

3.9.4: Geology- Iron and its Ores

Perhaps the most useful feature of thermochemical equations is that they can be combined to determine ΔH_m values for other chemical reactions. For example, iron forms several oxides, including iron(II) oxide or wüstite (FeO), iron(III) oxide or hematite (Fe_2O_3), and finally, iron(II,III) oxide or magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$ or Fe_3O_4). These oxides form by thermochemical reactions which depend on, and influence, their environment by producing or absorbing heat. Hematite exists in several phases (denoted α -hematite; β , & γ -maghemite; and ϵ), and they are all different from ordinary rust, which is also often given the formula Fe_2O_3 ^[1]. Fe_2O_3 is the chief iron ore used in production of iron metal. FeO is nonstoichiometric. Magnetite is the most magnetic of all the naturally occurring minerals on Earth. Naturally magnetized pieces of magnetite, called lodestone, will attract small pieces of iron. We'll see evidence below that Fe_3O_4 is not simply a mixture of FeO and Fe_2O_3 .



Iron(II) oxide, wüstite



Iron(III) oxide, hematite

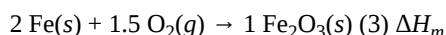
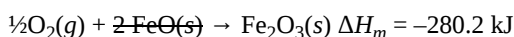
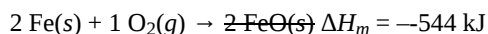


Iron(II,III) oxide, Magnetite

Consider, for example, the following two-step sequence. Step 1 is reaction of 2 mol Fe(s) and 1 mol $\text{O}_2(\text{g})$ to form 2 mol FeO(s) :

(1) $2 \text{Fe(s)} + 1 \text{O}_2(\text{g}) \rightarrow 2 \text{FeO(s)} \Delta H_m = -544 \text{ kJ} = \Delta H_1$ In step 2 the 2 moles of FeO react with an additional 0.5 mol O_2 yielding 1 mol Fe_2O_3 : (2) $2 \text{FeO(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) \Delta H_m = -280.2 \text{ kJ} = \Delta H_2$ (Note that since the equation refers to moles, not molecules, fractional coefficients are permissible.) The net result of this two-step process is production of 1 mol Fe_2O_3 from the original 2 mol Fe and 1.5 mol O_2 (1 mol in the first step and 0.5 mol in the second step). All the FeO produced in step 1 is used up in step 2.

On paper this net result can be obtained by *adding* the two chemical equations as though they were algebraic equations. The FeO produced is canceled by the FeO consumed since it is both a reactant and a product of the overall reaction



Experimentally it is found that the enthalpy change for the net reaction is the *sum* of the enthalpy changes for steps 1 and 2: $\Delta H_{\text{net}} = -544 \text{ kJ} + (-280.2 \text{ kJ}) = -824 \text{ kJ} = \Delta H_1 + \Delta H_2$ That is, the thermochemical equation (3) $2 \text{Fe(s)} + 1.5 \text{O}_2(\text{g}) \rightarrow 1 \text{Fe}_2\text{O}_3(\text{s}) \Delta H_m = -824 \text{ kJ}$ is the correct one for the overall reaction.

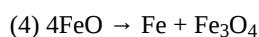
In the general case it is always true that *whenever two or more chemical equations can be added algebraically to give a net reaction, their enthalpy changes may also be added to give the enthalpy change of the net reaction.*

This principle is known as **Hess' law**. If it were not true, it would be possible to think up a series of reactions in which energy would be created but which would end up with exactly the same substances we started with. This would contradict the law of conservation of energy. Hess' law enables us to obtain ΔH_m values for reactions which cannot be carried out experimentally, as the next example shows.

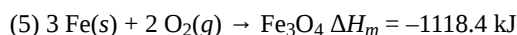
Example 1

Magnetite has been very important in understanding the conditions under which rocks form and evolve. Magnetite reacts with oxygen to produce hematite, and the mineral pair forms a buffer that can control the activity of oxygen. One way magnetite is formed is decomposition of FeO .

FeO is thermodynamically unstable below 575 °C, disproportionating to metal and Fe_3O_4 ^[2].



The direct reaction of iron with oxygen does not occur in nature, because iron does not occur in the elemental form in the presence of oxygen, but we know the enthalpy of reaction from laboratory studies:

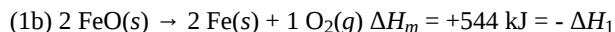


Calculate the enthalpy change for Reaction (4) from the enthalpies of other reactions given on this page.

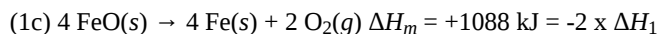
Solution

We use the following strategy to manipulate the three experimental equations so that when added they yield Eq. (4):

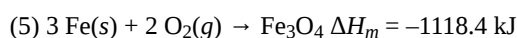
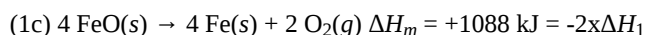
a) Since the target reaction (4) has FeO on the left, but the reaction (1) above with ΔH_{m1} has FeO on the right, we can reverse it, changing the sign on ΔH_{m1} :



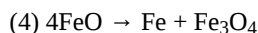
But the target reaction requires 4 mol of FeO on the left, so we need to multiply this reaction, and its associated enthalpy change, by 2:



b) Since the target equation has 1 mole of Fe_3O_4 on the right, as does equation (5) above, we can combine equation (5) with (1c):



Combining the equations and canceling 2O_2 on the left and right, and canceling 3 Fe on the left, leaving 1 Fe on the right, we get equation (4):



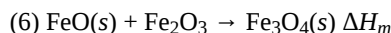
The enthalpy change will be the sum of the enthalpy changes for (1c) and (5):

$$\Delta H_m = -2\Delta H_{m1} + \Delta H_{m5}$$

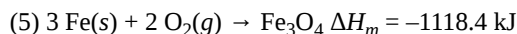
$$\Delta H_m = +1088 \text{ kJ} + (-1118.4) = -30.4 \text{ kJ}$$

Example 2

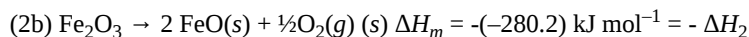
Fe_3O_4 is not simply a mixture of FeO and Fe_2O_3 , but a novel structure. Prove this by using thermochemical equations on this page to calculate the enthalpy for reaction (6) below. If the enthalpy change is zero, no significant chemical change occurs.



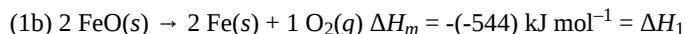
Solution: It appears that we could start with (5) which has Fe_3O_4 on the right, like the target equation:



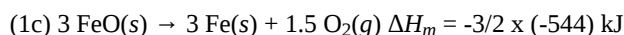
We can introduce the Fe_2O_3 needed on the left of the target equation by using the reverse of Equation (2), changing the sign on ΔH_m :



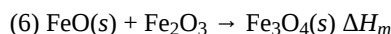
This will introduce 2 FeO on the right, and we want 3 FeO on the left in the target equation. There are also 3 Fe on the left of Equation (3) that need to be canceled. We can accomplish both by adding the reverse of Equation (1):



Since the target equation has 1 FeO on the left, we need to multiply (1b) by 3/2 or 1.5:



Combining (5), (2b), and (c) we get the target equation, and the ΔH is calculated by combining the corresponding ΔH_1 values:



$$\Delta H_1 = -1118 \text{ kJ} + (-280.2 \text{ kJ}) + (-3/2) \times (-544 \text{ kJ}) = -22 \text{ kJ}$$

Since this is a significantly exothermic change, it appears that a chemical change occurs when FeO and Fe_2O_3 combine to make Fe_3O_4 . Significant enthalpy changes occur when solutions are prepared (the dangerous heating observed when water is added to sulfuric acid is a prime example), but these always indicate that bonds have been broken or formed.

References

1. en.Wikipedia.org/wiki/Fe₂O₃
2. Greenwood, Norman N.; Earnshaw, A. (1997), Chemistry of the Elements (2nd ed.), Oxford: Butterworth-Heinemann, ISBN 0080379419

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