THERMODYNAMICS & THERMOCHEMISTRY

1. THERMODYNAMICS

It is the study of flow of energy. It encompasses the study of flow of heat as well as mass.

2. THERMODYNAMICS TERMINOLOGY

2.1 System

The part of the Universe under observation is called system.

2.2 Surrounding

The part of the Universe not under observation is called Surrounding.

System + Surrounding = Universe

2.3 Types of system

2.3.1 Open System : A system in which both flow of mass and heat is possible.

2.3.2 Closed System : A system in which flow of heat is possible but flow of mass is not possible.

2.3.3 Isolated System : A system in which neither heat nor mass can flow in or out.

3. STATE OF A SYSTEM

The state variables (P, V, T, n) describes the condition of a system. On changing any one or more of these variables the state of the system changes.

4. PROPERTIES OF SYSTEM

All the properties of a system can be categorized into one of the following two types :

4.1 Extensive Properties

Such properties of a system which depends on the mass or the total number of particles in the system are categorized as Extensive Properties. eg. Total Energy, volume.

4.2 Intensive Properties

Such properties of a system which depends on concentration and does not depend on the mass or the total number of particles in the system are categorized as Intensive properties. eg. Pressure, Density, Reractive Index.

5. STATE AND PATH FUNCTIONS

Such thermodynamic functions which depend only on the initial and final states of the system and not on the path followed are called **state functions** eg. Internal energy, Enthalpy and the functions which depend on the path followed while changing from one state to the other are called **path functions.** eg. work heat.

6. THERMODYNAMIC EQUILIBRIUM

A system is said to be under thermodynamic equilibrium when none of the state variables are changing and it satisfies the three equilibriums.

6.1 Mechanical Equilibrium

There is no mechanical motion and the pressure and the volume of the system is not changing.

6.2 Thermal Equilibrium

There is no flow of heat and the temperature of the system does not change with time.

6.3 Chemical Equilibrium

If any chemical reaction is taking place in the system then the rate of forward reaction is equal to the rate of backward reaction which means that the overall moles of the system is constant.

7. INTERNAL ENERGY

It is the sum total of the components of energy of the system due to the internal factors. It is denoted by U (sometimes by E). Since the system under observation is an ideal gas thus the internal energy of the system is dependent only on the kinetic energy of the gas and therefore is only a function of temperature. $U \propto T$. Since internal energy depends only on temperature thus, it is a **state function.**

8. MODES OF ENERGY TRANSFER

There are two methods to alter the internal energy of a system viz. **Heat and work.**

8.1 Heat

Heat is the energy transferred due to temperature difference between the system and the surrounding. On heating, the kinetic energy of the molecules increases and therefore the internal energy increases.

8.2 Work

Work is the energy spent to overcome an external force. When the system does work against an external pressure (expansion) it tends to reduce the internal energy and on the other hand when the system contracts due to the external pressure it tends to increase the internal energy.

9. FIRST LAW OF THERMODYNAMICS

The first law of Thermodynamics states that Energy can neither be created nor destroyed.

$\Delta U = q + w$

Conventions : In the above system if work is done by the system then w is negative and if work is done on the system then w is positive. Also, if heat flows into the system then q is positive and if heat flows out of the system then q is negative.

10. REVERSIBILITY

A process whose direction can be changed by an infinitesimal change to the system or surroundings and which can be reversed by retracing the original path and the system is restored to the initial state. The driving force of a reversible process is very-very small and such a process is extremely slow. For a process to be reversible there must not be any dissipative forces and also the system should be in a Quasi Static State.

10.1 Quasi Static State

A quasi static state means that the system seems to be static at all intervals of time but actually is not. The motion is so slow that it is almost impossible to detect the motion and the system seems to be in equilibrium with the surroundings at all instants of time.

11. EXPANSION WORK

It is the work done due to the volume changes of the gas. The mathematical expression for the expansion work is $w = -\int P_{ex}dV.$

Always remember, be it expansion or compression we always take the external pressure as the driving force. For a reversible process,

$P_{ex} \approx P_{GAS}$ and $w = -\int P_{GAS}dV.$

If we draw a process curve between P and V then the work done is represented by the area covered under the P-V graph as shown in Fig.

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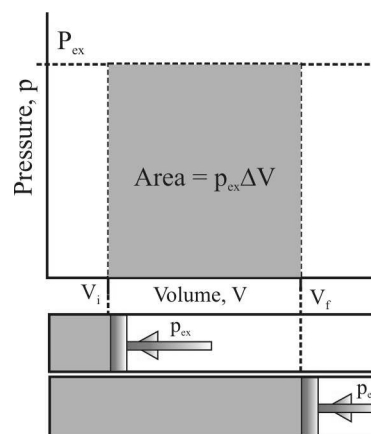
NOTE

Sign of w : If the volume of the system is increasing then the sign of **w is –ve** and if volume is decreasing **w is +ve**

Sign of ΔU : If the temperature of the system is decreasing or the product pressure and volume (PV) is reducing then the sign of **ΔU is –ve** else, the sign of **ΔU is +ve.**

Sign of q : The sign of q needs to be determined using the first law of thermodynamics.

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12. CYCLIC PROCESS

A cyclic process is one which comes back to its initial state. The graph of a cyclic process is always a closed graph. For a cyclic process, $\Delta U_{net} = 0$ and $q_{net} = -w_{net}.$

13. ENTHALPY (H)

Enthalpy is another thermodynamic function (like internal energy, work and heat) which we study in various thermodynamic processes. It is also a state function like internal energy. It is defined as the sum of the energy stored in the system and the energy used in doing work. Mathematically, $H = U + PV$. At constant pressure $\Delta H = q_p$ and at constant volume $\Delta U = q_V$.

14. HEAT CAPACITY (C)

The heat capacity of the system is the amount of heat needed to raise the temperature of the system by 1ºC or 1K.

$C = q/\Delta T$.

14.1 Molar Heat Capacity

The **molar heat capacity** of a system (C_M) is the amount of heat needed to raise the temperature of one mole gas by 1ºC or K.

$$C_M = \frac{q}{n\Delta T}$$

The **molar heat capacity of a system at constant pressure** (C_p) is the amount of heat needed to raise the temperature of one mole gas the system by 1ºC at constant pressure.

$C_p = q_p /n\Delta T$.

The **molar heat capacity of a system at constant volume** (C_V) is the amount of heat needed to raise the temperature of one mole gas by 1ºC at constant volume.

$C_V = q_V /n\Delta T$.

Thus, we can say that : $\Delta H = nC_p\Delta T$ and $\Delta U = nC_V\Delta T$ and $C_P = C_V + R$.

Type of Gas	C_V	C_P	$\gamma = C_P/C_V$
monotomic	3R/2	5R/2	5/3 = 1.67
diatomic	5R/2	7R/2	7/5 = 1.4
Non-linear Polyatomic	3R	4R	4/3 = 1.34

15. TYPES OF THERMODYNAMIC PROCESSES

There are four important types of processes to be studied in this chapter. The basic meanings and difference of these four processes are :

15.1 Isothermal Process

These processes are the ones in which the temperature is constant throughout the process.

$\Delta U = 0; \quad \Delta H = 0$

$w = -2.303 \, nRT \log_{10}(V_2/V_1) = -2.303 \, nRT \log_{10}(P_1/P_2)$

$q = +2.303 \, nRT \log_{10}(V_2/V_1) = +2.303 \, nRT \log_{10}(P_1/P_2)$

15.2 Adiabatic Process

These processes are the ones in which the heat exchanged with the surroundings is zero. Such processes are defined by the equation

$TV^{\gamma-1} = \text{constant}, \quad T^\gamma P^{1-\gamma} = \text{constant}, \quad PV^\gamma = \text{constant}.$

$q = 0 \quad \Rightarrow \quad w = \Delta U$

$\Delta U = nC_V\Delta T = (P_2V_2 - P_1V_1)/(\gamma-1) . = (nR\Delta T)/(\gamma - 1)$

$\Delta H = nC_P\Delta T$

15.3 Isochoric Process

These processes are the ones in which the volume remains constant. Since the change in volume is zero therefore we can say that

$w = 0$

$\Delta U = nC_V\Delta T = q_V \qquad \Delta H = nC_P\Delta T$

15.4 Isobaric Process

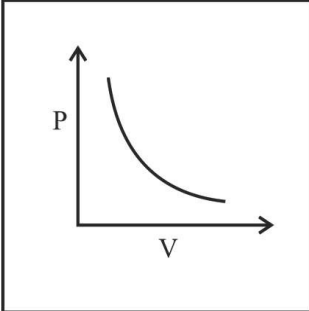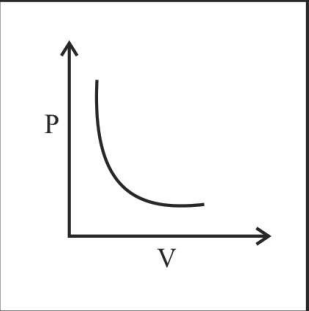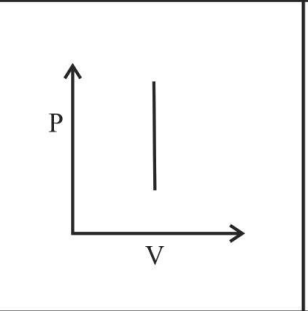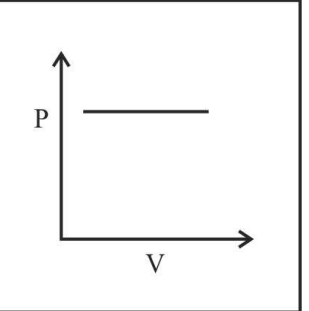These are the processes in which the pressure remains constant.
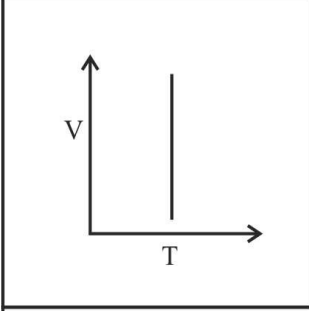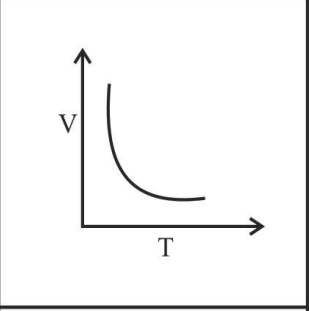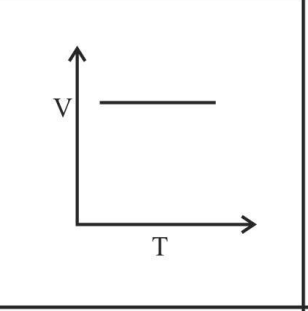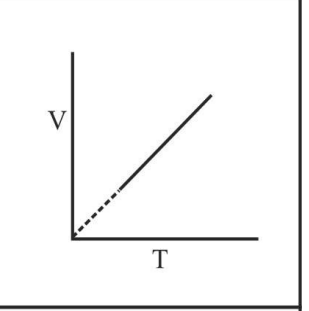
$w = -P\Delta V = -nR\Delta T$
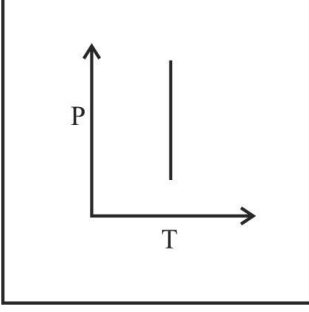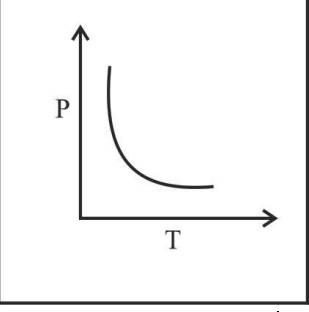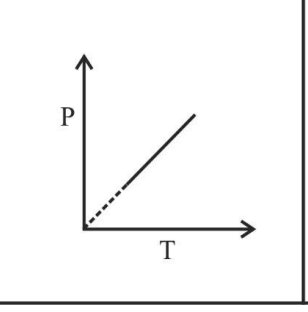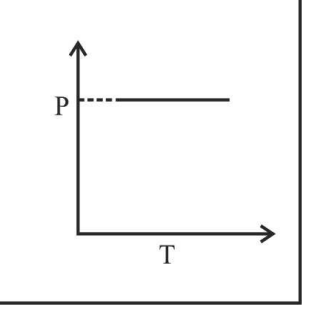
$\Delta U = nC_V\Delta T$

$\Delta H = nC_P\Delta T$

NOTE

All these processes are happening on a system containing an ideal gas therefore we can apply $PV = nRT$ at any stage that we find suitable.

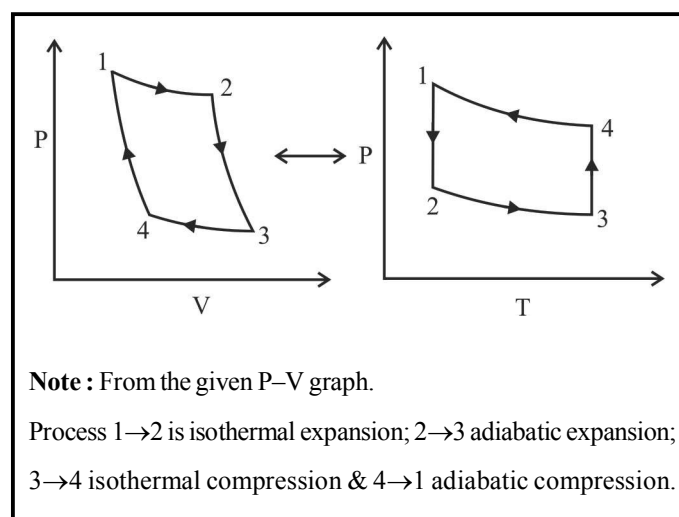| Isothermal	Adiabatic	Isochoric	Isobaric

NOTE

Although the graph of isothermal and adiabatic processes are similar in nature it should be noted that the P-V graph of an adiabatic process is steeper than that of an isothermal process.

16. GRAPH TRANSFORMATION

When a thermodynamic process is plotted in terms of two state variable it can be transformed into a graph involving the other state variable by doing the following :

1. Identify the type of curve given, whether it is P-V, V-T or P-T graph.

2. Then, Identify every step of the process

3. Then one by one convert every step into the required graph bearing in mind critical points like, an expansion process will remain an expansion process and so on.

4. A cyclic process should remain cyclic whichever graph we make.

Note : From the given P–V graph.

Process $1\rightarrow2$ is isothermal expansion; $2\rightarrow3$ adiabatic expansion; $3\rightarrow4$ isothermal compression & $4\rightarrow1$ adiabatic compression.

17. IRREVERSIBLE PROCESS

For an irreversible process the work done is given by $W = -\int P_{EXT} dV$. We cannot take the external pressure to be equal to the pressure of the gas in these processes.

18. FREE EXPANSION

If the external pressure of the gas is zero that is the gas is expanding against vaccum then the work done is always zero, this is called the case of free expansion. In this process the gas does no work as there is no effort put in expansion process. If no heat is supplied to the gas then there is no change in temperature too. That is why such a process is both Isothermal and Adiabatic.

19. POLYTROPIC PROCESS

It is a generalized form of any thermodynamic process which has a form $PV^n =$ **constant** where n is a real number. For an isothermal process $n = 1$ and for an adiabatic process $n = \gamma$. The heat capacity of a polytropic process can be calculated using the first law of thermodynamics and comes out to be :

$C = C_V - R/(n-1).$

20. NEED FOR SECOND LAW

The first law talks about the conservation of energy in a process but does not speak of the feasibility of a process. It does not tell whether a process will happen on its own i.e. whether the process is spontaneous or not. A spontaneous process is one which happens on its own. Example, heat always flows spontaneously from higher temperature to lower temperature : Nothing in the first law mentions that the opposite process cannot happen. According to first law any process where energy remains conserved is feasible. But we need some other basis for feasibility of a process. This is where the second law is important.

21. TYPES OF PROCESSES

21.1 Spontaneous processes

Spontaneous processes have a natural tendency to take place and no external work is needed to carry out these processes. All natural processes are spontaneous.

21.2 Non-Spontaneous processes

They are driven by external work and cannot take place naturally.

22. CONCEPT OF ENTROPY

❋ Matter has a natural tendency to get disordered or randomised

❋ Energy has a tendency to become disordered or dispersed.

It was concluded that any such process in which the total randomness of the universe (system + surrounding) increases is a spontaneous process. **Entropy is a measure of randomness or disorder.** It is a state function represented by S. We can safely say that in a spontaneous process there is a tendency for increase in entropy. Hence the statement of second law :

The entropy of an isolated system/Universe tends to increase OR In a spontaneous process the entropy of the Universe increases.

$\Delta S = q_{rev}/T.$

$$\Delta S_{TOTAL} = \Delta S_{SYSTEM} + \Delta S_{SURROUNDING} > 0$$

(for a sponataneous change)

Thus, **In a reversible process the entropy of the Universe remains constant i.e. $\Delta S_{Total} = 0$**

22.1 Entropy changes in a Thermodynamic Process

The entropy changes in an thermodynamic process can be mathematically calculated by the equation :

$\Rightarrow \Delta S = nC_V \ln (T_2/T_1) + nR \ln (V_2/V_1).$ This expression can be simplified for the four processes studied earlier as :

Isothermal process : $\Delta S = nR \ln (V_2/V_1)$

Isochoric process : $\Delta S = nC_V \ln (T_2/T_1)$

For isobaric process : $\Delta S = nC_P \ln (T_2/T_1)$

Adiabatic process : $\Delta S = 0$ ($q_{rev} = 0$)

22.2 Important points to Remember

1. Entropy of a system remains constant in a reversible adiabatic process. Therefore, it is also known as **"isentropic process".**

2. Entropy of an ideal gas will always increase in isothermal expansion.

3. In a reversible adiabatic process the entropy of both system and surroundings remains the same and there is no overall change in entropy as well.

$$\Delta S_{SYSTEM} = \Delta S_{SURROUNDINGS} = \Delta S_{TOTAL} = 0$$

4. In a reversible isothermal expansion the entropy of surroundings will always decrease to balance the increase in system's entropy to make the overall entropy constant.

5. In free expansion the entropy of the system always increases and that of surrounding remains constant. Free expansion is both isothermal and adiabatic and is irreversible.

23. GIBB'S FREE ENERGY

Gibb's Free energy function gives us a very convenient parameter to judge the spontaneity of a process from system's perspective. At a constant temperature and pressure, $\Delta G = -T\Delta S_{TOTAL}$ and for a process to be spontaneous, **$\Delta G < 0$.** The change in Gibb's free energy can also be represented in terms of the system parameters as :

$\Delta G_{SYS} = \Delta H - T\Delta S_{sys}$ at a constant temperature.

24. THERMOCHEMICAL EQUATION

A chemical equation which gives us all the information like energy changes associated with a chemical reaction and phases of various reactants and products is called Thermochemical Equation.

All reactions can be categorized into one of the following two categories :

24.1 Endothermic Reactions

Are those chemical reactions which absorb energy.
(ΔH = positive)

24.2 Exothermic Reactions

Are those chemical reactions which release energy.
(ΔH = negative)

For a chemical reaction, $\Delta H_{REACTION} = H_{PRODUCTS} - H_{REACTANTS}$

The change in enthalpy during a chemical reaction occurs due to breaking and making of bonds.

Also, $\Delta H = \Delta U + \Delta n_g RT$.

25. ENTHALPY OF REACTIONS

Enthalpy change can be calculated for all reactions and is sometimes called the Heat of Reaction. Let's take a look at various types of reactions and enthalpy changes associated with them :

25.1 Enthalpy of Formation ΔH_f^0

It is the heat absorbed or released when one mole of a compound is formed from its constituent elements under their standard elemental forms. The enthalpy for formation of the following substances is taken to be zero under 1 bar pressure and 298 K.
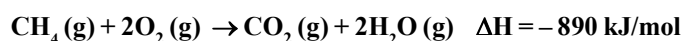
$\Delta H_f^0 (O_2, g) = 0$ $\Delta H_f^0 (S, Rhombic) = 0$

$\Delta H_f^0 (C, graphite) = 0$ $\Delta H_f^0 (P, white) = 0$
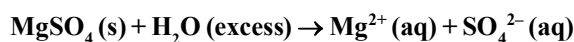
$\Delta H_f^0 (Br_2, l) = 0$ $\Delta H_f^0 (H^+, aq) = 0$

25.2 Enthalpy of Combustion

It is the heat released or absorbed when one mole of a substance undergoes combustion in presence of oxygen.

$$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g) \quad \Delta H = -890 \text{ kJ/mol}$$

25.3 Enthalpy of Solution

It is the heat released or absorbed when 1 mole of a compound is dissolved in excess of a solvent (water).

$$MgSO_4 (s) + H_2O \text{ (excess)} \rightarrow Mg^{2+} (aq) + SO_4^{2-} (aq)$$
$$\Delta H^0_{Sol} = -91.211 \text{ kJ/mol}$$

25.4 Enthalpy of Hydration

It is the energy released or absorbed when 1 mole of anhydrous or partially hydrated salt undergoes hydration by the addition of water of crystallisation. e.g.
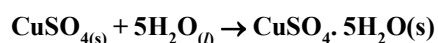
$$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4 . 5H_2O(s)$$
$$\Delta H_{HYD} = -78.9 \text{ kJ/mol}$$

25.5 Enthalpy of Neutralization

It is the heat released or absorbed when one equivalent of an acid undergoes neutralisation with one equivalent of a base. e.g.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O (l)$$
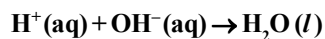
$\Delta H_R = -57.3 \text{ kJ/mol}$

26. HESS LAW OF CONSTANT HEAT SUMMATION

Since enthalpy is a state function thus for a reaction which takes place in steps the net change in enthalpy can be calculated by adding the enthalpy changes of each step. This is called the **Hess Law.**

27. BORN HABER CYCLE

The entire thermodynamics process of formation of an ionic crystal lattice is called Born Haber cycle. An ionic compound is formed from its constituents through a series of steps involving conversion of atoms/molecules into gaseous phase for ion formation, ionisation and electron gain to form ions and then the reaction of gaseous ions to form solid lattice.

28. BOND DISSOCIATION ENTHALPY

The energy needed to break the bonds of one mole molecules is called the Bond Dissociation Enthalpy of the substance. It is defined per mol of molecule. eg. Bond dissociation enthalpy of H_2 is 436 kJ/mol

29. HEAT OF ATOMIZATION

It is defined as the energy required to convert any substance to gaseous atoms. This is defined per mol of the gaseous atoms. For example Heat of atomisation of H will be 218 kJ/mol atoms.

30. RESONANCE ENERGY

Many compounds exhibit resonance. Due to resonance they exist in a structure which is different from the expected one and more stable.

Resonance energy $= \Delta H^0_f \text{(actual)} - \Delta H^0_f \text{(calculated)}$