Thermochemistry

The branch of chemistry which deals with energy changes taking place in chemical reactions is called thermochemistry.

Heat of reaction:

The amount of heat evolved or absorbed in a chemical reaction is called the heat of reaction.

Standard states:

When each of the reactants and products of a chemical reaction is in its standard state then heat change of the reaction will be standard heat of reaction.

Standard enthalpy of compounds:

Standard enthalpy of a compound is the heat of that reaction in which the constituent elements of the compound in their standard state react to yield 1 mole of the compound in its standard state.

* Change of Internal Energy in a Chemical Reaction :

Let us consider a system having internal energy U_R that undergoes a chemical change giving rise to another chemical system having internal energy U_p. Then, change in internal energy is given as :

$$\Delta U = U_p - U_R.$$

U_p → Internal energy of product
U_R → Internal energy of reactants

∵ U_p and U_R are definite quantities, ΔU must also be a definite quantity.

Let us consider a chemical reaction taking place at constant temp and constant volume.

∴ From 1st law eqⁿ,

$$\boxed{\Delta U = q_v} \quad [\because \text{At const. } V, \omega = 0].$$

Change of Enthalpy in a Chemical Reaction :

Let us consider the enthalpy of reactant and product that undergo a chemical reaction as H_R and H_p respectively. Then, change in enthalpy is given as,

$$\Delta H = H_p - H_R. \longrightarrow (1).$$

where, $H_p = U_p + PV_p. \longrightarrow (II)$

$H_R = U_R + P.V_R. \longrightarrow (III)$

where P is constant.

∴ Eqn (1) $\Rightarrow \Delta H = (U_p + PV_p) - (U_R + PV_R).$

$\Rightarrow \Delta H = (U_p - U_R) + P(V_p - V_R).$

$\Rightarrow \Delta H = \Delta U + P.\Delta V.$

$\Rightarrow \Delta H = q_v + P.\Delta V$ $\quad [\because \Delta U = q_v]$.

Let, q_p be the heat change involved in the chemical reaction taking place at constant pressure. Then,

$$\boxed{\Delta H = q_p}$$

Sign Convention :

(a) **Sign of ΔU:** (i) If $U_R > U_p$, the reaction will be exothermic.

$\therefore \Delta U = U_p - U_R$ will be negative.

Hence, in all exothermic reactions taking place at a constant temp^{r}, ΔU has a negative sign.

(ii) If $U_R < U_p$, then the reaction will be endothermic.

$\therefore \Delta U = U_p - U_R$ will be positive.

Hence, in all endothermic reactions taking place at a constant temp^{r}, ΔU has a positive sign.

(b) **Sign of ΔH:**

(i) If $H_R > H_p$, the reaction will be exothermic.

$\therefore \Delta H = H_p - H_R$ will have negative sign.

Hence, in all exothermic reactions taking place at a constant temp^{r}, ΔH has a negative sign.

(ii) If $H_p > H_R$, then the reaction will be endothermic

$\therefore \Delta H = H_p - H_R$ will be positive.

Hence, in all endothermic reactions, taking place at a constant temp^r, ΔH has a positive sign.

Relation between q_p and q_v:

We know,

$$\Delta H = \Delta U + P.\Delta V. \longrightarrow (1)$$

where ΔV is the change in volume.

$\because q_v = \Delta U$ and $q_p = \Delta H$, eqn (1) becomes,

$$q_p = q_v + P.\Delta V.$$

$$\Rightarrow q_p = q_v + P(V_2 - V_1). \longrightarrow (11)$$

$\because$ For n moles of an ideal gas,

$$PV = nRT$$

$\therefore$ $PV_1 = n_R RT$.

$PV_2 = n_p RT$.

where, n_R and n_p are the no. of moles of gaseous reactants and products and V_1 and V_2 are their volumes respectively.

$\therefore$ Eqn (11) $\Rightarrow q_p = q_v + n_p RT - n_R RT$.

$\Rightarrow q_p = q_v + RT(n_p - n_R)$.

$\Rightarrow q_p = q_v + \Delta n_g (RT)$.

$\Rightarrow \boxed{\Delta H = \Delta U + \Delta n_g RT}$.

where, Δn_g is the difference in the no. of moles of the gaseous products and gaseous reactants.

Case 1:

If $n_p > n_R$, $\Delta n_g > 0$ ie. Δn_g is +ve.

Then, $q_p > q_v$.

Case II:

If $n_p < n_R$, $\Delta n_g < 0$, i.e. Δn_g is -ve.

Then, $q_p < q_v$.

Case III:

If $n_p = n_R$, $\Delta n_g = 0$.

Then $q_p = q_v$.

Enthalpy of Combustion :

The enthalpy of combustion of a substance, at a given temperature and under atmospheric pressure is defined as the enthalpy change (ΔH) accompanying the complete combustion of one mole of the substance at that Temp^{r}.

If the temperature is 25°C, the enthalpy change is called the standard enthalpy of combustion.

e.g. (a) Combustion of carbon :

$$C(g) + O_2(g) \longrightarrow CO_2(g) \quad , \quad \Delta H^\circ = -393.5\ kJ.$$

(b) Combustion of hydrogen :

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) \quad , \quad \Delta H^\circ = -286.2\ kJ.$$

* Enthalpy of combustion can be used to determine enthalpies of reactions.

Let us consider a general chemical reaction.

$$A + B \longrightarrow C + D.$$

Let their standard enthalpies be, H_A°, H_B°, H_C° and H_D° respectively.

$$\therefore \Delta H = \Sigma H_{(products)} - \Sigma H_{(reactants)}.$$

$$\Rightarrow \Delta H^\circ = (H_C^\circ + H_D^\circ) - (H_A^\circ + H_B^\circ).$$

But,

$H^\circ = \Delta H_f^\circ$.

$\therefore \Delta H^\circ = \{\Delta H_f^\circ(C) + \Delta H_f^\circ(D)\} - \{\Delta H_f^\circ(A) + \Delta H_f^\circ(B)\}$.

$\Rightarrow \boxed{\Delta H^\circ = \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants})}$.

Standard Enthalpy of Neutralization of an acid :

It is the amount of heat evolved when 1 gram equivalent of the given acid is completely neutralized by a base in dilute solutions at 25°C and 1 atm pressure.

e.g. $H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O(l)$.

or $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O(l)$.

Standard Enthalpy of Neutralisation of a base :

It is the amount of heat evolved when 1 gram equivalent of the given base is completely neutralized by an acid in dilute solution at 25°C and 1 atm pressure.

e.g. $KOH_{(aq)} + \frac{1}{2} H_2SO_4(aq) \longrightarrow KHSO_4(aq) + H_2O(l)$,

$\Delta H^\circ = -57.4 \text{ kJ mol}^{-1}$.

Enthalpy of Solution :

The amount of heat evolved or absorbed when 1 mole of the solute is dissolved in a given amount of the solvent is called the enthalpy of solution of the solute

at that concentration and temp°.

Integral enthalpy of solution:

It is defined as the enthalpy change when one mole of a solute is dissolved in a solvent to give a solution of a specified concentration.

Enthalpy of dilution:

Change of enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to another is called enthalpy of dilution.

Differential enthalpy of solution:

It is defined as the enthalpy change produced when 1 mole of a solute is dissolved in such a large volume of solution of a specified concentration that the addition of 1 mole of solute does not affect the ~~different~~ concentration.

Enthalpy of precipitation:

The heat evolved in the precipitation of one mole of a sparingly soluble substance on mixing dilute solutions of appropriate electrolytes is called enthalpy of precipitation of that substance.

Hess's law of constant heat summation:

The law states that the amount of heat evolved or absorbed in a process, including a chemical change, is the

same whether the process takes place in one or several steps.

Let us consider a process where the system changes from state A to state B in one step. and the heat exchanged in this ~~state~~ change is q.

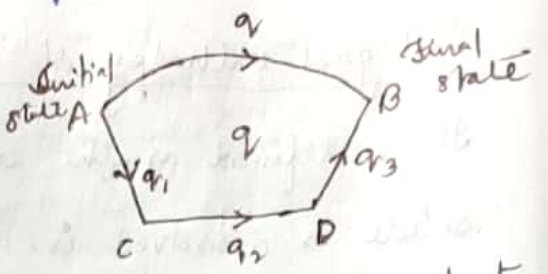


Fig: Hess's law of constant heat summation.

Now, let the system changes from state A to state B in three steps involving a change from A to C, C to D and then finally from D to B. If q_1, q_2 and q_3 are the amount of heat exchanged in the 1st, and and 3rd step respectively, then according to Hess's Law,

$$q = q_1 + q_2 + q_3$$

i.e. The enthalpy of a reaction depends only on the initial ~~and~~ reactants and final products and not at all on the intermediate products that may be formed, and also on the path in which the change is brought about.

Applications of Hess's Law:

① Calculation of Enthalpies of reactions:

e.g. Heat evolved when carbon burns in oxygen to form carbon monoxide can be measured with the

help of Hess's Law.

$$C_{(s)} + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad , \quad \Delta H^\circ = ?$$

But, C(s) can be converted to $CO_2(g)$ in a single or two steps as follows —

① In a single step:

$$C_{(s)} + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta H^\circ = -393.5 \text{ kJ}.$$

② In two steps:

$$C_{(s)} + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad , \quad \Delta H^\circ = x.$$

$$CO_{(g)} + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad , \quad \Delta H^\circ = -282.0 \text{ kJ} = y \text{ (say)}.$$

∴ By applying Hess's Law,

$$x + y = -393.5$$

$$\Rightarrow x = -393.5 - (-282.0)$$

$$\Rightarrow x = -111.5$$

∴ ΔH° for the combustion of carbon to give carbon monoxide is -111.5 kJ.

② Determination of enthalpies of slow reactions:

Hess's law is extremely useful in determining enthalpies of those reactions which take place extremely slowly and can't be completed in meaningful time. e.g. The transformation of rhombic sulphur into monoclinic sulphur is so slow that direct measurement of enthalpy change is not possible. But

the enthalpies of combustion of rhombic sulphur and monoclinic sulphur are known.

$S_{(rhombic)} + O_{2(g)} \longrightarrow SO_{2(g)}$; $\Delta H^\circ = -297.5\ kJ$ ⟶ (I)

$S_{(monoclinic)} + O_{2(g)} \longrightarrow SO_{2(g)}$; $\Delta H^\circ = -300.0\ kJ$ ⟶ (II)

$\therefore$ (I) − (II) ⇒ $S_{(rhombic)} \longrightarrow S_{(monoclinic)}$, $\Delta H^\circ = 2.5\ kJ$

or $S_{(monoclinic)} \longrightarrow S_{(rhombic)}$, $\Delta H^\circ = -2.5\ kJ$.

③ Calculation of enthalpies of formation:

e.g. It is impossible to determine experimentally the enthalpy of formation of benzene from its elements, viz. carbon and hydrogen. However, it can be calculated from the enthalpy of combustion of benzene and the enthalpies of formation of water and carbon dioxide.

$$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)} \quad ; \quad \Delta H^\circ = ?$$

Step 1: Thermochemical equations are:

(i) $C_6H_{6(l)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}$, $\Delta H^\circ = -3267.7\ kJ$

(ii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$, $\Delta H^\circ = -393.5\ kJ$.

(iii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$, $\Delta H^\circ = -286.2\ kJ$.

Step 2: (ii) × 6 and (iii) × 3 ⇒

(iv) $6C_{(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)}$, $\Delta H^\circ = -2361.0\ kJ$.

(v) $3H_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow 3H_2O_{(l)}$, $\Delta H^\circ = -858.6\ kJ$.

$\therefore$ (iv) + (v) − (i) ⇒ $6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)}$, $\Delta H^\circ = +48.1\ kJ$.

$\therefore$ The enthalpy of benzene is $+48.1\ kJ$.

④ Calculation of Enthalpies of hydration:

e.g. Anhydrous $CuSO_4$ (a white powder) can be easily obtained by heating the commonly available blue crystals of $CuSO_4 \cdot 5H_2O$ and then dessicating it. Let, the heats of solution of anhydrous and hydrated salt be ΔH_1 and ΔH_2 respectively as obtained from a calorimeter.

When anhydrous $CuSO_4$ is dissolved in enough water, it first gives hydrated $CuSO_4$.

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O(s).$$

which then dissolves to give the final ($CuSO_4$ aq.) solution. ΔH for the hydration process may then be calculated as follows,

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

i.e. ΔH_2 can be calculated since ΔH_1 and ΔH_3 are experimentally determined.

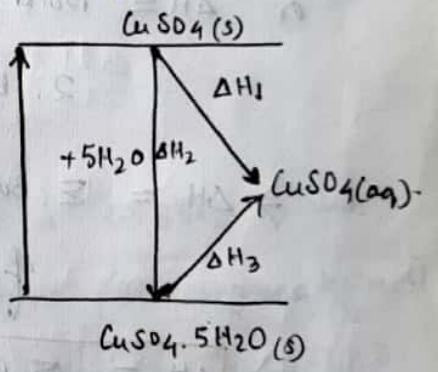


fig: Enthalpy changes in the solution process.

Bond Energy:

It is defined as the average amount of energy required to dissociate one mole i.e. Avogadro's no. of a given type of bonds present in the compound, into isolated gaseous atom.

e.g. $H_2(g) \longrightarrow 2H(g)$, $\Delta H = 435.1$ kJ.

Bond-energy is also called the enthalpy of formation of the bond.

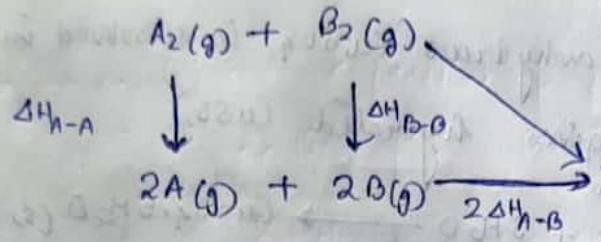
Applications of Bond energies:

(a) Determination of enthalpies of reactions:

Let us consider a reaction,

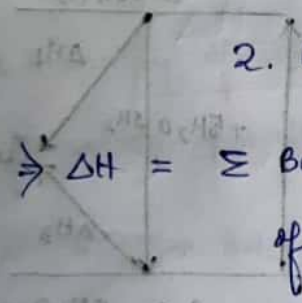
$$A_2(g) + B_2(g) \longrightarrow 2AB(g).$$

The thermal changes may be expressed in the following cycle and Hess's law can be applied.



$$\therefore \Delta H = \Delta H_{A-A} + \Delta H_{B-B} - 2\Delta H_{A-B}.$$

or ΔH = Bond energy of $A_2(g)$ + Bond energy of $B_2(g)$ − 2. Bond energy of $AB(g)$.



$\Rightarrow \Delta H$ = Σ Bond energy of reactants − Σ Bond energy of products.

$$\Rightarrow \boxed{\Delta H = \Sigma B.E.(R) - \Sigma B.E.(P)}$$

(b) Determination of enthalpies of formn of compounds:

e.g. Let us consider the formation of acetone.

$$3C_{(s)} + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-CH_3.$$

(acetone)

$$\therefore \Delta H_f = \left[3\left(\Delta H_{H-H}\right) + \frac{1}{2}\left(\Delta H_{O-O}\right) + 3\left(\Delta H_{C(s)\rightarrow C(g)}\right)\right] -$$

$$\left[2\left(\Delta H_{C-C}\right) + 6\left(\Delta H_{C-H}\right) + \Delta H_{C=O}\right].$$

$\Rightarrow \Delta H_f = \left[3\times 435.1 + \frac{1}{2}\times 493.1 + 3\times 719.6\right] - \left[2\times 347.3 + 6\times 416.2 + 711.3\right]$.

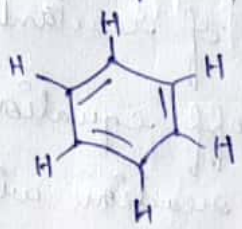
$\Rightarrow \Delta H_f = -192.4\ kJ\ mol^{-1}$.

© Determination of resonance energy:

eg. Let us consider the dissociation of benzene:

$$C_6H_{6(g)} \longrightarrow 6C_{(g)} + 6H_{(g)}.$$

Kekule's structure of benzene ring is,



$\therefore \Delta H_d = 3(\Delta H_{C-C}) + 3(\Delta H_{C=C}) + 6(\Delta H_{C-H})$.

$= 3\times 343.3 + 3\times 615.0 + 6\times 416.2$

$= 5384.1\ kJ\ mol^{-1}$.

But, the actual ΔH_d of benzene is $5535.1\ kJ\ mol^{-1}$.

i.e. The actual structure of benzene (Resonance hybrid) is more stable than the Kekule's structure by 151 kJ.

The Resonance hybrid of benzene is,

Variation of Enthalpy of Reaction with Temperature: The Kirchhoff eqⁿ:

Let us consider a general reaction:

$$aA + bB \longrightarrow cC + dD.$$

$\therefore \Delta H = \Sigma H_{products} - \Sigma H_{reactants}$

$$\Rightarrow \Delta H = (cH_C + dH_D) - (aH_A + bH_B) \longrightarrow (1)$$

Differentiating w.r.t. T and keeping P constant,

$$\left[\frac{\partial \Delta H}{\partial T}\right]_P = c\left(\frac{\partial H_C}{\partial T}\right)_P + d\left(\frac{\partial H_D}{\partial T}\right)_P - a\left(\frac{\partial H_A}{\partial T}\right)_P - b\left(\frac{\partial H_B}{\partial T}\right)_P$$

$$\Rightarrow \left[\frac{\partial \Delta H}{\partial T}\right]_P = c.C_{P,C} + d.C_{P,D} - a.C_{P,A} - b.C_{P,B}$$

$$\Rightarrow \left[\frac{\partial \Delta H}{\partial T}\right]_P = \Delta C_P. \longrightarrow (11)$$

where,

ΔC_P = Sum of heat capacities of products − Sum of heat capacities of reactants.

Eqn (11) is called Kirchoff equation. It states that the variation of ΔH of a reaction with temperature at constant pressure is equal to ΔC_P of the system.

i.e. $$\boxed{\left[\frac{\partial \Delta H}{\partial T}\right]_P = \Delta C_P}$$

$$\Rightarrow d(\Delta H) = \Delta C_P . dT . \longrightarrow (111)$$

Eqn (111) can be integrated if we consider a small temperature change and the heat capacities are to assumed to be independent of temperature.

$$\therefore \int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P . dT. \longrightarrow (1v)$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta C_P . (T_2 - T_1).$$

$$\Rightarrow \boxed{\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P.} \longrightarrow (v)$$

If the temperature range is very large, then,

$$C_P = \alpha + \beta T + \gamma T^2 . \longrightarrow (vi)$$

where α, β and γ are constants for a given species.

$$\therefore \Delta C_p = \left[(c\alpha_C + d\alpha_D) - (a\alpha_A + b\alpha_B)\right] + \left[(c\beta_C + d\beta_D) - (a\beta_A + b\beta_B)\right]T + \ldots\ldots$$

$$= \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \ldots \longrightarrow (VII).$$

$\therefore$ Substituting eqn (VII) into eqn (III), ~~dH~~ ~~dT~~ and integrating between T_1 and T_2, we get,

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2)\, dT.$$

$$\Rightarrow \boxed{\Delta H_2 - \Delta H_1 = \Delta\alpha(T_2 - T_1) + \frac{1}{2}\Delta\beta(T_2^2 - T_1^2) + \frac{1}{3}\Delta\gamma(T_2^3 - T_1^3)} \longrightarrow (VIII)$$

Eqn (VIII) is the integrated Kirchoff equation.

Flame and Explosion Temperatures:

The combustion of a gaseous fuel in air takes place so suddenly that the heat produced during combustion does not get any opportunity to be dissipated to the surroundings. The combustion process is thus equivalent to an adiabatic process practically. The entire amount of heat produced thus goes to heat the gases produced during combustion as also the unreacted nitrogen.

The maximum temperature attained by the flame-zone due to the heat liberated by the combustion of the fuel under adiabatic conditions at

constant pressure is known as the flame temperature. If, on the other hand, the combustion is carried out under adiabatic conditions at constant volume, the maximum temp^{r} attained is called explosion temperature.

For an isobaric adiabatic process, the flame temp^{r} can be calculated using the Kirchhoff eq^{n},

$$d(\Delta H)/dT = \Delta C_p$$

$$\Rightarrow d(\Delta H) = \Delta C_p \cdot dT.$$

Integrating, we have,

$$\int d(\Delta H) = \Delta C_p + \int_{T_i}^{T_f} \cdot dT.$$

$$\Rightarrow \Delta H = \Delta C_p (T_f - T_i).$$

Hence, knowing ΔH, ΔC_p and T_i, the final temperature T_f can be calculated.