Chem Factsheet

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Ellingham Diagrams

To succeed in this topic you will need to:
- understand the concepts of enthalpy and entropy
- understand the concept of Gibbs' Free Energy
- use the equation that links changes in enthalpy and entropy, and temperature.

After working through this Factsheet you will be able to:
- understand that Ellingham diagrams show how Gibbs' Free Energy changes vary with temperature
- appreciate that the gradient of the line in an Ellingham diagram relates to entropy change
- explain how Ellingham diagrams determine the relative ease of reducing a given metal oxide
- explain why carbon monoxide is the reducing agent for iron(III) oxide in the blast furnace
- explain whether carbon or hydrogen is the better reducing agent for a metal oxide.

Background

Harold Ellingham was a British chemist who first produced diagrams showing how the temperature of a system affects the stability of metal oxides in 1944. His diagrams can be used to predict the temperature at which an equilibrium exists between one mole of oxygen, a metal and its oxide – i.e. the temperature when the Gibbs' Free Energy change of a reaction (ΔG) equals zero.

Fig. 1 Equilibrium between zinc, oxygen and zinc oxide

$$2\,Zn(s) + O_2(g) \rightleftharpoons 2\,ZnO(s)$$

This means they can be used to determine how easy it is to reduce a metal oxide to a metal and so to compare the stabilites of metal oxides.

This is important in extractive metallurgy - the process of removing valuable metals from their ores and refining the extracted metals into a purer form.

The Diagrams

Ellingham diagrams show how ΔG varies with temperature for reactions in which **one mole of oxygen at 1 atm pressure** is combined with the pure metal (or other elements such as carbon or hydrogen).

Fig. 2 Reactions for ΔG for the formation of oxides

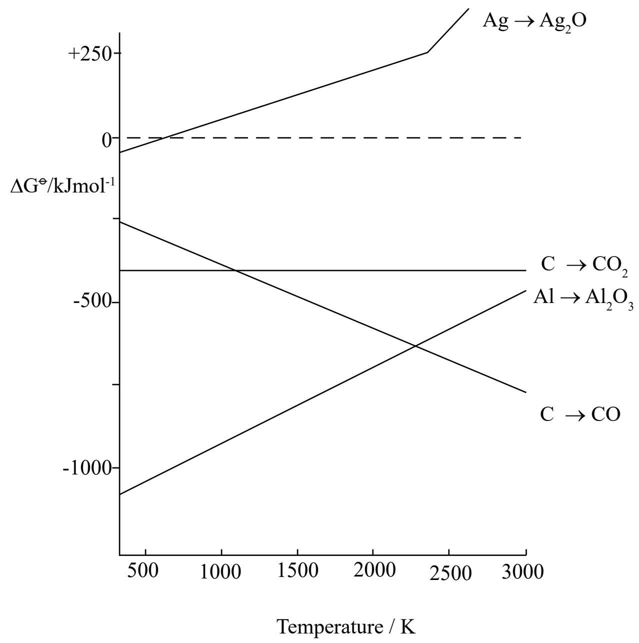
$$\tfrac{4}{3}Al + O_2 \rightarrow \tfrac{2}{3}Al_2O_3$$
$$4Ag + O_2 \rightarrow 2Ag_2O$$
$$C + O_2 \rightarrow CO_2$$
$$2C + O_2 \rightarrow 2CO$$

Ellingham diagrams are essentially a graph of the equation for Gibbs' Free energy change: $\Delta G = \Delta H - T\Delta S$.

This can be written as $\Delta G = -\Delta S.T + \Delta H$ which can then be compared to the standard equation for a straight line, y =mx + c.

When ΔG is plotted on the y-axis against T on the x-axis, a straight line is produced with a gradient (m) equal to $-\Delta S$ for the formation of the oxide and a y-intercept (c) equal to ΔH for the formation of the oxide.

Fig. 3 Ellingham diagram: the stability of various oxides



Questions

1. From Fig. 3 determine which reactions have a negative entropy change.
2. Explain, using an equation, why the line representing the formation of carbon monoxide has a negative gradient.
3. Explain, using an equation, why the line representing the formation of carbon dioxide has a gradient of zero.
4. Suggest why the gradient of the line representing the formation of silver oxide changes at approximately 2400K.

Extracting Metals

For a reaction to be spontaneous, ΔG must be negative. Therefore, when a line crosses ΔG=0, the reaction to form the metal oxide is no longer spontaneous at that temperature. However, the reverse reaction will become feasible, so the metal oxide will spontaneously decompose.

Question

5. (a) Write an equation for the decomposition of silver(I) oxide into its elements
   (b) From Fig. 3, estimate the temperature at which silver(I) oxide will spontaneously decompose.

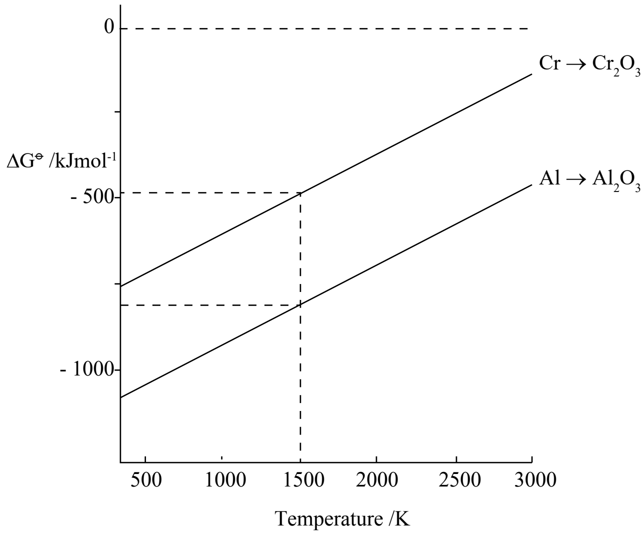
In theory, heating a metal oxide to the temperature at which the ΔG for the formation of that oxide becomes positive is one way of producing the pure metal, since the metal oxide will spontaneously decompose into its elements. However, in practice, uneconomically high temperatures are often required for the reaction and so it is not done on an industrial scale.

Relative stability of oxides

The ΔG at any given temperature for the formation of an oxide is also a measure of the stability of that oxide at that temperature. The more negative the ΔG, the more stable the oxide.

A metal which forms a more stable oxide is a potential reducing agent for a less stable oxide.

Fig. 4 Ellingham diagram for Al_2O_3 and Cr_2O_3



The ΔG for the formation of aluminium oxide at 1500K is more negative than that for the formation of chromium(III) oxide. Therefore, aluminium oxide is more thermodynamically stable than chromium(III) oxide. This means that aluminium is a potential reducing agent for the less stable chromium(III) oxide at 1500K.

The following reaction can therefore be predicted:

$$Cr_2O_3\,(s) + 2\,Al\,(s) \rightarrow Al_2O_3\,(s) + 2\,Cr\,(s)$$

This reaction is of industrial importance in the production of chromium.

The ΔG for the reaction at 1500K can be calculated.

Ellingham diagrams are drawn for the reaction of metals with one mole of oxygen gas, so using this the above equation is more correctly written as:

$$\tfrac{2}{3}Cr_2O_3(s) + \tfrac{4}{3}Al(s) \rightarrow \tfrac{2}{3}Al_2O_3(s) + \tfrac{4}{3}Cr(s)$$

Fig. 5 Calculating ΔG_{1500K}

$$\tfrac{4}{3}Al(s) + O_2\,(g) \rightarrow \tfrac{2}{3}Al_2O_3(s)$$

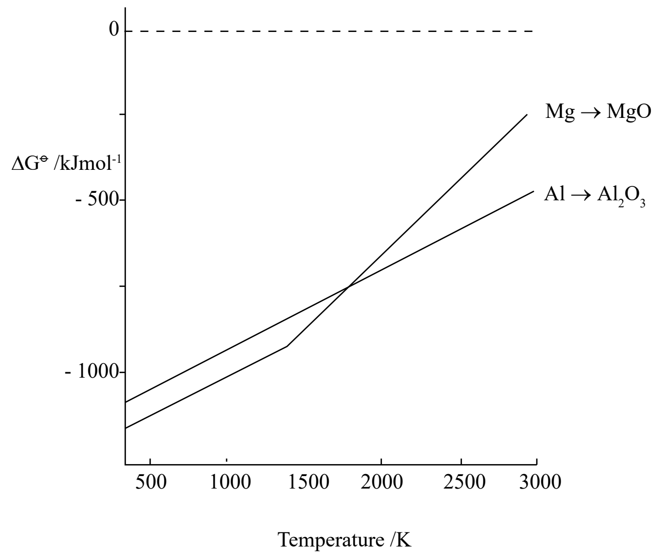
$$\tfrac{2}{3}\,Cr_2O_3(s) \rightarrow \tfrac{4}{3}\,Cr(s) + O_2(g)$$

[Note: the chromium reaction in Fig. 5 is the reverse of that described on an Ellingham diagram so the ΔG is positive.]

The overall $\Delta G_{reaction}$ $= -798 + 493$
$= -305\ kJmol^{-1}$
[negative ΔG implies a spontaneous reaction]

Question

Fig. 6 Ellingham diagram for MgO and Al_2O_3



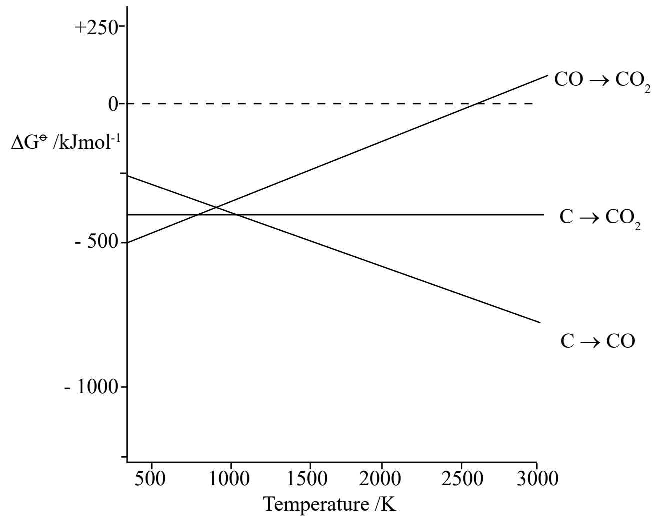
6. (a) Use Fig. 6 to determine which oxide is the most thermodynamically stable at 1000K and at 2500K?
   (b) At what temperatures would you predict magnesium to act as a reducing agent for aluminium oxide? Explain your answer.

Carbon and its Oxides

As seen in Fig.7 there are 3 Ellingham lines for the different reactions of carbon and carbon monoxide:

$C + O_2 \rightarrow CO_2$
$2C + O_2 \rightarrow 2CO$
$2CO + O_2 \rightarrow 2CO_2$

Fig. 7 Ellingham diagrams for the formation of oxides of carbon



The oxide with the most negative ΔG at a given temperature is formed as this is the most thermodynamically stable at that given temperature.

Question

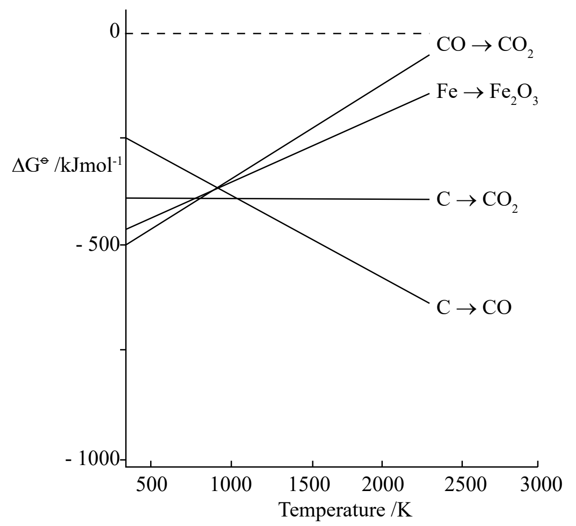
7. From Fig. 7 suggest the most thermodynamically stable oxide of carbon at 500K, 900K and 2000K.

Reducing Iron(III) Oxide

Iron(III) oxide gets reduced at the top of the blast furnace where the temperatures are approximately 800-850K. At these temperatures it can be seen from the Ellingham diagram in Fig 8 that carbon monoxide is a stronger reducing agent than carbon.

The line for the $CO \rightarrow CO_2$ process has a more negative ΔG than $C \rightarrow CO_2$ and $C \rightarrow CO$ processes at these temperatures.

Fig. 8 Ellingham diagram for Fe_2O_3 and oxides of carbon



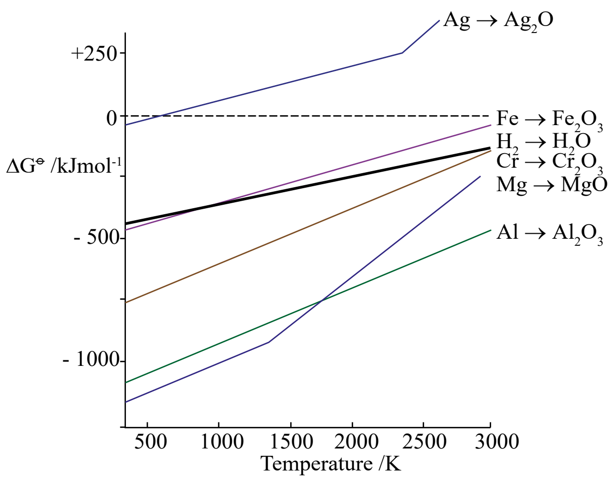
It can be predicted that at higher temperatures, carbon will act as the reducing agent producing CO at temperatures higher than approximately 1100K.

The Better Reducing Agent – Hydrogen or Carbon?

Remember, when choosing a reducing agent for a metal oxide, the ΔG for the formation of the oxidised reducing agent must be more negative than the metal oxide at the given temperature.

Fig. 9 shows that hydrogen is unable to reduce many oxides as water does not have a more negative ΔG than many metal oxides at any temperature, apart from Ag_2O. It can, however, reduce iron(III) oxide at temperatures above approximately 800K.

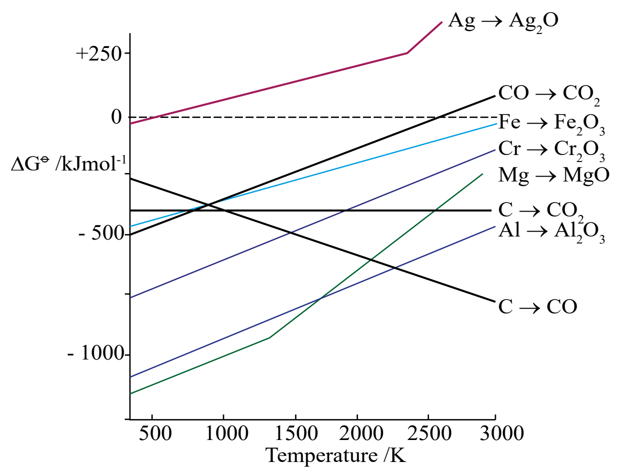
Fig. 9 Ellingham diagram for the formation of various oxides including water



From Fig. 10 it can be seen that, in theory, carbon becomes an increasingly powerful reducing agent as the temperature increases since the line for $C \rightarrow CO$ has a negative gradient.

However, in the reduction of chromium(III) oxide, the chromium formed reacts with carbon at these high temperatures and chromium carbide impurities are formed which give the product undesirable properties. The more favourable method of extracting chromium is reduction of chromium(III) oxide by aluminium as described previously.

Fig. 10: Ellingham diagram for the formation of various oxides including oxides of carbon



Question

8. (a) From Fig. 10, predict the temperatures at which carbon could theoretically reduce aluminium oxide.
   (b) Suggest the oxide of carbon that will be produced in the reaction.

Answers

1. The formation of silver(I) oxide and aluminium oxide.
   [reactions with negative entropy changes can be identified by having a line with a positive gradient - remember the gradient of the line = -ΔS]
2. The formation of carbon monoxide has a positive entropy change. The system becomes more disordered as 2 moles of gaseous product are formed from 1 mole of gas and 2 moles of solid.
3. The formation of carbon dioxide has a very low entropy change since 1 mole of gaseous reactants become 1 mole of gaseous products and so the disorder of the system does not change significantly.
4. The gradient changes at approximately 2400K as this corresponds to the boiling point of silver. Therefore the reaction at temperatures higher than approximately 2400K involve a greater negative entropy change as 5 moles of gaseous reactants become 2 moles of solid products. Before silver boils, the reactants are less disordered and so the change in disorder is less marked.
5. (a) $2Ag_2O \rightarrow 4Ag + O_2$
   (b) approximately 550 – 600K
6. (a) 1000K = MgO
   2500K = Al_2O_3
   (b) Temperatures below approximately 1750K because magnesium oxide is more thermodynamically stable than aluminium oxide at these temperatures meaning magnesium oxide will be formed in preference to aluminium oxide.
7. 500K = CO_2
   900K = CO_2
   2000K = CO
8. (a) anything above approximately 2300K (the point at which the $C \rightarrow CO$ and $Al \rightarrow Al_2O_3$ lines intersect)
   (b) carbon monoxide

Acknowledgements: *This Factsheet was researched and written by* ***Martin Scott. ISSN 1351-5136***