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ATOMIC ENERGY CENTRAL SCHOOL-KUDANKULAM

Handout –Module-3/5

Subject-Chemistry **Class-XI**

Lesson No.-Unit-6 (Thermodynamics)

Name of the topic-Enthalpy,Enthalpy of Transition,Enthalpies of Reaction

ENTHALPY

- It is the sum of internal energy and pV-energy of the system.
- Enthalpy is measure of total energy of a thermodynamic system. It includes the internal energy, which is the energy required to create a system, and the amount of energy required to make space for it by displacing its environment and establishing its volume and pressure.
- The enthalpy of a system is defined as,$H=U+PV$
- H is the enthalpy of the system
- U is the internal energy of the system
- P is the pressure at the boundary of the system and its environment.
- V is the volume of the system
- It is a state function and extensive property.
- The absolute value of H of a system cannot be measured directly. Thus change in enthalpy ΔH is more useful than its absolute value
- Unit of enthalpy is(SI) joule

- Enthalpy is preferred expression of system of energy in many chemical and physical measurements, because it simplifies certain descriptions of energy transfer.
- ΔH is +ve for endothermic reactions
- ΔH is –Ve for exothermic reactions
- $\Delta H = H_2 - H_1$
- or $\Sigma Hp = \Sigma HR$
- Relation between ΔH and Qp
- At constant atmospheric pressure we already derived an equation
- $Q_p = \Delta U + P\Delta V$
- And for change in enthalpy at constant pressure in the system we got…….
- $\Delta H = \Delta U + P\Delta V$
- So if external atmospheric pressure and pressure of gas in the system are same , then from above two equations we can derive
- $\Delta H = Q_p$
- Thus change in enthalpy of a system = heat transferred at constant pressure.
- We know that at constant pressure ΔH and ΔU are related as…
- $\Delta H = \Delta U + P\,\Delta V$
- for solids and liquids ΔV and is very small and can be neglected
- Hence $\Delta H = \Delta U$
- but what about gaseous reactions?
- Let n1 be the initial moles of gaseous reactants and n2 be the final moles of gaseous product.
- We know that change in enthalpy is given as …..
- $\Delta H = \Delta U + P\,\Delta V$

- $= \Delta U + P(V_2 - V_1)$
- $\Delta H = \Delta U + PV_2 - PV_1$
- Where V_1 is the volume of gaseous reactants
- V_2 is the volume of gaseous products
- suppose the gases are behaving ideally then….
- We can apply ideal gas equation $PV = nRT$ for both reactants and products
- For gaseous reactants $PV_1 = n_1RT$
- For gaseous product $PV_2 = n_2RT$
- $\Delta H = \Delta U + n_2RT - n_1RT$
- $\boldsymbol{\Delta H = \Delta U + (n_2 - n_1)RT}$
- $\boldsymbol{\Delta H = \Delta U + \Delta n_g RT}$
- Δn_g = number of moles of gaseous product – number of moles of gaseous reactants.
- but we know that ……..
- $\Delta H = Q_p$ and $\Delta U = Q_v$
- $Q_p = Q_v + \Delta n_g RT$
- Work done in terms of change in moles can be written as-
- **We know that at constant pressure and temperature....**
- $\boldsymbol{W = -P\Delta V}$
- **But** $\boldsymbol{PV_1 = n_1RT}$ **and**
- $\boldsymbol{PV_2 = n_2RT}$
- **∴ PV2 – PV1 = (n2 – n1)RT**
- $\boldsymbol{P\Delta V = \Delta nRT}$
- ∴ $\boldsymbol{W = -\Delta nRT}$

- Standard Enthalpy of Reaction
- Enthalpy of reaction expressed at the standard state conditions is called standard enthalpy of reaction (ΔH^0).
- Standard state of a substance at a specified temperature is its pure form at one bar pressure.
- Thermodynamic data is taken usually taken at 298K
- Standard states of certain elements and compounds are

EXAMPLES :- $H_2(g)$, Na (s), C(graphite) , $C_2H_5OH(l)$, $CaCO_3(s)$, $CO_2(g)$, $H_2O(l)$

- **Factors Affecting Enthalpy of Reaction**
- (i) Physical state of reactants and products.
- (ii) Allotropic forms of elements involved.
- (iii) Chemical composition of reactants and products.
- (iv) Amount of reactants.
- (v) Temperature**.**
- **Enthalpy of phase transition**
- Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remainsconstant (at 273 K).
- **Enthalpy of fusion**
- $H_2O(s) \rightarrow H_2O(l)$; $\Delta^0 H\, fusion = 6$ *kj/mol*
- Here $\Delta\, ^0H$ *fusion is enthalpy of fusion in standard* state. If water freezes, then process is reversed and equal amount of heat is given off to the surroundings.The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta\, fusH^0$
- **Enthalpy of vaporisation**

- Amount of heat required to vaporise one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its standard enthalpy of vaporization or molar enthalpy ofvaporization, $\Delta vapH^0$.
- $H_2O(l) \rightarrow H_2O(g) \qquad \Delta vapH^o= +40.79kj/mol$
- Melting of a solid is endothermic, so all enthalpies of fusion are positive.
- **Enthalpy of Solution**
- It is the Enthalpy change when one mole of a substance is dissolved in large excess of solvent, so that on further dilution no appreciable heat change occurs.
- Dissolution can be viewed as occurring in three steps:
- Breaking solute-solute attractions (endothermic), see for instance lattice energy U_l in salts.
- Breaking solvent-solvent attractions (endothermic), for instance that of hydrogen bonding
- Forming solvent-solute attractions (exothermic), in solvation
- The value of the enthalpy of solvation is the sum of these individual steps.
- $\Delta Hsolution= \Delta Hhyd + U1$
- Dissolution of ammonium nitrate in water is endothermic. The energy released by solvation of the ammonium ions and nitrate ions is less than the energy absorbed in breaking up the ammonium nitrate ionic lattice and the attractions between water molecules.
- Dissolving potassium hydroxide is exothermic, as more energy is released during solvation than is used in breaking up the solute and solvent.
- **Enthalpy of sublimation**
- Standard enthalpy of sublimation, Δ *subH0 is the change in enthalpy when one* mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).
- Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or ‘dry ice’ sublimes at 195K with *subH0=25.2 kJ mol–1 ;*

- **Enthalpy of Neutrilisation**
- It is the enthalpy change that takes place when 1 g-equivalent of an acid (or base) is neutralised by 1 g-equivalent of a base (or acid) in dilute solution. Enthalpy of neutralisation of strong acid and strong base is always constant, i.e., 57.1 kJ.
- Enthalpy of neutralisation of strong acid and weak base or weak acid and strong base is not constant and numerically less than 57.1 kJ due to the fact that here the heat is used up in ionisation of weak acid or weak base. This is known as enthalpy of ionisation of weak acid / or base.
- HCN + NaOH → NaCN +H2O
- ΔHneutrilisation=-12kj/mol at 25degree celcius.
- The heat of ionization for the above reaction is equal to (–12 + 57.3) = 45.3 kJ/mol at 25 °C.
- **Enthalpy of Atomisation**
- It is the enthalpy change occurring when one mole of the molecule breaks into its atoms.
- $H_2(g) \rightarrow 2H(g)$; $\Delta\, aH^0 = 435.0$ *kJ mol–1*
- You can see that H atoms are formed by breaking H–H bonds in dihydrogen. The enthalpy change in this process is known as enthalpy of atomization, Δ atomisation(a)H^0. *It is the* enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.
- $Na(s) \rightarrow Na(g)$; $\Delta\, aH^0 = 108.4$ *kJ mol–1*
- In this case, the enthalpy of atomization is same as the enthalpy of sublimation.
- **Enthalpy of Dilution.**
- It is the enthalpy change, when one mole of a substance is diluted from one concentration to another.molecule breaks into its atoms.
- **Enthalpy of Transition**

- It is the enthalpy change when one mole of the substance undergoes transition from one allotropic form to another
- **Enthalpy of Formation (ΔH_f)**
- It is heat change when one mole of compound is obtained from Its constituent elements.
- Enthalpy of formation at standard state is known as standard enthalpy of formation $\Delta fH°$ and is taken as zero by convention. It also gives the idea of stability.
- $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$
- $2C(\text{graphite}) + 3H_2 + 1/2O_2 \rightarrow C_2H_5OH$
- **Standard enthalpy of formation**
- Standard enthalpy of formation for one mol of a compound from its constituent elements in their most stable state of aggregation (reference state) is called standard molar enthalpy of formation $\Delta H^0{}_f$ substance.
- The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure. For example, the reference state of dihydrogen is H2 gas and those of dioxygen, carbon and sulphur are O_2 gas, C_{graphite} and S_{rhombic} respectively.
- **Enthalpy of Combustion**
- It is the Enthalpy change taking place when one mole of a compound undergoes complete combustion In the presence of oxygen (ΔHc.)
- ΔHc because process of combustion is exothermic.
- Consider-
- $C_2H_2(g) + 5/2O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ $\Delta_rH° = -1300$ KJ
- When <u>one mole of a substance</u> is completely oxidized in its standard state, the standard enthalpy change is called as the standard enthalpy of combustion
- **BOND ENTHALPY**

- It is the average amount of energy required to break one mole of bonds in gaseous molecules.
- **Bond Dissociation Enthalpy**
- The energy required to break the particular bond in a gaseous molecule is called bond dissociation enthalpy. It is definite in quantity and expressed in kJ mol-1.
- In diatomic molecule, bond dissociation enthalpy = Bond enthalpy
- In polyatomic molecule, bond dissociation enthalpy ≠ Bond Enthalpy
- ΔH = [sum of bond enthalpies of reactants] – [sum of bond enthalpies of product
- **Factors affecting bond enthalpy**
- (i) Size of atoms
- (ii) Electronegativity
- (iii) Bond length
- (iv) Number of bonding electrons
- $H_2O_{(g)} \rightarrow OH_{(g)} + H_{(g)} \quad \Delta_r H^\circ = 499\ kJ$
- $OH_{(g)} \rightarrow O_{(g)} + H_{(g)} \quad \Delta_r H^o = 428\ kJ$
- $H_2O_{(g)} \rightarrow 2H_{(g)} + O_{(g)} \quad \Delta_r H^o = 927\ kJ$

- **BOTH O-H BOND ENTHALPY VALUE IS NOT SAME**
- Thus average bond enthalpy will be 927/2 =463.5kJ
- ΔH^o (O-H) = 463.5 kJ
- Enthalpy of a reaction= Sum of the bond enthalpies of reactants –sum of the bond enthalpies of products
- For the reaction-
- $H_2(g) + I_2(g) \rightarrow 2HI(g)$

- $\Delta Hreaction = \sum bond\Delta Hreactants - \sum bond\Delta\, Hproducts$

Bond Enthalpy for polyatomic molecules

- In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ.
- CH_4 (g) →CH_3 (g)+H(g); = +427kj/mol
- CH_3 (g)→ CH (g)+ H(g); = +439kj/mol
- CH_2 (g)→ CH(g) + H(g); = +452kj/mol
- CH(g)→ C(g) + H(g); = +347kj/mol
- Therefore CH_4 (g)→ C(g)+ 4H(g); = 1665kj/mol

  In such cases we use mean bond enthalpyof C – H bond
- For example in CH4, $\Delta_{C-H}H^0$ *is calculated as:*
- $\Delta_{C-H}H^0 = \frac{1}{4}\, \Delta a H^0$
- $=1665/4$

  $= 416$ kJ mol^{-1}
