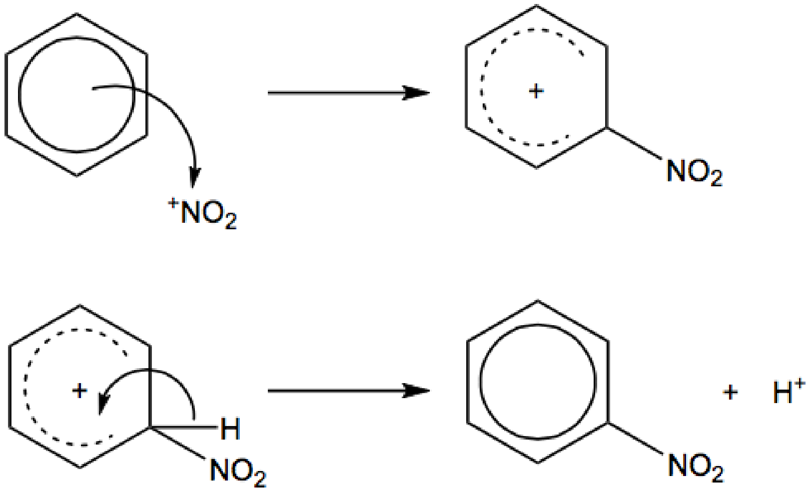
Accept equations having correct reactants.

(iii)
$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

Accept: $HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$ *Accept* $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$ *.*

Accept equivalent two step reactions in which sulfuric acid first behaves as a strong acid and protonates the nitric acid, before behaving as a dehydrating agent removing water from it.

(iv)



curly arrow going from benzene ring to N of $^+NO_2/NO_2^+$

carbocation with correct formula and positive charge on ring

curly arrow going from C–H bond to benzene ring of cation

formation of organic product nitrobenzene ***AND*** H^+

Accept mechanism with corresponding Kekulé structures.

*Do **not** accept a circle in M2 or M3. Accept first arrow starting either inside the circle or on the circle.*

M2 may be awarded from correct diagram for M3.

M4: Accept $C_6H_5NO_2 + H_2SO_4$ *if* HSO_4^- *used in M3.*

c. (i)

Name: ethane-1,2-diol

Class: alcohol«s»

Accept ethan-1,2-diol / 1,2-ethanediol.

*Do **not** accept “diol” for Class.*

(ii)
two ***AND*** two hydrogen environments in the molecule
OR
two ***AND*** both CH_2 and OH present

(iii)
$^+CH_2OH$

Accept CH_3O^+*.*

Accept $[\bullet CH_2OH]^+$ *and* $[\bullet CH_3O]^+$*.*

Do not accept answers in which the charge is missing.

(iv)
oxygen-hydrogen «bond»/O–H «in hydroxyl»

d. $K_\mathrm{b} \approx \frac{[\mathrm{OH^-}]^2}{[\mathrm{C_6H_5NH_2}]} = 10^{-9.13}/7.413 \times 10^{-10}$

$[\mathrm{OH^-}] = \sqrt{0.0100 \times 10^{-9.13}} = 2.72 \times 10^{-6}$

$[\mathrm{H^+}] = \frac{1\times10^{-14}}{2.72\times10^{-6}} = 3.67 \times 10^{-9}$

OR

pOH = 5.57

pH = –log $[H^+]$ = 8.44

Accept other approaches to the calculation.
*Award **[4]** for correct final answer.*
Accept any answer from 8.4 to 8.5.

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]
d. [N/A]