5.3 HESS'S LAW

Answer Key

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:

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

1. $C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$ $\Delta H_1 = -393\ kJ\ mol^{-1}$
2. $2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$ $\Delta H_2 = -484\ kJ\ mol^{-1}$ ⇒ +242   (reverse and divide by 2 →)
3. $2\,CO\,(g) + O_2\,(g) \rightarrow 2\,CO_2\,(g)$ $\Delta H_3 = -566\ kJ\ mol^{-1}$ ⇒ +283   (reverse and divide by 2 →)

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$H_2O(g) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$
$$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2}O_2(s)$$

$$C(s) + O_2(g) + H_2O(g) + CO_2(g) \rightarrow CO_2(g) + H_2(g) + \tfrac{1}{2}O_2(g) + CO(g) + \tfrac{1}{2}O_2(g)$$
$$C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$$

$$\Delta H_{rxn} = -393 + 242 + 283 = \boxed{+132\ kJ\ mol^{-1}}$$

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

reverse →	1.	C (s)	+	$2\ H_2$ (g)	→	CH_4 (g)	$\Delta H_1 = -75\text{kJ mol}^{-1}$ ⇒ +75
	2.	C (s)	+	O_2 (g)	→	CO_2 (g)	$\Delta H_2 = -393\text{ kJ mol}^{-1}$
	3.	$2\ H_2$ (g)	+	O_2 (g)	→	$2\ H_2O$ (g)	$\Delta H_3 = -484\text{ kJ mol}^{-1}$

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

$CH_4(g) \rightarrow C(s) + 2H_2(g)$

$C(s) + O_2(g) \rightarrow CO_2(g)$

$+\ 2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

$CH_4(g) + C(s) + O_2(g) + 2H_2(g) + O_2(g) \rightarrow C(s) + 2H_2(g) + CO_2(g) + 2H_2O(g)$

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

$\Delta H_{rxn} = +75 - 393 - 484 = -802\text{ kJ mol}^{-1}$

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:

divide by 2 →	1.	$2\ H_2$ (g)	+	O_2 (g)	→	$2H_2O$ (l)	$\Delta H_1 = -600\text{ kJ mol}^{-1}$ ⇒ -300
reverse divide by 2 →	2.	$2\ H_2O_2$ (aq)	→	$2\ H_2O$ (l)	+	O_2 (g)	$\Delta H_2 = -200\text{ kJ mol}^{-1}$ ⇒ +100

$H_2(g) + O_2(g) \rightarrow H_2O_2(aq)$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

$+\ \frac{1}{2}O_2(g) + H_2O(l) \rightarrow H_2O_2(aq)$

$H_2 + O_2 + H_2O \rightarrow H_2O + H_2O_2$

$H_2 + O_2 \rightarrow H_2O_2$

$\Delta H_{rxn} = -300 + 100 = -200\text{ kJ mol}^{-1}$

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

$$Fe_2O_3\,(s) + 3\,CO\,(g) \rightarrow 2\,Fe\,(s) + 3\,CO_2\,(g)$$

Using the equations below calculate the enthalpy of the reaction.

multiply by 3 → 1. $C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$ $\Delta H_1 = -393\ kJ\ mol^{-1}$ ⇒ −1179

reverse → 2. $2\,Fe\,(s) + 1.5\,O_2\,(g) \rightarrow Fe_2O_3\,(s)$ $\Delta H_2 = -822\ kJ\ mol^{-1}$ ⇒ +822

reverse multiply by 3 → 3. $C\,(s) + 0.5\,O_2\,(g) \rightarrow CO\,(g)$ $\Delta H_3 = -111\ kJ\ mol^{-1}$ ⇒ +333

$3C_{(s)} + 3O_2 \rightarrow 3CO_2$

$Fe_2O_3 \rightarrow 2Fe + 1.5O_2$

$+\ 3CO \rightarrow 3C + 1.5O_2$

$3C + 3O_2 + Fe_2O_3 + 3CO \rightarrow 3CO_2 + 2Fe + 3C + 3O_2$

$Fe_2O_3 + 3CO \rightarrow 3CO_2 + 2Fe$

$\Delta H_{rxn} = -1179 + 822 + 333 = \boxed{-24\ kJ\ mol^{-1}}$

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

Hess's Law is useful when determing enthalpies of rxn for specific rxns that are difficult to determine experimentally. Instead, more practical rxns that ~~can produce~~ are intermediate steps leading to the overall rxn can be done, and according to Hess's Law, the energy of the rxn of interest will be equal to the sum of the ΔH of the intermediate steps. An example would be $2H_2(g) + C(s) \rightarrow CH_4(g)$ This is difficult to measure experimentally, so instead it can be found through combustion of C & H_2 and combustion of methane.

others: used for rxns that are slow, dangerous, used for calculating more energy-efficient industrial processes

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.

multiply by 16 → 1. C (s) + O_2 (g) → CO_2 (g) ΔH_1 = -393 kJ mol^{-1} ⇒ -6288

multiply by 18 → 2. H_2 (g) + 1/2 O_2 (g) → H_2O (g) ΔH_2 = -242 kJ mol^{-1} ⇒ -4356

reverse multiply by 2 → 3. 8 C (s) + 9 H_2 (g) → C_8H_{18} (g) ΔH_3 = + 208 kJ mol^{-1} ⇒ - 416

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.

a) $2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

b) $16C + 16O_2 \rightarrow 16CO_2$

$18H_2 + 9O_2 \rightarrow 18H_2O$

~~16C + 18H2 →~~

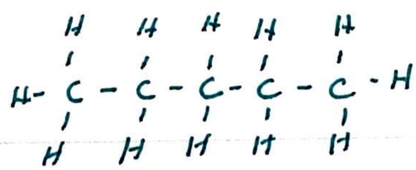
+ $2C_8H_{18} \rightarrow 16C + 18H_2$

$16C + 16O_2 + 18H_2 + 9O_2 + 2C_8H_{18} \rightarrow 16CO_2 + 18H_2O + 16C + 18H_2$

$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

$\Delta H_{rxn} = -6288 - 4356 - 416 = -11060$ kJ (for 2 moles octane)

$= -5530$ kJ mol^{-1}

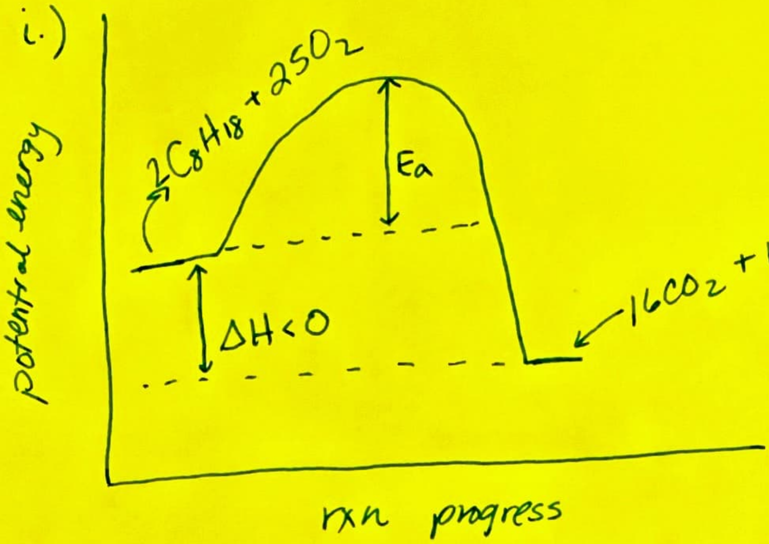
c)  or  both alkanes and differ by a factor of 3×(CH_2)

d) octane due to longer hydrocarbon chain = more LDF

Hess's Law Worksheet (Algebraic) Answer key

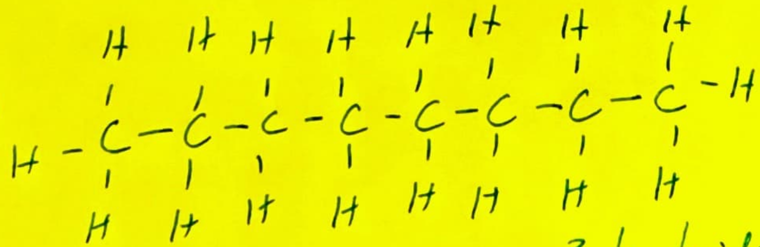
(6) e) this is an <u>exothermic</u> rxn

i.)



ii) Since energy is released, the products are lower in energy than the reactants. this means the products are <u>lower</u> in energy than the reactants, meaning they are <u>more stable</u>.

f)



all carbon atoms sp^3 hybridized