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.

Example

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

From the following measured 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)	$\Delta H = (+185) + (-76)$ $= +109$ kJ mol^{-1} (deduced enthalpy change)

Problems

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

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

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

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

1. $C (s) + 2 H_2 (g) \rightarrow CH_4 (g)$ $\Delta H_1 = -75 kJ\ mol^{-1}$

2. $C (s) + O_2 (g) \rightarrow CO_2 (g)$ $\Delta H_2 = -393\ kJ\ mol^{-1}$

3. $2 H_2 (g) + O_2 (g) \rightarrow 2 H_2O (g)$ $\Delta H_3 = -484\ kJ\ mol^{-1}$

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. $2 H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$ $\Delta H_1 = -600\ kJ\ mol^{-1}$

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

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)	→	CO_2 (g)	ΔH_1 = -393 kJ mol^{-1}
2.	H_2 (g)	+	1/2 O_2 (g)	→	H_2O (g)	ΔH_2 = -242 kJ mol^{-1}
3.	8 C (s)	+	9 H_2 (g)	→	C_8H_{18} (g)	ΔH_3 = + 208 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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ANSWERS:

1.

1. x 2
2. reverse
3. reverse

ΔH = 264 $kJmol^{-1}$

÷ 2

<u>ΔH = + 132 $kJmol^{-1}$</u>

2.

CH_4 (g) + $2O_2$ (g) → CO_2(g) + $2H_2O$(g)

1. reverse
2. no change
3. no change

<u>ΔH = -802 $kJmol^{-1}$</u>

3.

H_2 (g) + $2O_2$ (g) → H_2O_2(aq)

1. nochange
2. reverse

<u>ΔH = -200 $kJmol^{-1}$</u>

4.

1. x3
2. reverse
3. reverse and x3

<u>ΔH = -24 $kJmol^{-1}$</u>

5.

Hess's law enables enthalpy changes which cannot be found experimentally to be deduced from other experimental results ;

Hess's Law shows which enthalpies can be measured and which can be deduced ;

For example 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. ;

For example reactions involving aluminum metal are very slow because aluminum metal reacts with oxygen gas in the air to form a protective coating of aluminum oxide which makes the metal unreactive ($4Al + 3O_2 \rightarrow 2Al_2O_3$);

Hess's Law Problems (ANSWERS)

6.

a)

C_8H_{18} (g) + 12 ½ O_2 (g) → $8CO_2$(g) + $9H_2O$(g) (1)

b)

1. x8 (1)
2. x9 (1)
3. reverse (1)

<u>ΔH = -5530 $kJmol^{-1}$</u> (1)

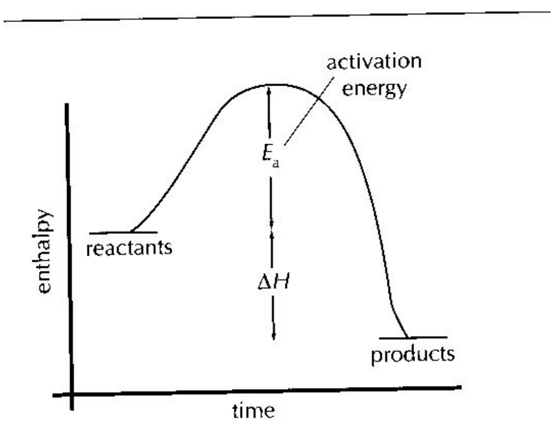
c) Correct sturcutural formula of pentane; (1)

Octane and pentane belong to the same homologous series of alkanes because they both have same general formula (C_nH_{2n+2}); (1)

Each member of the alkane homologous series differs from the previous member by one CH_2 group; (1)

d) Octane would have the higher boiling point; (1)
It has more electrons so the van der waals forces between the molecules are stronger; (1)
Therefore more heat energy needs to be absorbed to break the van der waals forces, giving it a higher boiling point; (1)

e)



labeled axes and products lower in energy than reactants ; (1)

Correct ΔH; (1)

Correct E_a; (1)

Products are more stable than the reactants because they have lower energy / enthalpy; (1)

f) sp^3 (1)