

WJEC A-LEVEL CHEMISTRY • UNIT 3

CHEMISTRY



EXAM QUESTION PACK

3.7 ENTROPY AND FEASIBILITY OF REACTIONS

SCORE

/61

PERCENTAGE

%

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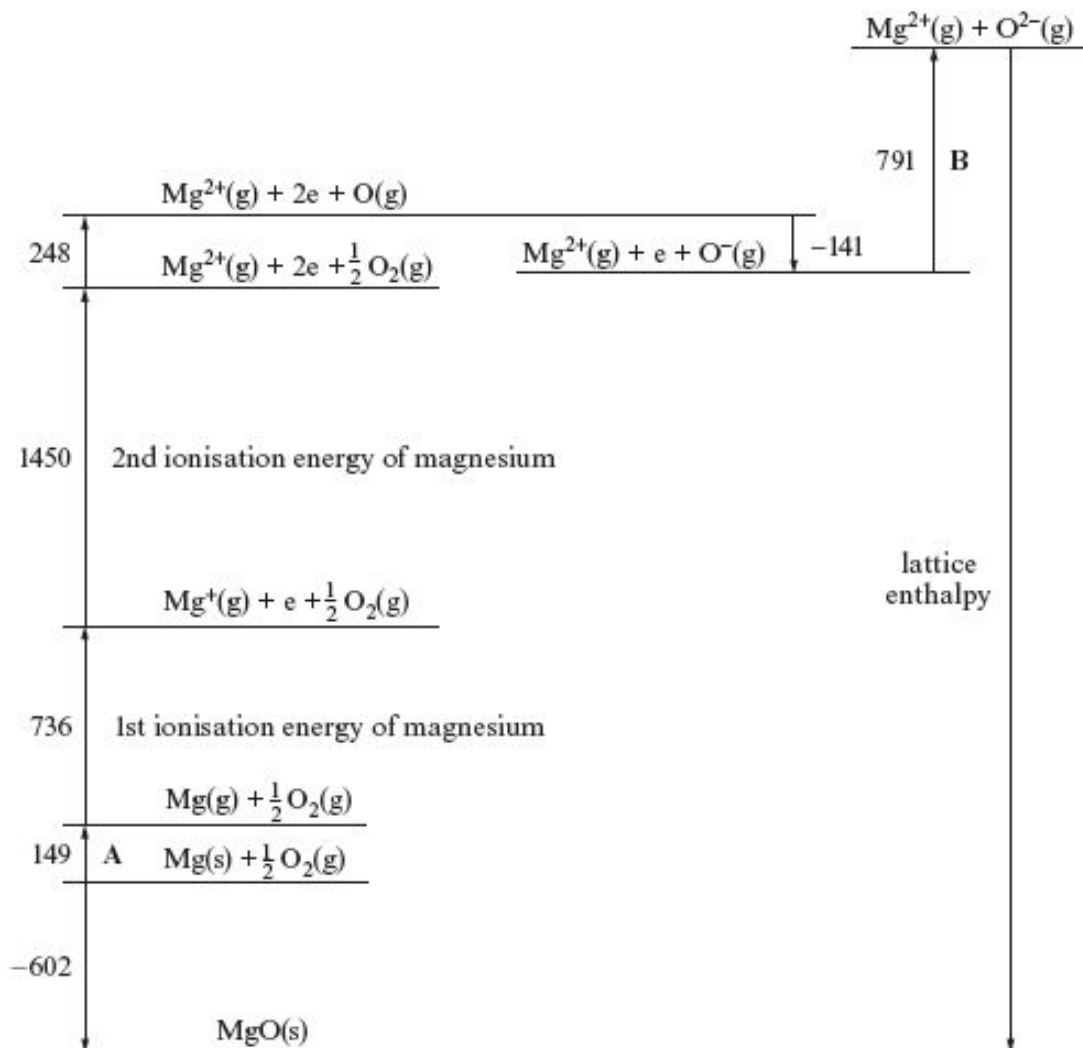
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1. Magnesium oxide, MgO , is a white solid with a very high melting temperature and it is used as the refractory lining in furnaces.

(a) The following Born-Haber cycle shows the enthalpy changes involved in the formation of magnesium oxide.

All enthalpy changes are in kJ mol^{-1} . The cycle is not drawn to scale.



- What is the name given to the enthalpy change labelled A? [1]
- State why the second ionisation energy of magnesium is greater than its first ionisation energy. [1]
- Suggest why the second electron affinity of oxygen, labelled B, is positive. [1]
- Calculate the value of the lattice enthalpy for magnesium oxide. [2]

- (b) Many metal oxides can be reduced to the metal by carbon monoxide. The equation for the reduction of magnesium oxide is given below.



The conditions under which reactions will occur can be predicted using enthalpy and entropy changes. The entropies of the substances involved in this reaction are shown in the table.

Substance	MgO(s)	CO(g)	Mg(s)	CO ₂ (g)
Entropy / JK ⁻¹ mol ⁻¹	26.9	197.7	32.7	213.7

- (i) Suggest a reason why the entropies of carbon monoxide and carbon dioxide are much higher than those of magnesium and magnesium oxide. [1]
 - (ii) Calculate the entropy change in this reaction. [1]
 - (iii) The enthalpy change, ΔH , for the reduction of magnesium oxide is 318.0 kJ mol⁻¹. Calculate the minimum temperature at which this reduction could occur. [3]
- (c) Magnesium oxide, MgO, lead(II) oxide, PbO, and aluminium oxide, Al₂O₃, all react with dilute acids to form aqueous ions – Mg²⁺(aq), Pb²⁺(aq) and Al³⁺(aq).

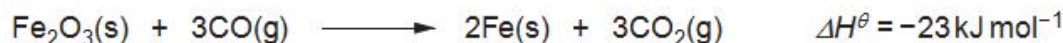
Suggest tests that would enable you to distinguish between solutions containing one of each of these ions. You should include the expected result for **each** test and are advised to record your tests and expected results in a table. [5]

QWC [2]

- (d) Aluminium chloride, AlCl₃, can be used to produce compounds including the chloroaluminate(III) ion, AlCl₄⁻.
- (i) Draw a dot and cross diagram to show the electron arrangement in the AlCl₄⁻ ion. You should show outer electrons only. [1]
 - (ii) Give **one** industrially important use in which the AlCl₄⁻ ion is involved. State the role of the ion in this use. [2]

Total [20]

2. Iron is extracted at high temperatures from the ore haematite, which contains iron(III) oxide, Fe_2O_3 . The process can be summarised by the equation below.



Some thermodynamic data for the substances in the reaction are shown in the following table.

(ii)

Substance	Standard enthalpy change of formation, $\Delta H_f^\theta / \text{kJ mol}^{-1}$	Standard entropy, $S^\theta / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{Fe}_2\text{O}_3(\text{s})$	-826	90
$\text{Fe}(\text{s})$	0	27
$\text{CO}(\text{g})$		198
$\text{CO}_2(\text{g})$	-394	213

- (a) Calculate the standard enthalpy change of formation of carbon monoxide. [3]

$$\Delta H_f^\theta = \dots\dots\dots \text{ kJ mol}^{-1}$$

- (b) Explain why the standard entropies of carbon dioxide and carbon monoxide are significantly greater than those of iron(III) oxide and iron. [1]

- (c) The standard entropy change for this reaction, ΔS^θ , is $+9 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (i) Calculate the free energy change, ΔG^θ , for this reaction at 298K. [2]

$$\Delta G^\theta = \dots\dots\dots \text{ kJ mol}^{-1}$$

(ii) Explain why this reaction is feasible at all temperatures.

[2]

(iii) Many industrial processes use high temperatures even when the reaction is feasible at low temperatures. Suggest why high temperatures are used.

[1]

(Total 9)

- (a) In the reaction below carbon monoxide is acting as a reducing agent.



Use oxidation states (numbers) to show that carbon monoxide is acting as a reducing agent in this reaction. [2]

- (b) State how the stabilities of the +II and +IV oxidation states vary down Group 4. [1]

- (c) You are given two solutions. One contains aqueous aluminium ions, Al^{3+} , and the other contains aqueous lead(II) ions, Pb^{2+} .

- (i) Describe a reaction to show that both of these ions exhibit amphoteric behaviour. Your answer should state the reagent(s) used, the names of any precipitates and any relevant observations. *Chemical equations are not required.* [4]

QWC [1]

- (ii) Describe what is seen when iodide ions are added to an aqueous solution of Pb^{2+} ions. Give the ionic equation for the reaction that occurs. [2]

- (d) Monomeric aluminium chloride is described as containing an electron-deficient species.

- (i) Explain, using monomeric covalent aluminium chloride, what is meant by *electron deficient* and why this leads to the ready formation of the Al_2Cl_6 dimer. You should show the structure of this dimer as part of your answer. [3]

- (ii) The electron-deficient nature of the aluminium chloride monomer results in the compound having an affinity for chlorine-containing species. This is important in catalysis and also in the production of specialised solvents. Give one example of the use of the monomer in either of these ways. [1]

- (iii) On heating, gaseous dimeric aluminium chloride molecules dissociate into the monomer.



- I State one reason why the entropy of this gaseous system is increasing. [1]

- II Use the equation

$$\Delta G = \Delta H - T\Delta S$$

to calculate the temperature at which the dissociation of gaseous Al_2Cl_6 molecules into gaseous AlCl_3 molecules just occurs spontaneously. The entropy change for this reaction, ΔS , is $88 \text{ J mol}^{-1} \text{ K}^{-1}$ and the enthalpy change, ΔH , is 60 kJ mol^{-1} . [2]

- (e) Solutions containing aqueous aluminium ions are weakly acidic because of the dissociation of one of the coordinated water molecules.



The acidity of this solution has been used to stop bleeding from minor cuts.

The expression for the equilibrium constant, in terms of concentrations, for the above system is shown below.

$$K_c = \frac{[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) [\text{H}^+(\text{aq})]}{[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})}$$

Use this expression to calculate the pH of a solution of aluminium ions of concentration 0.10 mol dm^{-3} . The equilibrium constant, K_c , for this system is $1.26 \times 10^{-5} \text{ mol dm}^{-3}$. [3]

Total [20]

2.

(a) $2 \times (0) + 3 \times (-394) - (-826) - 3 \times \Delta H_f^\circ(\text{CO}) = -23$ (1)

$$2 \times (\Delta H_f^\circ(\text{Fe})) + 3 \times (\Delta H_f^\circ(\text{CO}_2)) - (\Delta H_f^\circ(\text{Fe}_2\text{O}_3)) - 3 \times \Delta H_f^\circ(\text{CO}) = -23$$
 (1)

$$-1182 + 826 + 23 = 3 \times \Delta H_f^\circ(\text{CO})$$

$$-333 = 3 \times \Delta H_f^\circ(\text{CO})$$

$$-111 \text{ kJ mol}^{-1} = \Delta H_f^\circ(\text{CO})$$
 (1) [3]

(b) Gases have higher entropies than solids as the molecules have a greater degree of freedom / disorder [1]

(c) (i) $\Delta G = \Delta H - T \Delta S = -23 - (298 \times 9/1000)$ (1)

$$= -25.7 \text{ kJ mol}^{-1}$$
 (1) [2]

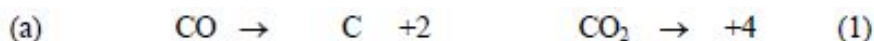
(ii) A reaction is feasible when ΔG is negative (1)

No temperature exists where ΔG is positive / ΔG is negative at all temperatures (1) [2]

(iii) Higher temperature used to increase rate of reaction [1]

Total [9]

3.



Increase of (positive) oxidation number = oxidation / reducing agents themselves
are always oxidised are always oxidised (1)

OR



Oxidation number of iodine reduced, reduction occurring, CO reducing agent (1) [2]

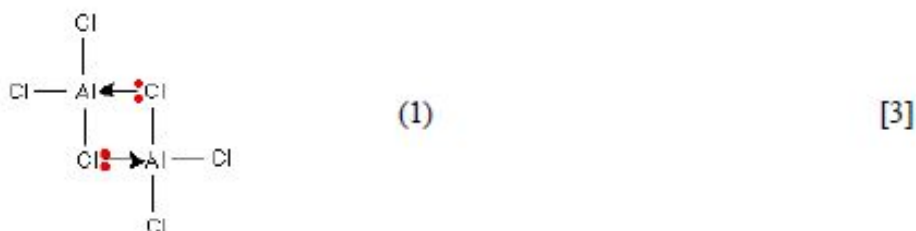
(b) +2 state becomes more stable down the group and +4 becomes less stable. [1]

(c) (i) Add (a little) sodium hydroxide solution (1) to each solution.
A white precipitate (1) of aluminium / lead(II) hydroxide (1) is seen.
When more sodium hydroxide solution is added these precipitates (dissolve giving
a colourless solution). (1) [4]

*QWC Legibility of text: accuracy of spelling, punctuation and grammar;
clarity of meaning.* [1]

(ii) Yellow precipitate (1) $\text{Pb}^{2+} + 2 \text{I}^- \rightarrow \text{PbI}_2$ [2]

(d) (i) The bonding of **aluminium** in the monomer has not completed the octet / suitable
diagram / 6 electrons in its outer shell (1)
When the dimer is formed this octet of bonded electrons is formed (1)



(ii) (As a catalyst) in the chlorination of benzene / making ionic liquids [1]

(iii) I The number of (gaseous) species is increasing, leading to less order [1]

II For the reaction to be just spontaneous $\Delta G = 0$ (1)

substituting $0 = 60\,000 - 88 T$

$T = 60\,000 / 88 = 682 \text{ K} / 409^\circ\text{C} \quad (1) \quad [2]$

$$(e) \quad K_c = \frac{[[Al(H_2O)_5(OH)]^{2+}(aq)][[H^+](aq)]}{[[Al(H_2O)_6]^{3+}(aq)]}$$

$$\therefore 1.26 \times 10^{-5} = [H^+]^2 / 0.10$$

$$\therefore [H^+]^2 = 1.26 \times 10^{-6} \quad [1]$$

$$\therefore [H^+] = \sqrt{1.26 \times 10^{-6}} = 1.12 \times 10^{-3} / 0.00112 \quad (1)$$

- error carried forward

$$pH = -\log_{10} [H^+] = -\log_{10} 1.12 \times 10^{-3} = 2.95 \quad (1) \quad [3]$$

Total [20]