Rafa Muñoa
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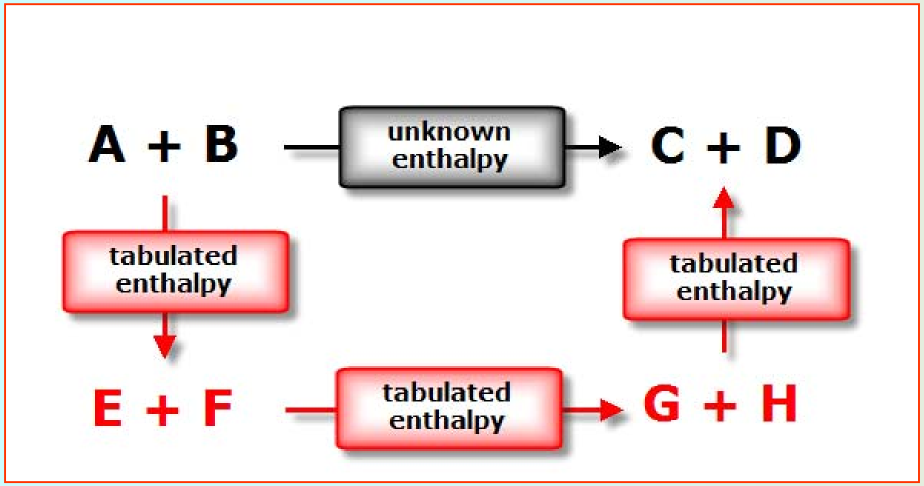
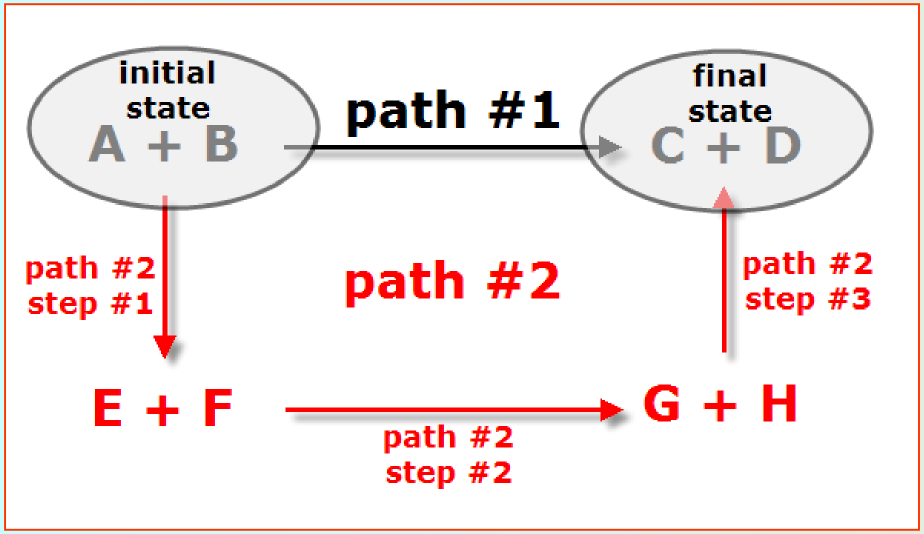
Hess's Law



Introduction

Many enthalpies of reaction are tabulated.

In this chapter we'll see how we can determine the enthalpy of a given reaction from those known (tabulated) values.



Enthalpy is a state function

Because enthalpy is a state function, the enthalpy change associated with a chemical process depends only on

- the **amount of matter** that takes part in that reaction
- the **initial state** of the reactants
- the **final state** of the products

Hess's Law

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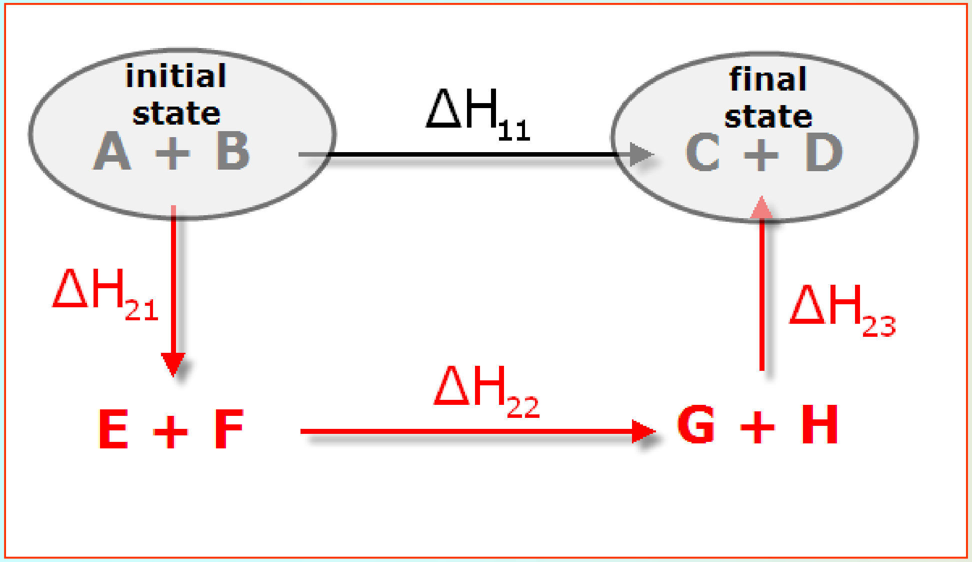

Enthalpy is a state function

As a result, given that we have two different paths to carry out a chemical reaction:

- path #1: in one unique step and the enthalpy is

$$\Delta H_{11}$$

- path #2: in three steps and the corresponding enthalpies are

$$\Delta H_{21},\ \Delta H_{22},\ \Delta H_{23}$$

then we can conclude that the enthalpies must meet the following relationship:

$$\Delta H_{11} = \Delta H_{21} + \Delta H_{22} + \Delta H_{23}$$

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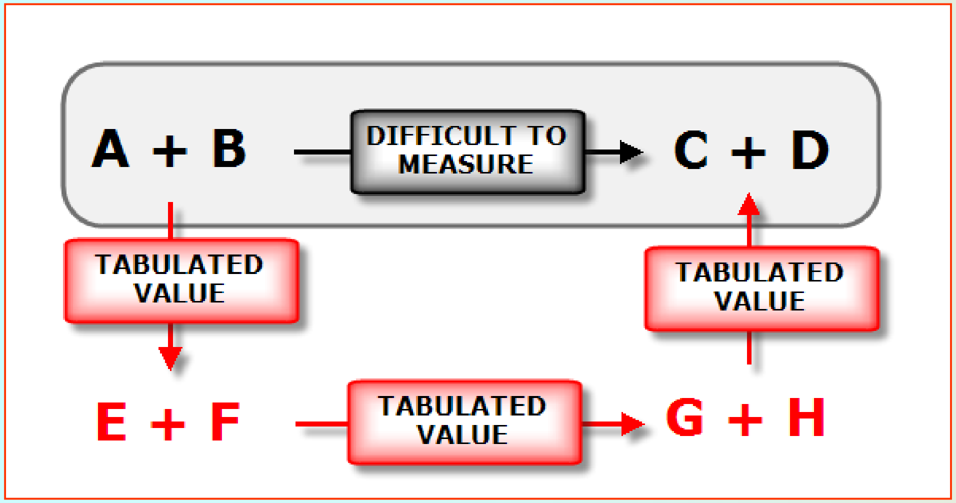

$$\Delta H_{11} = \Delta H_{21} + \Delta H_{22} + \Delta H_{23}$$

Hess's Law

Hess's laws states that if a reaction is carried out in a series of steps the enthalpy for the reaction will equal to the sum of the enthalpies for the individual steps.

This allows us to calculate the enthalpy change for a vast number of reactions from a small number of tabulated values.

This law provides a useful means of calculating enthalpies that are difficult to measure directly.

Hess's Law

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Sample Exercise #1

The following enthalpies are known:
- the enthalpy of combustion of C to CO_2 is −393.5 kJ/mol C,
- the enthalpy of combustion of CO to CO_2 is −283.0 kJ/mol C

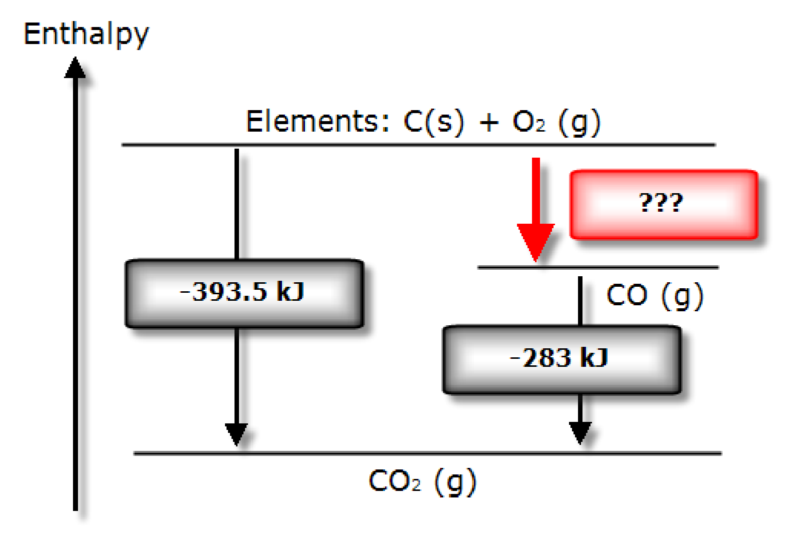
Using the data provided, determine the enthalpy of combusion of C to CO.

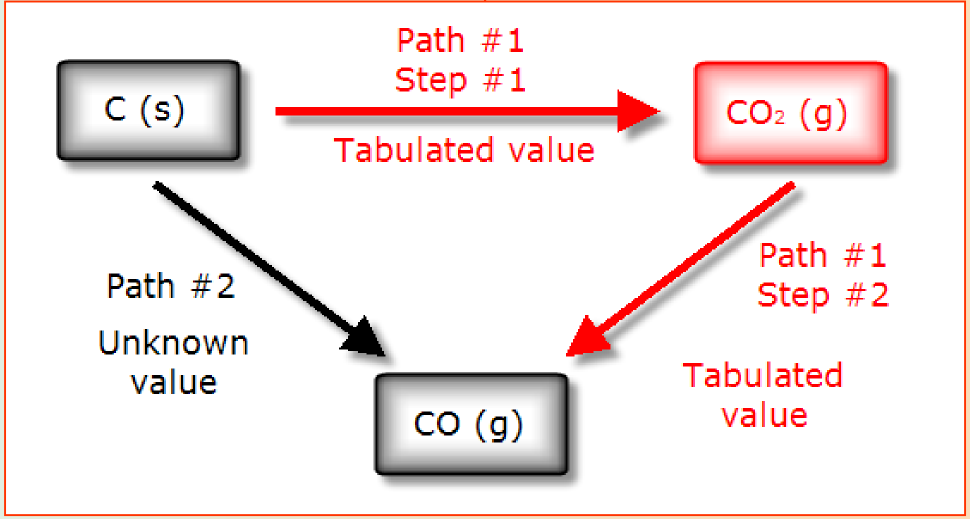
Strategy

We are going to follow these steps:

- #1: write the equations related to the data provided
- #2: combine the equations and their enthalpies to get the one we need to calculate

Graphic representations





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Step #1

$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)\quad \Delta H_1 = -393.5\ kJ$

$CO\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow CO_2\ (g)\quad \Delta H_2 = -283.0\ kJ$

$C\ (s) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)\quad \Delta H = ???$

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Sample Exercise #1

The following enthalpies are known:
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Strategy

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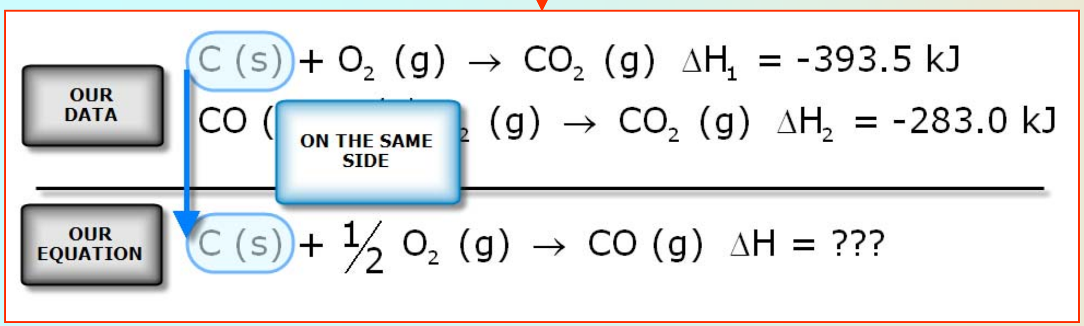
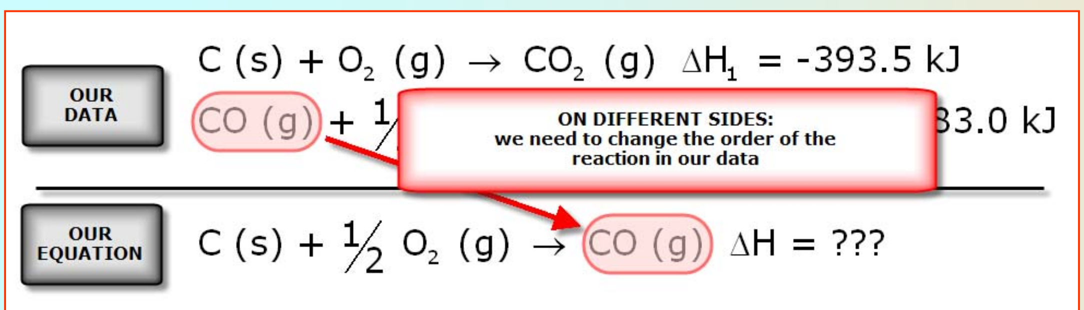
•#2: combine the equations and their enthalpies to get the one we need to calculate

Step #2





Combining the equations

We need to compare the sides of the compounds in our data and in our equation. We see that

•C(s) is a reactant in both equations, so we leave the data as it is

•CO(g) is a reactant in the data and a product in our equation; therefore we need to swap sides in the data and change the sign of the value of enthalpy

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Using the data provided, determine the enthalpy of combusion of C to CO.

Strategy

We are going to follow these steps:

- #1: write the equations related to the data provided
- #2: combine the equations and their enthalpies to get the one we need to calculate

Combining the equations

After changing sides to fit the data into our equation and cancelling out substances that appear on both sides, we get the enthalpy for our reaction

OUR DATA

$$C\,(s) + O_2\,(g) \rightarrow \cancel{CO_2\,(g)} \quad \Delta H_1 = -393.5\text{ kJ}$$

$$\cancel{CO_2\,(g)} \rightarrow CO\,(g) + \cancel{\tfrac{1}{2}\,O_2\,(g)} \quad \Delta H_2 = +283.0\text{ kJ}$$

OUR EQUATION

$$C\,(s) + \tfrac{1}{2}\,O_2\,(g) \rightarrow CO\,(g) \quad \Delta H = \mathbf{-110.5\text{ kJ}}$$

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Hess's Law

Sample Exercise #2

Calculate ΔH for the reaction

$$2\ C(s) + H_2\ (g) \rightarrow C_2H_2\ (g)$$

given the following reactions and their respective enthalpy changes:

$$C_2H_2\ (g) + 2.5\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + H_2O\ (l) \quad \Delta H_1 = -1299.6\ kJ$$

$$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g) \quad \Delta H_2 = -393.5\ kJ$$

$$H_2\ (g) + 0.5\ O_2\ (g) \rightarrow H_2O\ (l)\ \Delta H_3 = -285.8\ kJ$$

Strategy

- Combine the equations and their enthalpies to get the one we need to calculate

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Hess's Law

Sample Exercise #2

Calculate ΔH for the reaction $2\ C(s) + H_2\ (g) \rightarrow C_2H_2\ (g)$

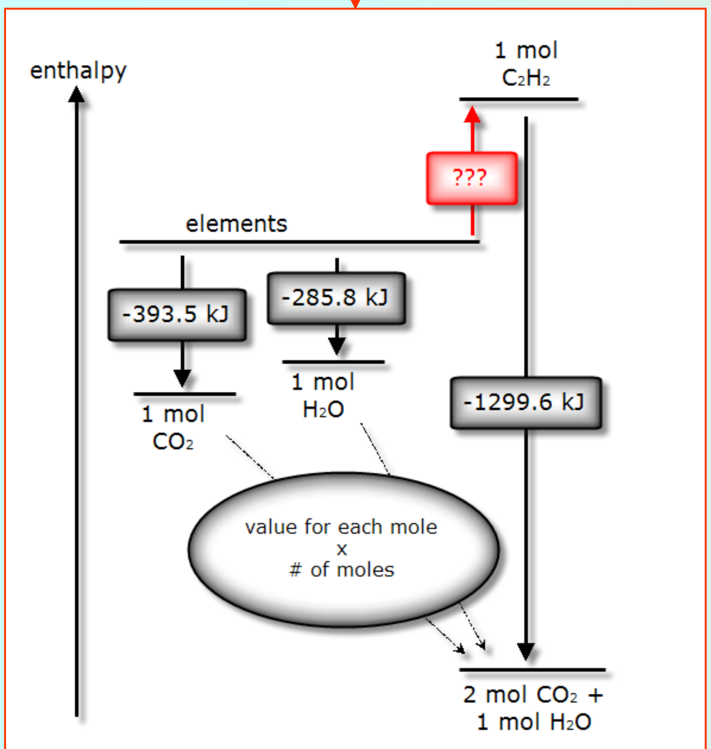
given the following reactions and their respective enthalpy changes:

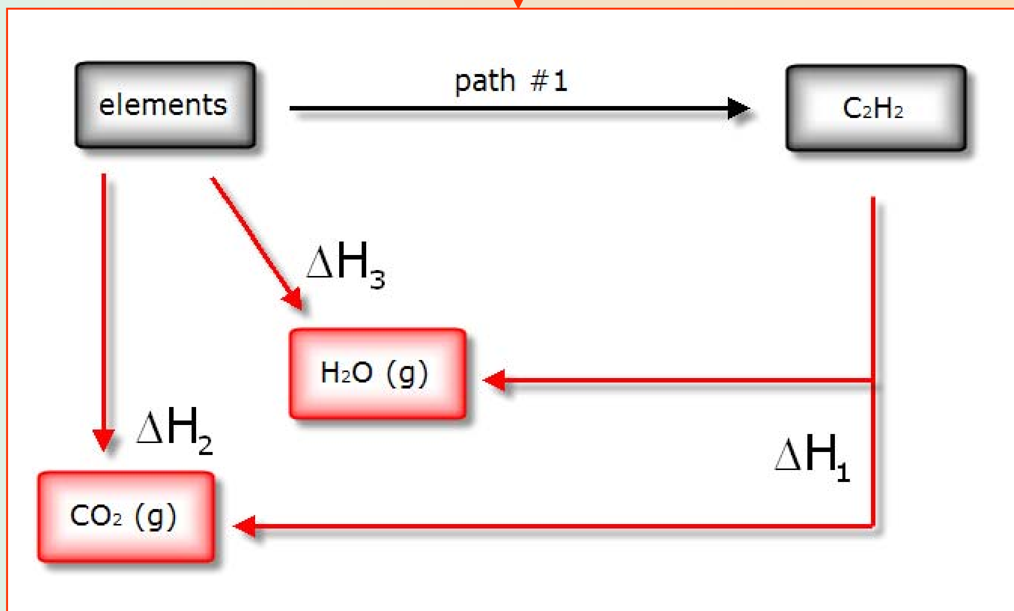
$C_2H_2\ (g) + 2.5\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + H_2O\ (l)\quad \Delta H_1 = -1299.6\ kJ$

$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)\quad \Delta H_2 = -393.5\ kJ$

$H_2\ (g) + 0.5\ O_2\ (g) \rightarrow H_2O\ (l)\ \Delta H_3 = -285.8\ kJ$

Graphic representations





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given the following reactions and their respective enthalpy changes:

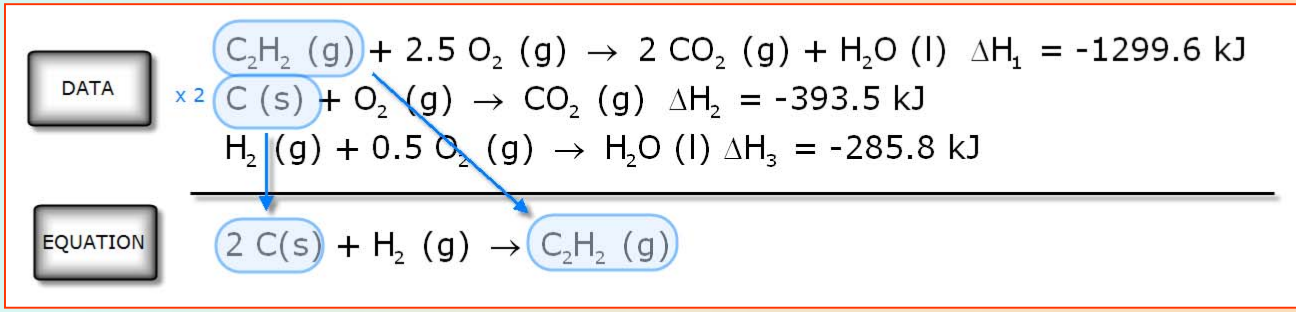
$C_2H_2\ (g) + 2.5\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + H_2O\ (l)\quad \Delta H_1 = -1299.6\ kJ$

$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)\quad \Delta H_2 = -393.5\ kJ$

$H_2\ (g) + 0.5\ O_2\ (g) \rightarrow H_2O\ (l)\quad \Delta H_3 = -285.8\ kJ$

Combining the first two equations is not enough; we need the help of the 3rd equation to

- eliminate oxygen and water
- introduce hydrogen



$2\ CO_2\ (g) + H_2O\ (l) \rightarrow C_2H_2\ (g) + 2.5\ O_2\ (g)\ \Delta H_1 = +1299.6\ kJ$

$2 \times [C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)\quad \Delta H_2 = -393.5\ kJ]$

$2\ C(s) + H_2O\ (l) \rightarrow C_2H_2 + 0.5\ O_2\ (g)$

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Sample Exercise #2

Calculate ΔH for the reaction

$$2\ C(s) + H_2\ (g) \rightarrow C_2H_2\ (g)$$

given the following reactions and their respective enthalpy changes:

$$C_2H_2\ (g) + 2.5\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + H_2O\ (l) \quad \Delta H_1 = -1299.6\ kJ$$
$$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g) \quad \Delta H_2 = -393.5\ kJ$$
$$H_2\ (g) + 0.5\ O_2\ (g) \rightarrow H_2O\ (l) \quad \Delta H_3 = -285.8\ kJ$$

Solution

$$\cancel{2\ CO_2\ (g)} + \cancel{H_2O\ (l)} \rightarrow C_2H_2\ (g) + \cancel{2.5\ O_2\ (g)} \quad \Delta H_1 = +1299.6\ kJ$$
$$2 \times \left[C\ (s) + \cancel{O_2\ (g)} \rightarrow \cancel{CO_2\ (g)} \quad \Delta H_2 = -393.5\ kJ\right]$$
$$H_2\ (g) + \cancel{0.5\ O_2\ (g)} \rightarrow \cancel{H_2O\ (l)} \quad \Delta H_3 = -285.8\ kJ$$

$$2\ C(s) + H_2\ (g) \rightarrow C_2H_2\ (g) \quad \Delta H = +226.8\ kJ$$

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OUR DATA

$N_2O_5(s) \rightarrow 2\,NO(g) + \frac{3}{2}\,O_2(g) \quad \Delta H = 223.7\ kJ$

$NO(g) + \frac{1}{2}$ … $NO_2(g) \quad \Delta H = -57.1\ kJ$

reverse the equation

OUR EQUATION

$2\,NO_2(g) + \frac{1}{2}\,O_2(g) \rightarrow N_2O_5(s) \quad \Delta H =$

OUR DATA

$2\,NO(g) + \frac{3}{2}\,O_2(g) \rightarrow N_2O_5(s) \quad \Delta H = -223.7\ kJ$

$NO(g) + \frac{1}{2}\,O_2(g) \rightarrow NO_2(g) \quad \Delta H = -57.1\ kJ$

reverse and multiply by 2

OUR EQUATION

$2\,NO_2(g) + \frac{1}{2}\,O_2(g) \rightarrow N_2O_5(s) \quad \Delta H =$

OUR DATA

$2\,NO(g) + \frac{3}{2}\,O_2(g) \rightarrow N_2O_5(s) \quad \Delta H = -223.7\ kJ$

$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g) \quad \Delta H = 114.2\ kJ$

OUR EQUATION

$2\,NO_2(g) + \frac{1}{2}\,O_2(g) \rightarrow N_2O_5(s) \quad \Delta H =$

OUR DATA

$\cancel{2\,NO(g)} + \frac{1}{2}\,O_2(g) \rightarrow N_2O_5(s) \quad \Delta H = -223.7\ kJ$

$2\,NO_2(g) \rightarrow \cancel{2\,NO(g)} + \cancel{O_2(g)} \quad \Delta H = 114.2\ kJ$

OUR EQUATION

$2\,NO_2(g) + \frac{1}{2}\,O_2(g) \rightarrow N_2O_5(s) \quad \Delta H = -109.5\ kJ$

General Strategy

The determination of an unknown enthalpy of a reaction using Hess's Law involves the following steps:

•#1: write / identify the target reaction (the reaction with the unknown value of enthalpy)

•#2: manipulate and combine the equations with known enthalpies to get the one we need to calculate:

- •change the sign of the enthalpy when you reverse an equation
- •multiply the number of moles and the enthalpy by the same factor

To do this, concentrate mainly on the places of compounds because elements can appear in more than one place.

•#3: add the manipulated equations to obtain the target equation and the unknown enthalpy