Thermochemistry

TOPICS COVERED

- Different type of heat reactions.
- Hess's law and its applications
  - Heat of Formation
  - Heat of Combustion
  - Heat of Decomposition

Hess's Law

- If a reaction can take place by more then one routes the overall change in enthalpy is the same whichever route is followed.

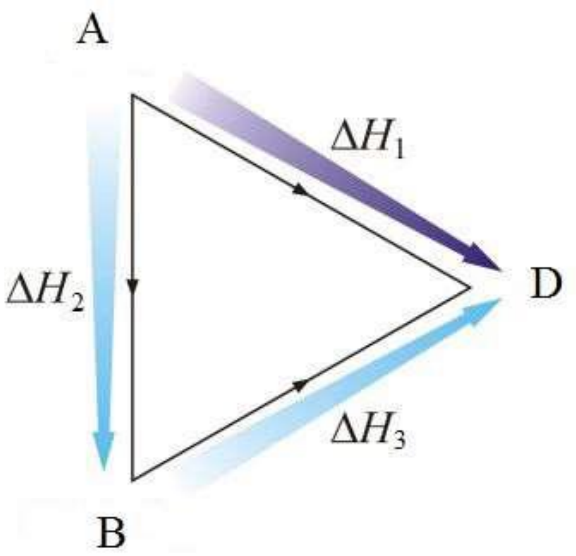
Illustration of Hess's Law

1. Let us assume that a reactant A gives product D directly by a single step and its change of enthalpy is ΔH_1.

2. Now the same reactant A produce D into two steps. First A is converted into B with an enthalpy change ΔH2 and in the 2nd step intermediate product B is converted in to D with enthalpy change ΔH3.

According to the **Hess's law**, we get

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$



- It follows also that the standard enthalpy change for the reaction D→A is -ΔH and for A→D is +ΔH.

Solved example

N_2 (g) + $2O_2$ (g) → $2NO_2$ (g) ; $\Delta H_1 = 68$ kJ

This reaction also can be carried out in two distinct steps, with enthalpy changes designated by ΔH2 and ΔH3 .

N2 (g) + O2 (g) → 2NO(g)	ΔH2 = 180 kJ
2NO(g) + O2 (g) → 2NO2 (g)	ΔH3 = – 112 kJ
N2 (g) + 2O2 (g) → 2NO2 (g)	ΔH2 + ΔH3 = 68 kJ

$$\Delta H1 = \Delta H2 + \Delta H3 = 68 \text{ kJ}$$

Different type of heat reactions

There are four different types of heat reactions.

Those are:

- Heat of formation
- Heat of decomposition
- Heat of combustion
- Enthalpy or Heat of Neutralisation

Heat of Formation

- The heat of formation of a compound may be defined as the quality of heat change during the formation of one mole of a substance from this constituent elements.
- For example, the standard enthalpy of formation of carbon dioxide would be the enthalpy of the following reaction under the conditions above:

$$C(s,graphite) + O_2(g) \rightarrow CO_2(g) \; ; \; \Delta H_f = -393.5 \text{ kJ/mol}$$

- Here all elements are written in their standard states, and one mole of product is formed. This is true for all enthalpies of formation.

Heat of Decomposition

- The amount of heat required to decompose 1 mole of a substance to its constituent elements is called Heat of Decomposition.

- Exampe- H_2O (l) = ½ O_2 (g) + ½ H_2 (g) ;
  $\Delta H = +285.5$ kJ/mol

Heat of Combustion

The heat of combustion of a compound or an element is defined as the amount of heat evolved, when 1 mole of a substance is burnt completely in oxygen at a given temperature at 1 atm. Pressure

CH_4 (g) + $2O_2$ (g) CO_2 (g) =$2H_2O$ (l) ; $\Delta H = -890$ kJ/mol

Standard Enthalpy of Formation ($\Delta Hf°$)

- Change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.

Conventional Definitions of Standard States

For a Compound

- For a gas, pressure is exactly 1 atm.
- For a solution, concentration is exactly 1 M.
- Pure substance (liquid or solid)

For an Element

- The form [N_2 (g), K(s)] in which it exists at 1 atm and 25°C.

A Schematic Diagram of the Energy Changes for the Reaction

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

ΔH° reaction = –(–75 kJ) + 0 + (–394 kJ) + (–572 kJ) = –891 kJ

Problem-Solving Strategy: Enthalpy Calculations

1. When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.
2. When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.
3. The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:
   $\Delta H^\circ_{rxn} = \Sigma n_p H_f^\circ$ (products) - ΣnrHf ° (reactants)
4. Elements in their standard states are not included in the $\Delta H_{reaction}$ calculations because ΔHf ° for an element in its standard state is zero.

Standard enthalpy of combustion

- Standard enthalpy of combustion is defined as the enthalpy change when one mole of a compound is completely burnt in oxygen with all the reactants and products in their standard state under standard conditions (298K and 1 bar pressure).
- For example:
- $H_2(g)+1/2O_2(g)\rightarrow H_2O(l);\Delta_cH° = -286 kJmol^{-1}$
- $C_4H_{10}(g)+13/2O_2(g)\rightarrow 4CO_2(g)+5H_2O(l);\ \Delta_cH° = -2658 kJmol^{-1}$

Bond Energies

- Energy must be added/absorbed to BREAK bonds (endothermic). Energy is released when bonds are FORMED (exothermic).
- ΔH = sum of the energies required to break old bonds (positive signs) plus the sum of the energies released in the formation of new bonds (negative signs).
- **ΔH = bonds broken – bonds formed**

- Example
- Using bond energies, calculate the change in energy that accompanies the following reaction:

$$H_2(g) + F_2(g) \rightarrow 2\ HF(g)$$

Bond Type	Bond Energy
H-H	432 kJ/mol
F-F	154 kJ/mol
H-F	565 kJ/mol

Change in energy = -544 kJ

References

Text Books

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THANK YOU