

### Unit 3, Lesson 06: Hess's Law of Heat Summation

A **state function** is a process which can occur many different ways, but the value of the function depends only on the final state, not on the steps in between.

For example, it doesn't matter how you get to school in the morning, as long as you get there. The route and method of transportation don't really matter. The overall result is the same, regardless of the path taken, so being at school is a state function.

The opposite of a state function is a **path function**, in which the steps taken do matter. The time taken to get to school and the distance covered are path functions.

Enthalpy (the total chemical potential energy of a substance due to its chemical bonds) is a state function. The enthalpy of a methane molecule is constant, regardless of whether that methane comes from a cow's burp, fermentation in a garbage dump or from an underground reservoir of natural gas.

The change in enthalpy ( $\Delta H$ ) for a reaction is also a state function. Even if a reaction can be performed by different reaction paths, the overall change in enthalpy will be the same, regardless of the path taken.

**Note:** the enthalpy of a substance does depend on the physical conditions of the molecule- its temperature, pressure and concentration. For this reason, enthalpy changes ( $\Delta H$ ) are usually measured under standard conditions such as SATP (25°C and 100 kPa pressure). For solutions, the standard state concentration is 1.00 mol/L concentration.

The symbol ( $\Delta H^\circ$ , read "ΔH nought") signifies that the enthalpy is a **Standard Enthalpy**, and was measured at 25 °C and 100 kPa.

**Hess's Law of Heat Summation:** if a reaction is carried out in a series of steps,  $\Delta H$  for the overall reaction is equal to the sum of the enthalpy changes for the individual steps (see diagrams, p 243, 244)

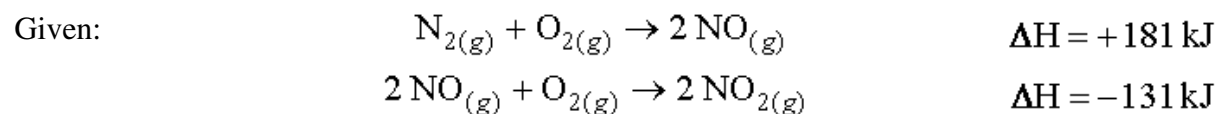
- the overall enthalpy change of a physical or chemical change depends only on the beginning conditions of the reactants and the final conditions of the products
- the enthalpy change is independent of the number or order of the steps in the reaction

This means that when a reaction can be expressed as the algebraic sum of two or more reactions, then the total enthalpy change is equal to the sum of the enthalpy changes for the intermediate steps.

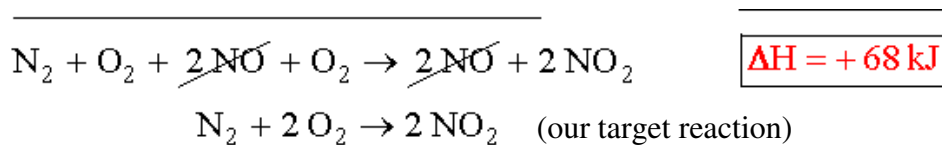
#### Rules for using Hess's Law

1. If the reaction is multiplied (or divided) by some factor,  $\Delta H$  must also be multiplied (or divided) by that same factor.
2. If the reaction is reversed (flipped), the sign of  $\Delta H$  must be changed from a negative to positive, or visa versa.

eg. Calculate  $\Delta H$  for the reaction:  $\text{N}_{2(g)} + 2 \text{O}_{2(g)} \rightarrow 2 \text{NO}_{2(g)}$  (the "target" reaction)

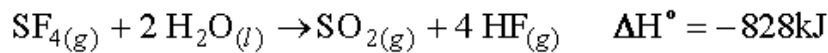
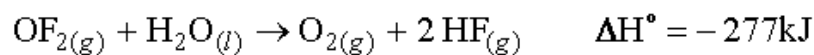


Adding these reactions, we get:

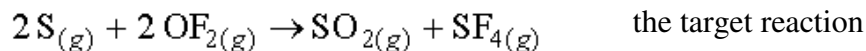


2) Let's try one that is a bit more complicated.

Given:



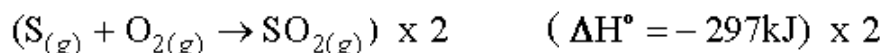
Calculate the value of  $\Delta H^\circ$  for the reaction:



**Step 1:** Pick any reactant or product from the target reaction to start with:

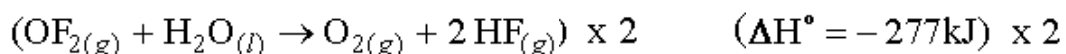
eg. we need 2 S atoms on the reactant side

- the only reaction with S atoms is the third reaction
- to get 2 S atoms, we need to multiply the whole third reaction and its  $\Delta H$  by a factor of 2
- write this down:



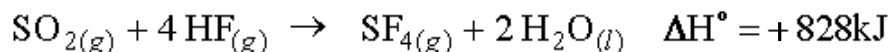
**Step 2:** Look at the next reactant in the target reaction:

- we need 2 OF molecules
- the only reaction with an OF molecule is the first reaction
- to get 2 OF molecules, we need to multiply the whole first reaction and its  $\Delta H$  by a factor of 2
- write this down:

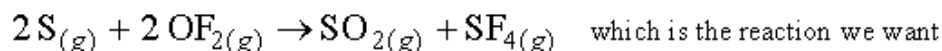
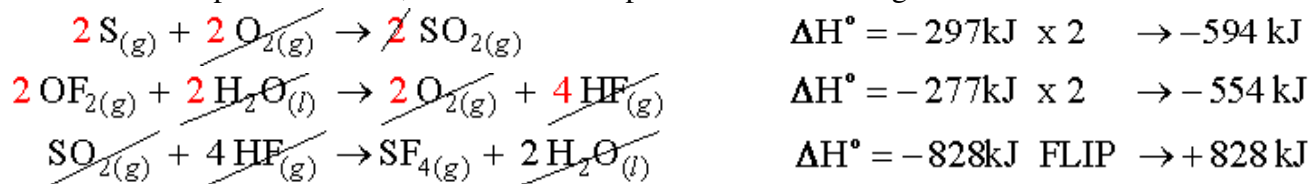


**Step 3:** Look at one of the products:

- there is 1  $\text{SF}_4$  molecule on the product side of the target reaction
- the only reaction with the  $\text{SF}_4$  molecule is the second reaction, but  $\text{SF}_4$  is on the reactant side
- to get the  $\text{SF}_4$  molecule on the product side, FLIP the second reaction
- because the reaction has been flipped, change the sign of  $\Delta H$  for this reaction to + 828 kJ
- write this down:



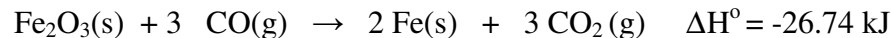
Now if we total up the reactions, we should end up with the overall target reaction:



$$\Delta H^\circ = -320 \text{kJ}$$

To calculate the  $\Delta H^\circ$  for the target reaction, add up  $\Delta H$  values for the individual reactions.

**Example #3:** Carbon monoxide (CO) is often used in metallurgy to remove oxygen from metal oxides and purify the free metal. The thermochemical equation for the reaction of CO with iron (III) oxide, Fe<sub>2</sub>O<sub>3</sub>, is:



Use this equation and the equation for the combustion of CO:



to calculate the value of  $\Delta H^\circ$  for the reaction:

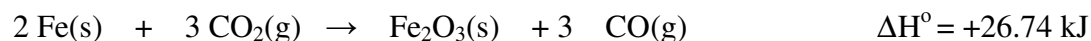


### Solution

Combine the equations in such a way that we can add them to get the final target equation. Then we add the corresponding  $\Delta H^\circ$ 's to obtain the  $\Delta H^\circ$  of the target equation.

**Step 1.** The target equation must have 2 Fe on the left, but the first equation above has 2 Fe on the right. To move it left, reverse the entire equation and remember to reverse the sign of  $\Delta H^\circ$ . When the equation is flipped over the Fe<sub>2</sub>O<sub>3</sub> also falls into the correct position.

**Step 2.** There must be 1½O<sub>2</sub> of the left, and we must be able to cancel *three* CO and *three* CO<sub>2</sub> when the equations are added. Multiply the second equation by 3 and we get the necessary coefficients. Multiply the  $\Delta H^\circ$  values for the second equation by 3 as well. The adjusted equations are:



**Step 3:** This adds up to the target equation and  $\Delta H^\circ$  of

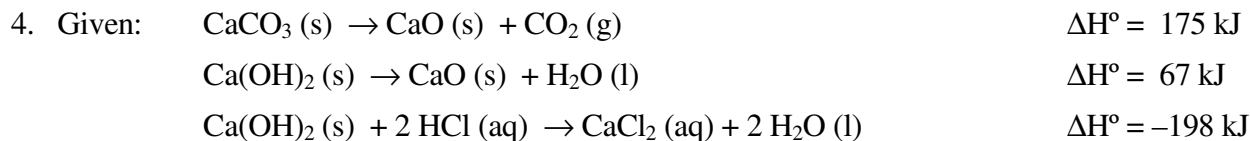


### Final notes:

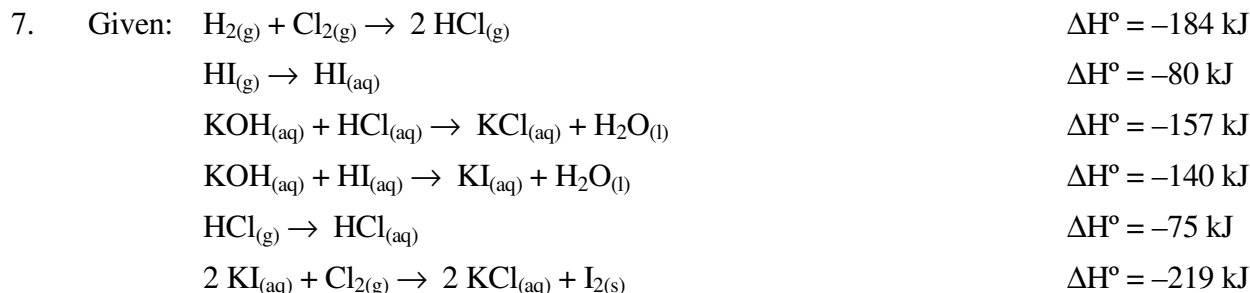
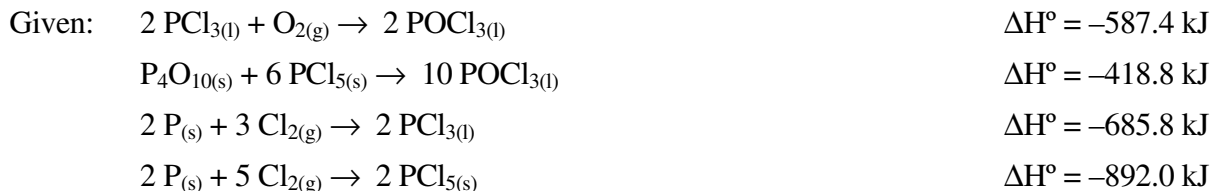
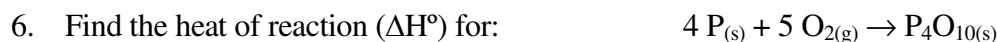
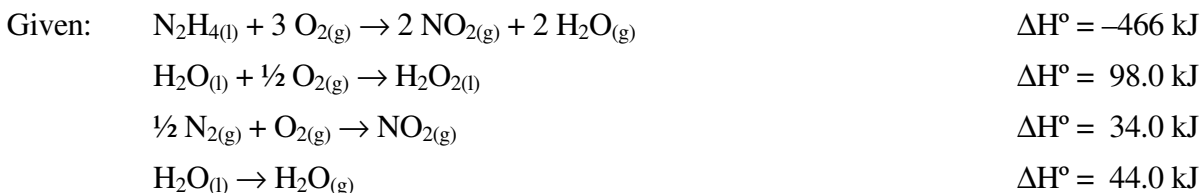
- The state of the reactants and products is important because it affects enthalpy. If necessary, convert substances to the correct state using a thermochemical reaction and include the  $\Delta H$  value for the phase change (change of state) in your calculation.
- $\Delta H^\circ$  is often listed as just  $\Delta H$ . If you are given  $\Delta H$ , assume that it was measured at standard conditions

**Homework:**

1. Read pages 243 – 246 in McGraw-Hill
2. Answer questions 13 – 16 on page 247
3. Read through investigation 5-B on pages 248-249 in preparation for tomorrow's lab. We will not use graphs to record temperature. Instead, prepare a data table similar to the one in Lab 4. Do not answer the extension question. The accepted value for  $\text{Mg(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{MgO(s)}$  is  $-601.6 \text{ kJ/mol}$ .



Find the  $\Delta H^\circ$  for:  $\text{CaCO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$



Calculate the heat of reaction ( $\Delta H^\circ$ ) for:  $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2 \text{HI}(\text{g})$

**Answers:**

4.  $-90. \text{ kJ}$  (the decimal indicates that the zero is significant, so 2 sig digs)
5.  $-642 \text{ kJ}$
6.  $-3271.2 \text{ kJ}$  or  $-3271 \text{ kJ}$  (both are acceptable answers)
7.  $+11 \text{ kJ}$