

## UNIT 6

## THERMODYNAMICS

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- ❖ The branch of chemistry which deals with energy changes associated with chemical reactions is called chemical energetics.

Eg:-  $C + O_2 \longrightarrow CO_2 + \text{Heat Energy}$

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{Heat} + \text{Light}$

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu + \text{Electrical Energy}$

### THERMODYNAMICS

- ❖ The term thermodynamics literally means flow of heat.
- ❖ It deals with the relation between heat and work.
- ❖ The word 'Thermo' means heat and 'dynamics' means work.
- ❖ The branch of science which deals with the study of energy changes associated with chemical reactions is called chemical thermodynamics.

### SYSTEM

- ❖ A specified part of the universe which is under observation is called a system.

### SURROUNDINGS

- ❖ The rest of the universe which is not a part of the system is called surroundings.

### TYPES OF SYSTEMS

#### OPEN SYSTEM

- ❖ A system which can exchange matter as well as energy with the surroundings is called as open system.
- ❖ Eg: Hot water placed in an open cup.

#### CLOSED SYSTEM

- ❖ A system which can exchange energy but not matter with the surroundings is called a closed system.
- ❖ Eg: Hot water placed in a closed cup.

#### ISOLATED SYSTEM

- ❖ A system which can neither exchange matter nor energy with the surroundings is called an isolated system.
- ❖ Eg: Hot water placed in a thermoflask.

#### HOMOGENEOUS SYSTEM

- ❖ In a homogeneous system, the physical properties and chemical composition are identical throughout the system.

#### HETEROGENEOUS SYSTEM

- ❖ In a heterogeneous system the physical properties and chemical compositions are different.

## **MACROSCOPIC PROPERTIES**

- ❖ The properties which depend on the bulk of the system are called macroscopic properties.
- ❖ Eg: Pressure, Temperature, Volume, Composition, Surface Tension, Viscosity, Density.
- ❖ Eg: In order to measure the temperature of water we do not deal with individual molecules but we consider the molecules in the bulk.

## **TYPES OF MACROSCOPIC PROPERTIES**

### **EXTENSIVE PROPERTIES**

- ❖ The properties of the system which depend on the amount of matter contained in it. Eg: Mass, Volume, Energy, Heat Capacity etc.

### **INTENSIVE PROPERTIES**

- ❖ The properties of the system which are independent of the amount of substance present in it are called intensive properties.
- ❖ Eg: Pressure, Temperature, Density, Viscosity, Specific heat capacity etc.

## **MACROSCOPIC SYSTEM**

- ❖ A system containing large amount of the substance is called a macroscopic system.

## **STATE OF A SYSTEM**

- ❖ A system is said to be in a certain state when the macroscopic properties have definite values.

## **STATE VARIABLES**

- ❖ The measurable properties which are required to determine the thermodynamic state of a system are called state variables.
- ❖ Eg: Pressure, Volume, Temperature, Composition etc.

## **STATE FUNCTION**

- ❖ A state function is the property of the system whose value depends only on the state of the system and independent of the path or manner by which the state is reached. Eg: Pressure, Volume, Internal Energy, Enthalpy etc.

## **PATH FUNCTION**

- ❖ A path function is a property of a system whose value depends on the path followed to reach the system.

## **PROCESS**

- ❖ A process is a method or operation by which a system changes from one state to another.

## **TYPES OF PROCESS**

### **ISOTHERMAL PROCESS**

- ❖ A process in which temperature remains constant.

### **ADIABATIC PROCESS**

- ❖ A process in which no heat enters or leaves the system.

### **ISOBARIC PROCESS**

- ❖ A process in which pressure remains constant.

### **ISOCHORIC PROCESS**

- ❖ A process in which volume of the system remains constant.

### **REVERSIBLE PROCESS**

- ❖ A process in which the change is carried out so slowly that the system and surroundings are always in equilibrium is called a reversible process.

### **IRREVERSIBLE PROCESS**

- ❖ A process which occurs suddenly or spontaneously such that it does not remain in equilibrium during the transformation.

## **WORK AND HEAT**

- ❖ Whenever a system changes from one state to another, the energy of the system also changes.
- ❖ Energy changes can occur either as heat or as work.
- ❖ Work is a form of energy that flows across the boundary of a system as a result of difference in pressure.
- ❖ Heat is a form of energy that flows across the boundary of a system as a result of a difference in temperature.
- ❖ It passes from a hot body to a cold body.

## **SIGN CONVENTION**

According to the International Convention, when

- ❖ Heat is absorbed by the system,  $q$  is positive
- ❖ Heat is evolved by the system,  $q$  is negative
- ❖ Work is done on the system,  $w$  is positive
- ❖ Work is done by the system,  $w$  is negative

## **PRESSURE-VOLUME WORK**

- ❖ It is the work done when the system expands or contracts against the external pressure.

- ❖ Consider a cylinder provided with a piston having an area of cross section 'A'.
- ❖ Let a gas of volume 'V' is enclosed in the cylinder.
- ❖ The pressure acting on the piston is 'P'.
- ❖ When the internal pressure is slightly more than the external pressure, the gas expands.
- ❖ As a result the piston moves a very small distance  $d\ell$ .
- ❖ Then, The change in volume,  $dv = A \cdot d\ell$

We know that,  $\text{Pressure} = \frac{\text{Force}}{\text{Area}}$

Or  $\text{Force} = \text{Pressure} \times \text{Area}$

- ❖ i.e., Force acting on the piston,  $F = P \times A$
- ❖ If a work,  $dw$  is done by the small movement of the piston, then

$$dw = \text{Force} \times \text{Distance}$$

$$dw = -P \times A \times d\ell \quad (\text{-ve sign indicates work is done by the system})$$

But  $A \times d\ell = dv$

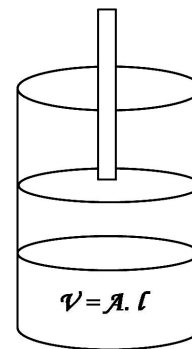
$$dw = -Pdv$$

- ❖ If the volume of the system changes from  $V_1$  to  $V_2$ , then the total work done is given by

$$W = -\int Pdv$$

$$W = -P(V_2 - V_1)$$

$$W = -P\Delta V$$



## INTERNAL ENERGY

- ❖ Every substance is associated with a definite amount of energy by virtue of its constitution.
- ❖ This energy possessed by the system is called the Internal Energy or Intrinsic Energy.
- ❖ It is denoted by E or U.
- ❖ It is the sum of translational kinetic energy ( $E_t$ ), rotational kinetic energy ( $E_r$ ), vibrational kinetic energy ( $E_v$ ), electronic energy ( $E_e$ ), nuclear energy ( $E_n$ ) and the interaction energy ( $E_i$ ) of the molecules.

$$\text{i.e., } E = E_t + E_r + E_v + E_e + E_n + E_i$$

## CHANGE IN INTERNAL ENERGY

- ❖ It is the heat evolved or absorbed in the reaction occurring at constant temperature and constant volume.

- ❖ If  $E_1$  and  $E_2$  are the internal energies of the system in the initial and the final states, then  $\Delta E = E_2 - E_1$
- ❖ The internal energy change of a reaction is determined with the help of Bomb Calorimeter.

### ZEROth LAW OF THERMODYNAMICS

- ❖ Zeroth law states that "when two bodies have equality of temperature with a third body, they inturn have equalities with each other".
- ❖ If two bodies A and B are in thermal equilibrium with another body C,
- ❖ then the bodies A and B will also be in thermal equilibrium with each other.
- ❖ The basic principle of thermometer is Zeroth Law.

### FIRST LAW OF THERMODYNAMICS

- ❖ The law states that energy can neither be created nor be destroyed or the total energy of the universe is a constant.

### FIRST LAW OF THERMODYNAMICS AND INTERNAL ENERGY

- ❖ Consider a system whose internal energy is  $E_1$ .
- ❖ If 'q' amount of heat is supplied, the internal energy of the system will increase to  $E_1 + q$ .
- ❖ If work is done on the system, the internal energy further increases and becomes  $E_2$ . Thus

$$\begin{aligned}
 E_2 &= E_1 + q + w \\
 E_2 - E_1 &= q + w \\
 \Delta E &= q + w \longrightarrow (1)
 \end{aligned}$$

- ❖ Equation (1) is the mathematical statement of first law of thermodynamics.
- ❖ If work is done by the system, the w is -ve.

$$\Delta E = q - w \longrightarrow (2)$$

- ❖ Consider a gas enclosed in a cylinder with a frictionless piston at a pressure 'P' and volume ' $V_1$ '.
- ❖ Let its internal energy be ' $E_1$ '.
- ❖ If 'q' amount of heat is supplied the gas expands the volume from  $V_1$  to  $V_2$  at constant pressure 'P'.
- ❖ Then work done by the system is given as

$$\begin{aligned}
 W &= -P(V_2 - V_1) \\
 W &= -P\Delta V
 \end{aligned}$$

- ❖ Substituting the value of W in equation (1), we get

$$\Delta E = q - P\Delta V \longrightarrow (3)$$

- ❖ For a process occurring at constant volume,

$$\Delta V = 0$$

$$P\Delta V = 0$$

$$\Delta E = q \longrightarrow (4)$$

- ❖ If  $\Delta E = 0$ , equation (1) becomes

$$0 = q + w$$

$$q = -W$$

- ❖ i.e., heat involved in a process is completely converted into work or vice versa.

### ENTHALPY OR HEAT CONTENT

- ❖ It is the sum of internal energy and the product of the pressure and volume.
- ❖ This is given by the relation,  **$H = E + PV$**
- ❖ Where H is the enthalpy, E is the internal energy, P is the pressure and V is the volume.

### ENTHALPY CHANGE

- ❖ If  $H_1$  is the enthalpy of a system in the initial state and  $H_2$  that of the final state, the change in enthalpy  $\Delta H$  is given by  **$\Delta H = H_2 - H_1$**
- ❖ The enthalpy change of a reaction is equal to the heat absorbed or evolved during a reaction at constant temperature and pressure.

### REACTION ENTHALPY

- ❖ The enthalpy change accompanying a reaction is called the reaction enthalpy.
- ❖ The enthalpy change of a chemical reaction is given by the symbol  $\Delta_r H$ .

$$\Delta_r H = \text{Sum of enthalpies of products} - \text{Sum of enthalpies of reactants}$$

$$\Delta_r H = \sum a_i H_{\text{pds}} - \sum b_i H_{\text{reactants}}$$

- ❖ Where  $a_i$  and  $b_i$  are the stoichiometric coefficients of the products and reactants respectively.

### RELATION BETWEEN $\Delta H$ AND $\Delta E$

- ❖ Let  $H_1$  be the enthalpy of the reactants and  $H_2$  that of the products.
- ❖ Then change in enthalpy is given by the equation

$$\Delta H = H_2 - H_1$$

$$\text{But } H = E + PV$$

$$H_1 = E_1 + P_1 V_1$$

$$H_2 = E_2 + P_2 V_2$$

$$\Delta H = (E_2 + P_2 V_2) - (E_1 + P_1 V_1)$$

$$\Delta H = (E_2 - E_1) + (P_2 V_2 - P_1 V_1)$$

- ❖ When the pressure is constant,

$$P_1 = P_2 = P$$

$$\Delta H = (E_2 - E_1) + P(V_2 - V_1)$$

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

❖ In the case of gases,  $PV = nRT$

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

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

$$P\Delta V = \Delta nRT$$

$$\Delta H = \Delta E + \Delta nRT$$

### STANDARD ENTHALPY OF REACTIONS ( $\Delta H^0$ )

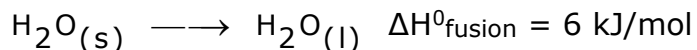
❖ It reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

### ENTHALPY CHANGES DURING PHASE TRANSFORMATIONS

❖ If a substance is transformed from one state to another, the change in enthalpy is called enthalpy of transition.

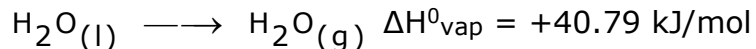
### STANDARD ENTHALPY OF FUSION ( $\Delta H^0_{\text{fusion}}$ )

❖ It is the enthalpy change accompanied by the melting of one mole of a solid substance in standard state.



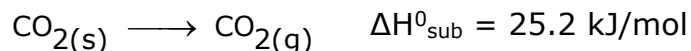
### STANDARD ENTHALPY OF VAPOURISATION ( $\Delta H^0_{\text{vap}}$ )

❖ It is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar).



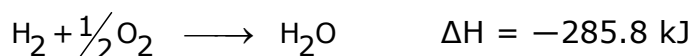
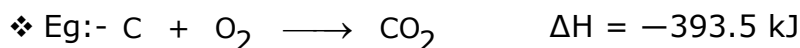
### STANDARD ENTHALPY OF SUBLIMATION ( $\Delta H^0_{\text{sub}}$ )

❖ It is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and at a standard pressure (1 bar).



### STANDARD ENTHALPY OF FORMATION ( $\Delta H^0_f$ )

❖ The enthalpy change accompanying the formation of one mole of a compound from its elements, all the substances being in their standard states is called standard enthalpy of formation.



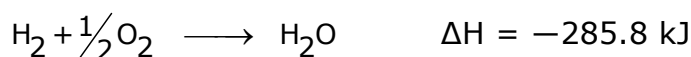
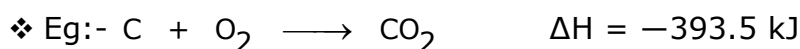
## EXOTHERMIC AND ENDOTHERMIC REACTIONS

- ❖ All chemical reactions are accompanied by energy changes.
- ❖ These changes appear in the form of evolution or absorption of heat. B
- ❖ Based on this, chemical reactions are classified into two types.

### EXOTHERMIC REACTIONS

- ❖ A chemical reaction which is accompanied by the evolution of heat energy is called an exothermic reaction.
- ❖ i.e., the total energy of the products is less than the enthalpy of the reactants.

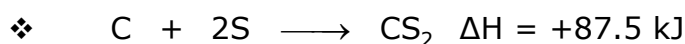
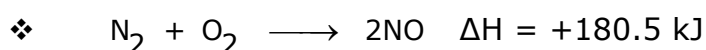
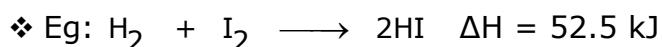
$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = -ve$$



### ENDOTHERMIC REACTIONS

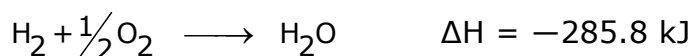
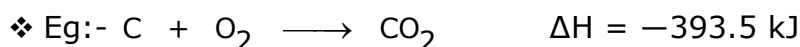
- ❖ A chemical reaction which is accompanied by the absorption of heat energy is called an endothermic reaction.
- ❖ i.e., total enthalpy of the products is greater than the total enthalpy of the reactants.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = +ve$$



### THERMOCHEMICAL EQUATIONS

- ❖ A chemical equation which indicates the heat change during the reaction.



### HEAT CAPACITY (C)

- ❖ Heat capacity of a system is defined as the quantity of heat required to raise the temperature of the system through  $1^\circ\text{C}$ .
- ❖ If  $q$  is the quantity of heat required to raise the temperature of the system from  $T_1$  to  $T_2$ , then  $C$  is given as



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

$$q = C \Delta T$$

- ❖ If  $dq$  is the quantity of heat required to raise the temperature of the system by  $dT$ , then  $C$  is given as

$$C = \frac{dq}{dT}$$

### HEAT CAPACITY AT CONSTANT VOLUME ( $C_v$ )

- ❖  $C_v$  is defined as the rate of change of internal energy with temperature at constant volume.
- ❖ For infinitesimally small changes, the first law of thermodynamics can be written as

$$dE = dq + dw$$

$$dE = dq - pdv$$

$$dq = dE + pdv$$

- ❖ At constant volume,  $dv = 0$

$$pdv = 0$$

$$dq_v = dE$$

$$C_v = \frac{dq_v}{dT} = \frac{dE}{dT} \text{ or } \left( \frac{\partial E}{\partial T} \right)_v$$

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v$$

### HEAT CAPACITY AT CONSTANT PRESSURE ( $C_p$ )

- ❖  $C_p$  is defined as the rate of change of enthalpy with temperature at constant pressure. At constant Pressure  $dv \neq 0$

$$dq_v = dE + pdv \dots \dots \dots (1)$$

- ❖ We have the relation

$$H = E + PV$$

$$dH = dE + PdV$$

$$dE = dH - PdV \dots \dots \dots (2)$$

- ❖ Substituting the value of (2) in eqn (1) we get

$$dq_v = dH - PdV + PdV$$

$$dq_v = dH$$

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

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

**RELATION BETWEEN  $C_p$  and  $C_v$** 

$$C_p = \frac{dH}{dT} \text{ and } C_v = \frac{dE}{dT}$$

$$C_p - C_v = \frac{dH}{dT} - \frac{dE}{dT} \dots\dots\dots(1)$$

❖ But  $H = E + PV$

$$PV = RT$$

$$H = E + RT$$

$$\frac{dH}{dT} = \frac{dE}{dT} + R \cdot \frac{dT}{dT}$$

$$\frac{dH}{dT} = \frac{dE}{dT} + R \dots\dots\dots(2)$$

❖ Substituting the value of (2) in eqn (1)

$$C_p - C_v = \frac{dE}{dT} + R - \frac{dE}{dT}$$

$$C_p - C_v = R$$

**SPECIFIC HEAT CAPACITY (c)**

❖ It is defined as the quantity of heat required to raise the temperature of unit mass of a substance by one degree.

❖ If  $q$  is the quantity of heat required to raise the temperature of the system by  $\Delta T$ , then

$$c = \frac{q}{m\Delta T}$$

**MOLAR HEAT CAPACITY**

❖ It is the quantity of heat required to raise the temperature of one mole of a substance by one degree.

**MEASUREMENT OF  $\Delta E$  and  $\Delta H$** 

❖ We can measure the energy changes associated with chemical or physical processes by an experimental technique called calorimetry.

**MEASUREMENT OF  $\Delta E$** 

❖ For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter.

❖ The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings.

❖ A combustible substance is burnt in pure dioxygen supplied in the steel bomb.

❖ Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored.

❖ Since the bomb calorimeter is sealed, its volume does not change.

- ❖ Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter.
- ❖ The temperature of the bath is recorded at the beginning and at the end of the reaction.
- ❖ The change in temperature is noted and is then converted to  $q_v$  by the equation,  

$$q_v = C\Delta T$$

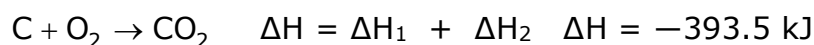
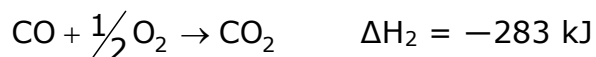
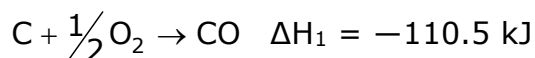
### MEASUREMENT OF $\Delta H$

- ❖ The enthalpy change may be measured by using a calorimeter.
- ❖ The calorimeter is immersed in an insulated water bath fitted with a stirrer and the thermometer.
- ❖ The temperature of the bath is recorded at the beginning and after the end of the reaction.
- ❖ The change in temperature may be noted.
- ❖ By knowing the heat capacity of the calorimeter system and the change in temperature, the heat absorbed or evolved may be calculated.
- ❖ This will give the enthalpy change,  $\Delta H$  of the reaction.
- ❖ In an exothermic reaction, heat is evolved and system loses heat to the surroundings.
- ❖ Therefore,  $q_p$  will be negative and  $\Delta H$  will also be negative.
- ❖ In an endothermic reaction, heat is absorbed,  $q_p$  is +ve and  $\Delta H$  will be positive.

### Hess's Law of Constant Heat Summation

- ❖ Hess's law states that the enthalpy change of a chemical reaction is the same, whether the change takes place in one step or several steps.
- ❖ Eg:  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -393.5 \text{ kJ}$

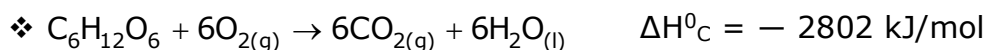
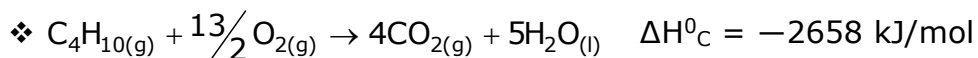
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### ENTHALPIES OF DIFFERENT TYPES OF REACTIONS

#### STANDARD ENTHALPY OF COMBUSTION ( $\Delta H^\circ_c$ )

- ❖ It is defined as the enthalpy change accompanied by the complete combustion of one mole of a substance, all the reactants and products being in their standard states at the specified temperature.



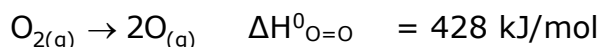
### ENTHALPY OF ATOMIZATION ( $\Delta H^0_{\text{a}}$ )

❖ It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gaseous phase.



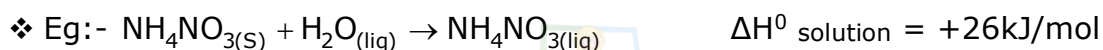
### BOND ENTHALPY

❖ It is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gaseous phase.



### ENTHALPY OF SOLUTION

❖ It is the enthalpy change when 1 mole of a substance is dissolved in a specified amount of solvent at a temperature.



### LATTICE ENTHALPY

❖ It is the enthalpy change when 1 mole of an ionic compound dissociates into its ions in gaseous state.



### DETERMINATION OF LATTICE ENTHALPY

#### BORN HABER CYCLE

❖ Determination of lattice enthalpy of NaCl.

❖ The formation of NaCl involves the following steps.

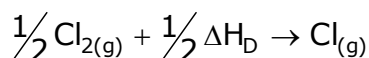
#### Conversion of metallic sodium to gaseous sodium atoms.

❖ The amount of energy required to convert one mole of metallic sodium to gaseous atoms is called sublimation energy,  $\Delta H_{\text{sub}}$



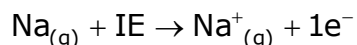
#### Conversion of gaseous chlorine molecule to gaseous chlorine atoms.

❖ The amount of energy required to dissociate one mole of gaseous chlorine molecule to gaseous chlorine atoms is called dissociation energy,  $\Delta H_{\text{D}}$ .

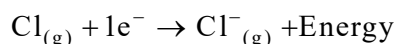


**Conversion of gaseous sodium atoms to sodium ions.**

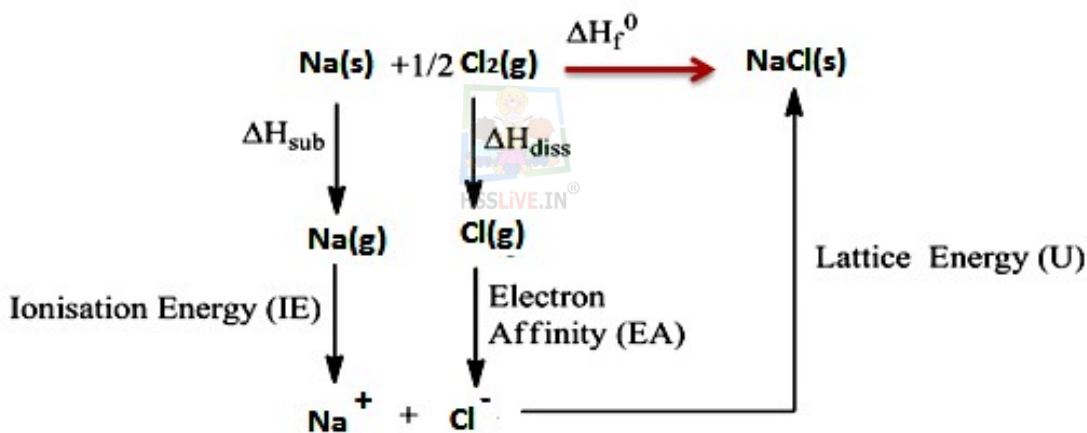
- ❖ The amount of energy required to convert one mole of gaseous sodium atoms to sodium ions is called Ionisation energy.

**Conversion of gaseous chlorine atom to chloride ions.**

- ❖ The amount of energy released when one mole of gaseous chlorine atom is converted to chloride ions is called electron affinity.

**Combination of gaseous sodium ions and chloride ions to form NaCl.**

- ❖ The amount of energy released when one mole of solid crystalline compound is formed from gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions is called lattice energy, U.
- ❖ The overall change is  $\text{Na}_{(s)} + \frac{1}{2}\text{Cl}_{2(g)} \rightarrow \text{NaCl}_{(s)}$

**Born Haber Cycle for Sodium Chloride****SPONTANEITY**

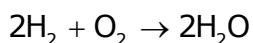
- ❖ The potential to proceed without the assistance of any external agency.

**SPONTANEOUS PROCESS**

- ❖ A process that occurs without the help of any external agency is called a spontaneous process.
- ❖ Eg: Flow of water from a high level to a low level.
- ❖ Flow of heat from a hot body to a cold body
- ❖ Flow of gases from a high pressure region to a low pressure region.
- ❖ Spontaneous process are of two types. They are
- ❖ **Process which requires no initiation**
- ❖ Evaporation of water from ponds, rivers, sea etc.  $\text{H}_2\text{O}_{(\text{liquid})} \rightarrow \text{H}_2\text{O}_{(\text{gas})}$
- ❖ Combination of NO and  $\text{O}_2$ .  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

### ❖ **Process which require some initiation**

- ❖ Combination of  $H_2$  and  $O_2$  should be initiated by an electric spark.



- ❖ Burning of carbon.  $C + O_2 \rightarrow CO_2$

### **ENTROPY**

- ❖ The degree of randomness or disorder of a system is determined by a property called Entropy.
- ❖ Entropy is the measure of disorder of the system.
- ❖ Change in entropy is represented by  $\Delta S$ .
- ❖  $\Delta S$  is related with  $q$  and  $T$  for a reversible reaction as  $\Delta S = \frac{q_{rev}}{T}$
- ❖ The greater the disorder in an isolated system, the higher is the entropy.
- ❖ The unit of entropy is  $JK^{-1}mol^{-1}$ .

### **SECOND LAW OF THERMODYNAMICS**

- ❖ This law gives the relationship between entropy and spontaneity.
- ❖ For a spontaneous process in an isolated system, the change in entropy is +ve. i.e.,  $\Delta S > 0$ .
- ❖ If the system is not isolated, the total energy change will be equal to the sum of change in entropy of the system and surroundings.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surroundings}$$

$$\Delta S_{universe} > 0$$

- ❖ The second law of thermodynamics states that the entropy of the universe always increases in the course of every spontaneous change.

### **ENTROPY AND SPONTANEITY**

- ❖ The total entropy change for the system and surroundings of a spontaneous process is given by  $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surroundings} > 0$   
i.e., when  $\Delta S_{total} > 0$ , the process is spontaneous.
- ❖ When a system is in equilibrium, the entropy is maximum and the change in entropy,  $\Delta S = 0$ .  
i.e., when  $\Delta S_{total} = 0$ , the process is at equilibrium.
- ❖ When  $\Delta S_{total} < 0$ , the process is non spontaneous.

### **FREE ENERGY AND FREE ENERGY CHANGE**

- ❖ Free energy is the maximum energy available from a system that can be

converted into work during a process.

- ❖ It is denoted by Gibbs energy or Gibbs function,  $G$ .

$$G = H - TS$$

- ❖ Gibbs function,  $G$  is an extensive property and a state function.
- ❖ The change in Gibbs energy for the system  $\Delta G_{\text{system}}$  can be written as

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

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

- ❖ The equation is called Gibbs Helmholtz equation.

### **PREDICTION OF SPONTANEITY IN TERMS OF $\Delta G$**

- ❖ The equation  $\Delta G_{\text{system}} = -T\Delta S_{\text{total}}$  may be used to predict the spontaneity of a process.
- ❖ For a spontaneous process,  $\Delta S$  is +ve so that  $\Delta G$  is -ve.
- ❖ Therefore, when  $\Delta G$  is -ve, the process will be spontaneous.
- ❖ For a process at equilibrium,  $\Delta S = 0$ , so that  $\Delta G = 0$ .
- ❖ Therefore, when  $\Delta G$  is zero, the process will be at equilibrium.
- ❖ For a non spontaneous process,  $\Delta S$  is -ve so that  $\Delta G$  is +ve.
- ❖ Therefore, when  $\Delta G$  is +ve, the process will be non spontaneous.

### **CONDITIONS FOR $\Delta G$ TO BE NEGATIVE**

- ❖ When  $\Delta H$  is -ve and  $\Delta S$  is +ve,  $\Delta G$  will be -ve and the process will be spontaneous.
- ❖ On the other hand when  $\Delta H$  is +ve and  $\Delta S$  is -ve,  $\Delta G$  will be +ve and the process will be non spontaneous.
- ❖ When  $\Delta H$  is +ve and  $\Delta S$  is negative,  $\Delta G$  will be -ve only when  $\Delta H < T\Delta S$ .
- ❖ Hence the reaction will be spontaneous only at high temperatures.
- ❖ When  $\Delta H$  is -ve and  $\Delta S$  is -ve,  $\Delta G$  will be -ve only when  $\Delta H < T\Delta S$ .
- ❖ Hence the reaction will be spontaneous only at low temperatures.

### **Gibbs Free Energy Change and Equilibrium**

- ❖ Consider the reversible reaction,  $A + B \rightleftharpoons C + D$
- ❖ The criterion for equilibrium is  $\Delta G = 0$
- ❖ Gibbs energy for a reaction in which all the reactants and products are in the standard state ( $\Delta G^0$ ) is related to the equilibrium constant of the reaction as

$$\Delta G = \Delta G^0 + RT \ln K$$

$$0 = \Delta G^0 + RT \ln K$$

$$\text{Or } \Delta G^0 = -RT \ln K$$

$$\Delta G^0 = -2.303 RT \log K$$

We know that

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K$$

$$\Delta G^0 = -RT \ln K$$

### Third Law of Thermodynamics

- ❖ The law states that "The Entropy of a perfectly crystalline substance is zero at absolute zero temperature".
- ❖ Third law helps to calculate the absolute entropies of pure substances at different temperatures.

## [PREVIOUS HSE QUESTIONS]

1. a) For the oxidation of iron  $4\text{Fe}_{(s)} + 3\text{O}_{2(g)} \longrightarrow 2\text{Fe}_2\text{O}_{3(s)}$  entropy change  $\Delta S$  is  $-549.4 \text{ J/K/mol}$  at 298K. In spite of the negative entropy change of this reaction, why is the reaction spontaneous? ( $\Delta_r H^0$  for the reaction is  $-1648 \times 10^3 \text{ J/mol}^{-1}$ ).

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \Delta S_{\text{surroundings}} = \frac{-\Delta H_r}{T}$$

$$\Delta S_{\text{surroundings}} = \frac{-(-1648) \times 10^3}{298} = 5530 \text{ JK}^{-1} \text{ mol}^{-1} \quad \Delta S_{\text{total}} = 549.4 + 5530$$

$$\Delta S_{\text{total}} = 4980.6 \text{ J/K/mol}$$

$\Delta S_{\text{total}} = +ve$ . Therefore, the reaction is spontaneous.

- 2 a) The enthalpy of combustion of  $\text{CH}_4(g)$ ,  $\text{C}(\text{graphite})$  and  $\text{H}_2(g)$  at 298K are  $-890.3 \text{ kJ mol}^{-1}$ ,  $-393.5 \text{ kJ mol}^{-1}$  and  $-285.8 \text{ kJ mol}^{-1}$  respectively. Calculate the enthalpy of formation of  $\text{CH}_4(g)$ .

$$\Delta H_{\text{formation}} = \Delta H_{\text{reactants}} - \Delta H_{\text{products}}$$

$$\Delta H_{\text{formation}} = -74.8 \text{ kJ/mol}$$

### Answer

b) Match the following:

1. $W = -\Delta U$	a) Enthalpy change
2. $\Delta U = 0$	b) Universal gas constant
3. $C_p - C_v$	c) Adiabatic process
4. $q_p$	d) Isothermal process
	e) Cyclic process

$W = -\Delta U$	Adiabatic
$\Delta U = 0$	Isothermal
$C_p - C_v$	Universal Gas Constant
$q_p$	Enthalpy Change



3. Find the temperature above which the reaction  $\text{MgO}_{(s)} + \text{C}_{(s)} \longrightarrow \text{Mg}_{(s)} + \text{CO}_{(g)}$  becomes spontaneous. (Given  $\Delta_r H^\circ = 490 \text{ kJ mol}^{-1}$  and  $\Delta_r S^\circ = 198 \text{ JK}^{-1}\text{mol}^{-1}$ ).

$$T = \frac{\Delta H}{\Delta S} \quad T = \frac{490 \times 10^3}{198} \quad T = 2474 \text{ K}$$

4. Enthalpy and entropy changes of a reaction are  $40.63 \text{ kJ/mol}$  and  $108.8 \text{ J/K/mol}$ . Predict the feasibility of the reaction at  $27^\circ\text{C}$ .

$$\Delta H = 40.63 \text{ kJ/mol} = 40630 \text{ J/mol} \quad T = 300 \text{ K} \quad \Delta S = 108.8 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S \quad \Delta G = 40630 - 300 \times 108.8$$

$$\Delta G = 40630 - 32640 = 7990 \text{ J/mol}$$

5) 3 mol of an ideal gas at 1.5 atm and  $25^\circ\text{C}$  expands isothermally in a reversible manner to twice its original volume against an external pressure of 1 atm. Calculate the work done. ( $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ )

$$V_1 = V \quad V_2 = 2V \quad n = 3 \text{ mol} \quad T = 25^\circ\text{C} = 298 \text{ K} \quad R = 8.314 \text{ J/K/mol}$$

$$w_{\text{rev}} = -2.303 n R T \log \frac{V_2}{V_1} \quad w_{\text{rev}} = -2.303 \times 3 \times 8.314 \times 298 \log 2$$

$$w_{\text{rev}} = -2.303 \times 3 \times 8.314 \times 298 \times 0.3010 \quad w_{\text{rev}} = -5152.38 \text{ J}$$

6) Calculate the work done for the reversible isothermal expansion of 1 mole of an ideal gas at  $27^\circ\text{C}$ , from a volume of  $10 \text{ dm}^3$  to a volume of  $20 \text{ dm}^3$ .

$$n = 1 \quad V_1 = 10 \text{ dm}^3 \quad V_2 = 20 \text{ dm}^3 \quad T = 27^\circ\text{C} = 300 \text{ K}$$

$$w_{\text{rev}} = -2.303 n R T \log \frac{V_2}{V_1} \quad w_{\text{rev}} = -2.303 \times 1 \times 8.314 \times 300 \times \log \frac{20}{10}$$

$$w_{\text{rev}} = -2.303 \times 8.314 \times 300 \times \log 2 \quad w_{\text{rev}} = -1728.9 \text{ J}$$

7) The equilibrium constant for a reaction is 5. What will be the value of  $\Delta G^\circ$ ? Given that  $R = 8.314 \text{ J/K/mol}$ ,  $T = 300 \text{ K}$ .

$$\Delta G^\circ = -2.303 RT \log K \quad \Delta G^\circ = -2.303 \times 8.314 \times 300 \times \log 5$$

$$\Delta G^\circ = -2.303 \times 8.314 \times 300 \times 0.6989 \quad \Delta G^\circ = -4014.58$$

8. Classify the following into intensive and extensive properties.

a) Internal Energy      b) Density      c) Heat Capacity      d) Temperature

Intensive property: Density, Temperature

Extensive property: Internal Energy, Heat Capacity

9. Calculate the change in internal energy for the conversion of one mole of water at  $100^\circ\text{C}$  to steam at 1 atm pressure. The heat absorbed and work done by the system are  $40.7 \text{ kJ}$  and  $3.1 \text{ kJ}$  respectively?

$$q = 40.7 \text{ kJ} \quad w = -3.1 \text{ kJ}$$

$$\Delta E = q + w \quad \Delta E = 40.7 - 3.1 \quad \Delta E = 37.6 \text{ kJ}$$

9. When a certain amount of gas is heated from 300K at constant volume, 627.5 kJ of heat was absorbed. Calculate the change in internal energy?

$$\Delta V = 0 \quad P\Delta V = 0 \quad w = 0 \quad q = 627.5 \text{ J}$$

$$\Delta E = q + w \quad \Delta E = 627.5 + 0 \quad \Delta E = 627.5 \text{ kJ}$$

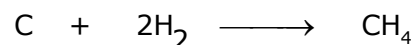
10. Calculate the amount of work done when one mole of a gas is allowed to expand from 1 litre to 5 litres against an external pressure of 1 atm.

$$P = 1 \text{ atm} \quad V_1 = 1 \text{ L} \quad V_2 = 5 \text{ L}$$

$$\Delta V = V_2 - V_1 \quad W = -P\Delta V \quad W = -1 \times 4 = -4 \text{ atm}$$

$$W = -4 \times 101.3 \text{ J} \quad W = -405.2 \text{ J}$$

11. The enthalpy of formation of methane at constant pressure is -75.83 kJ at 300K. Calculate  $\Delta E$  at 300K.



$$\Delta H = -75.83 \text{ kJ} = -75830 \text{ J} \quad R = 8.314 \quad T = 300 \text{ K}$$

$$\Delta E = \Delta H - \Delta nRT \quad \Delta E = -75830 - (-1) \times 8.314 \times 300$$

$$\Delta E = -75830 + 2494.2 \quad \Delta E = -73335.8 \text{ J} \quad \Delta E = -73.34 \text{ kJ}$$

12. The enthalpy change for a reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  is -93 kJ at 300 K.

Calculate the value of  $\Delta E$ .

$$\Delta H = -93 \text{ kJ} = -93000 \text{ J} \quad R = 8.314 \quad \Delta n = -2 \quad T = 300 \text{ K}$$

$$\Delta E = \Delta H - \Delta nRT \quad \Delta E = -93000 - (-2) \times 8.314 \times 300$$

$$\Delta E = -93000 + 4988.4 \quad \Delta E = 88011.6 \text{ J} \quad \Delta E = 88.011 \text{ kJ}$$

13. The quantity of heat required to raise the temperature of 25 g of ethylene glycol by 1K is 60.8J. Calculate the specific heat capacity of ethylene glycol.

$$Q = 60.8 \text{ J} \quad m = 25 \text{ g} \quad \Delta T = 1 \text{ K}$$

$$c = \frac{q}{m\Delta T} \quad c = \frac{60.8}{25 \times 1} \quad c = 2.43 \text{ Jg}^{-1}\text{K}^{-1}$$