5.3 HESS'S LAW

Hess's Law is a variation of the first law of thermodynamics and is model for determining the enthalpy change of reactions that can't be found experimentally (from experiment). It is a useful law because there are many reactions where the enthalpy change cannot be measured directly by experiment because the reaction does not go to completion, a protective oxide layer forms on a reactant, the reactants do not combine easily or the reaction may be too slow or too dangerous. Hess's Law is therefore an indirect method of finding the enthalpy change (ΔH) from other experimental results.

Hess's law states that the energy change in converting reactants into products is the same regardless of the pathway taken, provided that the conditions of the reactants and products are the same.

You are not required to be able to state Hess's Law but you need to be able to use it to deduce the enthalpy change of a reaction by manipulating enthalpy changes of known reactions found experimentally.

Solving Hess's Law Calculations by Manipulating Equations

In Hess's Law problems with two or three steps, manipulate the reactions for which ΔH is has been measured by:

- multiplying by some factor
- reversing
- multiplying and reversing
- dividing
- or leaving unchanged

until the equations "add" and "cancel" to give the reactants and products. Add the ΔH values to give the deduced ΔH for the required equation. NOTE: The same manipulation must be done to ΔH as well. For example if you reverse an equation reverse the sign of ΔH.

<u>Example</u>

<u>Deduce</u> the enthalpy change for the reaction $2\,NO\,(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g)$

From the following <u>measured</u> enthalpy changes

Given that 1. $N_2\,(g) + O_2\,(g) \rightarrow 2\,NO\,(g)$ $\Delta H = -185\ kJ\ mol^{-1}$

And 2. $N_2\,(g) + 2\,O_2\,(g) \rightarrow 2\,NO_2\,(g)$ $\Delta H = -76\ kJ\ mol^{-1}$

Solution

The measured enthalpy changes must be manipulated so that N_2 is cancelled out, because it is not required in the reaction for which you are solving for ΔH.

reverse Equation 1 and ΔH to put NO on the LHS, products side	$2\,NO(g)$	$\rightarrow$	$N_2(g)$	+	$O_2(g)$	$\Delta H = +185\ kJ\ mol^{-1}$
leave Equation 2 unchanged	$N_2(g)$	+	$2\,O_2(g)$	$\rightarrow$	$2\,NO_2(g)$	$\Delta H = -76\ kJ\ mol^{-1}$

add the equations together including your ΔH values.

$$2\,NO(g) + N_2(g) + 2\,O_2(g) \rightarrow N_2(g) + O_2(g) + 2\,NO_2(g)$$

Cancel out the N_2 on the LHS and RHS. Cancel out the 2 O_2 on the LHS and 1 O_2 on the RHS to give 1 O_2 on the LHS

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g) \qquad \Delta H = (+185) + (-76) = +109\ kJ\ mol^{-1}$$

(deduced enthalpy change)

Problems

1. Use the data below to deduce the ΔH for the reaction:

$$\mathbf{C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)}$$

1. $C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1 = -393\ kJ\ mol^{-1}$
2. $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \qquad \Delta H_2 = -484\ kJ\ mol^{-1}$
3. $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g) \qquad \Delta H_3 = -566\ kJ\ mol^{-1}$

2. Use the data below to deduce the heat of reaction when gaseous methane combusts in excess oxygen.

1.	C (s)	+	2 H_2 (g)	$\rightarrow$	CH_4 (g)	ΔH_1 = -75kJ mol^{-1}
2.	C (s)	+	O_2 (g)	$\rightarrow$	CO_2 (g)	ΔH_2 = -393 kJ mol^{-1}
3.	2 H_2 (g)	+	O_2 (g)	$\rightarrow$	2 H_2O (g)	ΔH_3 = -484 kJ mol^{-1}

3. Deduce the enthalpy change for the reaction of hydrogen and oxygen to form hydrogen peroxide. What will be the enthalpy change for the reaction below? Given that:

1.	2 H_2 (g)	+	O_2 (g)	$\rightarrow$	$2H_2O$ (l)	ΔH_1 = -600 kJ mol^{-1}
2.	2 H_2O_2 (aq)	$\rightarrow$	2 H_2O (l)	+	O_2 (g)	ΔH_2 = -200 kJ mol^{-1}

4. The production of iron involves carbon monoxide reacting with iron oxide to form iron and carbon dioxide

$$\mathbf{Fe_2O_3\ (s) \quad + \quad 3\ CO\ (g) \quad \rightarrow \quad 2\ Fe\ (s) \quad + \quad 3\ CO_2\ (g)}$$

Using the equations below calculate the enthalpy of the reaction.

1.	C (s)	+	O_2 (g)	→	CO_2 (g)	ΔH_1 = -393 kJ mol^{-1}
2.	2 Fe (s)	+	1.5 O_2 (g)	→	Fe_2O_3 (s)	ΔH_2 = -822 kJ mol^{-1}
3.	C (s)	+	0.5 O_2 (g)	→	CO (g)	ΔH_3 = -111 kJ mol^{-1}

5. (M00) Explain giving **one** example, the usefulness of Hess's Law in determining ΔH values. [4]

6. Octane (C_8H_{18}) a component of petrol burns in excess oxygen to produce carbon dioxide and gaseous water as the products.

a) Write a balanced equation for the combustion of octane.

b) Calculate the enthalpy change for the combustion of octane from the data given below.

1.	$C (s)$	+	$O_2 (g)$	$\rightarrow$	$CO_2 (g)$	$\Delta H_1 = -393 \text{ kJ mol}^{-1}$
2.	$H_2 (g)$	+	$1/2\ O_2 (g)$	$\rightarrow$	$H_2O (g)$	$\Delta H_2 = -242 \text{ kJ mol}^{-1}$
3.	$8\ C (s)$	+	$9\ H_2 (g)$	$\rightarrow$	$C_8H_{18} (g)$	$\Delta H_3 = + 208 \text{ kJ mol}^{-1}$

c) If octane has the formula C_8H_{18} deduce and draw the structural formula of pentane. Describe why they belong to the same homologous series.

d) Pentane and octane are liquids at room temperature. State and explain which molecule would have the higher boiling point.

e) Draw an enthalpy level diagram for the combustion of octane.

i) Indicate on the diagram the enthalpy change of the reaction and activation energy

ii) Compare the relative stabilities of the bonds of the reactants and products. [4]

f) (HL only) State the hybridization around the carbon atoms in octane.

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