Thermodynamics & Thermochemistry

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First Law of thermodynamics

$$\Delta U = Q + W$$

ΔU is change in internal energy of the system

Q is heat added **to** the system

W is work done **by** the system

Note that It is the thermodynamic expression of conservation of energy principle

Work done by system (W)

$$W = - \int_{V_1}^{V_2} P \, dV$$

When P is constant: $= -P_{ext} \Delta V$

For an ideal gas: $PV = nRT$

For reversible process for ideal gas:

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} \, dV \qquad = - nRT \ln \frac{V_2}{V_1}$$

Enthalpy Of a System (H)

$$H = E + pV$$

H represents total energy of the system
E represent internal energy

Note that H takes into account internal energy as well as energy gained from doing work equal to PV

E is sum of $K.E. + P.E.$ of system and is an intrinsic value of system

$$\Delta H = \Delta E + p\Delta V$$

Increase in H is heat absorbed at constant pressure

Heat of Reaction

At constant volume (q_v) $\longrightarrow$ $= \Delta E$

At constant pressure (q_p) $\longrightarrow$ $= \Delta H$

$$q_p = q_v + \Delta n_g RT$$

Where $\Delta n_g = \sum$ moles of gaseous product $- \sum$ moles of gaseous reactant

Note : for reactions involving only solids and liquids
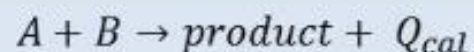
$$\Delta H \cong \Delta E$$

Exothermic And Endothermic Reaction
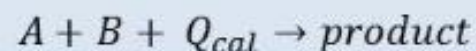
A reaction is exothermic when heat is evolved

$$\Delta H_{products} < \Delta H_{reactants}$$ → $A + B \rightarrow product + Q_{cal}$

A reaction is endothermic when heat is absorbed

$$\Delta H_{products} > \Delta H_{reactants}$$ → $A + B + Q_{cal} \rightarrow product$

Note that in thermochemistry reactions are generally carried out in open vessels which means pressure is constant and equal to atmospheric pressure   → $\Delta H = q_p$

Heat of Formation (H_f)

Heat change accompanying the formation of 1 mole of compound from its constituting element(s) under standard conditions

Standard condition for thermochemistry : 1 atm pressure and $25°C$ T

Note that $\Delta H_f{}^0$ for any element in its standard state is zero by convention

Heat of Solution

Heat evolved or absorbed when one mole of solute is dissolved completely in excess of solvent

Note that it can be positive or negative

Example : $KCl\ (s) + aq. \rightarrow KCl(aq)$ $\Delta H_s = 4.4\ cal$

Note that it is different from heat of hydration where new bond between water molecules and substance is being made

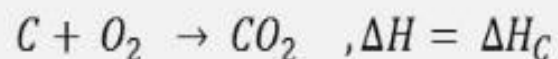## Heat Of Combustion (ΔH_c)

Heat evolved when 1 mole of burnt completely in oxygen

Example: $C + \frac{1}{2}O_2 \rightarrow CO$, $\Delta H \neq \Delta H_C$

$C + O_2 \rightarrow CO_2$, $\Delta H = \Delta H_C$

Note that heat of combustion is measured at constant volume which gives ΔE and from it ΔH_C is derived

Heat of Neutralisation

It is defined for an acid or a base

It is heat evolved when 1 equivalent of acid / base is neutralized by a strong base / acid respectively

$$\Delta H_{(neutralisation)} = \Delta H_{(ionisation)} + \Delta H(H^+ + OH^-)$$

$$= \Delta H_{(ionisation)} - 13.7 kcal / eq$$

Note that for strong acids $\Delta H_{(ionisation)} =$ zero

$\therefore \Delta H_{(neutralisation)}$ for weak acids $< 13.7 kcal$

Greater the value of heat of neutralisation (negative value) of an acid, more will be its strength

Heat of Hydration

Heat change accompanying formation of 1 mole of a specified hydrate from 1 mole of an anhydrous substance with required number of moles of water

Example : $CaCl_{2(s)} + 6H_2O \rightarrow CaCl_2 \cdot 6H_2O$ $\Delta H_{hydration}$

Note that heat of hydration is always negative

Hess's Law of Constant Heat Summation

At constant pressure the total enthalpy change for a chemical reaction is same whether the reaction takes place in one or more steps

$$A \rightarrow D \;;\; \Delta H = q$$

$$A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$$
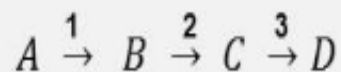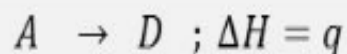
$$\Delta H_1 = q_1 \quad \Delta H_2 = q_2 \quad \Delta H_3 = q_3$$

$$\therefore \quad q = q_1 + q_2 + q_3$$

Note that it is a special case of first law of thermodynamics

Application of Hess's Law

$$\Delta H^0{}_{for\ any\ reaction} = \sum \Delta H^0{}_{f\ (product)} - \sum \Delta H^0{}_{f(reactant)}$$

Note that write balanced equation for the reaction as a first step for finding $\Delta H_{(reaction)}$

Also for finding $\Delta H^0{}_f$ write all reactant and products in their phase i.e. solid / liquid / gas

Kirchhoff's Law At Constant Pressure

$$\int_{T_1}^{T_2} d\Delta H = \Delta C_p \int_{T_1}^{T_2} dT$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

$$\Delta C_p = \sum C_{p(products)} - \sum C_{p(reactants)}$$

Note : ΔH depends on temperature and from Kirchhoff's equation we can calculate heat of reaction at another temperature

Kirchhoff's Law At Constant Volume

$$\int_{T_1}^{T_2} d\Delta E = \Delta C_v \int_{T_1}^{T_2} dT$$

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

$$\Delta C_v = \sum C_{v(products)} - \sum C_{v(reactants)}$$

Note that heat capacities of all substances taking part in reaction must be included

Bond Energy

Average amount of energy required to break bonds present in 1 mole of compound

Note that original compound and dissociation products must be in gaseous state

Note that in this process heat is always given to the system
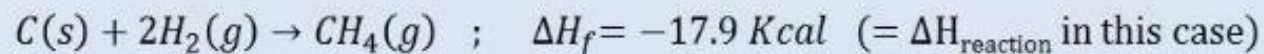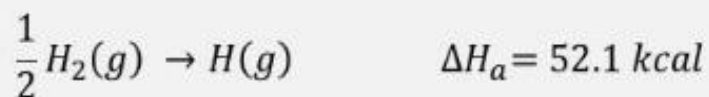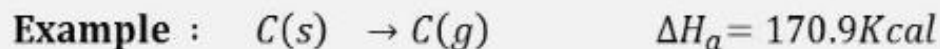
Bond energy is always positive

Calculation of Bond Energy

Bond energy calculation need knowledge of

Heat of formation (ΔH_f) of substance

Heat of atomization of its constituents (ΔH_a)

Example : $C(s) \rightarrow C(g)$ $\Delta H_a = 170.9 Kcal$

$\frac{1}{2} H_2(g) \rightarrow H(g)$ $\Delta H_a = 52.1 \, kcal$

$C(s) + 2H_2(g) \rightarrow CH_4(g)$; $\Delta H_f = -17.9 \, Kcal$ $(= \Delta H_{reaction}$ in this case)

Then Bond energy of $C - H$ bonds (x) is given by

$$\Delta H_a(C) + 4[\Delta H_a(H)] + 4x = \Delta H_f$$

Resonance Energy

For a compound resonance energy is measure of extra stability of conjugated system as compared to corresponding number of isolated double bonds

$$\text{Resonanace Energy} = \Delta H_{experimental} - \Delta H_{calculated}$$

Note : As resonance in a molecule gives it stability, it is always negative

Entropy Change of an Ideal Gas

1   For an ideal gas   ➡️ $PV = nRT$

2   Isothermal process ($\Delta T = 0$)   ➡️

$$\Delta S_T = 2.303 nR \log \frac{P_1}{P_2}$$

$$= 2.303 nR \log \frac{V_2}{V_1}$$

3   Isobaric process ($\Delta P = 0$)   ➡️ $\Delta S_P = 2.303 n\, C_P \log \frac{T_2}{T_1}$

Entropy Change For an Ideal Gas

Isochoric process ($\Delta V = 0$) ⟹ $\Delta S_v = 2.303 n C_v \log \dfrac{T_2}{T_1}$

At any temperature and pressure / volume

$$\Delta S = 2.303 n C_P \log \frac{T_2}{T_1} - 2.303 nR \log \frac{P_2}{P_1}$$

Or

$$\Delta S = 2.303 n C_v \log \frac{T_2}{T_1} + 2.303 nR \log \frac{V_2}{V_1}$$

Entropy Change Accompanying Change Of Phase

Solid changing to liquid ➡️ $$\Delta S_f = \frac{\Delta H_f}{T_f}$$

ΔH_f is molar heat of fusion and T_f is the freezing point of solid

Liquid changing to vapor ➡️ $$\Delta S_v = \frac{\Delta H_v}{T_b}$$

ΔH_v is molar heat of vaporisation and T_b is the boiling point of liquid

Note that both ΔH_v and ΔH_f are positive as transformation require energy And both processes are accompanied with an increase in entropy

Gibbs Free Energy (ΔG)

Maximum work for a spontaneous reaction is equal to ΔG

$$w_{max} = \Delta G$$

$$\Delta G = \Delta H - T\Delta S$$ → This equation serves as a criterion for spontaneity of a reaction or process

Note that for spontaneous reaction : $\Delta G < 0$

Accordingly ΔH and ΔS will be positive or negative depending on reaction

Free Energy Change Of Ideal Gas In Isothermal Process

$$dG = VdP - SdT$$

→ Valid when system reversibly undergoes change in pressure and also in temperature

$$dG = VdP = nRT\frac{dP}{P}$$

← For an ideal gas , at constant temperature

$$\Delta G = 2.303nRT\, log\frac{P_2}{P_1}$$

→ Initial and final states are designated by 1 and 2 respectively

Clausius-Clapeyron Equation

$$P = A \exp(-\Delta H_{vap} / R T)$$

A is a constant

R is gas constant

T is in kelvin

The vapor pressure of a liquid steadily increase as the temperature increases

$$\ln\frac{P_1}{P_2} = \frac{\Delta Hva_p}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Note that above expression helps in calculation of vapor pressure at different temperature if vapor pressure at a temperature is known