

CHEMICAL THERMODYNAMICS AND ENERGETICS

Introduction:-

Thermodynamics is a branch of science which deals with the inter conversion of various forms of energies. It also governs transformation of heat into work and vice-versa.

Energy may be defined as any property which can be produced from or converted into work. The various forms of energy. Which are

- i) Kinetic energy
- ii) Potential energy
- iii) Electrical energy
- iv) Radiant energy
- v) Chemical energy
- vi) Mass energy
- vii) Nuclear energy

Chemical Thermodynamics is the branch of thermodynamics which deals with the study of processes involving Chemical energy only.

Objectives of thermodynamics:-

- i) To predict the feasibility of a branch.
- ii) To predict the yield of the products.
- iii) To deduce important generalizations and their mathematical expressions like distribution law, Phase rule.

Limitations of thermodynamics:-

- i) It deals with macroscopic quantities and not with microscopic quantities.
- ii) It predicts feasibility but does not tell about the rate of reaction.
- iii) It concerns only with initial and final states and does not deal with path by which change is brought.

Terms used in thermodynamics.

System :- It is Part of the universe which is selected for thermodynamics investigation.

Surrounding :-

The part of the universe other than the system is called surroundings.

The system and surroundings are separated by a real or imaginary boundary.

Types of Systems :-

(a) On the basis of compositions, the system may be

- i) Homogeneous System :-** A System having uniform nature throughout and consists of one phase only.
- ii) Heterogeneous System :-** A system which is not uniform throughout and consist of more than one phase.

(b) On the basis of exchange of mass and energy, the system may be

- i) Isolated System :-** The system which can neither exchange energy nor mass with the surroundings such system is sealed and insulated.

For e.g. Piece of ice in thermos flask

- ii) Closed System :-** The system which can exchange energy with the surroundings but not mass.

For e.g. heating of solid iodine in a sealed container. Here the solid iodine sublimates to iodine vapours but iodine vapours cannot escape from container.

- iii) Open System:-** The system which can exchange mass as well as energy with the surroundings.

For e.g. Tea in a cup or solution of CuSO_4 in a beaker.

- 1. State of the System :-** The conditions of existence of a system when its macroscopic properties have definite value is called state of the system.

- 2. State function:-** State function is a quantity or property the change in the value of which depends only on the initial and final states of the system and is independent of path.

• THERMODYNAMIC PROPERTIES

- i) Intensive properties:-** The properties of the system which do not depend upon the amount of Substance Present. For e.g. - Temperature, Pressure, Viscosity, Surface tension, Density, refractive index and Specific heat etc.
- ii) Extensive properties :-** The Properties of the system which depend upon the amount of substance in the system. For e.g. – mass, volume, energy, enthalpy and work etc.

- **THERMODYNAMIC PROCESSES**

- i) **Isothermal Process :-** The Process in which temperature of the system remains constant ($\Delta T = 0$)
- ii) **Isobaric Process :-** The Process in which the pressure of the system remains constant ($\Delta P = 0$)
- iii) **Isochoric Process :-** The Process in which the volume of the system remains constant ($\Delta V = 0$)
- iv) **Adiabatic Process :-** The Process in which the system does not exchange heat with the surroundings. ($\Delta q = 0$)
- v) **Reversible Process :-** The Process in which direction may be reversed at any stage such process is slow in equilibrium conditions. It takes infinite time to occur. It is an ideal process and cannot observed in reality.
- vi) **Irreversible Process :-** The process which may not be reversible. All natural processes are irreversible in nature.
- vii) **Cyclic Process :-** The process in which system returns to its original state after a number of reactions. For such process $\Delta U = 0, \Delta H = 0$

- **Thermodynamic equilibrium:**

It involves simultaneous existence of following three equilibria:-

- (i) **Mechanical equilibrium** i.e. when no work is done on the system or done by the system.
- (ii) **Thermal equilibrium:** - i.e. Temperature remains constant throughout the system including the surroundings.
- (iii) **Chemical equilibrium** i.e. composition of system remains constant and definite.

A system is said to be in thermodynamic equilibrium if it satisfy all the above three equilibria.

- **WORK AND HEAT**

Work is a mode of energy transfer to or from a system with reference to the surroundings. When the system is in equilibrium no work is being done. It appears only during a change of state of the system. Work is of many types and the product of two factors.

$$\text{i.e. work} = \text{intensity Factor} \times \text{capacity Factor}$$

Where intensity factor is a measure of force responsible for work and capacity factor is a measure of extent for which work is done.

- **(a) Mechanical work:-** Consider a gas in a cylinder fitted with a frictionless piston. The Pressure exerted by the gas on the piston can be balanced by applying pressure from outside on the piston. This is called external pressure (p_{ext} .) This external pressure p_{ext} . is used to calculate work during irreversible expansion or contraction of the gas.

Suppose gas expands through a distance 'l'

$$\text{Work (W)} = - \text{force} \times \text{displacement} = - p_{\text{ext}} \times A \times l$$

$$W_{\text{irr}} = p_{\text{ext}} \times \Delta V \quad [\because A \times l = \Delta V]$$

$$W_{\text{irr}} = p_{\text{ext}} \times (V_2 - V_1)$$

Where V_1 and V_2 are the Volumes of the initial and final states of the system resp. p_{ext} - Intensity Factor, ΔV - Capacity Factor

Mechanical work is given by expression $W_{\text{irr}} \geq - p_{\text{ext}} \cdot \Delta V$

maximum work is possible if p_{ext} is maximum. This is possible when process is reversible. $W_{\text{rev}} \geq W_{\text{irr}}$

Work done in isothermal reversible expansion of an ideal gas is given by

$$W_{\text{rev}} = - 2.303nRT \log_{10} \frac{V_2}{V_1} = -2300 nRT \log_{10} \frac{P_1}{P_2}$$

- **(b) Electrical work** = Potential difference \times Quantity of electricity
= Volt (intensity factor) \times Coulomb (Capacity factor)

Sign conventions.

If Work is done on the system $W = +ve$

If work is done by the system $W = -ve$

Units of work :-

SI or MKS unit of work is joule or N.m., CGS. unit of work is erg or dyne. cm

$$1 \text{ Joule} = 10^7 \text{ erg}$$

- Heat (q) - It may be defined as the amount of energy that flows between system and surroundings due to difference in temperature.

- **Internal Energy (U)**

It is the definite quantity of energy possessed by a substance and depends upon its chemical nature, temperature, pressure and volume. It is a state function whose absolute value cannot be determined as it is a sum of many types of energies such as translational energy, rotational energy, vibrational energy, electronic energy, bonding energy, absolute value of each type cannot be determined.

$$U = U_{\text{trans}} + U_{\text{Rota}} + U_{\text{vib}} + U_{\text{bonding}} + U_{\text{electronic}}$$

Change in internal energy ΔU can be calculated

$$\Delta U = U_2 - U_1$$

- It is an extensive property and is a state function.
- Internal energy depends on temperature, pressure, volume and quantity of matter.
- No change in internal energy in cyclic process.
- Internal energy change (ΔU) per mole is calculated by using formula (from Bomb Calorimeter)

$$\Delta U = \frac{Z \times \Delta T \times M}{m}$$

Z - Heat capacity of calorimeter

ΔT - Rise in temp, M - molar mass

m - Amount of substance taken.

Expression For P-V work (Pressure constant)

Consider a certain amount of gas at pressure p, volume V and temp. T enclosed in a cylinder fitted with frictionless rigid movable piston upward through a distance 'd' by external Force f

$$W = \text{opposing force} \times \text{distance}$$

$$W = -f \times d$$

-ve sign signifies when the piston moves against an opposing force.

The force opposing the expansion is the constant external pressure p_{ex}

$$f = p_{\text{ex}} \times A$$

$$\therefore W = -P_{\text{ex}} \times A \times d$$

$$Ad = \Delta V = V_2 - V_1$$

$$W = -p_{\text{ex}} \Delta V$$

$$W = -p_{\text{ex}} (V_2 - V_1)$$

When gas expands, work is done by the system $V_2 > V_1$, $-p_{\text{ex}} \times \Delta V = -ve$

When gas compressed, Work is done on the system. $V_2 < V_1$, $-p_{\text{ex}} \times \Delta V = +ve$

Expression for Maximum Work.

Consider 'n' moles of an ideal gas enclosed in a cylinder fitted with frictionless movable rigid piston expanded isothermally and reversibly from initial volume V_1 to final volume V_2 at temp T.

Expansion takes place in a number of infinitesimally small steps. During each step P_{ex} external pressure is infinitesimally smaller than the pressure P of gas. The gas will expand slowly. Now according to Boyle's law the pressure P of gas will decrease. The expansion continues until the falling pressure of gas p_{ex} . At this stage the expansion stops and the system reaches mechanical equilibrium with surroundings.

When the volume of the gas increases by an infinitesimal amount dV in a single step. Small amount of work done is given by

$$dW = -p_{\text{ex}} dV$$

$$P - p_{\text{ex}} = dP \text{ or } p_{\text{ex}} = P - dP$$

$$dW = - (P - dP) dV$$

$$dW = -P \cdot dV + dp dV$$

$$dW = -p \cdot dv + dP \cdot dV$$

$$dW = -P \cdot dV$$

Total amount of work during expansion from volume V_1 to V_2

$$\int_1^2 dw = - \int_{V_1}^{V_2} P \cdot dV$$

$$W_{\text{max}} = - \int_{V_1}^{V_2} P \cdot dV$$

Ideal gas equation for n-moles

$$PV=nRT \quad \text{Or } P = \frac{nRT}{V}$$

$$W_{\max} = \int_{V_1}^{V_2} nRT \cdot \frac{dV}{V}$$

$$W_{\max} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$W_{\max} = -nRT \ln \frac{V_2}{V_1}$$

$$W_{\max} = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

T=Constant' Accor to Boyle's law

$$P_1 V_1 = P_2 V_2 \quad \text{or } \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W_{\max} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

- **Relation between ΔH and ΔU for Chemical reactions.**

ΔH and ΔU are related by at constant pressure as

$$\Delta H = \Delta U + P \cdot \Delta V$$

$$\Delta H = \Delta U + P \cdot \Delta V$$

$$\Delta H = \Delta U + P (V_2 - V_1)$$

$$\Delta H = \Delta U + PV_2 - PV_1$$

Where V_1 - Volume of gas phase reactant, V_2 - volume of gas phase product. From ideal gas equation $PV = nRT$

Suppose n_1 moles of gaseous reactant produce n_2 moles of gaseous products.

$$PV_1 = n_1 RT \quad \text{and} \quad PV_2 = n_2 RT$$

$$\therefore \Delta H = \Delta U + n_2 RT - n_1 RT$$

$$\Delta H = \Delta U + RT (n_2 - n_1)$$

$$\boxed{\Delta H = \Delta U + \Delta n RT}$$

- **Derive $\Delta H = \Delta U + P \cdot \Delta V$ -**

$$H_1 = U_1 + P_1 V_1 \text{ and } H_2 = U_2 + P_2 V_2$$

$$\Delta H = H_2 - H_1$$

$$\therefore \Delta H = U_2 + P_2 V_2 - (U_1 + P_1 V_1)$$

$$\Delta H = (U_2 - U_1) + (P_2 V_2 - P_1 V_1)$$

Since at const P, $P_1 = P_2 = P$

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

$$\boxed{\therefore \Delta H = \Delta U + P \Delta V}$$

First Law of Thermodynamics

It states that **energy can neither be created nor be destroyed although it can be converted from one form to another**. This means that the total energy of the universe remains constant. This law was put forward by Mayer and Helmholtz.

Mathematical formulation

$$q = \Delta U - W$$

ΔU - change in internal energy, q - heat change, W - Work

Sign conventions

- If work is done on the system, W is positive
- If work is done by the system, W is Negative
- If heat is absorbed by the system, q or ΔH is positive.
- If heat is given out by the system, q or ΔH is negative.
- If energy is absorbed by the system. ΔU is positive
- If energy is released. ΔU is negative. i.e. internal energy of system decreases.
- P-V work done in isothermal irreversible expansion $W_{\text{irr}} = -P_{\text{ext}} \Delta V$
- P-V work done in isothermal reversible expansion

$$W_{\text{rev}} = -2.303 nRT \ln \frac{V_2}{V_1} = -2.303 nRT \ln \frac{P_1}{P_2}$$

- For isothermal reversible process

$$\Delta U=0, q=-W, \therefore W=nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

- $q = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$
- $H = U + PV$
- $\Delta H = \Delta U + P \cdot \Delta V$
- $\Delta H = \Delta U + \Delta nRT$ For an isothermal expansion $\Delta T = 0$

$$\Delta H = \Delta U = 0$$

- For an isothermal isobaric expansion at Constant T and P, $q = -W$
 $\Delta U = 0, \Delta H = 0$
- For Isochoric process, $\Delta V = 0, q = \Delta U$
- For an adiabatic process $q=0, \Delta U = W$
- For a cyclic Process $\Delta U = 0, q = -W$
- For adiabatic reversible expansion of gas
 - (a) $TV^{\gamma-1} = \text{Constant}$
 - (b) $TP^{(1-\gamma)} = \text{Constant}$
 - (c) $PV^{\gamma} = \text{constant}$
- Both q and W are not state functions since their values depend upon the path by which the change is carried but the quantity q+W is a state function.
- $\therefore \Delta U$ is a state function.
- **Enthalpy or Heat Content (H)**

Majority of reactions are carried in open vessels therefore these are subjected to constant pressure conditions heat changes under such conditions are different from heat changes at constant volume conditions therefore a new thermodynamic function enthalpy H is defined.

$$H = U + PV$$

Enthalpy is a state function and is an extensive property.

The absolute value of H cannot be calculated but change in enthalpy ΔH can be calculated.

For exothermic reactions $\Delta H < 0$

For endothermic reactions $\Delta H > 0$

- The change in enthalpy

$$\Delta H = \Delta U + P \cdot \Delta V$$

$$\Delta H = \Delta U + \Delta nRT$$

(a) When $\Delta n = 0$, then $\Delta H = \Delta U$

(b) If $\Delta n > 0$, then $\Delta H > \Delta U$

(c) If $\Delta n < 0$, then $\Delta H < \Delta U$

- Enthalpy changes when a substance undergoes phase transition.
- For reactions involving solids and liquids only, $\Delta H = \Delta U$
- For reactions involving solid, liquid and gases the value of Δn is evaluated by the difference in number of moles of gaseous reactant and products.
- Enthalpy change is (ΔH) calculated using calorimeter (an open vessel)

$$\Delta H = Z \times \Delta T \times \frac{M}{m}$$

Z - Heat capacity of calorimeter system

ΔT - Change in temperature

M- Molecular mass of substance.

m - Amount of the substance.

This method is not suitable For

- (a) Reactions which are extremely slow
- (b) Reactions which are accompanied by very small enthalpy change.
- (c) Reactions which do not go to completion
- Exothermic reactions are chemical reactions, which proceed with evolution of heat $H_p < H_R$, $\Delta H = H_p - H_R = -ve$
 $\Delta H = \Delta U = -ve$ For exothermic reactions.
- Endothermic reactions are chemical reactions which proceed with absorption of heat by reacting substance.
 $H_p > H_R$, $\Delta H = H_p - H_R = +ve$
 $\Delta H = \Delta U = +ve$ For endothermic reactions.

- **Bond Energy and Bond Dissociation Energy**

Bond dissociation energy is the energy required to break one mole of a particular type of bonds in gaseous molecule. It's units are kJmol^{-1}

(i) In diatomic molecules the term bond energy and bond dissociation energy have same meaning.

e.g. For H_2 - molecule, the value is 433 kJmol^{-1}

(ii) In Polyatomic molecules containing more than one similar bonds, the bond energy is average of bond dissociation energies of various similar bonds.

- To calculate enthalpy changes in a reaction

$$\Delta H = \sum \text{Bond energies of Reactant bonds} - \sum \text{Bond energies of product bonds}$$

- **HEAT OF REACTION :-**

Heat of reaction is the quantity of heat evolved or absorbed in a reaction. It is denoted by ΔH and expressed in joules (J) or kilo Joules (kJ)

$$\Delta H = \sum H_p - \sum H_R$$

When heat of the reaction is expressed at the standard states, then it is called standard heat of reaction and is denoted as ΔH° .

VARIOUS FORMS OF HEATS OF REACTIONS

- **Heat of Formation :-** Enthalpy change accompanying the formation of 1 mole of a compound from it's elements. It is taken as zero.

If an element exists in more than one allotropic forms. The most stable allotropic form is taken as standard form. Standard enthalpies of formation of graphite and rhombic sulphur are taken as zero.

$$\Delta H^\circ_{\text{Reaction}} = \Delta H^\circ_f(\text{Products}) - \Delta H^\circ_f(\text{Reactants})$$

- **Heat of combustion:-** The amount of heat liberated during the complete combustion of one mole of a substance in the presence of excess of oxygen is known as a heat of combustion or enthalpy of combustion.

Since combustion reactions, Hence $\Delta H^{\circ}_{\text{Combustion}} < 0$

- **Heat of dissolution:-** It is the heat change taking place when one mole of the substance is dissolved in large excess of solvent so that on further dilution no appreciable heat change occurs.



- **Heat of Vaporization :-** It is the heat required to change one mole of the liquid substance completely into vapour at the boiling point



- **Heat of fusion:-** It is the heat required to change one mole of the solid substance completely into liquid at the melting point.



- **Heat of sublimation:-** It is the heat required to change one mole of solid substance directly into vapours completely below the melting point.



- **Heat of hydrogenation: -** It is the enthalpy change occurring when 1 mole of an unsaturated organic compound is fully hydrogenated.
- **Heat of transition:-** It is the heat change when one mole of the substance undergoes transition from one allotropic form to another.



- **Heat of Neutralization: -** It is the heat change occurring when 1 gm-equivalent of an acid (or base) is neutralized by 1 gm-equivalent of base (or acid) in dilute solutions.
- It may be remembered that heat of neutralization of strong acid - strong base is always constant.

i.e. $\Delta H_{\text{neutralization}} = -57.1 \text{ kJ} = -13.7 \text{ Kcal}$



The enthalpy of neutralization is the quantity of heat liberated in the combination of H^+ and OH^- ions in solutions to form one mole of water.

The heat of neutralization of strong-acid weak base or weak acid strong base is less than 57.1 kJ. This is because some heat is required to dissociate weak electrolyte completely into ions.

The heat required for dissociation of one mole of weak electrolyte (acid/base) is referred to as heat of ionization



The smaller the heat of neutralization the weaker is that acid (or base) involved.

- The absolute value of heat of neutralization of HF is more than 57.1 kJ (68 kJ). This is due to very high heat of hydration of fluoride ion.
- **Heat of hydration:** - It is the heat change occurring when one mole of anhydrous substance undergoes complete hydration. (i.e. combine with the required number of water molecules to form hydrated salt.)



Hydration is an exothermic process because it involves the bonding of water molecules and central metal ion.

Its value can be found out from enthalpies of solution of the anhydrous salt and the hydrated salt, during the process of dissolution of anhydrous salt. The hydration as well as dissolution takes place. Thus

$$\text{Heat of solution of anhydrous salt} = \left(\text{Heat of hydration of anhydrous salt} \right) - \left(\text{Heat of solution of hydrated salt} \right)$$

- **Heat of ionization:-**

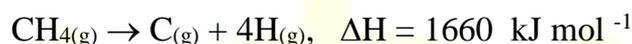
The heat change that accompanies the removal of an electron from each atom or ion in 1 mole of gaseous atom or ions is called an enthalpy of ionization.

For e.g. - $\text{Na}_{(g)} \rightarrow \text{Na}^+_{(g)} + \bar{e}$ $\Delta H_{\text{ion}} = 494 \text{ kJ mol}^{-1}$

i.e. 494 kJ of heat are required to ionize one mole of Na.

- **Heat of atomization:- (ΔH_{ato})**

The heat change accompanying the dissociation of all the molecules in one mole of a gas phase substance into gaseous atoms is called Heat of atomization



- **Heat of Solution (ΔH_{soln}):-**

The heat change in a process in which one mole of a substance is dissolved in a specified quantity of a solvent so as to form a solution of particular concentration at a given temperature.

For e.g. - When 1 mole of NaCl is dissolved in water to form 1M solution 4 kJ heat are absorbed.

Enthalpy of solution of NaCl is + 4 kJ mol⁻¹

Enthalpy of solution of KCl is + 17.2 kJ mol⁻¹

- **Heat of dilution:-**

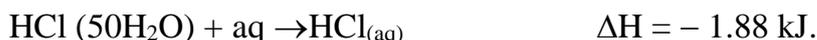
The heat change that occurs when a solution of one concentration is diluted to form the solution of another concentration.

When 1 mole of HCl is dissolved in 50 moles of water heat of solution is given by $\text{HCl}_{(g)} + 50 \text{ H}_2\text{O}_{(l)} \rightarrow \text{HCl} (50 \text{ H}_2\text{O})$, $\Delta H = - 73.26 \text{ kJ}$

When 1 mole HCl is dissolved in large quantity of water i.e. when solution is infinitely dilute. The heat of solution is given by



The infinitely dilute solution means. The solution is so dilute that further dilution causes no thermal effects.



∴ Heat of dilution is – 1.88 kJ.

HEAT CAPACITY:- It is heat required to raise the temperature of the system by one degree. For one mole of a pure substance. It is called molar heat capacity (c_m)

Types of heat capacity.

(i) Heat capacity at constant volume $C_v = \left[\frac{\partial E}{\partial T} \right]_v$

(ii) Heat capacity at constant Pressure $C_p = \left[\frac{\partial H}{\partial T} \right]_p$

For ideal gas $C_p - C_v = R$

R – gas constant $C_p > C_v$.

- Since molar heat capacities of solids are approx equal to one another i.e.

$$\Delta C_p = \Delta C_v = 0.$$

∴ ΔH involving only solids do not change appreciably with temperature

$$C_p / C_v = \gamma$$

- The value of γ depends on the atomicity of gaseous molecules.

$$\gamma = 1.66 \text{ For monoatomic gases (He, Ne, Ar- etc.)}$$

$$\gamma = 1.40 \text{ For diatomic gases.}$$

$$\gamma = 1.33 \text{ For (O}_2, \text{H}_2, \text{N}_2 \text{ etc) triatomic gases [SO}_2, \text{O}_3 \text{ etc.]}$$

- **Dulong and Petit law:-** The product of specific heat and molar mass of any metallic element equal to 6.4 approximately .

$$S_p \text{ heat} \times \text{molar mass} = 6.4 \text{ approx.}$$

This law is applicable to solid elements except Be, B, C and Si

- Clausius - Claperon equation :-

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \Delta H_v - \text{molar heat of vaporization.}$$

LAWS OF THERMO CHEMISTRY

- **Laplace and Lavoisier Law:-** According to this law, heat absorbed or evolved in a chemical reaction is opposite and equal to heat change when the reaction is reversed.

ZEROETH LAWS OF THERMODYNAMICS

According to this law, if two systems A and B separately are in thermal equilibrium with another system C, then system A and B will also be in thermal equilibrium with each other.

SECOND LAWS OF THERMODYNAMICS

The first law of the thermodynamics does not help us to predict whether the process in question can occur spontaneously or not (i.e. whether it is feasible or not) and if so, in which direction. The answer to this problem is provided by second law of thermodynamics. This statement of the law is developed in terms of the entropy criterion. The second law states that entropy of isolated system tends to increase and reaches a maximum value. This means that the most stable state of an isolated system is the state of maximum value. This means that the most stable state of an isolated system is the state of maximum entropy. There are several other statements of the second law.

- i) **Clausius** stated that it is impossible to transfer heat from a cold to hot reservoir without doing some work.
- ii) **Kelvin** stated that it is impossible to convert all the heat taken from source to work, without losing some of it to colder reservoir.
- iii) **Caratheodary** postulated that in the neighborhood of every equilibrium state of a closed system, there was stated which cannot be reached.
- iv) **Boltzmann** stated that, nature tends to pass from a less probable to a more probable condition. The condition of maximum probability is the one of the maximum randomness.

Entropy (S.) It is the extensive thermodynamic property of the system which provides a measure of it's degree of disorder or randomness. It is denoted by S

The change in entropy during the process is given by the ratio of heat absorbed by the system (q) in a reversible manner to the temperature (T) at which it is absorbed

$$\Delta S = (S_2 - S_1) = \frac{q_{rev}}{T}$$

SPONTANEOUS AND NON - SPONTANEOUS PROCESSES

- **Spontaneous Process:-** The Physical or Chemical Process which occurs in a particular set of conditions either of its own or after proper initiation is known as spontaneous process.

For a process to be spontaneous in isolated system, $\Delta S = +ve$

For a process to be in open system

$$\Delta S = \text{total} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

If system changes from A to B, either reversibly or irreversibly entropy change is given as

$$\Delta S_{\text{sys}} = \frac{q_{rev}}{T}, \quad \Delta S_{\text{surr}} = \frac{-q_{rev}}{T}$$

i.e. $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ – For reversible

$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ – For irreversible

Second law of Thermodynamics states that the entropy of the universe always increase during the course of any spontaneous change.

ENTROPY CHANGES IN PROCESSES.

(i) Entropy change during isothermal reversible expansion of an ideal gas

$$\Delta S = \frac{q_{rev}}{T}$$

Acco. to Ist law $\Delta U = q + W$

For Isothermal, $\Delta U = 0$

$\therefore q = -W$.

$$W_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} \quad q = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_2}{P_1}$$

For 1 mole of gas at constant T.

$$\Delta S = \frac{q}{T} = \frac{nRT}{T} \ln \frac{V_2}{V_1} = nR \ln \frac{V_2}{V_1} \quad \Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}$$

ii) Entropy change during adiabatic reversible expansion.

In such process $q=0$ at all stages hence $\Delta S=0$, reversible adiabatic processes are called isentropic process.

iii) Entropy change when pressure is constant, $\Delta S = C_p \ln \frac{T_1}{T_2}$

iv) Entropy change when volume is constant, $\Delta S = C_v \ln \frac{T_2}{T_1}$

v) Entropy change during phase transition, $\Delta S = S_2 - S_1 = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T} \quad \Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

GIBB'S ENERGE (G)

Gibb's energy of a system is a thermodynamic quantity. The decrease in value of a G during process is equal to useful work done by system.

$$(-\Delta G = -W_{useful})$$

It is the amount of energy freely available from a system at particular T.

During any process change Gibb's energy

$$\Delta G = G_2 - G_1$$

$$\Delta G = \Delta H - T\Delta S$$

This expression called Gibb's Helmholtz education

CRITERION OF SPONIANEITY

- **Exoergonic reaction:-** An exoergonic reaction which is accompanied by decrease of Gibb's energy.

i.e. a reaction for which ΔG is -ve. All spontaneous process are exoergonic

- **Endoergonic reactions** - Which is accompanied by increase in Gibbs energy i.e. for which $\Delta G = +ve$. All non-spontaneous processes are endoergonic reactions.

- **Effect of T on spontaneity.**

i) for exothermic reaction,

$$\Delta H = -ve$$

$$T\Delta S = +ve \text{ or } -ve$$

If $T\Delta S$ is +ve, then ΔG always -ve, If $T\Delta S$ is -ve, then for ΔG to be -ve

T should be low

Thus exothermic reactions are favored by decrease in temperature

ii) For endothermic reactions.

$$\Delta H = +ve, T\Delta S = +ve \text{ or } -ve$$

If $T\Delta S$ is -ve, then $\Delta G > 0$ (reaction is non-spontaneous)

If $T\Delta S$ is +ve, then ΔG to be -ve, T is high.

Sr. No.	Sign of ΔH	Sign of ΔS	$\Delta G = \Delta H - T\Delta S$	Remarks.
1.	-ve	+ve	Always -ve	Spontaneous at all T
2.	+ve	-ve	Always +ve	non-spontaneous at all T
3.	+ve	+ve	+ve at low T -ve at high T	Non-spontaneous at low T spontaneous at high T
4.	-ve	-ve	-ve at low T +ve at high T	Spontaneous at low T. Non-spontaneous at high T

COUPLED REACTIONS: - A non-spontaneous reaction can be made spontaneous by coupling. When non-spontaneous reactions ($\Delta G = +ve$) is coupled with another reaction for which ΔG is highly -ve then both reactions occur simultaneously.

For e.g



The change in free energy for both reactions.

$$\Delta G^0 = -56.2 \text{ kJmol}^{-1} \text{ is } -ve$$

then reduction of Fe_2O_3 with CO is spontaneous.

- **ΔG and Equilibrium Constant**

For a reversible reaction at constant T and P. The equilibrium composition of reaction mixture corresponds to lowest pt. on Gibb's energy and progress of reaction curve.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium

$$Q = K, \Delta G = 0$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K.$$

$$\Delta G^\circ = -2.303 RT \log_{10} K$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$RT \ln K = T \Delta S - \Delta H^\circ$$

For endothermic $\Delta H^\circ = +ve$ K- Small

For exothermic, $\Delta H^\circ = -ve$, K -large.

- ***Change in Gibb's energy and EMF of cell***

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

$$\Delta G = -nFE_{\text{cell}}$$

If reactant and product in their standard state .

$$\Delta G^\circ = -nFE_{\text{cell}}$$

THIRD LAW OF THERMODYNAMICS

The entropy of a substance at absolute zero (0K) is taken to be zero. The importance of law is to calculate absolute entropies of pure substance at different T.

For a solid at TK

$$S_T - S_0 = \Delta S = \int_0^T \frac{C_p \cdot dT}{T} = C_p \ln T$$

$$\Delta S = 2.303 C_p \log T$$

Where S_T and S_0 are entropies at TK and 0K

For liquid and gases: - The absolute entropy at given T.

$$S = \int_0^{T_f} C_p(s) \frac{dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} C_p(l) \frac{dT}{T} + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_b}^T C_p(g) \frac{dT}{T}$$

This law is true only for substances which exist in perfect crystalline form at 0K

The Third law of Thermodynamics.

At absolute zero of temperature the entropy of every substance may become zero and it does become zero in the case of a perfectly crystalline solid.

▪ Determination of Absolute Entropies of solids liquids and gases:-

For an infinitesimally small change of state of a substance or a system the entropy

change is given by - $(ds) = \frac{dq}{T}$

If the change takes place at constant P.

$$\text{then } (\delta s)_p = (\delta q)_p/T \quad \therefore \left(\frac{\partial S}{\partial T}\right)_p = (\partial q/\partial T)_p \times \frac{1}{T}$$

By definition on

$$(\delta q/\delta T)_p = C_p \quad (\delta s/\delta T)_p = C_p \times 1/T$$

at constant pressure $ds = (C_p/dT) \times dT$

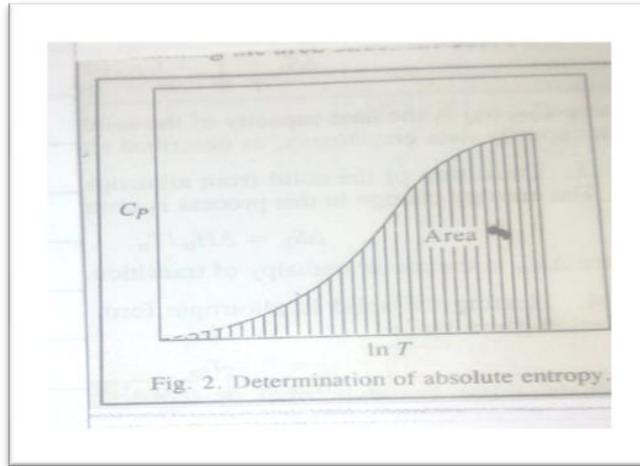
For a perfectly crystalline substance the absolute entropy $S=0$, at $T=0$, therefore we write

$$\int_{S=0}^{S=S} ds = \int_{T=0}^{T=T} \left(\frac{C_p}{T}\right) dT \quad (C_p/T), \quad S_T = \int_0^T \frac{C_p \cdot dt}{T} = \int_0^T C_p \cdot d(\ln T) \dots (I)$$

where S_T is the absolute entropy of the crystalline solid under examination at temp T.

The integral in equation (I) is evaluated by measuring C_p at various temperatures between $T = 0$ and T. Then plotting C_p against T and determine the area under the curve between $T=0$ and T. This area gives value of S_T

Since it is not possible to obtain the value of C_p at absolute zero. heat capacities are measured up to 15 K and value of absolute zero is obtained by extrapolation. A graph of C_p Vs $\ln T$ is then plotted and extrapolated to absolute zero of temp. The area under graph gives S_T at temp T.



Determination of absolute entropy equation (I) can be written as -

$$S_T = \int_0^T cp \frac{dT}{T} = \int_T^T cp \cdot \frac{dT}{T} \dots\dots\dots(2)$$

When $10 < T < 15$ K

The first integral is evaluated with the help of Debye-Theory of heat capacities of crystalline substance at which $0 < T < 15$ K

$$C_P = C_V = aT^3 -$$

Where a - is an empirical constant and equation (2) is known as Debye - T^3 Law.

Equation (2) may be written as -

$$S_T = \int_0^{T^\infty} aT^3 \cdot \frac{dT}{T} + \int_{T^\infty}^T cp \cdot \frac{dT}{T} = \frac{1}{3} a(T^\infty)^3 + \int_{T^\infty}^T cp \cdot \frac{dT}{T} \dots\dots\dots(4)$$

The second integral of equation (2) is evaluate from experimental measurement of heat capacity combining heat capacity data and enthalpy data on phase transformation the absolute entropy of a substance whether solid, liquid or gas at temperature T can be determined.

Suppose it is required to determine absolute entropy of gas at 25^0C under atmospheric pressure. This would be equal to some of entropy changes in following process each of which is brought about reversibly.

It is assumed that the substance in solid state exists in two allotropic forms α and β .

1. Heating the crystalline solid from absolute zero to temp. T Where $10 < T^\infty < 15$ K and evaluating entropy change with the aid of Debye's Theory.

Let entropy change be Δs_1 , then

$$\Delta S_1 = \int_0^T aT^3 \frac{dT}{T} = \frac{1}{3} a(T^\circ)^3 \dots (5)$$

2. Heating the crystalline solid from T° & to T_{tr} Where, T_{tr} is the transition temperature at which crystalline solid changes from allotropic form α to allotropic form β .

The entropy change in this process

$$\Delta S_2 = \int_{T^\circ}^{T_{tr}} C_p \cdot S(\alpha) dT \dots (6)$$

Where $C_p S(\alpha)$ is the heat capacity of the solid in allotropic form α

ΔS_2 is evaluated by integration of heat capacity data graphically.

3. Transition of the solid from allotropic form α to allotropic form β at the transition temp. T_{tr} . The entropy change in this process

$$\Delta S_3 = \Delta H_{tr} / T_{tr} \dots (7)$$

Where ΔH_{tr} molar enthalpy of transition.

4. Heating the solid in allotropic form β to its fusion point T_f . The entropy change in this process is given by

$$\Delta S_4 = \int_{T_{tr}}^{T_f} C_p \cdot S(\beta) dT \dots (8)$$

Where $C_p S(\beta)$ is the heat capacity of the solid in allotropic form β .

5. Changing the solid in allotropic form β into liquid state at the fusion temperature T_f . The entropy change of this process.

(Entropy of fusion) is given by

$$\Delta S_5 = \Delta H_f / T_f \dots (9)$$

6. Heating the liquid from its freezing point (T_f) to its boiling point (T_b). The entropy change involved in this case is given by

$$\Delta S_6 = \int_{T_f}^{T_b} C_{p,l} \ln T \dots (10)$$

Where $C_{p,l}$ heat capacity of substance in liquid state. This can be evaluated by plotted $C_{p,l}$ Vs $\ln T$ between temp T_f and T_b .

7. Changing the liquid into gaseous state at temp. T_b . The entropy change ΔS , is the molar entropy of vaporization and is given by.

$$\Delta S_7 = \frac{\Delta H_v}{T_b}$$

ΔH_v – is entropy of vaporization per mole of substance.

8. Heating the gas from T_b to required temp i.e. 25°C (298.15 K). The entropy change involved here is

$$\Delta S_8 = \int_{T_b}^{298.15} C_{p,g} d \ln T$$

Where C_p – is the heat capacity of the substance in gaseous state at const. p. ΔS_8 is evaluated by plotting $C_{p,g} \ln T$

$\ln T$, between Temp. T_b and 298.15 K and noting area below curve.

The absolute entropy of the gas at 298.15 K (25°C) S_T is equal to the sum of all the entropy changes above.

Thus $S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 + \Delta S_7 + \Delta S_8$

Limitations of Law

- (i) Glassy solids even at 0K entropy greater than zero.
- (ii) Solids have mixtures of isotopes do not have zero entropy at 0K for entropy of solid Cl_2 is not zero at absolute 0K
- (iii) Crystals of CO_2 , N_2O , NO , H_2O etc. do not have perfect order even at 0K thus $S \neq 0$

Some important Points

1) Joule relationship between mechanical work done (W) and heat produced (H) is

$$W \propto H \text{ or } W = JH$$

Where J is called mechanical equivalent of heat. It's value is $J = 4.184 \times 10^7$ ergs

Thus work done when 1 calorie of heat is produced = 4.184 J

2) Work done by a gas for isothermal irreversible expansion from volume V_1 to volume V_2 against a constant external pressure P is $W_{\text{irr}} = -P \cdot \Delta V$

3) Accor to first law of thermodynamics

$$\Delta U = q + w$$

Where q - heat absorbed w – work done

4) Sign conventions for ΔU , q and W.

If energy is absorbed by the system $\Delta U = +ve$

If energy is released by the system $\Delta U = -ve$

If work is done on the system. $W = +ve$

If work is done by the system. $W = -ve$

If heat is absorbed by the system $q = +ve$

If heat is given out by the system $q = -ve$

5) $\Delta H^{\circ}_{\text{Reaction}} = \Delta H^{\circ}_{\text{f (Products)}} - \sum \Delta H^{\circ}_{\text{f (Reactants)}}$

6) $\Delta H_{\text{Reaction}} = \sum \text{B.E of Reactants} - \sum \text{B.E of Products}$

7) Enthalpy $H = U + PV$

Enthalpy change $\Delta H = \Delta U + P \Delta V$

8. Heat Capacity, $C = \frac{q}{T_2 - T_1}$

q - Heat absorbed to raise temp from T_1 to T_2

9. $C_v = (\partial u / \partial T)_v$ and $C_p = (\partial H / \partial T)_p$

10. $C_p - C_v = R$.

11. Work done in isothermal reversible expansion

$$W_{\text{max}} = -2.303 nRT \log_{10} \frac{V_2}{V_1} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

12. For reversible adiabatic expansion.

$$PV^{\gamma} = \text{constant}, TV^{\gamma-1} = \text{constant} \text{ and } TP^{1-\gamma/\gamma} = \text{constant}$$

13. Work done during adiabatic expansion of n - moles of an ideal gas

$$q_v = nC_v (T_2 - T_1)$$

14. $q_v = \Delta U$ and $q_p = \Delta H$

15. $q_p = q_v + \Delta nRT$ or $\Delta H = \Delta U + \Delta nRT$

16. Kirchoff's equation is $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$.

17. Change in internal energy (for combustion) is determined by bomb calorimeter -

$$\Delta U = C \times \Delta T \times M/m$$

C - heat capacity of the calorimeter

$\Delta t - (t_2 - t_1)$ = rise in temp

m - Mass of substance taken

M - Molecular mass of substance.

18. Efficiency of heat engine $\eta = w/q = T_2 - T_1 / T_2 = q_2 - q_1 / q_2$

q_2 - heat absorbed at T_2 q_1 - heat absorbed by system at T_1 , W = work done

19. Entropy change $\Delta S = q_{\text{rev}} / T$

20. $\Delta S_{\text{System}} + \Delta S_{\text{Surr}} \geq 0$

= sign reversible process (Equilibrium) and sign > to irreversible process.

21. $\Delta S_{\text{fusion}} = \Delta H_{\text{fusion}} / T_f$

22. Gibbs's energy = $G = H - TS$, $\Delta G = \Delta H - T\Delta S$

24. $\Delta G^0 = \sum G^0_{\text{(Products)}} - \sum G^0_{\text{(Reactants)}}$

25. If ΔG is - Ve, Process is Spontaneous

If ΔG is + Ve, Process is non - Spontaneous

If $\Delta G = 0$ Process is in equilibrium

26. $\Delta G = W_{\text{useful}}$

27. Clausius - Clapeyron equation

For Liquid - \leftrightarrow vapour equilibrium

28. $\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

29. Vant Hoff reaction isotherm $\Delta G = \Delta G^0 + RT \ln k_p$

30. Total differential equation $dG = Vdp - S.dT$

31. At constant temp T. $\left(\frac{\partial q}{\partial p} \right)_p = V$

At constant Pressure P $\left(\frac{\partial q}{\partial p} \right)_p = - S$

32. $\Delta G^0 = n FE^0$

33. $\Delta G^0 = - RT \ln K$

34. Entropy change For ideal gas (For Imole)

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

At const. T, $\Delta S = R \ln V_2/V_1 = R \ln P_1/P_2$

At const. V, $\Delta S = C_v \ln T_2/T_1$

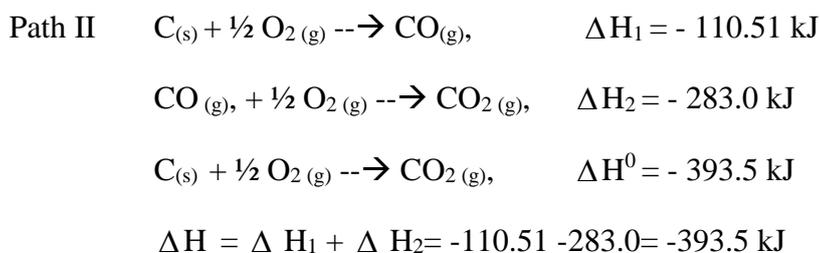
At const. P, $\Delta S = C_p \ln T_2/T_1$

HESS'S LAW OF CONSTANT HEAT SUMMATION

Law States that the enthalpy change (or heat evolved or absorbed) in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

Illustration of Hess's Law by considering the formation of carbon dioxide from carbon and oxygen carbon can be converted into I CO₂ by two ways

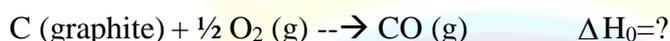




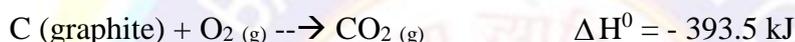
Applications of Hess's Law

1. If it is not possible to determine experimentally the enthalpy of reaction it can be calculated by Hess's law.

For e.g. the enthalpy of formation of CO cannot be determined experimentally



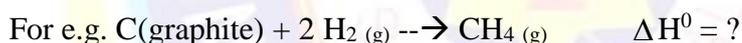
because some of the carbon can be oxidized to CO_2 . However the enthalpies of following reactions can be determined from which enthalpy of formation of CO can be calculated.



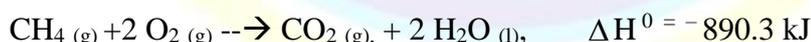
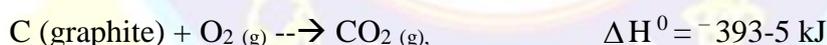
Reversing equation (II) and adding to equation (I). We get



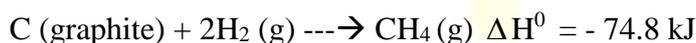
- 2) It can be used to calculate enthalpy of reaction which do not occur directly



This reaction does not occur directly its ΔH^0 can be calculated from the following reactions whose ΔH^0 values are known.



Between (I) + 2 x equation (II) – equation (III) gives



- 3) The enthalpy of Formation of any compound from its elements can be calculated.
- 4) The enthalpy of combustion can be calculated.

KIRCHHOFF'S EQUATION:-

The heat of reaction varies with temperature. The verification of ΔH or ΔG with

temperature is given by Kirchhoff's equation as - $\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_p$

H_2 and H_1 are enthalpy changes at temperatures T_2 and T_1 resp. ΔC_p is change in heat capacity at constant pressure.

$$\Delta C_p = \sum C_p \text{ of products} - \sum C_p \text{ reactants similarly}$$

U_2 and U_1 are internal energy changes at T_2 and T_1 resp and ΔC_v is the change at heat capacities at constant volume.

$$\Delta C_v = \sum C_v \text{ of products} - \sum C_v \text{ reactants similarly}$$

Kirchhoff's equation is given by
$$\frac{\Delta V_2 - \Delta V_1}{T_2 - T_1} = \Delta C_v$$

Born - Haber's Cycle:-

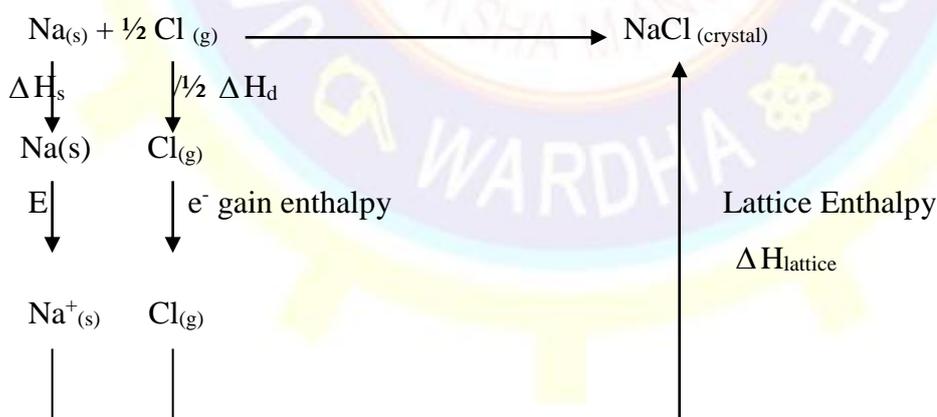
This cycle relates lattice energy (U) of a crystal to other thermo chemical parameters like heat of Sublimation, formation dissociation, ionization energy electron affinity etc.

Lattice energy :- (U) It is the energy evolved when one mole of the crystalline solid is formed from its constituent ion in their free gaseous state



$$U = +782 \text{ KJ/mol. } \Delta H_{\text{lattice}} = -782 \text{ KJmol}^{-1}$$

Formation of NaCl Crystal involves several steps. ΔH_f of NaCl will be the algebraic sum of all the energy terms involved in these steps.



By Hess's law $\Delta H_s + \text{IE} + \frac{1}{2} \Delta H_d + \Delta H_{\text{eg}} + \Delta H_{\text{lattice}} = \Delta H_f$

Actual sign of the enthalpy depends on endothermic or exothermic nature of each step (lattice and e gain enthalpy are generally -ve)

Born Haber cycle are generally used to calculate lattice energy. Which are difficult to measure experimentally.

- Resonance energy:** - The difference between the observed heat of formation of the actual compound and that of resonating structure which has the lowest internal energy (obtained by calculation) is called the resonance energy.

$$\text{Resonance Energy} = \Delta H_f \text{ of actual compound (observed (experimental))} - \Delta H_f \text{ of resonating structure having lowest. Internal energy (calculated)}$$

Resonance energy = observed heat of formation - calculated heat of formation

