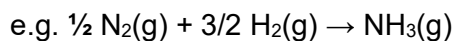


Thermodynamics

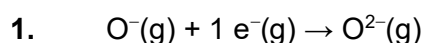
Important definitions

For each of the transformations represented by the equations **1-5**, name the enthalpy change and provide a full definition.



Name: *The standard molar enthalpy change of formation of ammonia*

Definition: *The enthalpy change when one mole of a compound is formed from its elements under standard conditions, all reactants and products in their standard states*

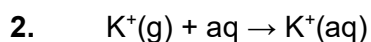


Name:

(1 mark)

Definition:

(1 mark)

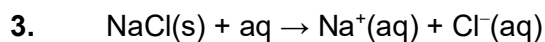


Name:

(1 mark)

Definition:

(1 mark)

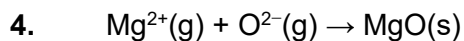


Name:

(1 mark)

Definition:

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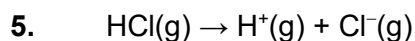


Name:

(1 mark)

Definition:

(1 mark)



Name:

(1 mark)

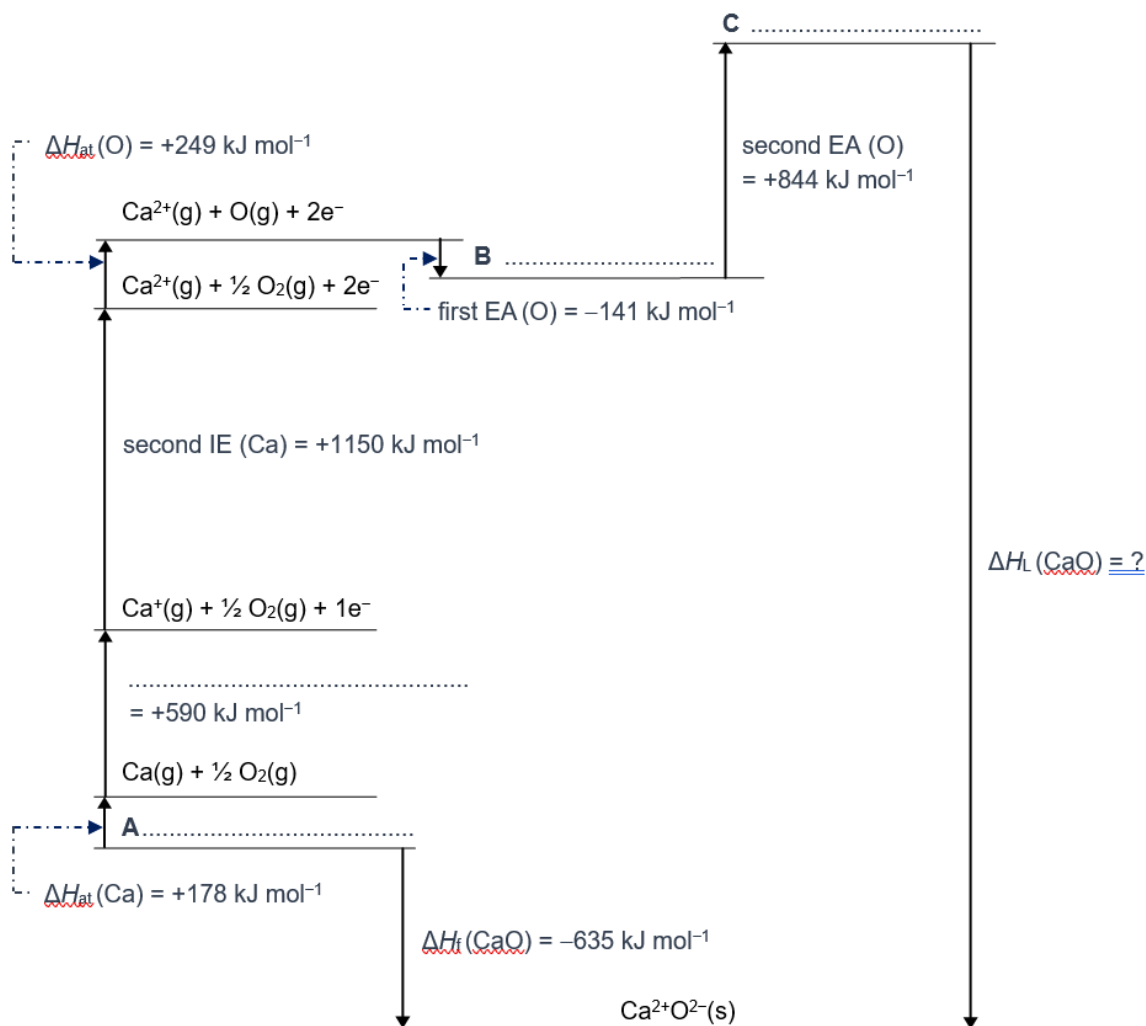
Definition:

(1 mark)

Born Haber cycles

In 1918, a chance meeting of two German scientists, Max Born and Fritz Haber led to a discussion of the manner in which an ionic compound is formed when a metal reacts with a non-metal. This resulted in the creation of what we know today as Born Haber cycles.

The Born Haber cycle for the formation of calcium oxide is shown in the diagram below;



1. Complete the cycle by adding suitable labels for the one missing enthalpy change and the missing intermediate species on the three stages labelled A-C. (7 marks)
2. Explain why the second electron affinity of oxygen is positive. (2 marks)
3. Use the values for the enthalpy changes given to calculate the lattice dissociation enthalpy for calcium oxide. (1 mark)

Enthalpy of solution

The tables below give some data on the lattice formation enthalpies for three different salts, and the enthalpies of hydration of the different ions in the salts.

Salt	Lattice formation enthalpy / kJ mol ⁻¹	Positive ion	Enthalpy of hydration / kJ mol ⁻¹	Negative ion	Enthalpy of hydration / kJ mol ⁻¹
LiCl	-848	Li ⁺	-545	Cl ⁻	-338
NaCl	-780	Na ⁺	-418	Br ⁻
KCl	-711	K ⁺	-351		

1. (a) Describe and explain the trend observed in the enthalpies of hydration of the group one ions.

(3 marks)

(b) The enthalpy of hydration of the bromide ion is not given in the table. Complete the table with a predicted value for the enthalpy of hydration of bromide ions.

(1 mark)

2. The enthalpy of solution of a salt can be calculated from its lattice enthalpy and the enthalpies of hydration of the individual ions in the salt.

Use the data in the table above to calculate the enthalpy of solution of each of the following salts. Show full working for your answers.

(6 marks)

Entropy

Entropy is a measure of the randomness of a system. The more disorder in a system the more positive the entropy.

1. For each of the pairs of systems below, circle the one with the higher entropy;

(a)

An ice cube

or

The puddle of water made when the ice cube melts

(b)

A firework before it explodes

or

The same firework after it has exploded

(2 marks)

2. Use your understanding of entropy to predict whether each of the reactions (a)-(d) have a positive or negative entropy change.

(4 marks)

- (a) $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
(b) $2 \text{Fe}_2\text{O}_3(\text{s}) + 3 \text{C}(\text{s}) \rightarrow 4 \text{Fe}(\text{s}) + 3 \text{CO}_2(\text{g})$
(c) $\text{C}_4\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_4\text{H}_{10}(\text{g})$
(d) $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$

3. Use the data below to now calculate the entropy changes for each of the reactions (a)-(d) and see if your predictions were correct.

Elements	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)
C(s)	+5.7
Fe(s)	+27.3
H ₂ (g)	+65.3
O ₂ (g)	+102.5

Inorganics	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)
Ag ⁺ (aq)	+72.7
AgCl(s)	+96.2
Cl ⁻ (aq)	+56.5
Fe ₂ O ₃ (s)	+87.4
H ₂ O(l)	+69.9
H ₂ O ₂ (l)	+109.6

Organics	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)
C ₄ H ₈ (g)	+305.6
C ₄ H ₁₀ (g)	+310.1
CO ₂ (g)	+213.6

(4 marks)

Gibbs free energy

1. The second law of thermodynamics states that for a reaction to be feasible, the **total** entropy has to increase i.e. $\Delta S_{\text{total}} > 0$.

The **total entropy change**, ΔS_{total} can be defined as;

$$\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$$

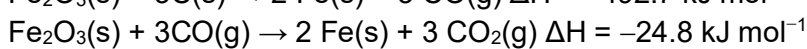
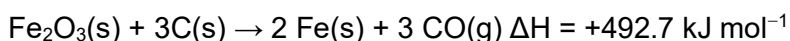
The entropy of the surroundings is affected by the enthalpy change of the reaction (e.g. in an exothermic reaction, heat energy is transferred to the surroundings and hence there is an increase in disorder). The relationship between the **enthalpy change of a reaction**, $\Delta H_{\text{reaction}}$ and the **entropy change of the surroundings**, $\Delta S_{\text{surroundings}}$ is given by;

$$\Delta S_{\text{surroundings}} = - \frac{\Delta H_{\text{reaction}}}{T}$$

If $-T\Delta S_{\text{total}}$ is equal to the **Gibbs free energy change**, ΔG , use the facts above to derive the equation;

$$\Delta G = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}} \quad (3 \text{ marks})$$

2. Iron can be extracted from haematite, Fe_2O_3 , using either C or CO_2 as the reducing agent;



(a) Use the data on the right to;

(i) Calculate the minimum temperature at which reduction with carbon is feasible. (2 marks)

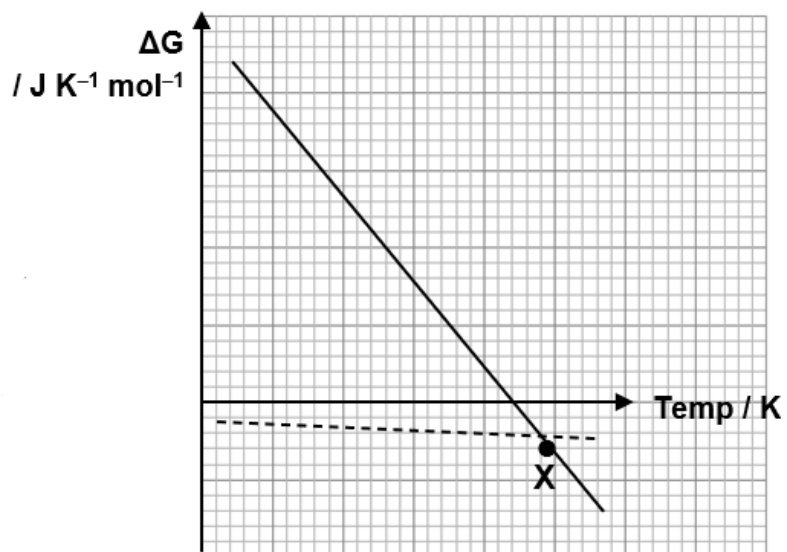
(ii) Prove by calculation that reduction with carbon monoxide is feasible at all temperatures. (2 marks)

Substance	S^\ominus ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{Fe}_2\text{O}_3(\text{s})$	87.4
$\text{Fe}(\text{s})$	27.3
$\text{C}(\text{s})$	5.7
$\text{CO}(\text{g})$	197.6
$\text{CO}_2(\text{g})$	213.6

(b) The lines on the graph on the next page (— and - - - -) show how the Gibbs free energy changes with temperature for each of the methods of reducing haematite described in part (a).

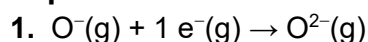
(i) Identify which line corresponds to reduction with carbon and which to reduction with carbon monoxide. (1 mark)

(ii) Calculate the temperature at point X (2 marks)



Thermodynamics – Answers

Important definitions

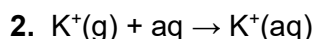


Name: Second electron affinity of oxygen

(1 mark)

Definition: The enthalpy change when a mole of electrons is added to a mole of gaseous oxygen ions each with a single negative charge, forming one mole of gaseous ions each with a two negative charge.

(1 mark)

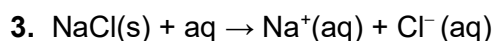


Name: Molar enthalpy of hydration

(1 mark)

Definition: The enthalpy change when one mole of gaseous ions dissolve in sufficient water to give an infinitely dilute solution

(1 mark)

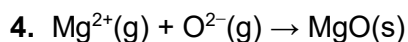


Name: Molar enthalpy change of solution

(1 mark)

Definition: The enthalpy change when one mole of an ionic substance dissolves in sufficient water to give an infinitely dilute solution

(1 mark)

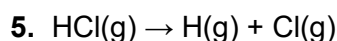


Name: Lattice formation enthalpy

(1 mark)

Definition: The enthalpy change when one mole of an ionic substance is formed from its gaseous ions under standard conditions

(1 mark)



Name: The H-Cl bond enthalpy in hydrogen chloride

(1 mark)

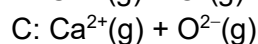
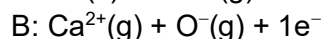
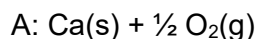
Definition: The enthalpy change when one mole of gaseous hydrogen chloride molecules breaks its covalent bond to form a gaseous hydrogen radical and a gaseous chlorine radical.

(1 mark)

Born Haber cycles

1. Missing enthalpy change is the first ionisation energy of calcium

(1 mark)



(2 marks for each of A-C; 1 mark for correct species, 1 mark for correct state symbols)

2. The second electron affinity is positive as you are adding an electron to an already negative ion. Therefore energy is needed to overcome the repulsion.

(2 marks)

$$\begin{aligned} 3. \quad \Delta H_L(\text{CaO}) &= 178 + 590 + 1150 + 249 + (-141) + 844 - (-635) \\ &= 2870 - (-635) \\ &= \underline{3505 \text{ kJ mol}^{-1}} \end{aligned}$$

(1 mark)

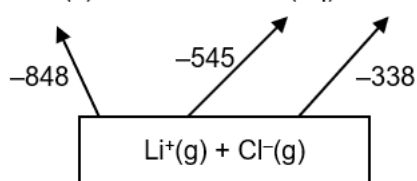
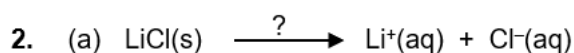
Enthalpy of solution

1. (a) As the ions increase in size, the enthalpy of hydration decreases.

(1 mark)

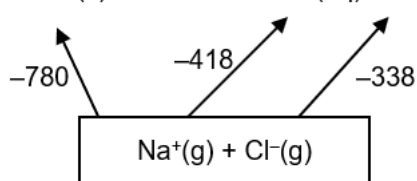
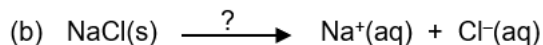
As the ions increase in size the positive ions are less attractive (lower charge to size ratio) and so the attractions formed between the water molecules of the positive ion are weaker (1 mark) and hence less energy is produced when they form (1 mark).

(b) As a bromide ion is bigger than a chloride ion, following the trend described above the enthalpy of hydration is smaller (less negative). The actual value is -304 kJ mol^{-1}



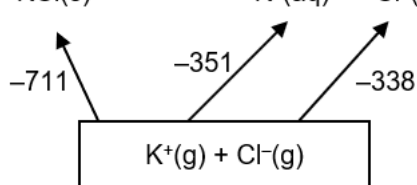
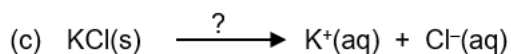
$$\Delta H_{\text{sol}}(\text{LiCl}) = -(-848) + -545 + -338 = \underline{-35 \text{ kJ mol}^{-1}}$$

(2 marks)



$$\Delta H_{\text{sol}}(\text{NaCl}) = -(-780) + -418 + -338 = \underline{+24 \text{ kJ mol}^{-1}}$$

(2 marks)



$$\Delta H_{\text{sol}}(\text{KCl}) = -(-711) + -351 + -338 = \underline{+22 \text{ kJ mol}^{-1}}$$

(2 marks)

Entropy

1. (a) The puddle of water

(1 mark)

(b) The firework after it has exploded

(1 mark)

2. (a) $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ Positive entropy change

(1 mark)

(b) $2 \text{Fe}_2\text{O}_3(\text{s}) + 3 \text{C}(\text{s}) \rightarrow 4 \text{Fe}(\text{s}) + 3 \text{CO}_2(\text{g})$ Positive entropy change

(1 mark)

(c) $\text{C}_4\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_4\text{H}_{10}(\text{g})$ Negative entropy change

(1 mark)

(d) $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ Negative entropy change

(1 mark)

3. (a) $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

$$\Delta S = (69.9 + 102.5) - (109.6) = \underline{+62.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(1 mark)

(b) $2 \text{Fe}_2\text{O}_3(\text{s}) + 3 \text{C}(\text{s}) \rightarrow 4 \text{Fe}(\text{s}) + 3 \text{CO}_2(\text{g})$

$$\Delta S = [(4 \times 27.3) + (3 \times 213.6)] - [(2 \times 87.4) + (3 \times 5.7)] = \underline{558.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(1 mark)

(c) $\text{C}_4\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_4\text{H}_{10}(\text{g})$

$$\Delta S = (310.1) - (305.6 + 65.3) = \underline{-60.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(1 mark)

(d) $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$

$$\Delta S = (96.2) - (72.7 + 56.5) = \underline{-33.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

(1 mark)

Gibbs free energy

1. If, $\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$, substituting in $\Delta S_{\text{surroundings}} = -\Delta H_{\text{reaction}} / T$, the equation becomes;

$$\Delta S_{\text{total}} = -\frac{\Delta H_{\text{reaction}}}{T} + \Delta S_{\text{system}} \quad (1 \text{ mark})$$

Multiplying everything by $-T$ we get;

$$-T\Delta S_{\text{total}} = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}} \quad (1 \text{ mark})$$

$$\text{Since, } -T\Delta S_{\text{total}} = \Delta G \text{ then, } \underline{\Delta G = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}}} \quad (1 \text{ mark})$$

2. (a) (i) For reduction with carbon;

$$\Delta S = [(2 \times 27.3) + (3 \times 197.6)] - [87.4 + (3 \times 5.7)] = +542.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

(1 mark)

The reaction becomes feasible when $\Delta G = 0$, so substituting into $\Delta G = \Delta H - T\Delta S$ we get

$$0 = 492.7 - (T \times 542.9/1000). \text{ Therefore, } 492.7 = 0.5429T \text{ and hence } \underline{T = 908 \text{ K}}$$

(1 mark)

(ii) For reduction with carbon monoxide;

$$\Delta S = [(2 \times 27.3) + (3 \times 213.6)] - [87.4 + (3 \times 197.6)] = +15.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

(1 mark)

The reaction becomes feasible when $\Delta G = 0$, so substituting into $\Delta G = \Delta H - T\Delta S$ we get

$0 = -24.8 - (T \times 15.2/1000)$. Therefore, $24.8 = -0.0152T$ and hence $T = -1630 \text{ K}$. Since the lowest temperature possible is 0 K, the reaction is feasible at all temperatures.

(1 mark)

(b) (i) Comparing $\Delta G = \Delta H - T\Delta S$ to $y = mx + c$ we can see a graph of ΔG (y-axis) vs. T (x-axis) will have a **gradient of $-\Delta S$** and a **y-intercept equal to ΔH** .

For reduction with C, $\Delta H = +492.7 \text{ kJ mol}^{-1}$, $\Delta S = +542.9 \text{ J K}^{-1} \text{ mol}^{-1}$ therefore line _____

For reduction with CO, $\Delta H = -24.8 \text{ kJ mol}^{-1}$, $\Delta S = +15.2 \text{ J K}^{-1} \text{ mol}^{-1}$ therefore line -----
(1 mark for correct identification)

(ii) At point X both reactions have an equal value for ΔG so we can say that;

$$492.7 - 0.5429T = -24.8 - 0.0152T$$

(1 mark)

Rearranging this becomes;

$$492.7 + 24.8 = 0.5429T - 0.0152T$$

$$517.5 = 0.5277T$$

$$T = 981 \text{ K}$$

(1 mark)