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THERMODYNAMICS AND THERMOCHEMISTRY

Thermodynamics deals with the study of different forms of energy, their interconversions and the quantitative relationships between them.

Inter conversion of heat energy with other forms of energy.

Systems: There are three types:

Open system: Can exchange matter and energy with the surrounding

Example: Water in an open beaker

Closed system: Can exchange energy but not matter with the surroundings

Example: Water in a closed beaker.

Isolated system: Cannot exchange both matter and energy with the surroundings

Example: Water in a thermally isolated closed container like thermos flask.

State function / Thermodynamic function:

Value depends only on the position of the system and not on the way it is attained

Examples: Temperature (T), Pressure (P), Volume (V), Internal Energy (E), Enthalpy (H), Entropy (S), Free energy (E)

Note: Work done (W) and heat absorbed (Q) depend on the path taken. So they are not state functions.

Intensive properties

They do not depend upon the amount of substance present in a system.

Examples: Temperature, density, surface tension etc.

Extensive properties

Depend upon the amount of substance in a system.

Examples: Mass, volume etc.

Process:

Defines the way in which a system changes its position from one thermodynamic state to another.

Types of process:

Isothermal, Adiabatic, Reversible, Irreversible, Isobaric, Isochoric etc.

Adiabatic process:

Is one where no heat is exchanged between the system and the surroundings.

Hence $dq = 0$

Takes place in a thermally isolated closed system.

Lesser the thermal conductance of the vessel, more efficient the process is

dw is the work done on the system. First law equation is $dE = dq + dw$.

Since dq is zero, $dE = dw$.

Work done = Increase in internal energy.

If work is done by the system, From first law, $dE = dq - dw$.

Since dq is zero, $dE = -dw$,

Work done = Decrease in internal energy

Isothermal process:

Is one where heat is exchanged between the system and the surroundings.

Higher the thermal conductance of the vessel, better is the way the process takes place

Temperature being constant, $dE = 0$

If work is done on the system, From first law, $dE = dq + dw$.

Hence, $dw = -dq$

(dE is zero). So work done = Amount of heat liberated.

If work is done by the system, From first law, $dE = dq - dw$.

Hence $dw = +dq$ (dE is zero).

So work done = Amount of heat absorbed.

Isobaric process:

Pressure remains constant. $\Delta P = 0$

Isochoric process:

Volume remains constant. $\Delta V = 0$

Cyclic process:

System returns to the initial state.

Initial and final states are the same.

Hence $\Delta E = 0$ and $\Delta H = 0$.

Internal energy (E)

Internal energy of the system is the energy possessed by it due to its chemical nature and its thermodynamic state

It is the sum of the rotational energy, vibrational energy, translational energy etc.

Internal energy of an element in their standard state is zero.

S.I unit of internal energy is 'U'

Enthalpy (H)

Enthalpy of a system is the total heat content of a system

$H = u + PV$ or $\Delta H = \Delta u + P\Delta V$ or $\Delta H = \Delta u + RT\Delta n$.

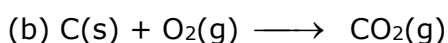
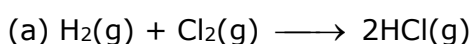
If ΔH is -90 kJ, at 298 K,

$\Delta u = \Delta H - RT\Delta n = -90 \text{ kJ} - (8.314 \times 10^{-3} \times 298 \times -2) = -85.04 \text{ KJ}$

Relationship between ΔH and ΔU and ΔE

$\Delta H = \Delta U + \Delta nRT$, where $\Delta n = n_p - n_r$

Case (i) $\Delta n = 0$



$\Delta H = \Delta U$

Case (ii) $\Delta n = +ve$

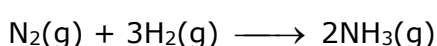


$\Delta n = +1$

$\Delta H > \Delta U$

Case (iii) $\Delta n = -ve$

$\Delta H < \Delta U$



$$\Delta n = -2$$

In case, the reactants and products are liquids or solids the volume change (ΔV) during the reaction is negligible i.e. $\Delta V = 0$. Hence $\Delta H = \Delta U$

- Measurement of ΔU :** Heat of a reaction at constant volume is represented as ΔU . It is done in a bomb calorimeter. Which is a strong steel vessel in which combustion of the experimental substance is carried out. It is surrounded by an insulated vessel containing water whose rise of temperature is noted. Knowing the heat capacity C of the calorimeter, ΔU can be calculated using the formula $\Delta U = C \times \Delta T \times \frac{M}{m}$
 Where ΔT = rise in temperature m = mass of the substance M = mol. Mass
- Measurement of ΔH :** Heat of reaction at constant pressure is ΔH . The change in enthalpy during the combustion reaction is measured in a similar calorimeter in the same manner. However the calorimeter is kept open to keep pressure constant.

First law of thermodynamics

Energy can neither be created nor be destroyed.

It can be converted from one form into another.

Mathematical form of first law of thermodynamics is $dU = dq + dw$ (w is the work done on the gas).

If work is done by the gas then the first law equation takes the form $dU = dq - dw$

Work done in an isothermal process given by

$$W = - 2.303 nRT \log \frac{V_2}{V_1} \text{ or}$$

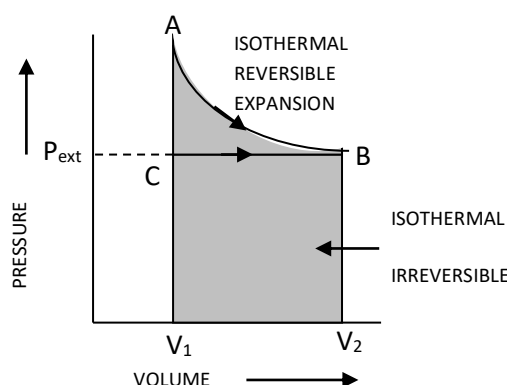
$$W = - 2.303 nRT \log \frac{P_1}{P_2}$$

Work done in an adiabatic process is given by $W = nC_v(T_1 - T_2)$

C_v is the molar heat capacity at constant volume.

Expansion against vacuum (Free expansion). For expansion of an ideal gas against vacuum (reversible or irreversible), as $P_{ext} = 0$, the work done (w) = 0

$W_{rev} > W_{irrev}$, $W_{rev} = W_{max}$ and $w_{rev} > w_{ad}$. For reversible expansion, as P_{ext} has the maximum value (only infinitesimally smaller than P_{int}), work done in reversible expansion is the maximum work for a given change in volume. Hence, $W_{rev} > W_{irrev}$. Also $W_{rev} > W_{ad}$.



Joule's relationship between mechanical work done (W) and heat produced (H):

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

Where J is called mechanical equivalent of heat. Its value is $J = 4.184 \times 10^7 \text{ ergs} = 4.184 \text{ joules}$. Thus, work done when 1 calorie of heat is produced = 4.184 joules.

Heat capacity, specific heat capacity and molar heat capacity:

- Heat capacity and Specific heat capacity. Heat capacity (C) of a substance is defined as the amount of heat required to raise the temperature of the **given substance** through 1°C .

Specific heat capacity (c) is the amount of heat required to raise the temperature of **1g** of the substance through 1° C.

Evidently, the amount of heat, q, required to raise the temperature from T₁ and T₂ of mass m gram of a sample having specific heat, c, can be calculated using the expression

$$q = m \times c \times (T_2 - T_1) = m \times c \times \Delta T$$

or using the heat capacity (C),

$$q = C \times \Delta T$$

$$\text{Thus, } C = \frac{q}{\Delta T} = \frac{\delta q}{dT} \text{ (for a small change)}$$

Note. Specific heat capacity of water is 1 cal g⁻¹ K⁻¹ or 4.184 J g⁻¹ K⁻¹

- 2. Molar heat capacity.** It is the amount of heat required to raise the temperature of 1 mole of the substance through 1°C. Thus, molar heat capacity $C_m = \frac{C}{n}$

Where C is the heat capacity of n moles of the substance.

- 3. Heat capacity at constant volume (C_v) and that at constant pressure (C_p).**

As q is not a state function, therefore C is also not a state function. Hence, to know the value of C, the conditions such as constant volume or constant pressure have to be specified which define the path. Thus, there are two types of heat capacities, which are

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p)

Now, according to 1st law of thermodynamics,

$$\delta q = dU + PdV$$

$$\therefore C = \frac{dU + PdV}{dT}$$

At constant volume, dV = 0, hence,

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \text{ or } C_v = \frac{dU}{dT} \text{ for ideal gas.}$$

At constant pressure,

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \dots (i)$$

As H = U + PV,

$$\therefore \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \dots (iii)$$

Combining (i) and (ii)

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \text{ or } C_p = \frac{dH}{dT} \text{ for ideal gas}$$

- 4. Relationship between C_p and C_v**

H = U + PV = U + RT (for 1 mole of ideal gas)

$$\therefore \frac{dH}{dT} = \frac{dU}{dT} + R$$

i.e., C_p = C_v + R

or C_p - C_v = R

Thus, C_p > C_v by the gas constant R, i.e., approx. 2 calories or 8.314 J

- 5. Ratio $\gamma = C_p/C_v$**

The ratio C_p/C_v, represented by γ , is as follows:

Nature of the gas:	Monoatomic (He, Ar etc.)	Diatomic (H ₂ , O ₂ , CO etc)	Triatomic (CO ₂ , H ₂ S etc)
$\gamma = C_p/C_v$	1.66	1.40	1.30

Internal energy of one mole of a monoatomic gas is $U = \frac{3}{2} RT$

$$\therefore C_v = \left(\frac{\partial U}{\partial T} \right) = \frac{3}{2} R$$

$$C_p = C_v + R = \frac{5}{2} R$$

$$\therefore \gamma = C_p/C_v = 5/3 = 1.66$$

$$\text{For diatomic gases, } C_v = \frac{5}{2} R, C_p = \frac{7}{2} R$$

$$\text{Hence, } \frac{C_p}{C_v} = \frac{7}{5} = 1.40$$

The ratio decreases with increase of temperature.

Spontaneous process: A process which takes place by itself without any external aid under given conditions is called spontaneous process.

Non spontaneous process: A process which does not take place by itself under the given conditions is called a non spontaneous process

Entropy (s): It is a measure of disorder of a system or randomness of a system. Entropy is a state function. The change in entropy during the process is given by $\Delta S = \frac{\Delta q}{T}$ where Δq is the quantity of heat absorbed at a given temperature T Kelvin. The unit of ΔS is J/K.

The change in entropy depends on initial and final states of the system

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Note: 1) Vapour state has highest entropy

2) Greater the number of chemical bonds, higher is the entropy.

For example: $S_{\text{acetylene}} < S_{\text{ethylene}} < S_{\text{ethane}}$

Criteria for spontaneity: Spontaneity of a process can be explained using the following factors

a) Enthalpy factor (ΔH)

b) Entropy factor (ΔS).

c) Free energy factor (ΔG).

Enthalpy factor alone can not explain spontaneity. For a spontaneous process, entropy increases. Thus

a) ΔS is +ve for a spontaneous process,

b) ΔS is -ve for a non spontaneous process

c) ΔS is zero for a process at equilibrium.

For a reversible process at equilibrium $\Delta S = \frac{q_{\text{rev}}}{T}$

According to first law of thermodynamics, $\Delta U = q + w$

For isothermal expansion of an ideal gas, $\Delta U = 0$.

$$\text{Hence, } Q_{\text{rev}} = -W_{\text{rev}} = n RT \ln \frac{V_2}{V_1}$$

$$= n RT \ln \frac{P_1}{P_2}$$

$$\Delta S = n R \ln \frac{V_2}{V_1}$$

$$\Delta S = n R \ln \frac{P_1}{P_2}$$

Entropy change for 1 mole of an ideal gas

At constant temperature (isothermal process)

$$\Delta S = R \ln \frac{V_2}{V_1}$$

$$\Delta S = R \ln \frac{P_1}{P_2}$$

At constant volume (isochoric process)

$$\Delta S = C_v \ln \frac{T_2}{T_1}$$

At constant pressure (isobaric process)

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

Second law of Thermodynamics: A spontaneous process is accompanied by an increase in total entropy. In other words entropy of the universe is continuously increasing.

In an isolated system, the change in entropy is positive. In an open system,

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Entropy of the system continuously increases and tends to attain equilibrium.

- 1) For an exothermic reaction, $\Delta S_{\text{system}} > 0$ & $\Delta S_{\text{surroundings}} < 0$
- 2) For an endothermic reaction, $\Delta S_{\text{system}} < 0$ & $\Delta S_{\text{surroundings}} > 0$
- 3) The entropy change for a cyclic process is zero.
- 4) The entropy change in the equilibrium state is zero ($\Delta S = 0$).
- 5) For natural processes, entropy of universe is increasing. $\Delta S_{\text{universe}} > 0$
- 6) In a reversible process, ΔS_{total} or $\Delta S_{\text{universe}} = 0$ and therefore $\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$
- 7) For adiabatic reversible process, $\Delta S_{\text{system}} = \Delta S_{\text{surroundings}} = \Delta S_{\text{total}} = 0$
- 8) In a spontaneous (irreversible process), ΔS_{total} or $\Delta S_{\text{universe}} > 0$,
i.e. in spontaneous processes, there is always increase in entropy of the universe.

Gibb's free energy (G): It is the difference between the initial state energy and equilibrium state energy. It is the energy which is available with the system to do useful work. It is given by $G = H - TS$ where TS is the non available energy.

Gibb's equation is given by $\Delta G = \Delta H - T\Delta S$. The free energy change for a process at 298 K and 1 atm pressure in which all the reactants and products are in their standard state is called standard free energy change and is denoted by ΔG^0 .

For a spontaneous process, $\Delta G < 0$

For a non spontaneous process, $\Delta G > 0$

For a process at equilibrium, $\Delta G = 0$

Two important conditions for thermodynamic feasibility of a chemical reaction are increase in entropy and decrease in free energy.

Predicting the feasibility of a reaction using Gibb's equation

a) $\Delta H < 0$ & $\Delta S > 0$

the reaction is spontaneous at all temperatures

b) $\Delta H < 0$ & $\Delta S < 0$

the reaction is spontaneous at low temperatures when $T\Delta S < \Delta H$.

c) $\Delta H > 0$ & $\Delta S > 0$

the reaction is spontaneous at high temperatures when $T\Delta S > \Delta H$.

d) $\Delta H > 0$ & $\Delta S < 0$ the reaction is non spontaneous at all temperatures.

The standard free energy change and standard cell potential are related as $\Delta G^0 = -nFE^0$ where E^0 is the standard EMF of the cell

a) Standard free energy of formation of an element is zero

b) Standard free energy of formation H^+ ion is zero.

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

$$W_{\max} = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

For isothermal expansion of an 'n' moles of ideal gas

$$\Delta G = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$$

Gibbs Energy change of a cell reaction $W_{\max} = nFE^\circ$

$$-\Delta G = W_{\max} = nFE^\circ$$

$$\Delta G^\circ = \sum G^\circ_{(\text{products})} - \sum G^\circ_{(\text{reactants})}$$

- Third law of thermodynamics:** "At absolute zero, the entropy of a perfectly crystalline substance is zero."

Eg: The sublimation energy of $I_2(s)$ is 57.3 kJ/mol and the enthalpy of fusion is 15.5 kJ/mol. The enthalpy of vaporisation of I_2 is

a) 41.8 kJ/mol b) -41.8 kJ/mol c) 72.8 kJ/mol d) -72.8 kJ/mol

Ans: (a)

$$\Delta H_{\text{sub}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vap}}$$

$$\Delta H_{\text{vap}} = 57.3 - 15.5 = 41.8 \text{ kJ/mol}$$

Eg: The change of energy on freezing 1.00 kg of liquid water at 0°C and 1 atm is

a) 236.7 kJ/kg b) 333.4 kJ/kg c) -333.4 kJ/kg d) -236.7 kJ/kg

Ans: (c)

Enthalpy of fusion of ice = +6 kJ/mol \therefore Enthalpy of freezing of water = -6 kJ/mol

$$\therefore \text{Enthalpy change on freezing 1000 g of water} = -\frac{6 \times 1000}{18} = -333.4 \text{ kJ}$$
- Zeroth law of thermodynamics:** If two systems are both in chemical equilibrium with a third system, they are in thermal equilibrium with each other. The zeroth law introduces the concept of thermometer to measure the temperature.

Thermochemistry deals with the study of enthalpy changes during physical and chemical process.

Physical changes involve processes like

melting of ice

boiling of a liquid

transition of a substance from one allotropic form to another

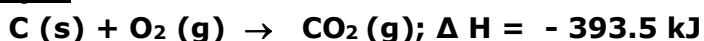
polymorphic changes etc.

Thermochemical equation

Balanced chemical equation in which the physical states of reactants and products are shown.

It indicates enthalpy change during physical or chemical processes.

Example:



Heat is liberated in an exothermic reaction. Hence ΔH is negative

Heat is absorbed in an endothermic reaction. So ΔH is positive.

Enthalpy of reaction

Enthalpy change involved when the number of moles of the reactants as indicated by the balanced chemical equation have completely reacted under the given condition

Enthalpy of reaction depends on

Quantity of reactants

Temperature of measurement

Condition of constant pressure or constant volume maintained during the reaction.

Physical state of the reactants and products

Standard enthalpy of formation:

Enthalpy change that occurs when one mole of compound is formed from its elements in their standard states.

At the standard state the temperature is 298K, pressure is 101.3 kPa

More the negative value of enthalpy of formation, stabler is the compound

Enthalpy of formation of HF and HCl are - 268.6 kJ and - 92.3 kJ respectively. So HF is stabler.

Enthalpy of formation may be positive or negative.

For an exothermic compound ΔH is -ve and for an endothermic compound ΔH is +ve.

Enthalpy of combustion:

Enthalpy change that occurs when one mole of a substance is burnt completely in air or oxygen.

Enthalpy of combustion is always negative.

Enthalpy of combustion indicates the stability of a substance.

Enthalpy of neutralization:

It is the change in enthalpy that occurs when one gram equivalent mass of an acid is completely neutralized by one gram equivalent mass of a base both in dilute solutions.

Enthalpy of neutralisation of a strong acid against a strong base is a constant and the value is - 57.3 kJ

Enthalpy of neutralisation when any one of them or both are weak is less than - 57.3 kJ

Enthalpy of ionisation of a weak acid is the difference between - 57.3 kJ and the actual value of enthalpy of neutralisation.

Enthalpy of ionisation is always positive.

Weaker the acid or base more is the enthalpy of ionisation.

Enthalpy of solution

It is the change in enthalpy that occurs when one mole of a solute is dissolved in excess solvent such that on further addition of the solvent, there should not be any heat change.

Heat is absorbed when ionic solids like ammonium chloride dissolve.

Heat is liberated if hydration takes place during dissolution

Example:

Heat is evolved during dissolution of conc. sulphuric acid, NH_3 , SO_2 , SO_3 etc.

Enthalpy of transition :

It is the change in enthalpy that occurs when one mole of an element changes from one allotropic form to another.

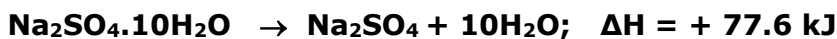
Example:

$P_{\text{White}} \rightarrow P_{\text{Red}}: \Delta H = - 18 \text{ kJ}$

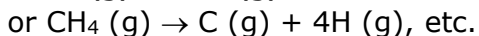
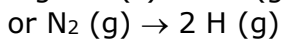
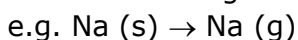
The negative sign shows that P_{Red} is more stable than P_{White} .

It is also the enthalpy change that occurs when one mole of a substance undergoes polymorphic change.

Example:



- **Enthalpy of atomization.** It is the amount of heat required to dissociate one mole of the substance into gaseous atoms.

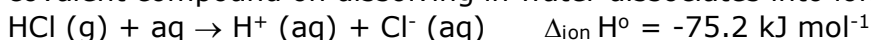


Effect of Temperature on Solubility/Calculation of Enthalpy of solution. If the solubility of a substance is known at two different temperatures, the mean molar enthalpy of solution over this temperature range can be calculated by applying an equation,

$$\text{Log} \frac{S_2}{S_1} = \frac{\Delta_{\text{sol}}H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Where S_1 and S_2 are solubilities at temperatures T_1 and T_2 respectively.

- **Enthalpy of ionization ($\Delta_{\text{ion}} H$).** It is the enthalpy change taking place when 1 mole of a covalent compound on dissolving in water dissociates into ions, e.g.,



- **Enthalpy of formation of ions.** To find $\Delta_f H^\circ$ for an ion, we take $\Delta_f H^\circ$ for H^+ ion in the solution = 0, e.g., to find $\Delta_f H^\circ$ for Cl^- ion in solution, from the above equation

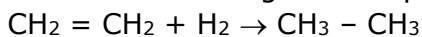
$$\Delta_r H^\circ = [\Delta_f H^\circ (\text{H}^+) + \Delta_f H^\circ (\text{Cl}^-)] - \Delta_f H^\circ (\text{HCl})$$

Knowing that $\Delta_r H^\circ = -75.2 \text{ kJ mol}^{-1}$,

$\Delta_f H^\circ (\text{HCl}) = -92.8 \text{ kJ mol}^{-1}$ and taking $\Delta_f H^\circ (\text{H}^+) = 0$, we get

$$\Delta_f H^\circ (\text{Cl}^-) = -168.0 \text{ kJ mol}^{-1}$$

- **Enthalpy of hydrogenation.** It is the enthalpy change that takes place when one mole of an unsaturated organic compound is completely hydrogenated, e.g.,



- **Enthalpy Changes During Phase Transitions.**

i) Enthalpy of fusion ($\Delta_f H$): It is the heat required to convert one mole of the solid substance into liquid at the melting point.

ii) Enthalpy of vaporisation ($\Delta_{\text{vap}} H$). It is the heat required to convert one mole of the liquid into vapour at the boiling point

iii) Enthalpy of sublimation ($\Delta_{\text{sub}} H$): It is the heat required to convert one mole of solid directly into vapours below the boiling point. It is equal to Heat of fusion + Heat of vaporisation,

Enthalpy of sublimation = enthalpy of fusion + enthalpy of vaporization.

$$\text{i.e., } \Delta_{\text{sub}} H = \Delta_{\text{fus}} H + \Delta_{\text{vap}} H$$

1st law of thermo chemistry: Lavoisier and Laplace law

The law states that the amount of heat required to decompose a compound into its elements is equal to the amount of heat liberated when the same amount of compound is formed from its elements.

Enthalpy of formation and decomposition are numerically equal but opposite in sign.

Enthalpy of formation of water is - 395.5 kJ and enthalpy of decomposition of water is + 393.5 kJ

Second law of thermo chemistry: Hess's law:

The enthalpy change that occurs during a chemical reaction is always a constant irrespective of the number of steps taken.

Enthalpy of a reaction does not depend on the method of formation.

Bond energy

Enthalpy of a reaction can also be calculated using bond energy.

Bond energy is the energy released when one mole of the bonds of a given type are formed.

$$\Delta H_{\text{reaction}} = \text{Bond energies of reactants} - \text{Bond energies of products.}$$