CHEMISTRY CLASS -XI

UNIT -6
THERMODYNAMICS

MODULE -3/5

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OUTLINE

- Enthalpy
- Enthalpy of phase transition
- Enthalpy of formation
- Enthalpy of combustion
- Enthalpy of solution
- Enthalpy of sublimation
- Enthalpy of dilution
- Enthalpy of atomisation
- Enthalpy of ionisation.
- Enthalpy of neutrilisation.
- Enthalpy of bond dissociation .

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
- $\Delta H = H_2 - H_1$

Numerical

- **Calculate the enthalpy of the reaction:**
  $N_2o_4(g) + 3CO(g)$ ———–>$N_2o(g) + 3CO_2(g)$
  Given that;$\Delta_f H^- CO(g) = – 110$ kj mol^{-1}; $\Delta_f HCo_2(g) =$ $– 393$ kj mol^{-1}
  $\Delta_f HN_2o(g) = 81$ kj mol^{-1}; $\Delta_f N_2O_4(g) = 9.7$ kj mol^{-1}
- Enthalpy of reaction (Δ_r,H) = [81 + 3 (- 393)] – [9.7 + 3 (- 110)]
  = [81 – 1179] – [9.7 – 330] = – 778 kj mol^{-1}

Relation between ΔH and Q_p

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 …..

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

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

$\Delta H = \Delta U + P\,V_2 - PV_1$

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 = n RT for both reactants and products

For gaseous reactants $PV_1 = n_1RT$

For gaseous product $PV_2 = n_2RT$

$\Delta H = \Delta U + n_2RT - n_1RT$

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

$\Delta H = \Delta U + \Delta n_g RT$

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….

$W = - P \Delta V$

BUT $PV_1 = n_1RT$ and

$PV_2 = n_2RT$

$\therefore PV_2 – PV_1 = (n_2 – n_1)RT$

$P \Delta V = \Delta nRT$

$\therefore \quad W = - \Delta nRT$

- Enthalpy of reaction expressed at the standard state conditions is called standard enthalpy of reaction (ΔH^o).
- 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 :- $H_{2(g)}$, $Na_{(s)}$, $C_{(graphite)}$, $C_2H_5OH_{(l)}$, $CaCO_{3(s)}$, $CO_{2(g)}$, $H_2O_{(l)}$

- **The reaction of cyanamide,$NH_2CN(s)$ with dioxygen was carried out in a bomb calorimeter and ΔU was found to be -742,7 KJ^{-1} mol^{-1} at 298 K. Calculate the enthalpy change for the reaction at 298 K.**
- **$NH_2CN\ (S) + 3/2O2(g) \longrightarrow N_2(g) + CO_2(g) + H_2o(l)$**
- $\Delta U = -\ 742.7\ KJ^{-1}\ mol^{-1}$; $\Delta n^g = 2 - 3/2 = +\ 1/2$ mol.
  R = 8.314 x 10-3$KJ^{-1}\ mol^{-1}$; T = 298 K
  According to the relation,$\Delta H = \Delta U + \Delta n^g RT$
  $\Delta H = (-\ 742.7\ kj) + (1/2\ mol) \times (8.314 \times 10^{-3}\ KJ^{-1}\ mol^{-1}) \times$ (298 K)
  $= -\ 742.7\ kj + 1.239\ kj = -\ 741.5\ kj.$

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**
- $H_2O(s)$-→ $H_2O(l)$; *oH fusion =6 kj/mol*
- Here *oH fusion is enthalpy of fusion in standard* state. 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, *fusH*o

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 specified amount of solvent, under standard condition.
- 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.
- ΔHsolution= ΔHhydration +Lattice enthalpy
- 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.
- $KOH(s) + Aq \rightarrow K^+(aq) + OH^-(aq)$

- **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 at infinite dilution**-The enthalpy change observed by dissolving 1 mole of a substance in infinite amount of solvent so that interaction between solute molecules are negligible is called enthalpy at infinite dilution.
- **Enthalpy of Hydration-**
- It is the enthalpy of one mol of an anhydrous salt by combination with specific number of moles of water.
- $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$
- ΔH=-78.2kj/mol

Enthalpy of sublimation

- Standard enthalpy of sublimation, $\Delta_{sub}H^{o}$ *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 $\Delta_{sub}H^{o} = 25.2\ kJ\ mol^{-1}$;

Enthalpy of Neutralisation

- 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.
- $H_2(g) \rightarrow 2H(g)$; $\Delta_a H^o = 435.0\ kJ\ mol^{-1}$
- 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, $\Delta_{atomisation(a)}H^o$. *It is the* enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.
- $Na(s) \rightarrow Na(g)$; $\Delta_a H^o = 108.4\ kJ\ mol^{-1}$
- In this case, the enthalpy of atomization is same as the enthalpy of sublimation.
- **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

- 1. **Enthalpy of Formation (ΔHf)**
- It is heat change when one mole of compound is obtained from Its constituent elements.
- $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$
- $2C(graphite) + 3H_2 + 1/2O_2 \rightarrow C_2H_5OH$
- $1/2N_2(g) + 3/2H_2(g) \rightarrow NH_3(g)$

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 ΔH^o_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 O2 gas, Cgraphite and Srhombic respectively.
- By convention the standard molar enthalpies of formation of free elements in their reference state are taken to be **zero.**

- **Given : $N_2(g) + 3H_2(g)$ ————> $2NH_3(g)$; $\Delta_{r\,H}^{-} = -92.4$ kj mot^{-1} What is the standard enthalpy of formation of NH_3 gas?**
- ΔH^{-} NH_3 (g) = – (92.4)/2 = – 46.2 kj mol^{-1}
- **Calculate the standard enthalpy of formation of CH_3OH. from the following data:**
  (i) $CH_3OH(l) + 3/2\ o_2\ (g)$ ———-> $CO_2\ (g) + 2H_2o\ (l)$; $\Delta_r H^{-} = -$ 726kj mol^{-1}
  (ii) $C(s) + o_2(g)$ ————>$Co_2\ (g)$; $\Delta_c H^{-} = -393$ kj mol^{-1}
  (iii) $H_2(g) + 1/2o_2(g)$ —————->$H_2o\ (l)$; $\Delta_f H^{-} = -286$ kj mol^{-1}
- The equation we aim at;
  $C(s) + 2H_2(g) + l/2o_2(g)$ ———> $CH_3OH\ (l)$;$\Delta_f H^{-} = \pm?$ … (iv)
  Multiply eqn. (iii) by 2 and add to eqn. (ii)
  $C(s) + 2H_2(g) + 2o_2(g)$ ————->$Co_2(g) + 2H_2o(l)$
  $\Delta H = -(393 + 522) = -965$ kj mol-1
- Subtract eqn. (iv) from eqn. (i)
  $CH_3OH(l) + 3/2o_2(g)$ ————> $Co_2(y) + 2H_2o(l)$; $\Delta H = -726$ kj mol^{-1}
  Subtract: $C(s) + 2H_2(y) + l/2o_2(g)$ ———-> $CH_3OH(l)$; $\Delta_f He = -$ 239 kj mol^{-1}

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

$C_2H_2(g) + 5/2O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ $\Delta_r H° = -1300$ 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

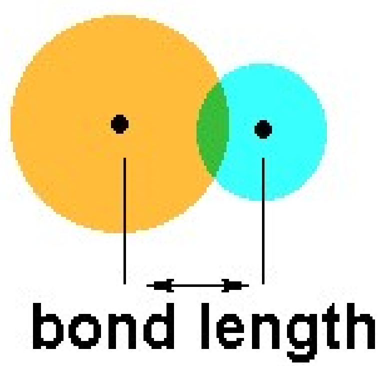
Let us solve.....

- **Enthalpy of combustion of carbon to carbon dioxide is – 393.5 J mol^{-1} ·Calculate the heat released upon formation of 35.2 g of Co_2 from carbon and oxygen gas.**
- The combustion equation is:
  $C(s) + o_2 (g) \longrightarrow Co_2(g)$; $\Delta cH = -393.5$ KJ mol^{-1}
  Heat released in the formation of 44g of Co_2 = 393.5 kj
  Heat released in the formation of -
- 35.2 g of Co_2=(393.5 KJ) x (35.2g)/(44g) = 314.8 kj

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 products]

- Factors affecting bond enthalpy
- (i) Size of atoms
- (ii) Electronegativity
- (iii) Bond length
- (iv) Number of bonding electrons



Ex :-1

Enthalpy change of a reaction

$$\Delta_r H^o = \sum \Delta H^o(\text{reactant}) - \sum \Delta H^o(\text{product}) \quad \text{.......} \quad (4.31)$$

Consider the reaction

$$H_2(g) + I_2(g) \longrightarrow 2\ HI(g)$$

The enthalpy is given by

$$\Delta_r H^o = [\Delta H^o(\text{H-H}) + \Delta H^o(\text{I-I})] - [2\Delta H^o(\text{H-I})]$$

Remember...

If reactants and products are diatomic molecules the Eq. (4.31) gives accurate results. The bond enthalpies are known accurately. For reactions involving polyatomic molecules the reaction enthalpies calculated via. Eq. (4.31) would be approximate and refer to averag bond enthalpies.

Bond Enthalpy –Polyatomic molecule

- 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) $\rightarrow CH_3$ (g)+H(g); $\Delta_{bond}H^0$= +427kj/mol
- CH_3 (g)$\rightarrow$ CH (g)+ H(g); $\Delta_{bond}H^0$= +439kj/mol
- CH_2 (g)$\rightarrow$ CH(g) + H(g); $\Delta_{bond}H^0$= +452kj/mol
- CH(g)$\rightarrow$ C(g) + H(g); $\Delta_{bond}H^0$= +347kj/mol
- Therefore CH_4 (g)$\rightarrow$ C(g)+ 4H(g); $\Delta_a H^0$= 1665kj/mol
- In such cases we use mean bond enthalpyof C– H bond.
- For example in CH_4, $\Delta_{C-H}H^o$ *is calculated as:*
- $\Delta_{C-H}H^o$= ¼ $\Delta_a H^0$
- *=1665/4*

  = 416 kJ mol–1

- ✓ $H_2O_{(g)} \rightarrow OH_{(g)} + H_{(g)} \quad \Delta_r H^\circ = 499\ kJ$
- ✓ $OH_{(g)} \rightarrow O_{(g)} + H_{(g)} \quad \Delta_r H^o = 428\ kJ$

- ✓ $H_2O_{(g)} \rightarrow 2H_{(g)} + O_{(g)} \quad \Delta_r H^o = 927\ kJ$

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

THANK YOU