

Revision Notes
Class - 11 Chemistry
Chapter 6 - Chemical Thermodynamics

Thermodynamics:

The study of flow of mass, heat and energy is the study of thermodynamics.

Thermodynamics terminology:

- **System:**

A notable part of the universe which is kept under observation is known as the system.

- **Surrounding:**

The remaining part of the universe except the system which isn't kept under observation is known as surroundings.

In general, it can be stated as;

Universe = System + Surrounding

- **Types of system:**

- a) **Open system –**

The system where flow of both, mass and heat energy take place.

Example: Human body.

- b) **Closed system –**

The system where flow of heat energy takes place but has constant mass.

Example: Pressure cooker.

- c) **Isolated system –**

The system where none of the flow takes place.

Example: Thermos flask.

State of system:

The state of the system can be defined and changed with respect to the changes in state variables i.e., P, V, T and n. These variables define the conditions of the system and change in any one of them, will change the state of the system.

Properties of system:

- **Intensive properties –**

Properties depending upon concentration and independent of mass or total number of particles in the system. They are pressure, refractive index, density, etc.

- **Extensive properties** –

Properties depending upon mass or total number of particles in the system. They are volume, total energy, etc.

State and path function:

- **State function** –

The function which will be independent of the path followed but will depend upon the initial and final states while bringing up the changes in the system.

Example: internal energy, enthalpy, etc.

- **Path function** –

The function which will depend upon the path followed while bringing up the changes in the system.

Example: work, heat, etc.

Thermodynamic equilibrium:

The system remains in equilibrium when the state variables do not change and the below three types of equilibrium are satisfied.

- **Mechanical equilibrium** –

The absence of mechanical motion, constant pressure and volume brings up the mechanical equilibrium.

- **Thermal equilibrium** –

The constant heat and temperature with respect to the time brings up thermal equilibrium.

- **Chemical equilibrium** –

The rate of forward reaction equal to the rate of backward reaction brings up the chemical equilibrium.

Internal energy:

The sum total of the components of the energy influenced by the internal factors of the system is known as internal energy; often denoted by U or E.

The system under observation acts as an ideal gas system which depends only upon kinetic energy and hence, is the function of temperature as $U \propto T$. Thus, internal energy is a state function.

Modes of energy transport:

- **Heat –**

The energy transferred due to temperature difference within the system and surroundings is known as heat (Q). When the system is heated, kinetic energy of the molecules is being increased which then increases the internal energy.

- **Work –**

The energy spent to overcome the external forces acting upon the system is known as work (W). When a system expands, the internal energy is reduced. Whereas, on contraction of the system the internal energy is increased.

First law of thermodynamics:

Energy can neither be created or destroyed is the first law of thermodynamics denoted as;

$$\Delta U = Q + W$$

The sign conventions are given as;

Work done by the system = - W

Work done on the system = + W

Heat flowing into the system = + Q

Heat flowing out of the system = - Q

Reversibility:

The process which can change its direction by very small i.e., infinitesimal change in the system or surrounding; retracing its original path reaching the same initial state. A process to follow reversibility, there must not be any dissipative forces and the system must be in Quasi Static State.

- **Quasi static state –**

Here, the system seems to be static at all time intervals but not actually in reality. The motion is so slow that the system seems to be in equilibrium with the surroundings.

Expansion work:

The work done due to changes in volume of the system is known as expansion work. Note that, let it be expansion or compression, we take external pressure as the driving force.

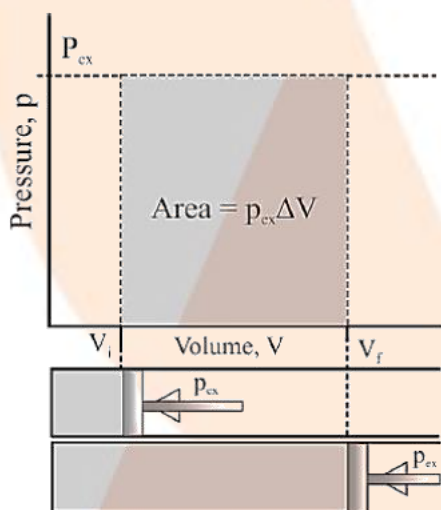
Mathematically, it can be represented as;

$$W = -\int P_{\text{ex}} dV$$

For reversible processes, external pressure is considered equal to the pressure of gas. Thus,

$$W = -\int P_{\text{gas}} dV$$

When a P – V graph is drawn, work done is represented as the area covered under it as shown;



Sign conventions:

- **W** –
Positive if the volume of the system is decreasing and negative when the volume of system is increasing.
- **ΔU** -

When the temperature of the system or product pressure or volume is reducing, it is negative; else is positive.

- **Q –**

This needs to be determined by the first law of thermodynamics.

Cyclic process:

A process which comes back to its original and initial state is known as a cyclic process. A closed graph determines this process and here, $\Delta U=0$ and $Q_{\text{net}} = -W_{\text{net}}$.

Enthalpy:

A thermodynamic state function defined as the sum of energy stored in the system and the energy used in doing work. Mathematically, can be represented as;

$$\Delta H = U + PV$$

- At constant P, $\Delta H = Q_p$.
- At constant V, $\Delta U = Q_v$.

Molar heat capacity:

- **At constant Pressure –**

The amount of heat needed to raise the temperature of one mole of gas by a degree at constant pressure. It can be stated as;

$$C_p = \frac{Q_p}{n\Delta T}$$

- **At constant Volume –**

The amount of heat needed to raise the temperature of one mole of gas by a degree at constant volume. It can be stated as;

$$C_v = \frac{Q_v}{n\Delta T}$$

We can now say that, $\Delta H = nC_p\Delta T$ and $\Delta U = nC_v\Delta T$.

Types of thermodynamic processes:

- **Isothermal process –**

Constant temperature process is known as isothermal process. Here, $\Delta U=0$ and $\Delta H=0$.

$$W = -2.303nRT \log \frac{V_2}{V_1} = -2.303nRT \log \frac{P_1}{P_2}$$

$$Q = 2.303nRT \log \frac{V_2}{V_1} = 2.303nRT \log \frac{P_1}{P_2}$$

- **Adiabatic process –**

When the heat exchanged with the surrounding is zero, such a process is known as adiabatic process. Here,

$$TV^{\gamma-1} = C, T^{\gamma}P^{1-\gamma} = C, PV^{\gamma} = C$$

where, C is constant.

$$Q=0 \Rightarrow W = \Delta U$$

Now,

$$\Delta U = nC_v \Delta T = \frac{(P_2 V_2 - P_1 V_1)}{(\gamma - 1)} = \frac{(nR \Delta T)}{(\gamma - 1)} \quad \text{and}$$

$$\Delta H = nC_p \Delta T$$

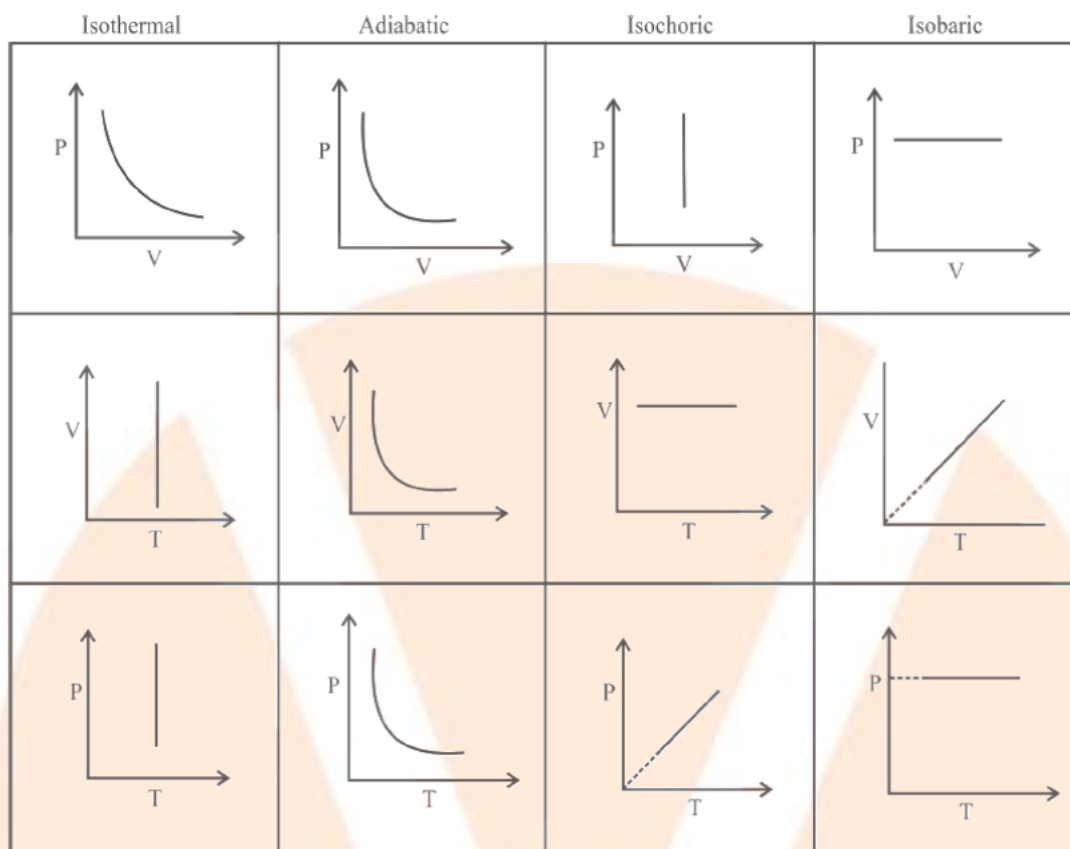
- **Isochoric process –**

Constant volume process is known as isochoric process. Here, $W = 0$, $\Delta H = nC_p \Delta T$ and $\Delta U = nC_v \Delta T = Q_v$.

- **Isobaric process –**

Constant pressure process is known as isobaric process. Here, $W = -P \Delta V = -nR \Delta T$, $\Delta H = nC_p \Delta T = Q_p$ and $\Delta U = nC_v \Delta T$.

Graphs:



Note that, the P – V graphs of isothermal and adiabatic processes are similar but the one for adiabatic is steeper than that of isothermal.

- **Irreversible process –**

Work done is given as, $W = -\int P_{\text{ex}} dV$ in the irreversible process. Here, we cannot say external pressure will be equal to that of pressure of gas.

- **Free expansion –**

In free expansion, the external pressure of the gas is zero i.e., the gas expanding against the vacuum will have work as zero. Thus, no heat will be supplied to the process showing no changes in the temperature. Hence, it is an isothermal and adiabatic process.

- **Polytropic process –**

A generalised form of any thermodynamic process which can be represented as $PV^n = \text{constant}$.

For isothermal processes, $n = 1$.

For adiabatic process, $n = \gamma$.

Thermochemical equation:

A chemical equation giving you all the information like phases of reactants and products in the reaction along with energy changes associated with the same is known as thermochemical equation.

Types of reaction:

- **Endothermic reaction –**

The chemical reactions that absorb energy are known as endothermic reactions. Here, $\Delta H = +ve$.

- **Exothermic reaction –**

The chemical reactions that release energy are known as exothermic reactions. Here, $\Delta H = -ve$.

For any chemical reaction,

$$\Delta H_{\text{Reaction}} = \Delta H_{\text{Products}} - \Delta H_{\text{Reactants}}$$

This change in enthalpy occurs due to making and breaking of bonds.

Hess law of constant heat summation:

For a reaction which takes place in stepwise manner, the net change in enthalpy can be calculated as the enthalpy changes in each step. The governing law is known as Hess law of constant heat summation.

Enthalpy of reactions:

- **Enthalpy of bond dissociation –**

The energy needed to break the bonds of one mole molecules is known as enthalpy of bond dissociation. It is defined per mole of molecule.

- **Enthalpy of combustion –**

The heat released or absorbed when a mole of a substance undergoes combustion in presence of oxygen is known as enthalpy of combustion.

- **Enthalpy of formation –**

The heat released or absorbed when a mole of compound is formed from its constituent elements under their standard elemental forms is known as enthalpy of formation.

- **Enthalpy of atomization –**

The energy required to convert any substance to gaseous atoms is known as enthalpy of atomization. It is defined per mole of the gaseous atoms.

- **Enthalpy of sublimation –**

The heat required to change a mole of substance from solid state to its gaseous state at STP is known as enthalpy of sublimation.

- **Enthalpy of phase transition –**

The phase transition from one phase to another releases or absorbs a particular standard enthalpy which is known as enthalpy of phase transition.

- **Enthalpy of ionization –**

The amount of energy an isolated gaseous atom will take to lose an electron in its ground state is known as enthalpy of ionization.

- **Enthalpy of solution –**

The heat released or absorbed when a mole of a compound is dissolved in excess of a solvent (mostly, water) is known as enthalpy of solution.

- **Enthalpy of dilution –**

The enthalpy change associated with the dilution process of a component in a solution at a constant pressure is known as enthalpy of dilution. It is defined as energy per unit mass or amount of substance.

Second law of thermodynamics:

The state of entropy of the entire universe, as an isolated system will always increase over time, is the standard statement of the second law of thermodynamics.

- **Need –**

The first law of thermodynamics states the conversion of energy in a process but does not explain the feasibility of the same. This point gave rise to the need for the second law of thermodynamics.

Types of processes:

- **Spontaneous process –**

The spontaneous process has the tendency to take place naturally and no external work is needed to carry out the same.

- **Non-spontaneous process –**

The non-spontaneous process is driven by external work and cannot be performed naturally.

Entropy:

The measure of randomness or disorder in the process or a body is known as its entropy. It is a state function and is represented as S.

Spontaneous process is the process in which total randomness of the universe tends to increase. Thus,

$$\Delta S = \frac{Q_{\text{rev}}}{T}$$

For spontaneous change, $\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$.

For reversible process where the entropy of the universe remains constant, $\Delta S_{\text{Total}} = 0$.

Entropy changes in thermodynamic processes:

The entropy changes in any thermodynamic process can be mathematically represented as;

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

- Isothermal process –

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

- Isochoric process –

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

- Isobaric process –

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

- Adiabatic process –

$$\Delta S = 0$$

Gibbs free energy:

This gives us the most convenient parameter to judge the spontaneity of the process from the perspective of the system. At constant temperature it can be represented as;

$$\Delta G_{\text{sys}} = \Delta H - T\Delta S_{\text{sys}}$$

At constant temperature and pressure, $\Delta G = -T\Delta S_{\text{Total}}$.

For process to be spontaneous, $\Delta G < 0$.

Third law of thermodynamics:

The entropy of the system will approach a constant value as its temperature approaches absolute zero is the empirical statement of the third law of thermodynamics.