

Thermodynamics.

- The branch of science which deals with the study of different forms of energy and quantitative relationship between them is known as thermodynamics.

When we confine our study to chemical changes and chemical substance only then it is known as chemical thermodynamics.

- Importance.

1. It helps us to predict whether any given chemical reaction can occur under the given set of conditions.
2. It helps in predicting the extent of reaction before the equilibrium is attained.
3. It helps to deduce some important laws like law of chemical equilibrium.

- Limitations.

1. It helps to predict the feasibility of a process but does not tell anything about the rate at which the process takes place.
2. It deals only with the initial and final states of a system but does not tell anything about the mechanism of the process.
3. It deals with the properties of the matter in bulk but does not tell anything about the individual atoms and molecules.

- System and Surrounding - The part of the universe chosen for thermodynamic consideration is called system and the remaining portion of the universe is called surrounding.

Universe = System + Surrounding.

- Open System - A system is said to be an open system if it can exchange both matter and energy with surrounding.
- Closed System - If a system can exchange only energy with surrounding but no matter exchange then it is called closed system.
- Isolated system - If a system can neither exchange energy nor matter with the surrounding is called isolated system.
- State of a system and State variable - The state of a system means the condition of the system which is describe in terms of certain observable properties such as temperature (T), Pressure (P) Volume (V) of the system. If any of these properties of the system changes then the system is said to be in different state and these properties are called State Variable.
- State function - A Physical Quantity is said to be state function if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained.
- Macroscopic system - If a system contain a large number of chemical species like atoms, ions or molecules, is called a macroscopic system.
- Extensive Properties - The properties which depend upon the quantity of the matter contain in the system is called extensive properties.
- Intensive Properties - The properties which depends upon the nature of the substance and are independent of the amount of the substance present in the system is called Intensive Properties.
- Thermodynamics equilibrium - A system is said to be in thermodynamics equilibrium if its macroscopic properties like temperature, pressure etc. do not change.

with time.

— Thermodynamics Process - A thermodynamics process is said to occur when the system changes from one state to another state.

a. Isothermal Process - When the temperature is constant during the process is called isothermal process.

b. Adiabatic Process - When a system is carried out in such a manner that there is no exchange of heat from system to surrounding is called adiabatic process.

c. Isochoric Process - It is a process during which the volume of the system is kept constant.

d. Isobaric - It is a process during which the pressure of the system is kept constant.

— An isothermal process occurs when the system has conducting walls or it is an open system. The container with conducting walls is called diathermic.

— An adiabatic process occurs when it is a closed system and has non-conducting (insulated) walls called adiabatic walls. The container with non-conducting walls is called adiabatic.

— Reversible and Irreversible Process - It is a process which is carried out slowly so that all changes occurring in the direct process can be exactly reversed and the system remains almost in a state of equilibrium with the surrounding at every stage of the process.

— Irreversible Process - It is a process which is not carried out slowly so that the successive steps of the direct process cannot be retraced and any change in the external condition disturbs the equilibrium.

— Internal energy - The energy stored within a substance or a system is called internal energy.

Difference

Reversible

1. The Process is Carried out slowly
2. At any stage during the Process equilibrium is not disturbed.
3. It takes infinite time for completion
4. It is only Imaginary and cannot be achieved in actual process
5. Work obtained in this process is maximum.

Irreversible

- The Process is rapidly.
- Equilibrium may exist only after the Process.
- It takes finite time.
- These Processes actually occur in nature.
- Work obtained in this process is not maximum.

— Internal energy change - If U_R is the internal energy of the reactants and U_P is the internal energy of the products then energy change $\Delta U = U_P - U_R$

If ΔU is negative then energy is evolved (Exothermic)

If ΔU is positive then energy is absorbed (Endothermic)

Important Points.

- (a) The Internal energy depends upon the Quantity of Substance contained in the system so it is an extensive property.
- (b) The internal energy of ideal gas is a function of temperature only. So in isothermal process the temperature remains constant, there is no change in internal energy so $\Delta U = 0$

— Work - work is said to have been done whenever the point of application of a force is displaced in the direction of the force. If F is the force and dl is the displacement then $W = F \times dl$

this type of work is called mechanical work.

— Electrical work - If the force is the E.M.F. and the displacement is the quantity of electricity flowing through the circuit then

Electrical work = E.M.F $\times$ Quantity of electricity.

— Work of expansion/Compression or Pressure-volume work.

It is the work done when the gas expands/contracts against the external pressure. It is a kind of mechanical work.

Consider a gas enclosed in a cylinder fitted with a frictionless piston.

Area of cross section of cylinder = $a \text{ cm}^2$.

Pressure on the piston = P

Distance through which gas expands = dl .

As pressure is force per unit area, force f acting on the piston will be $f = P \times a$.

Work done by the gas = $f \times dl$.

$$= P \times a \times dl.$$

But $a \times dl = dv$, a small increase in the volume of the gas.

Hence the small amount of work done by the gas is

$$dw = P \times dv.$$

If gas expands from V_1 initial volume to V_2 final volume.

$$w = \int_{V_1}^{V_2} P \, dv = P \int_{V_1}^{V_2} 1 \cdot dv.$$

$$= P(V_2 - V_1) = P \Delta V.$$

If the work done on the system for compression work will be positive and if the work done by the system then the work will be negative for work of expansion.

— Work done in isothermal reversible expansion of an ideal gas - The small amount of work done dw when the gas expands through a small amount of volume dv against the external pressure P_{ext} is.

$$dw = -P_{ext} \, dv.$$

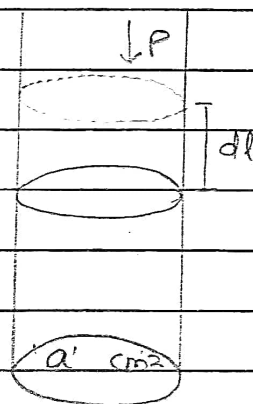
In a reversible expansion $P_{ext} = P_{int} - dP$.

$$dw = -(P_{int} - dP) \times dv.$$

$$= -P_{int} \times dv + dP \times dv$$

$$\because dP \times dv \Rightarrow 0$$

$$= -P_{int} \times dv.$$



work done when the gas expand from V_1 to V_2

$$W = -P_{\text{ext}} \int_{V_1}^{V_2} dV.$$

For ideal gas $PV = nRT$

$$P = \frac{nRT}{V}.$$

$$\text{So } W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT [\log V]_{V_1}^{V_2}.$$

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

$\therefore$ At Constant temperature $P_1 V_1 = P_2 V_2$

$$\text{then } \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

In the irreversible expansion external pressure remain constant but in reversible expansion external pressure has to be decrease continuously so as to remain smaller than the internal pressure.

Reversible work of expansion is the maximum work.

- Heat - heat is another mode of energy exchange between the system and the surroundings as a result of the difference of temperature between them. It is represented by Q

When heat is given by the system to the surrounding then Q have negative sign.

When heat is absorbed by the system from the surrounding then Q have positive sign.

S.I. unit of Q is Joules. It is usually measured in term Calories.

A Calorie is defined as the quantity of heat required to raise the temperature of 1 gram water through 1°C

$$1 \text{ Calorie} = 4.184 \text{ Jule}$$

$$1 \text{ Jule} = 0.2390 \text{ Calorie}.$$

Internal energy is a state function, work and heat are not state function because their values do not depend on the initial and final state but depend upon the path followed.

$$\Delta U = Q + W$$

- First law of thermodynamics - It is simply the law of Conservation of energy.

Energy can neither be created nor destroyed although it may be converted from one form to another.

or.

The energy of an isolated system is constant.

Let the initial internal energy of the system = U_1 ,

If it absorbs heat Q , its internal energy will be = $U_1 + Q$

If further work W is done on the system, the internal energy will further increase and become = $U_1 + Q + W$

$$U_2 = U_1 + Q + W$$

$$U_2 - U_1 = Q + W$$

$$\Delta U = Q + W$$

If the work done is the work of expansion, then $W = -PdV$

$$\text{then } \Delta U = Q - PdV$$

For an isothermal change $\Delta U = 0$. For reversible

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

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

For isothermal expansion of an ideal gas against vacuum

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

For adiabatic change $Q = 0$

$$\text{then } \Delta U = W$$

- Internal energy change - It is the heat absorbed or evolved at constant volume.

If a process is carried out at constant pressure the work of expansion is $w = -P\Delta V$ — (1)

According to first law of thermodynamics.

$$Q = \Delta U - w \quad \text{where } Q \text{ is the heat absorbed.}$$

$$= \Delta U + P\Delta V.$$

$$Q = (U_2 - U_1) + P(V_2 - V_1)$$

$$= (U_2 + PV_2) - (U_1 + PV_1)$$

The thermodynamic quantity $U + PV$ is called the heat constant or enthalpy of the system and it is represented by H .

$$\text{then } H_1 = U_1 + PV_1$$

$$H_2 = U_2 + PV_2$$

$$\text{then } Q = H_2 - H_1 = \Delta H.$$

Enthalpy change of a system is equal to heat absorbed or evolved by the system at constant pressure.

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

- The energy stored within the substance or the system that is available for conversion into heat is called heat content or enthalpy of the substance or system.

Main points about internal energy and Enthalpy.

1. Both are state function.
2. Both are extensive properties.
3. The absolute value of neither internal energy nor enthalpy can be determined.
4. Internal energy change is the heat evolved or absorbed at constant volume. While enthalpy change is that at constant pressure. $\Delta U = Q_V$ $\Delta H = Q_P$
5. In a cycle system, when the system returns to its original state after a number of changes $\Delta U = 0$ or $\Delta H = 0$.

— Relationship between Heat of reaction at constant pressure and that at constant volume. —

$$Q_P = \Delta H \text{ and } Q_V = \Delta U$$

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

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

for ideal gas.

$$= \Delta U + PV_2 - PV_1$$

$$\because PV_1 = n_1 RT.$$

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

$$PV_2 = n_2 RT.$$

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

Where $\Delta n = n_2 - n_1$; number of moles of the gaseous product and those of the gaseous reactants.

$$Q_p = Q_v + \Delta n_g RT.$$

$$R = 8.314 \text{ J/Kmol}$$

— Condition for $Q_p = Q_v$ or $\Delta H = \Delta U$

1. When reaction is carried out in a closed vessel so that volume remains constant $\Delta V = 0$.
2. When reaction involves no gases reactants and products.
3. When reaction involves gases reactants and products but their no of moles are equal.

— When a real gas is allowed to expand adiabatically from high pressure to low pressure through a fine hole it is cooling except H_2 and He which get warmed up. This effect is called Joule-Thomson effect.

— During adiabatic expansion of real gas enthalpy remain constant so it is called isenthalpic process.

— The temperature at which a real gas shows no cooling or heating effect on adiabatic expansion is called inversion temperature.

— H_2 and He have very low inversion temperature so they show heating effect at room temperature during adiabatic expansion.

— During isothermal expansion of an ideal gas.

$$\Delta U = 0 \text{ and } \Delta T = 0$$

$$\therefore \Delta H = \Delta U + \Delta PV = \Delta U + nR\Delta T = 0 + 0 = 0.$$

Heat Capacity - It is defined as the amount of heat required to raise the temperature of the system through 1°C . It is defined by C .

$$C = \frac{Q}{T_2 - T_1} = \frac{Q}{\Delta T}$$

- Specific heat Capacity - It is defined as the amount of heat required to raise the temperature of 1 gram of the substance through 1°C .

- Molar heat Capacity - It is defined as the amount of heat required to raise the temperature of one mole of the substance through 1°C . It is represented by C_m .

$$C_m = \frac{C}{n}$$

The amount of heat Q required to raise the temperature from T_1 to T_2 of mass m gram of a sample and having specific heat C can be calculated by

$$Q = m \times C \times (T_2 - T_1)$$

$$= m \times C \times \Delta T.$$

$$\text{or } Q = C \times \Delta T.$$

a. Heat Capacity at Constant Volume - The heat supplied to a system to raise its temperature through 1°C keeping the volume of the system constant is called heat capacity at constant volume and represented by C_v .

b. Heat Capacity at Constant Pressure - The heat supplied to a system to raise its temperature through 1°C keeping the external pressure constant is called heat capacity at constant pressure and represented by C_p .

$$- \quad dQ = du + PdV. \quad dQ = C \Delta T.$$

$$\text{then } C = \frac{du + PdV}{dT}.$$

When V constant.

$$\text{then } dV = 0.$$

then $C_v = \frac{du}{dT}$.

Rate of change of internal energy with temperature at Constant Volume.

$$C_p = \frac{du}{dT} + P \cdot \frac{dv}{dT} \quad \text{--- (I)}$$

and. $H = U + Pv$.

$$\text{then } \frac{dH}{dT} = \frac{du}{dT} + P \cdot \frac{dv}{dT} \quad \text{--- (II)}$$

By (I) and (II).

$$C_p = \frac{dH}{dT} \quad \text{Rate of change of enthalpy with temperature at Constant Pressure.}$$

— Relation between C_p and C_v —

If the volume of the system is kept constant and the heat is added then no work is done by the system. then the total heat is used up completely to increase the internal energy. Again if the pressure of the system is constant then some work of expansion is also done by the system. then if at constant pressure some extra heat is required for doing the work of expansion. then $C_p > C_v$

$$C_p - C_v = \frac{dH}{dT} - \frac{du}{dT}$$

But $H = U + Pv$ and $Pv = nRT$.

$$\text{then } nRT = H - U.$$

$$nR = \frac{H}{T} - \frac{U}{T} \therefore nR = \frac{dH}{dT} - \frac{dU}{dT}$$

$$C_p - C_v = \frac{dH}{dT} - \frac{dU}{dT} = nR.$$

For 1 mole $n=1$ then $C_p - C_v = R = 8.314 \text{ Joules.}$

Nature of gas:- Monoatomic Diatomic Triatomic

$\gamma = \frac{C_p}{C_v}$	1.66	1.40	1.30
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Exothermic Reactions - Those reactions which are accompanied by the evolution of heat. It's called Exothermic reaction.

Endothermic Reaction - Those reactions in which heat is absorbed are called endothermic reactions.

- Exothermic and Endothermic reactions in terms of ΔH .

$$\Delta H = \text{Heat contents of Product} - \text{Heat contents of reactant} \\ = H_p - H_r.$$

ΔH is negative for exothermic reactions.

ΔH is Positive for endothermic.

- Thermochemistry - The branch of Chemistry which deals with the heat changes in chemical reactions is called thermochemistry.

- Thermochemical equation - When a balanced chemical equation not only indicates the quantities of the different reactants and products but also indicates the amount of heat evolved or absorbed then the equation is called thermochemical equation.

- Heat of Reaction or Enthalpy of Reaction or enthalpy change of reaction - The amount of heat evolved or absorbed in a chemical reaction when the number of moles of the reactant as represented by the chemical equation have completely reacted is called Enthalpy of Reaction.

Factors on which the heat of reaction depend.

1. Quantities of the reactants involved.
2. Physical state of reactants and products.
3. Allotropic modifications.
4. Concentration of solution.
5. Temperature.
6. Condition of Constant Pressure and Constant volume.

- Standard enthalpy of reaction - The standard enthalpy of a reaction is the enthalpy change accompanying the reaction when all the reactants and products are taken in their standard states. It is represented as ΔH° or $\Delta H^\ominus$

Latest enthalpy IUPAC symbols.

Enthalpy of reaction $\Delta_r H$.

Enthalpy of Combustion $\Delta_c H$.

Enthalpy of formation $\Delta_f H$.

Enthalpy of Vaporisation $\Delta_{vap} H$.

- Enthalpy of Combustion - It is defined as the heat change (usually the heat evolved) when 1 mole of substance is completely burnt or oxidized in oxygen.

- Standard Enthalpy of Combustion - It is the amount of heat evolved when one mole of substance under standard condition (298 K, 1 bar pressure) is completely burnt to form the products also under standard condition. It is represented by $\Delta_c H^\circ$

- Calorific value - It is the amount of heat in calories or Joules produce from complete combustion of one gram of the fuel or the food.

- Balance diet - The food consisting of carbohydrates, oils, fats, vitamins, proteins, mineral salts etc which provides the necessary calories is called a balance diet.

- Enthalpy of formation - It is defined as the heat change when 1 mole of the substance is formed from.

elements under given Conditions of temperature and Pressure. It is represented by $\Delta_f H$.

- Standard enthalpy of formation - It is defined as the enthalpy change accompanying the formation of 1 mole of the substance in the standard state from its elements. It is represented by $\Delta_f H^\circ$.
- Enthalpy of Neutralization - It is defined as the heat change when one gram equivalent of the acid is neutralized by a base, the reaction being carried out in dilute aqueous solution.
- Enthalpy of Solution - The enthalpy of solution of a substance in a particular solvent is defined as the enthalpy change when 1 mole of the substance is dissolved in a specified amount of the solvent. However if such a large volume of the solvent is taken that further addition of the solvent does not produce any more heat change, it is called enthalpy of solution at infinite dilution.
- Lattice energy or lattice enthalpy - Dissociation of the ionic solid into free ions. The energy required for this process is called lattice energy or lattice enthalpy.

Lattice enthalpy of an ionic compound is the enthalpy change that occurs when one mole of the ionic compound dissociates into ions in the gaseous state.

- Important Consequence of lattice enthalpies.
 1. Greater the lattice enthalpy, more stable the ionic compound.
 2. Greater the lattice enthalpy of an ionic compound, less is its solubility in water.
- Enthalpy of atomization - When one mole of a given substance dissociates into gaseous atoms, the enthalpy change in the process is called enthalpy of atomization.

- **Enthalpy of ionization** - When a Covalent Compound on dissociation in water splits to produce ions in the solution, the enthalpy change in the process is called enthalpy of ionization.
- **Enthalpy of Hydration** - The amount of enthalpy change when one mole of the anhydrous salt combine with the required number of moles of water so as to change into the hydrated salt is called the enthalpy of hydration.
- **Enthalpy of hydrogenation** - The amount of heat change that take place when one mole of an unsaturated organic compound is completely hydrogenated is called enthalpy of hydrogenation.
- **Enthalpy of allotropic transformation** - The enthalpy change that take place when one mole of one form of allotropic modification change to another is called enthalpy of allotropic transformation.
- **Enthalpy of fusion** - Enthalpy change during the transformation of one mole of a solid substance into its liquid state at its melting point is called enthalpy of fusion.
- **Enthalpy of Vaporisation** - The amount of heat required to convert one mole of a liquid into its vapour state at its boiling point is called molar enthalpy of vapourisation.
- **Enthalpy of Sublimation** - Energy required during the conversion of one mole of a solid into its vapour at a given temperature below melting point is called enthalpy of sublimation.
- **Hess's Law of Constant Heat Summation** - The total amount of heat change in a reaction is depends only upon the nature of the initial reactant and nature of the final products and is independent of the path or the manner by which this change is brought about.

The thermochemical equation can be treated as algebraic equations which can be added, subtracted, multiplied or divided.

- Bond energy - It is the amount of energy released when one mole of bonds are formed from the isolated atoms in the gaseous state or the amount of energy required to dissociate one mole of bond present between the atoms in the gaseous molecules. It is represented by $\Delta_b H$

Bond energy usually means bond dissociation energy. It is the energy required so taken as positive.

Bond energy should be Δ_u° and Bond enthalpy be Δ_H°

Uses -

When a chemical reaction takes place, some bonds of the reacting molecules are broken whereas some new bonds of the products molecules are formed. Knowing the bond energies of the various bonds involved, the enthalpy change of the reaction can be calculated.

- Limitation of first law - It provides no information concerning the feasibility of the process whether the process is possible or not.

- Spontaneous process - A process which under some given conditions may take place by itself or by initiation independent of the rate is called a spontaneous process or.

A process which can take place by itself or has an urge or tendency to take place is called spontaneous process.

- Non-spontaneous process - A process which can neither take place by itself nor by initiation is called a non-spontaneous process.

— driving force — This force which is responsible for the spontaneity of a process is called the driving force.
Nature of driving force.

a. Tendency for minimum energy — It is a common observation that in order to require maximum stability, every system tends to have minimum energy.

Hence one may conclude that a tendency to attain minimum energy, a negative value of enthalpy change might be responsible for a process or a reaction to be spontaneous.

Limits (Q) A number of reactions are known which are endothermic for which ΔH is positive but still they are spontaneous. example.

1. Evaporation of water or melting of ice.
2. Dissolution of salt like NH_4Cl , KCl .
3. Decomposition of CaCO_3 on heating.
4. Decomposition of N_2O_5 at room temperature.

(Q9) A number of reactions are known for which ΔH is zero but still they are spontaneous. example.

1. Reaction between acetic acid and ethyl alcohol.
2. Expansion of an ideal gas into vacuum.

Hence it may be concluded that the energy factor or enthalpy factor cannot be the sole criterion for predicting the spontaneity or the feasibility of a process. Thus some other factor must also be involved. This factor is the tendency for maximum randomness.

The resultant of the above two tendencies which give the overall tendency for a process to occur is called the driving force of the process.

- Entropy - It is a measure of randomness or disorder of the system. It is represented by 'S'

The greater the randomness the higher is the entropy. Crystalline solid state has lowest entropy, the gaseous state has the highest entropy

Like internal energy and enthalpy, it is a state function. The change in its value during a process called the entropy change and is given by $\Delta S = \sum S_{\text{prod}} - \sum S_{\text{react}}$.

$$\Delta S = \frac{Q}{T}$$

Entropy change during a process is defined as the amount of heat (Q) absorbed isothermally and reversibly divided by the absolute temperature (T) at which the heat is absorbed. It is an extensive property. Its S.I unit is $\text{J K}^{-1} \text{mol}^{-1}$.

- Entropy of fusion - It is the change in entropy when 1 mole of a solid substance change into liquid form at the melting temperature. $\Delta_f S = \frac{\Delta_f H}{T_m}$

- Entropy of vaporisation - It is the entropy change when 1 mole of a liquid changes into vapour form at its boiling point. $\Delta_v S = \frac{\Delta_v H}{T_v}$

- Entropy of sublimation - It is the entropy change when 1 mole of the solid changes into vapour at a particular temperature. $\Delta_s S = \frac{\Delta_s H}{T}$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

Spontaneity in terms of Entropy.

1. If ΔS_r is Positive, the process is spontaneous.
2. If ΔS_r is Negative, the direct process is non-spontaneous and reverse is spontaneous.
3. If ΔS_r is zero, the process is in equilibrium.

In a cyclic process the net entropy change $\Delta S = 0$.

In a reversible process $\Delta S = 0$

In an irreversible process $\Delta S > 0$

— Statement of second law of thermodynamics

All spontaneous processes or naturally occurring processes are thermodynamically irreversible.

or.

Without the help of an external agency, a spontaneous process cannot be reversed. Heat cannot by itself flow from a colder to a hotter body.

or.

The complete conversion of heat into work is impossible without leaving some effects elsewhere.

or.

All spontaneous processes are accompanied by a net increase of entropy. For all the spontaneous processes the total entropy change is positive.

or.

The entropy of the universe is continuously increasing.

— Gibbs free energy — It is that thermodynamic quantity of a system the decrease in whose value during a process is equal to the maximum possible useful work that can be obtained from the system. It is denoted by G

$$\Delta G = \Delta H - T\Delta S$$

it is known as Gibbs energy equation.

Where $\Delta G = G_2 - G_1$, change in Gibbs free energy.

$\Delta H = H_2 - H_1$, enthalpy change of the system.

$\Delta S = S_2 - S_1$, Entropy change of the system.

If ΔG is negative, the process will be spontaneous.

If ΔG is zero, the process is in equilibrium.

If ΔG is positive then the direct process is non-spontaneous and reverse process is spontaneous.

— An endothermic reaction which may be non-spontaneous at low temperature may become spontaneous at high temperature.

— An exothermic reaction which may be non-spontaneous at high temperature may become spontaneous at low temperature.

— Standard free energy change of a reaction — It is defined as the change in free energy which takes place when the reactants in the standard state are converted into the products in their standard state.

— Standard free energy of formation — It is defined as the free energy change which takes place when 1 mole of the compound is formed from its elements taken in their standard states.

$$\Delta_r G^\circ = -2.303 RT \log K ; \quad K = \text{equilibrium constant}$$

$$\text{or.} \\ K = \frac{T \Delta_r S^\circ - \Delta_r H^\circ}{RT}$$

— Third law of thermodynamics —

The entropy of a perfectly crystalline solid approaches zero as the temperature approaches absolute zero.

The entropy of all Perfectly crystalline Solids may be taken as zero at the absolute zero of temperature.

or.

At absolute zero a Perfectly crystalline solid has a perfect order of its Constituent Particles. There is no disorder at all. Hence the absolute entropy is taken as zero.

The entropy per mole of the substance under standard conditions at the specified temperature is called standard molar entropy S_m°

A simplified expression for the absolute entropy of solid at temperature T is.

$$S = 2.303 C_p \log T.$$

where C_p is the heat capacity of the substance at constant pressure

For liquid and gaseous substance the total absolute entropy at the given temperature will be the sum of all the entropy changes which the substance has to undergo in order to reach that particular state starting from the crystalline solid at absolute zero. Thus the complete expression will be.

$$S = \int_0^{T_f} \frac{C_p(s)}{T} \cdot dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{vap}}{T_{vap}} + \int_{T_b}^T \frac{C_p(g)}{T} \cdot dT.$$

Q.1. To what type of system the following belong.

- (i) Tree (ii) Pond (iii) Animals (iv) Tea Placed in a kettle.
(v) Tea Placed in thermos flask. (vi) Tea Placed in a cup.

Ans. (i) Open (ii) open (iii) open (iv) Closed (v) Isolated
(vi) open system.

Q.2. Separate out of following into extensive and intensive.
Volume, temperature, Pressure, boiling point, Free energy.

Ans. Volume and free energy are extensive.
Temperature, Pressure and boiling point are intensive.

Q.3. Can the absolute value of internal energy be determined
Why or Why not.

Ans. No, Because it is the sum of different types of energies
Some of which cannot be determined.

Q.4. Show that the product of Pressure and Volume has the
dimension of energy.

Ans. $P \times V = \frac{\text{Force}}{\text{Area}} \times \text{Area} \times \text{length} = \text{Force} \times \text{length} = \text{Work} = \text{Energy}.$

Q.5. For the same increase in volume, why work done is more if
the gas is allowed to expand reversibly at higher temperature.

Ans. For isothermal reversible expansion $W = -P_{int} \times \Delta V$. At
higher temperature internal Pressure of the gas is more.

Q.6. Why standard heat of formation of diamond is not zero.
though it is an element.

Ans. The standard state chosen for Carbon is graphite and
not diamond.

Q.7. Is the bond energy of all the four C-H bond in CH_4 molecule
equal, if not then why. How is the C-H bond energy than.

reported.

Ans. No. Because after breaking of C-H bonds one by one the electronic environments change. The reported value is the average value of the bond dissociation energies of the four C-H bonds.

Q.8. Same mass of diamond and graphite are burnt in oxygen. Will the heat produced be same or different.

An. Heat evolved will be different. This is because they have different crystal structure.

Q.9. Water can be lifted into the water tank at the top of the house with the help of a pump. Then why is not considered to be spontaneous.

An. A spontaneous process should continue taking place by itself after initiation. But this is not so in the given case because water will go up so long as the pump is working.

Q.10. Rank the following in the order of increasing entropy.

(a) 1 mole of $H_2O(l)$ at $25^\circ C$ and 1 atm. pressure.

(b) 2 mole of $H_2O(s)$ at $0^\circ C$ and 1 atm. pressure.

(c) 1 mole of $H_2O(v)$ at $100^\circ C$ and 1 atm. pressure.

(d) 1 mole of $H_2O(l)$ at $0^\circ C$ and 1 atm. pressure.

Ans. $b < d < a < c$.

Q.11. Under what condition the heat evolved or absorbed in a reaction is equal to its free energy change.

An. As $\Delta G = \Delta H - T\Delta S$ thus $\Delta G = \Delta H$ only when either the reaction is carried out at $0^\circ K$ or the reaction is not accompanied by any entropy change $\Delta S = 0$.

Q.12. Which out of the following can be determine, Absolute

Internal energy, absolute enthalpy, absolute entropy.

An. Absolute entropy.

Q.13. At a certain temperature T , the endothermic reaction $A \rightarrow B$ proceeds virtually to the end. Determine.

a. Sign of ΔS for this reaction.

b. Sign of ΔG for the reaction $B \rightarrow A$ At the temperature T

c. The possibility of reaction $B \rightarrow A$ Proceeding at a low temperature

Ans. (a) Energy factor oppose, so enthalpy factor must favour, so ΔS must be positive.

(b) For $A \rightarrow B$ ΔG is negative and for $B \rightarrow A$ ΔG is positive

(c) For $B \rightarrow A$ ΔH is negative and ΔS is also negative. ΔS oppose the process but at low temperature, $T\Delta S$ may be so low that ΔH is greater in magnitude than $T\Delta S$, and the process will be spontaneous.

Q.14. An exothermic reaction $A \rightarrow B$ is spontaneous in the backward direction, what will be the sign of ΔS for the forward reaction.

An. Backward reaction will be endothermic thus energy factor oppose the backward reaction. As backward reaction is spontaneous, randomness factor must favour, so ΔS will be positive for backward and Negative for forward reaction.

Q.15. Predict in which of the following entropy increase/decrease

(a) A liquid crystallized into a solid.

(b) Temperature of a solid is raised from 0°K to 115°K .

(c) $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

(d) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$

An. (a) Decrease because randomness is decrease

(b) increase because the particles start vibrating about their equilibrium position. randomness increase.

- (c) Increase - because the reactant is solid and product have gaseous substance.
- (d) Increase - because the product have large number of particles.

Q.16. Comment on the validity of the statements, give reason.

- (a) Thermodynamically, an exothermic reaction is sometimes not spontaneous.
- (b) The entropy of steam is more than that of water at its boiling pt.
- (c) The equilibrium constant for a reaction is one or more, if $\Delta_r G^\circ$ for it is less than zero.

An (a) True, This is because $\Delta G = \Delta H - T\Delta S$. For exothermic reaction ΔH is negative and $T\Delta S$ is positive (entropy factor oppose the process) and $T\Delta S > \Delta H$ so ΔG will be positive and process will not be spontaneous.

(b) True, because at the same temperature gaseous state have more randomness.

(c) $-\Delta G^\circ = RT \log K$, if ΔG° is less than zero then it is negative and K will be positive. Hence K will be greater than 1.

Q.17. Give reason.

(a) Neither Q nor W is a state function but $Q+W$ is a state function.

An. $\Delta U = Q + W$ and ΔU is a state function.

(b) The dissolution of ammonium chloride in water is endothermic still it dissolves in water.

An. On dissolution entropy increases ΔS is positive though ΔH is positive but if $T\Delta S > \Delta H$ then according to the eqn. $\Delta G = \Delta H - T\Delta S$, ΔG will be negative. Hence the process is spontaneous.

(c) A real crystal has more entropy than an ideal crystal.

An. A real crystal has some disorder due to the presence of defects whereas ideal crystal has no disorder so a real crystal has more entropy.