

## 03.

## Chemical Thermodynamics

## SYSTEM AND SURROUNDING

A system is that part of the universe which is under thermodynamic study and the rest of the universe is surroundings.

**Boundary:** The real or imaginary surface separating the system from the surroundings is called the boundary.

**Homogeneous system:** When a system is uniform throughout, it is called a Homogeneous System, e.g., a pure single solid liquid or gas, mixtures of gases, are true solution of a solid in a liquid. A homogeneous system is made of one phase only. A phase is defined as a homogeneous, physically distinct and mechanically separable portion of a system.

**Heterogeneous system:** A heterogeneous system is one which consists of two or more phases, in other words it is not uniform throughout, e.g. ice in contact with water, ice in contact with vapour, etc. Here ice, water, and vapour constitute separate phases.

## THERMODYNAMIC SYSTEMS

There are three types of thermodynamic systems depending on the nature of the boundary.

- 1. Isolated system:** When the boundary is both sealed and insulated, no interaction is possible with the surroundings. Therefore, an isolated system is one that can transfer neither matter nor energy to and from its surroundings.
- 2. Closed system:** A closed system is one which cannot transfer matter but can transfer energy in the form of heat, work and radiation to and from its surroundings.
- 3. Open system:** In such a system the boundary is open and un-insulated. Therefore, an open system is one which can transfer both energy and matter to and from its surroundings.
- 4. Adiabatic systems:** Those systems in which no thermal energy passes into or out of the system are said to be adiabatic systems.

## INTENSIVE PROPERTIES

A property which does not depend on the quantity of matter present in the system, is known as Intensive property.

## EXTENSIVE PROPERTIES

A property that does depend on the quantity of matter present in the system, is called as Extensive property.

## COMMON PROPERTIES OF A SYSTEM

Intensive properties		Extensive properties
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point	Enthalpy, Entropy

## STATE OF A SYSTEM

A thermodynamic system is said to be in a certain state when all its properties are fixed. The fundamental properties which determine the state of a system are pressure (P), temperature (T), volume (V), mass and composition. Since a change in the magnitude of such properties alters the state of the system, these are referred to as State variables or State functions or Thermodynamic parameters. A change of system from the initial state to final state (2nd state) will be accompanied by change in the state variables. For a pure gas, the composition is fixed automatically, as it is constant per cent. The remaining state variables P, V, T are interrelated in the form of an algebraic relationship called the Equation of State. Thus for one mole of a pure gas, the equation of state is

$$PV = RT$$

where R is gas constant.

If of the three state variables (P, V, T), P and T are specified, the value of third (V) is fixed automatically and can be calculated from the equation of state. The variables (P and T) which must be necessarily specified to define the state of a system, are designated as Independent state variables. The remaining state variable (V) which depends on the value of P and T, is called Dependent state variable.

An important characteristic of a state variable (or state function) is that when the state of a system

is altered, the change in the variable depends on the initial and final states of the system. For example, if we heat a sample of water from  $0^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ , the change in temperature is equal to difference between the initial and final temperatures.

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 1 \text{ } 25^{\circ}\text{C}$$

The way in which the temperature change is brought about has no effect on the result.

### THERMODYNAMIC PROCESSES

When a thermodynamic system changes from one state to another, the operation is called a Process. These processes involve the change of conditions (temperature, pressure and volume).

#### Types of thermodynamic processes:

- 1. Isothermal Processes :** In these processes the temperature remains fixed. This is often achieved by placing the system in a thermostat (a constant temperature bath).  
For an isothermal process,  $dT = 0$ .
- 2. Adiabatic Processes:** In these processes no heat can flow into or out of the system,  
For an adiabatic process,  $dp = 0$
- 3. Isobaric Processes:** These processes take place at constant pressure.  
For an isobaric process,  $dp = 0$
- 4. Isochoric Processes :** In these processes the volume remains constant.  
For isochoric processes  $dV = 0$ .
- 5. Cyclic Process:** When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process,  
For a cyclic process,  $dE = 0, dH = 0$
- 6. Reversible process:** A thermodynamic reverse process is one that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.
- 7. Irreversible process:** When a process goes from the initial to the final state in a single step and cannot be carried the reverse order, it is said to be an irreversible process.

### WORK

When a change in the state of a system occurs energy is transferred to or from the surroundings. This energy may be transferred as heat or mechanical work, 'work' force  $\times$  distance. Types: Type of work used in thermodynamics

- 1. Electrical work:**

Electrical work done = E.M.F  $\times$  quantity of electricity. This type of work is involved in case of reactions involving ions.

- 2. Work of expansion or pressure - volume work:**

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

**Units of work :** In CGS system the unit of work is erg which is defined as the work done when a resistance of 1 dyne is moved through a distance of 1 centimetre. Since the erg is so small, a bigger unit, the joule (J) is now used.

$$1 \text{ joule} = 10^7 \text{ ergs}$$

$$\text{or } 1 \text{ erg} = 10^{-7} \text{ J}$$

For large quantities of work, kilojoule (kJ) is used.

$$1 \text{ kJ} = 1000 \text{ J}$$

### HEAT (q)

It is another mode of energy exchanged between system and the surrounding as a result of the difference of temperature between them.

**Units:** Unit of heat is calorie (cal). Since heat and work are interrelated, SI unit of heat is the joule (J)

$$1 \text{ joule} = 0.2390 \text{ calorie}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

$$\text{or } 1 \text{ kcal} = 4.184 \text{ kJ}$$

**Sign convention of Heat :** If the heat flows from surroundings into the system to raise energy of the system, it is taken to be positive,  $+q$ . If heat flows from the system into the surroundings, lowering the energy of the system, it is taken to be negative,  $-w$ .

**Sign convention of work (W):** If work is done on a system by surroundings and energy of the system is thus increased, it is taken to be positive,  $+w$ . If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative,  $-w$ .

### Summary of Sign Conventions

Heat flows into the system,  $q$  is  $+ve$  ;

Heat flows out of the system,  $w$  is  $-ve$

Work is done on the system,  $w$  is  $+ve$  ;

Work is done by the system,  $w$  is  $-ve$

### Note:

Work done by a system is not a state function because their values do not depend merely on the initial and final states but depend upon the path followed.

### FIRST LAW OF THERMODYNAMICS

It is the Law of Conservation of Energy to the thermodynamic systems. It states that: the total energy of an isolated system remains constant though it may change from one form to another, or Energy can neither be created nor destroyed although it may be converted from one form to another.

When a system is changed from state A to state B, it undergoes a change in the internal energy from  $E_A$  to  $E_B$ . Thus, we can write

$$\Delta E = E_B - E_A$$

This energy change is brought about by the evolution or absorption of heat and/or by work being done by the system. Because total energy of the system must remain constant, we can write the mathematical statement of the First Law as:

$$\Delta E = q - w$$

where  $q$  = amount of heat supplied to the system, and

$w$  = work done by the system

Thus, First Law may also be stated as, the net energy change of a closed system is equal to the heat transferred to the system minus the work done by the system.

When the gas expands against an applied constant pressure by volume  $\Delta V$ , then total mechanical work done is given by the relation

$$w = -P \times \Delta V$$

$$\Delta E = q - P \times \Delta V$$

### ENTHALPY OF A SYSTEM

In a process carried at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy ( $E$ ), as no PV work is done. But in a constant - pressure process, the system (a-gas) also expends energy in doing PV work. Therefore, total heat content of a system at constant pressure is equivalent to the internal energy  $E$  plus PV energy. This is called the enthalpy of the system and is represented by the symbol  $H$ . Thus, enthalpy is defined by the equation

$$H = E + PV$$

In the equation  $E$ ,  $P$ ,  $V$  are all state functions. Thus  $H$ , the value of which depends on the value of  $E$ ,  $P$ ,  $V$  must also be a function of state. Hence its value is independent of the path by which state of the system is changed.

### Change in Enthalpy:

Enthalpy change of a system may be defined as the amount of the increase in internal energy of the

system and the pressure -volume work done, i.e. the work of expansion.

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

According to the First Law,

$$\Delta E = q - w$$

where  $q$  = heat transferred

When change in state occurs at constant pressure,

$$\Delta H = q_p$$

This relationship is usually written as,

$$\Delta H = q_p$$

where subscript  $p$  means constant pressure.

**Units :** Units of  $\Delta H$  are kilocalories (kcal) or kilojoule (kJ).

### Sign Conventions of Enthalpy:

$$\Delta H = H_2 - H_1$$

$\Delta H$  is positive if  $H_2 > H_1$ , and the process of reaction will be endothermic.

$\Delta H$  is negative if  $H_1 > H_2$  and the reaction will be exothermic.

### INTERNAL ENERGY

A thermodynamic system containing some quantity of matter has within itself a definite quantity of energy. This energy includes not only the translation kinetic energy of the molecules but also other molecular energies such as rotational, vibrational energies. The kinetic and potential energy of the nuclei and electrons within the individual molecules also contribute to the energy of the system. The total of all the possible kinds of energy of a system, is called its Internal Energy. The internal energy of a system, like temperature, pressure, volume, etc. is determined by the state of a system and is independent of the path by which it is obtained. Hence internal energy of a system is a state function. Since the internal energy of a system depends on the mass of the matter contained in a system, it is classed as an extensive property. **Symbol representation of Internal energy and Sign conventions:**

The internal energy of a system is represented by the symbol  $E$ . It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics we are concerned only with the energy changes when a system changes from one state to another.

If  $\Delta E$  be the difference of energy of the initial state ( $E_{in}$ ) and the final state ( $E_f$ ), we can write

$$\Delta E = E_f - E_{in}$$

$\Delta E$  is +ve if  $E_p$  is greater than  $E_{in}$  and -ve if  $E_p$  is less than  $E_{in}$ .

**Units:**

S.I unit for internal energy of a system is the joule (J). Another unit is calorie. 1 cal is 4.184 J.

**Relation Between  $\Delta H$  and  $\Delta E$** 

Calorific value of many gaseous fuels are determined in constant volume calorimeters. These values are, given by

$$q_u = \Delta E$$

When any fuel is burnt in the open atmosphere, additional energy of expansion, positive or negative, against the atmosphere is also involved. Thus value of  $q$  actually realized, i.e.,  $q_p$   $\neq$   $\Delta H$ , may be different from the equation.

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

If gases are involved in a reaction, then account for most of the volume change as the volumes of solids and liquids are negligibly small in comparison.

**SECOND LAW OF THERMODYNAMICS**

A process which proceeds of its own accord, without any outside assistance, is termed a spontaneous or natural process. The reverse process which does not proceed on its own, is referred to as a nonspontaneous or unnatural process.

The tendency of a process to occur naturally is called the spontaneity, e.g., Spontaneous processes

**1. Rolling ball :**

A ball rolls down-hill spontaneously but it will not roll uphill unless work is done on it.

**2. Heat flow :**

When two balls of metal, one hot and one cold, are connected, heat flows spontaneously from the hot ball to the cold one, never from cold to hot. It requires work to transfer heat from one place to the other, say, by means of refrigerator pump.

**Some important criteria of spontaneous physical and chemical changes:**

1. Spontaneous change is one-way or unidirectional.
2. For a spontaneous change to occur, time is no factor. A spontaneous reaction may take place rapidly or very slowly.
3. If the system is not in equilibrium state (unstable), a spontaneous change is inevitable. The change will continue till the system attains the state of

equilibrium.

4. Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed. To take the system away from equilibrium, some external work must be done on the system.
5. Spontaneous change is accompanied by decrease of internal energy or enthalpy ( $\Delta R$ ).

**ENTROPY (S)**

It is a thermodynamic state quantity that is a measure of the randomness or disorder of molecules of the system.

The change in disorder accompanying a process from start to completion is represented by  $\Delta S$ . The entropy of a system is a state function and depends only on the initial and final states of the system. The change in entropy,  $\Delta S$ , for any process is given by the equation,

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

When  $S_{\text{final}} > S_{\text{initial}}$ ,  $\Delta S$  is positive,

A process accompanied by an increase in entropy tends to be spontaneous. The entropy of the system increases if it goes from less orderly state to more orderly state and vice-versa. This concept of entropy has led to the conclusion that all substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy. In case of a perfect crystal the entropy is zero. This is Third law of Thermodynamics. Entropy change for an ideal gas. Entropy is a state function and its value depends on two of the three variables T, P and V.

**(a) T and V as variables:**

$$\Delta S = 2.303 n C_u \log \frac{T_2}{T_1} + 2.303 R \log \frac{V_2}{V_1}$$

**(b) P and T as Variables:**

$$\Delta S_u = 2.303 \times n \times C_u \log \frac{T_2}{T_1}$$

Entropy change during a process is defined as the amount of heat evolved or absorbed isothermally and reversibly divided by the absolute temperature at which the heat is evolved or absorbed

$$[\Delta S = q_{\text{rev}}/T]$$

**Unit of entropy change:** JK<sup>-1</sup> mol<sup>-1</sup>

**Entropy change during phase transformations:**

**1. Entropy of fusion :**

It is the change in entropy when 1mole of a solid substance changes into liquid form at the melting temperature.

$$\Delta S_{\text{fusion}} = S_{\text{liq}} - S_{\text{solid}} = \Delta H_{\text{fusion}}/T_m$$

**2. Entropy of vaporization :** It is the entropy change when 1 mole of a liquid changes into vapours at its boiling temperature.

$$\Delta S_{\text{vap}} = S_{\text{liq}} - \Delta H_{\text{vap}}/T_b$$

**3. Entropy of sublimation :** It is the entropy change when 1mole of the solid changes into vapour at a particular temperature .

$$\Delta S_{\text{sub}} = S_{\text{vap}} - S_{\text{solid}} = \Delta H_{\text{sub}}/T_m$$

**Note:**

Entropy increases not only when a solid melts or sublimates .or decomposes to give one or more gases or a liquid evaporates. It also increases when the number of molecules of products is greater than the molecules of reactants.

**The Second Law of Thermodynamics**

The second law of thermodynamics states that whenever a spontaneous process takes place, it is accompanied by increase in the total energy of the universe. Term 'universe' to mean system and the surrounding.

$$\Delta S_{\text{univ}} = S_{\text{syst}} + \Delta H_{\text{surr}}$$

The second law, tells that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases.

$$\Delta S_{\text{univ}} > 0.$$

When a reversible process occurs, the entropy of the system remains constant,

$$\Delta S_{\text{univ}} = 0$$

Since the entire universe is undergoing spontaneous change, the second law can be most generally and concisely stated as the entropy of the system is constantly increasing. In term of entropy second law of thermodynamic may be defined as - all spontaneous processes are accompanied by a net increase of entropy, i.e., for all the spontaneous processes, the total entropy changes  $\Delta S$  is positive.

**Third Law of Thermodynamics**

The entropy of all crystalline solids may be taken as zero at the absolute zero of temperature. It is used in the calculation of absolute entropy of any substance in any state at any temperature.

$$\lim_{T \rightarrow 0} S = 0$$

As the temperature is raised, the molecules begin to vibrate. The number of ways in which the vibrational energy can be distributed increases with increase in temperature and the entropy of the solid increases steadily as the temperature increases. At the melting point of a solid, there is a discontinuous jump in entropy because there are many more ways of arranging the molecules in the liquid than in the solid. An even greater jump in entropy is observed at the boiling point because molecules in the gas are free to occupy a more larger volume and randomness increase.

**THERMOCHEMISTRY**

We know that every substance has a definite amount of energy known as the intrinsic energy or internal energy, E. Its exact value cannot be determined but the change in internal energy,  $\Delta E$ , can be accurately measured experimentally. When the internal energy of reactants ( $E_r$ ) is greater than the internal energy of the products ( $E_p$ ), difference of internal energy,  $\Delta E$ , is released as heat energy.

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

$$\text{or } \Delta E = E_p - E_r$$

Such a reaction is called exothermic reaction. If the internal energy of the products ( $E_p$ ) is greater than that of the reactants ( $E_r$ ), heat is absorbed from the surroundings. Such a reaction is called endothermic reaction. The amount of heat released or absorbed in a chemical reaction is termed the heat of reaction. The energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and the formation of new bonds. Thus thermochemistry provides useful information regarding the bond energies.

**Unit of energy change:**

Calorie (cal.), kilocalorie (1 kcal = 1000 cal), Joule (J) and kilojoule (kJ). 1 cal = 4.18 J and 1 kcal = 4.18 kJ.

**ENTHALPY OF A REACTION**

Thermochemical measurements are made either at Constant volume or Constant pressure. The magnitudes of changes observed under the two conditions are different. The change in internal energy ( $\Delta E$ ) is the heat change accompanying a chemical reaction at constant volume because no external work is performed. However at constant pressure not only does the change in internal energy take place but

work is also involved because of expansion or contraction. Enthalpy of a system is defined as the sum of internal energy and product of its pressure and volume,

$$\text{i.e. } H = E + PV$$

where  $E$  = internal energy ;

$P$  = pressure, of the system

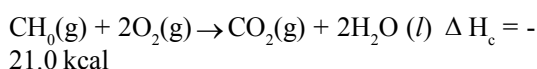
$V$  = volume of the system.

It is also called Heat content.

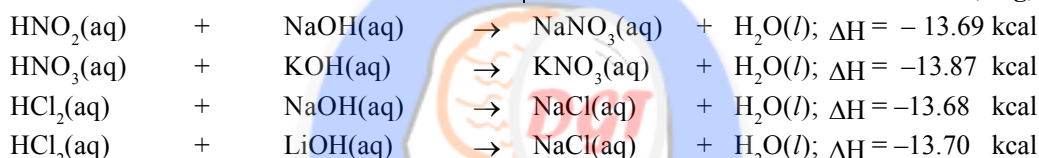
### HEAT OF COMBUSTION ( $\Delta H_c$ )

It is defined as the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.

e.g, heat of combustion of methane is -21.0 kcal (= 87.78 kJ) as shown by the equation.

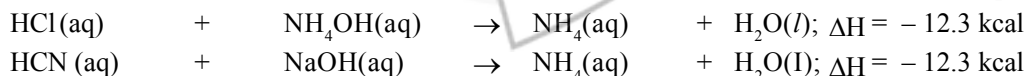


Heat of combustion of a substance ( $\Delta H_c$ ) is always negative, i.e heat energy is evolved during

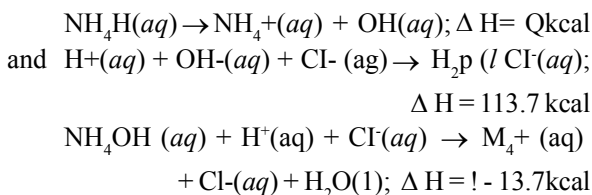


The heat of neutralisation of a strong acid and strong base is -13.7 kcal, no matter which acid or base is employed. This regularity has been explained satisfactorily with the help of the theory of ionisation. If HA and BOH represent any strong acid and any strong base respectively and equivalent amounts of these in dilute solution be mixed, we have

The heat of neutralisation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxyl ions, when weak acids or weak bases are neutralised by strong bases or strong acids respectively, the heat of neutralisation differs widely from -13.7 kcal. This is shown by the following examples:



In such cases the neutralisation process involves not only the union of hydrogen and hydroxyl ions but also the dissociation of the weak acid or base. Thus measured heat of neutralisation is, equal to the heat given out in the union of  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  ions plus the heat accompanying the dissociation of weak acid or weak base, neutralisation of  $\text{NH}_4\text{OH}$  with HCl, can be represented as :



the process of combustion.

**Unit:** cal  $\text{g}^{-1}$  or kcal  $\text{g}^{-1}$  or kJ  $\text{g}^{-1}$

### HEAT OF SOLUTION

It is defined as the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature. For example, when one mole of copper sulphate is dissolved in water so that we get one molar solution, the heat absorbed is 78.5 kJ. If the solution so obtained is further diluted, there will again be a change in enthalpy. If we go on diluting the solution, a stage will come when further dilution produces no thermal effect. This state is called the state of infinite dilution.

### HEAT OF NEUTRALISATION OF CHEMICAL THERMODYNAMICS

**The heat of neutralisation is defined as the change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or vice versa in dilute solution, e.g,**

But the measured heat of neutralisation is -12.3 kcal, therefore

$$Q - 13.7 = -12.3$$

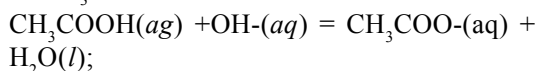
$$Q = 13.7 - 12.3 = 1.4 \text{ kcal}$$

Hence the heat of dissociation of  $\text{NH}_4\text{OH}$  is 1.4 kcal, i.e 1.4 kcal of heat is absorbed when one mole of ammonium hydroxide is dissociated into ions. In general, the heat of dissociation of a weak acid or weak base may be defined as the change in enthalpy of the system when one mole of it is dissociated into ions.

### HEAT OF IONIZATION OF WEAK ACIDS AND WEAK BASES

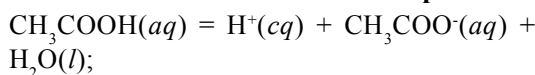
It may be defined as the change in heat content

when one mole of weak acid or weak base is completely ionized in solution, e.g. neutralization of  $\text{CH}_3\text{COOH}$  with  $\text{NaOH}$

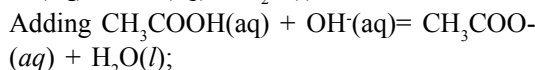
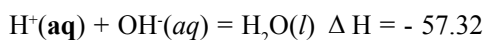


$$\Delta H = -55.78 \text{ kJ}$$

**Reaction can be written in two step :**



$$\Delta H = x \text{ kJ}$$



$$\Delta H = (x - 57.32) \text{ kJ}$$

On comparison, we get

$$x - 57.32 = -55.78,$$

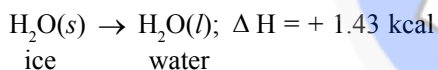
$$x = 1.54$$

Therefore heat of ionization of acetic acid

$$= +1.54 \text{ kJ}$$

### HEAT OF FUSION

It is defined as the heat change (or enthalpy change) when one mole of a solid substance is converted in to the liquid state at its melting point. e.g. melting of one mole of ice at its melting point,  $0^\circ\text{C}$  or  $273 \text{ K}$ . The process can be represented as

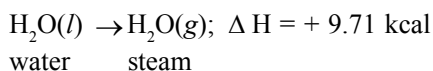


and is accompanied by the absorption of  $1.43 \text{ kcal}$  of heat. From the values of heats of fusion of various substances we can compare their magnitudes of intermolecular forces. Greater the heat of fusion of a substance higher the magnitude of intermolecular forces.

### HEAT OF VAPORISATION

It is the heat change (or enthalpy change) when one mole of liquid is converted into vapour or gaseous state it boiling point.

e.g., when one mole of water is converted into steam at  $100^\circ\text{C}$  or  $373 \text{ K}$ , the heat absorbed is  $9.71 \text{ kcal}$  which is the heat of vaporisation of water. The change can be represented as :



The heats of vaporisation of ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) and benzene ( $\text{C}_6\text{H}_6$ ) are  $7.29 \text{ kcal mol}^{-1}$  and  $7.36 \text{ kcal mol}^{-1}$  respectively. The values of heats of vaporisation can also be used for the

comparison of the magnitude intermolecular forces of attraction in liquids.

### HEAT OF SUBLIMATION

Sublimation is a process when a solid changes directly into gaseous state without changing into liquid state it occurs at a temperature below the melting point of the solid. Heat of sublimation is defined as the heat change (or enthalpy change) when one mole of a solid is directly converted into the gaseous state at a temperature below its melting point.

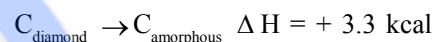
e.g., the heat of sublimation of iodine is  $14.92 \text{ kcal mol}^{-1}$ . It can be represented as



### HEAT OF TRANSITION

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

e.g., the transition of diamond into amorphous carbon may be represented as



Similarly,  $\text{S}_{\text{monoclinic}} \rightarrow \text{S}_{\text{rhombic}}$

and  $\text{P}_{\text{white}} \rightarrow \text{P}_{\text{red}} \quad \Delta H = -1.028 \text{ kcal}$   
where  $-0.016 \text{ kcal}$  and  $-1.028 \text{ kcal}$  are heats of transition of monoclinic sulphur to rhombic sulphur and white phosphorus to red phosphorus respectively.

### HESS'S LAW OF CONSTANT HEAT SUMMATION

We know that heat changes in chemical reactions are equal to the difference in internal energy ( $\Delta E$ ) or heat content ( $\Delta H$ ) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since  $\Delta E$  and  $\Delta H$  are functions of the state of the system, the heat evolved or absorbed in a given reaction must be independent of the manner in which the reaction is brought about. Thus it depends only on the initial state and final states of the system and not the manner or the steps in which the change takes place. This generalisation is known as Hess's Law and may be stated as

*If a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat change is same no matter by which method the change is brought about.*

## OBJECTIVE TYPE QUESTIONS

1. The value of  $\Delta S$  is negative for which of the following process?  
 a) Burning of rocket fuel  
 b) Dissolution of sugar  
 c) Sublimation of iodine;  
 d) Freezing of water
2. Which one of the following statements is wrong?  
 a) The branch of chemistry which deals with energy changes involved in chemical reactions, is called chemical energetics.  
 b) Renewable source of energy is also called non-conventional source of energy.  
 c) Non-renewal source of energy is also called conventional source of energy.  
 d) Coal, lignite, natural gas, crude petroleum oil, uranium etc. renewable sources of energy.
3. Carbon and carbon monoxide burn in oxygen to give carbon dioxide according to the equations.  

$$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \quad \Delta H = -394 \text{ kJ} \dots(\text{i})$$

$$2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}); \quad \Delta H = -569 \text{ kJ} \dots(\text{ii})$$
 The heat of formation of carbon monoxide would be  
 a) -109.5 kJ                      b) +109.5 kJ  
 c) +108.5 kJ                      d) -108.5 kJ
4. What is the enthalpy changed for  $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$  if heat of formation of  $\text{H}_2\text{O}(\text{l})$  and  $\text{H}_2\text{O}_2(\text{l})$  are -188 and -286 kJ/mole respectively?  
 a) -196 kJ/mole                      b) 196 kJ/mole  
 c) 948 kJ/mole                      d) -948 kJ/mole.
5. Combustion of hydrogen in a fuel cell at 300 K is represented as  

$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$$
 If  $\Delta H$  and  $\Delta G$  are -241.60 kJ mol<sup>-1</sup> and -228.40 kJ per mole of  $\text{H}_2\text{O}$ , the value of  $\Delta S$  for the aforesaid process is  
 a) 4.4 kJ                      b) -88 J  
 c) +88 J                      d) -44 J
6. All the naturally occurring processes proceed spontaneously in a direction which leads to  
 a) increase in enthalpy of system  
 b) decrease in entropy of system  
 c) increase in entropy of system  
 d) increase in entropy of universe
7. A gas absorbs 100 calories of heat energy and is compressed from 10.0 litres to 5.0 litres by applying an external pressure at 2.0 atm. The change in internal energy for the gas is  
 a) 312 cal                      b) 342 cal  
 c) 426 cal                      d) 562 cal
8. The enthalpy of neutralisation of sodium hydroxide and sulphuric acid is -57 kJ mol<sup>-1</sup> and with ethanoic acid -55.0 kJ mol<sup>-1</sup>, because  
 a) ethanoic acid is a monobasic acid, but sulphuric acid is a dibasic  
 b) ethanoic acid is only partly ionised, hence neutralisation is incomplete.  
 c) ethanoic acid is a weak acid and hence requires less sodium hydroxide for neutralisation.  
 d) some heat is used to ionise the ethanoic acid completely.
9. Given that :  

$$\text{C} + \text{O}_2 \rightarrow \text{CO}_2; \quad \Delta H = -X \text{ kJ}$$

$$2\text{CO}_2 \rightarrow 2\text{CO}; \quad \Delta H = -Y \text{ kJ}$$
 The enthalpy of formation of carbon monoxide will be  
 a)  $Y - 2X$                       b)  $\frac{2X - Y}{2}$   
 c)  $\frac{Y - 2X}{2}$                       d)  $2X - Y$
10. A hypothetical reaction  $\text{X} \rightarrow 2\text{Y}$  proceeds by the following sequence of steps  

$$\frac{1}{2}\text{X} \rightarrow \text{Z}; \quad \Delta H = q_1$$

$$\text{Z} \rightarrow 2\text{W}; \quad \Delta H = q_2$$

$$\text{W} \rightarrow \frac{1}{2}\text{Y}; \quad \Delta H = q_3$$
 The values of  $\Delta H$  of reaction is  
 a)  $q_1 + q_2 + q_3$   
 b)  $2q_1 + 2q_2 + 3q_3$   
 c)  $2(q_1 + q_2 + 2q_3)$   
 d)  $2(q_1 + q_2 + q_3)$
11. The values of  $\Delta H_f$  of  $\text{C}_2\text{H}_2(\text{g})$  and  $\text{C}_6\text{H}_6(\text{g})$  are respectively 230 and 85 kJ mol<sup>-1</sup>. The standard enthalpy change for trimerisation of acetylene to benzene is  
 a) 205 kJ mol<sup>-1</sup> of benzene  
 b) 605 kJ mol<sup>-1</sup> for benzene  
 c) -605 kJ mol<sup>-1</sup> of benzene





- $\text{H}_2(\text{g}) \rightarrow + \text{H}(\text{g}) + \text{OH}(\text{g}); \Delta H = 498 \text{ kJ mol}^{-1}$   
 $\text{OH}(\text{g}) \rightarrow + \text{H}(\text{g}) + \text{O}(\text{g}); \Delta H = 428 \text{ kJ mol}^{-1}$   
 From the above data, the value of  $\Delta H_{\text{O}-\text{H}}$  bond is  
 a) 498 kJ mol<sup>-1</sup>                      b) 428 kJ mol<sup>-1</sup>  
 c) 463 kJ mol<sup>-1</sup>                      d) 70 kJ mol<sup>-1</sup>
26. Work done in vaporiation of one mol of water at 373 K against the pressure of 1 atmosphere is approximately  
 a) - 3100.0 J                              b) 31.20 J  
 c) - 20.2 J                                d) + 2p.2 J
27. Given the following:  $\text{C}(\text{s}) \rightarrow + \text{C}(\text{g}); \Delta H = 170.9 \text{ kcal mol}^{-1}$   
 $\Delta H_2(\text{g}) \rightarrow + \text{H}(\text{g}), \Delta H = 52.0 \text{ kcal mol}^{-1}$   
 $\frac{1}{2} H_f(\text{CH}_4) = - 17.89 \text{ kcal mol}^{-1}$   
 The average C-H bond energy in  $\text{CH}_4$  would be  
 a) +99.2 kcal                              b) -99.2 kcal  
 c) +24.8 kcal                              d) -24.8 kcal.
28. Given:  
 (i)  $2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) \rightarrow + \text{C}_2\text{H}_4(\text{g}); \Delta H = 716.7 \text{ kJ}$   
 (ii)  $\text{C}(\text{graphite}) \rightarrow + \text{C}(\text{g}), \Delta H = 716.7 \text{ kJ}$   
 (iii)  $\text{H}_2(\text{g}) \rightarrow + 2\text{H}(\text{g}), \Delta H = 435.9 \text{ kJ}$   
 (iv) C - H bond energy as 416 kJ  
 The C - C bond energy would be  
 a) 2875.65 kJ mole<sup>-1</sup>  
 b) -2875.65 mole<sup>-1</sup>  
 c) +329.65 kJ mol<sup>-1</sup>  
 d) -392.65 kJ mol<sup>-1</sup>
29. Which of the following expression gives the value of heat capacity of 1 mol of ideal gas at constant pressure?  
 a)  $\frac{dE}{dT}$                                       b)  $\frac{dS}{dT}$   
 c)  $\frac{dH}{dT}$                                       d)  $\frac{dH}{dP}$
30.  $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \Delta H = -x\text{kJ}$   
 The value of  $\Delta H$  represents  
 a) enthalpy of solution of copper (II) sulphate  
 b) enthalpy of hydration of copper (II) sulphate  
 c) enthalpy of hydrolysis of copper (II) sulphate  
 d) lattice energy of copper (II) sulphate.
31. A system X undergoes following changes.  
 $\text{X} \rightarrow \text{W} \rightarrow \text{Z} \rightarrow \text{X}$
- $(P_1 V_1 T_1) (p_2 V_2 T_1) (P_3 V_2 T_2) (P_1 V_1 T_1)$   
 The overall process may be called  
 a) reversible process  
 b) cyclic process  
 c) cyclic as well as reversible  
 d) isochoric process.
32. In an oven, using coal (assume the coal is 80% carbon in weight), insufficient oxygen is supplied such that 60% of carbon is converted to  $\text{CO}_2$  and 40% carbon is converted to CO. The heat generated, when coal is burnt in this fashion would be  
 Given:  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 394 \text{ kJ}$   
 $\text{C}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow + \text{CO}(\text{g}) + 111 \text{ kJ}$   
 a) 183,200 kJ                              b) 187,200 kJ  
 c) 185,200 kJ                              d) 181,200 kJ
33. In the above example, by using good oven all the carbon is converted into  $\text{CO}_2$  alone. The percentage lost in heat for inefficient oven would be  
 a) 50%                                        b) 40%  
 c) 30.25%                                d) 20%
34. The variation of enthalpy of reaction is given by the .  
 a) Clapyron's equation  
 b) Hess's law  
 c) Gibb's equation  
 d) Kirchoff's equation
35. One mole of  $\text{H}_2\text{SO}_4$  is completely neutralised with 2 moles of NaOH in dilute solutions. The amount of heat evolved during the process is  
 a) 57.0 kJ                                      b) > 57.0 kJ  
 c) < 57.0 kJ                                d) > 114.0 kJ
36. The process;  $\text{CH}_3\text{COOH} \rightarrow + \text{CH}_3\text{COO}^- + \text{H}^+$ , should be  
 a) exothermic  
 b) endothermic  
 c) neither exothermic nor endothermic  
 d) exothermic or endothermic depending upon tern perature.
37. Gobar gas obtained by bacterial fermentation of animal refuse contains mainly methane. If heat of combustion of  $\text{CH}_4$  is 809 kJ, then gobar gas produced per day for small village community of 100 families, assuming that each family has to be supplied 20,000 kJ of energy per day to meet all needs and that the methane content in gobar gas is 80% by weight, it would be

- a) 41.0 kg                      b) 49.0 kg  
c) 49.44 kg                     d) 22 kg
38. A man submits to a diet of 9,500 kJ per day and expends energy in all forms to a total of 12,000 kJ per day. If the energy lost was stored as sucrose (1632 kJ per 100 g), then number of days the man will take to lose 1 kg of sucrose (ignoring water loss) would be  
a) 6 days                        b) 6.53 days  
c) 5 days                        d) 4 days
39. The bond dissociation energies of four bonds C - A, C - B, C - D and C - E are respectively 240, 382, 276 and 486 kJ/mole. The atom with smallest size is  
a) B                                b) C  
c) A                                d) E
40. Which of the following process should be endothermic?  
a)  $C(s) + O_2(g) \rightarrow CO_2(g)$   
b)  $A^+(g) + X^-(g) \rightarrow AX(s)$   
c)  $O^-(g) + e^- \rightarrow O^{2-}(g)$   
d)  $Na^+(g) + e^- \rightarrow Na(g)$
41. A substance A(g) with molecular mass 40 has  $\Delta H_f^\circ = 0$ . What is true about it?  
a) A is a molecular solid  
b)  $A(s) \rightarrow A(l)$  is an exothermic process  
c) A is an element  
d) A is a ionic solid
42. For the equilibrium  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$  at 298 K,  $K_p = 1.8 \times 10^{-7}$ ; the value of  $\Delta G^\circ$  would be  
a) 44.80 kJ mol<sup>-1</sup>                b) 45.80 kJ mol<sup>-1</sup>  
c) 38.80 kJ mol<sup>-1</sup>                d) 80.80 kJ mol<sup>-1</sup>
43. Which one of the following statements is not correct?  
a) For isochoric process,  $dE = 0$   
b) For isothermal process,  $dT = 0$   
c) For adiabatic process,  $dQ = 0$   
d) For isobaric process,  $dP = 0$
44. The heats of solution of anhydrous  $CuSO_4$  and hydrated  $CuSO_4 \cdot 5H_2O$  are -66.5 and 11.7 kJ/mole respectively. Calculate the heat of hydration of  $CuSO_4$  to  $CuSO_4 \cdot 5H_2O$ .  
a) 54.8 kJ                        b) - 54.8 kJ  
c) - 78.2 kJ                      d) none of these
45. According to Gibb's Helmholtz equation  
a)  $\Delta G = \Delta H$   
b)  $\Delta G > \Delta H$   
c)  $\Delta G$  can be  $>$  or  $<$   $\Delta H$   
d)  $\Delta G < \Delta H$ .
46. Given that  
 $H_2O(l) \rightarrow H_2O(g); \Delta H = +43.7$  kJ  
 $H_2O(s) \rightarrow H_2O(l); \Delta H = +6.05$  kJ  
The value of  $\Delta H$  (Sublimation of ice) is  
a) 49.75 kJ mol<sup>-1</sup>                b) 37.65 kJ mol<sup>-1</sup>  
c) 43.7 kJ mol<sup>-1</sup>                d) -43.67 kJ mol<sup>-1</sup>
47. When a solid is heated to its melting point  $T_1$  and then to its boiling point  $T_2$  then changes of  $\Delta S$  with T can be represented as
- 
48. For a reaction which one of the following is not a condition for spontaneous change or an equilibrium?  
a)  $\Delta H = -ve$  and  $T \Delta S = 0$   
b)  $\Delta G = +ve$  and  $\Delta H = 0$   
c)  $\Delta H = T \Delta S$   
d)  $\Delta H < T \Delta S$ ,  $\Delta S$  is -ve and reaction is exothermic
49. When one mole is heated at constant volume, temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which of the following statement is correct?  
a)  $Q = W = 500J$ ,  $\Delta U = 0$   
b)  $Q = \Delta U = 500J$ ,  $W = 0$   
c)  $Q \neq W = 500 J$ ,  $\Delta U = 0$   
d)  $\Delta U = 0$ ,  $Q = W = - 500 J$ .
50.  $\Delta S^\circ$  and  $\Delta H^\circ$  for combustion of methane are 186 JK<sup>-1</sup> and -74.8 kJ mol<sup>-1</sup> respectively. The value of  $\Delta E^\circ$  for the process would be  
a) unpredictable                b) (74.8 - R) kK-1  
c) 74.78 kJ                        d) (596R - 74.8) kJ.
51. Given the reaction:  $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ ;  $\Delta H = 40$  kJ.  
The  $\Delta H$  is specifically called  
a) Heat of formation of CO

- b) Heat of combustion  
c) Heat of reaction  
d) Heat of hydrogenation of C = O bond.
52. Given the following data  
 $C + O_2 \rightarrow CO_2, \Delta H = -94 \text{ kcal}$   
 $CO + \frac{1}{2} O_2 \rightarrow CO_2; \Delta H = 67.7 \text{ kcal}$   
 The heat of formation of CO calculated from the data would be  
 a) +40.4 kcal                      b) +26.3 kcal  
 c) -26.3 kcal                      d) -52.6 kcal
53. Following reaction occurs in an automobile  
 $2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2 + 18H_2O(g)$   
 This sign of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  respectively will be  
 a) +, -, +                              b) +, +, -  
 c) -, +, +                              d) -, +, -
54. Enthalpy of  $CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH$  negative. If enthalpy of combustion of  $CH_4$  and  $CH_3OH$  are  $x$  and  $y$  respectively, then which of the following relation is correct?  
 a)  $x > y$                               b)  $x = y$   
 c)  $x < y$                               d)  $x \geq y$
55. What is correct about heat of combustion?  
 a) It is +ve in some cases while -ve in others.  
 b) It is applicable to gaseous substances only.  
 c) It is always -ve.  
 d) It is always +ve.
56. Which one of the following is likely to have largest value?  
 a) Heat of dissociation of a diatomic molecule  
 b) Heat of fusion of the same substance as solid  
 c) Heat of vaporisation of the same substance as a liquid  
 d) Heat of sublimation of the same
57. In thermodynamics, a process is called reversible when  
 a) surroundings and system change into each other  
 b) there is no boundary between system and surroundings  
 c) the surroundings are always in equilibrium with the system  
 d) the system changes into the surroundings spontaneously.
58. The heat of neutralisation of  $HCl$  and  $NaOH$  is  
 a) zero                                      b) -57.3 kJ
- c) +57.3 kJ                              d) none of these
59.  $2Zn + O_2 \rightarrow 2ZnO \Delta G^\circ = -616 \text{ J}$   
 $2Zn + S_2 \rightarrow 2ZnS \Delta G^\circ = -293 \text{ J}$   
 $S_2 + 2O_2 \rightarrow 2SO_2 \Delta G^\circ = -408 \text{ J}$   
 $\Delta G^\circ$  for the following reaction is :  
 $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$   
 a) -717 J                              b) -314 J  
 c) -501 J                              d) +731 J.
60.  $XY$ ,  $X_2$  and  $Y_2$  are diatomic molecules if  $\Delta H_{x-x}$ ,  $\Delta H_{y-y}$  and  $\Delta H_{x-y}$  are in the ratio of 2 : 1 : 2 and enthalpy of formation of  $XY$  from  $X_2$  and  $Y_2$  is  $-100 \text{ kJ mol}^{-1}$ . The value of  $\Delta H_{x-x}$  in  $\text{kJ mol}^{-1}$  is  
 a) 200                                      b) 400  
 c) 250                                      d) 500.
61.  $Ba^{2+}(aq) + 8O_4^{2-}(aq) \rightarrow BaSO_4(s); \Delta H = -22.4 \text{ kJ}$   
 The heat change represented by above equation is called  
 a) heat of formation of  $BaSO_4$   
 b) heat of precipitation  
 c) heat of association  
 d) integral heat of formation
62. The heat evolved in the combustion of benzene is given by the equation:  
 $C_6H_6(l) + 7\frac{1}{2} O_2(g) \rightarrow 3H_2O(l) + 6CO_2(g),$   
 $\Delta H = 781.0 \text{ kcal mol}^{-1}$   
 Which of the following quantities of heat energy will be evolved when 39 g of benzene is burnt in an open container?  
 a) 122.25  $\text{kcal mol}^{-1}$   
 b) 390.5  $\text{kcal mol}^{-1}$   
 c) 1562.0  $\text{kcal mol}^{-1}$   
 d) 586.75  $\text{kcal mol}^{-1}$
63. Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atom is 208 kcal at  $25^\circ\text{C}$ . The bond energy of H-H bond will be  
 a) 104 kcal                              b) 10.4 kcal  
 c) 104 kcal                              d) 52 kcal
64. At  $27^\circ\text{C}$  latent heat of fusion of a compound is  $2930 \text{ J mol}^{-1}$  Entropy change is  
 a)  $9.07 \text{ J mol}^{-1} \text{ K}^{-1}$   
 b)  $0.977 \text{ J mol}^{-1} \text{ K}^{-1}$   
 c)  $10.77 \text{ J mol}^{-1} \text{ K}^{-1}$   
 d)  $9.77 \text{ J mol}^{-1} \text{ K}^{-1}$
65. The enthalpy of formation steadily change from  $-17.89 \text{ kcal mol}^{-1}$  to  $-49.82 \text{ kcal mol}^{-1}$  in going

- from  $\text{CH}_4$  to  $\text{C}_2\text{H}_6$  to  $\text{C}_8\text{H}_{18}$ . The value of  $\Delta G^\circ_f$  however, shows the opposite trend - 12.12 kcal mol<sup>-1</sup> to - 4.14 kcal mol<sup>-1</sup>. The correct reason for this is
- number of possible isomers increases with the increase in the number of C atoms
  - number of C - C bonds increases in relation to C-H bonds
  - formation of  $\text{C}_n\text{H}_{2n+2}$  from  $n\text{C}$  and  $(n+1)\text{H}_2$  molecules cause considerable decrease in entropy and  $\Delta S$  becomes more negative with increase in value of n.
  - none of the above reason is correct.
66. Which of the following changes at constant T, p can be associated with positive value of work as per conversions?
- $\text{Sn(s)} + 2\text{F}_2(\text{g}) \rightarrow \text{SnF}_4(\text{s})$
  - $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
  - $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
  - $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO(s)} + \text{CO}_2(\text{g})$ .
67. For the process: dry ice  $\rightarrow \text{CO}_2(\text{g})$
- $\Delta H$  is -ve while  $\Delta p$  + ve.
  - 10.4 kcal
  - both  $\Delta H$  and  $\Delta p$  are +ve
  - $\Delta H$  is +ve while  $\Delta p$  is -ve
68.  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}$ ;  $\Delta H = 44$  kcal.  
 $2\text{Na(s)} + 2\text{HCl(g)} \rightarrow 2\text{NaCl(s)} + \text{H}_2(\text{g})$ ;  
 $\Delta H = -152$  kcal.
- For the reaction,  $\text{Na(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$ ,
- $\Delta H = ?$
- 54 kcal
  - 98 kcal
  - 196 kcal
  - 108 kcal
69. For the reaction  $\text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(l)}$ , which one is true?
- $\Delta H = \Delta E - RT$
  - $\Delta H = \Delta E + RT$
  - $\Delta H = \Delta E + 2RT$
  - $\Delta H = \Delta E - 2RT$
70. For hypothetical reversible reaction,
- $$\frac{1}{2}\text{A}_2(\text{g}) + \frac{3}{2}\text{B}_2(\text{g}) \rightleftharpoons \text{AB}_3(\text{g})$$
- the values of  $\Delta H = -20$  kJ while the values of standard entropies of  $\text{A}_2$ ,  $\text{B}_2$ ,  $\text{AB}_3$  are 60, 40, 50 JK<sup>-1</sup> mol<sup>-1</sup> respectively. The temperature at which the above reaction attains equilibrium will
- approximately, be
- 400 K
  - 500 K
  - 250 K
  - 200 K.
71. The enthalpy change for a given reaction at 298K is - x J mol<sup>-1</sup>. If the reaction occurs spontaneously at 298 K, then entropy change at that temperature
- can be negative but numerically larger than  $x/298$
  - can be negative but numerically smaller than  $x/298$
  - cannot be negative
  - cannot be positive
72. For a process to be spontaneous, the entropy of the
- system must increase
  - surroundings must increase
  - surroundings must decrease
  - universe must increase
73. An exothermic reaction is one in which the reacting substances
- have more energy than the products
  - have less energy than the products
  - have the same energy as the products
  - are at a higher temperature than the products
74. Which statement is correct about entropy
- The value of entropy of pure crystalline is zero at absolute zero
  - The value of entropy of pure crystalline is positive at absolute temperature
  - The value of entropy of all crystalline is zero at absolute temperature
  - The value of entropy of pure crystalline is zero at 0°C.
75. In certain chemical reaction  $\Delta H = 150$  kJ and  $\Delta S$  is 100 JK<sup>-1</sup> at 300 K. The value of  $\Delta G$  would be
- zero
  - 300 kJ
  - 330 kJ
  - 120 kJ
76. The internal energy change ( $\Delta H$ ) of a process does not depend upon
- amount of substance undergoing the change
  - temperature
  - path of the process
  - nature of substance undergoing the change.
77.  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ ;  $\Delta H^\circ = -68$  Kcal .....(i)
- $\text{K} + \text{H}_2\text{O} + \text{aq} \rightarrow \text{KOH(aq)} + \frac{1}{2}\text{H}_2$ ;  $\Delta H^\circ = -48$

- Kcal ... (ii)
- $\text{KOH} + \text{aq} \rightarrow \text{KOH}(\text{aq}); \Delta H^\circ = -14$
- Kcal. ... (iii)
- For the above data, the standard heat of formation of KOH in kcal is
- a)  $-68 + 48 - 14$       b)  $-68 - 48 + 14$   
 c)  $68 - 48 + 14$       d)  $68 + 48 + 14$
78. The heats evolved in combustion of rhombic and monoclinic sulphur are respectively 70960 and 71030 cal m respectively. What will be heat of conversion of rhombic sulphur to monoclinic?
- a) 70960 cal      b) 71030 cal  
 c) -70 cal      d) +70 cal
79. From the following which is the correct relation?
- a)  $\Delta U = \Delta Q - W$   
 b)  $\Delta W = \Delta U + \Delta Q$   
 c)  $\Delta U = \Delta W - \Delta Q$   
 d) None of these
80. Which of the following thermochemical equation will represent the enthalpy of formation of  $\text{OH}^-$  (aq) ion?
- a)  $\frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{H}_2(\text{g}) + e^- + \text{aq} \rightarrow \text{OH}^-(\text{aq})$   
 b)  $\text{H}_2\text{O} \dots \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$   
 c)  $\text{H}^+(\text{aq}) + \text{O}^{2-}(\text{aq}) \rightarrow \text{HO}^-(\text{aq})$   
 d) None of these
81. Given:  $\text{C} + 2\text{S} \rightarrow \text{CS}_2; \Delta H^\circ = +117 \text{ kJ}$   
 $\text{C} + \text{O}_2 \rightarrow \text{CO}_2; \Delta H^\circ = -393 \text{ kJ}$   
 $\text{S} + \text{O}_2 \rightarrow \text{SO}_2; \Delta H^\circ = -297 \text{ kJ}$
- The value of  $\Delta H_{\text{combustion}}$  of carbon disulphide in  $\text{kJ mol}^{-1}$  is
- a) -1104      b) +1104  
 c) +807      d) -807
82. For a system in equilibrium,  $\Delta G = 0$ , under conditions of constant
- a) temperature and pressure  
 b) temperature and volume  
 c) pressure and volume  
 d) energy and volume
83. Given:  $\text{C}(\text{diamond}) + \text{O}_2 \rightarrow \text{CO}_2; \Delta H = -395 \text{ kJ}$   
 $\text{C}(\text{graphite}) + \text{O}_2 \rightarrow \text{CO}_2; \Delta H = 393 \text{ kJ}$
- The heat of formation of diamond from graphite is
- a) +2.0 kJ      b) -1.5 kJ  
 c) -7.88 kJ      d) +78.8 kJ
84. If  $\Delta H_{\text{vap}}$  of pure water at  $100^\circ\text{C}$  is  $40.627 \text{ kJ mol}^{-1}$ . The value of  $\Delta S_{\text{vap}}$  is
- a)  $108.91 \text{ kJ mol}^{-1}$       b)  $108.91 \text{ JK}^{-1} \text{ mol}^{-1}$   
 c)  $606.27 \text{ JK}^{-1} \text{ mol}^{-1}$       d)  $808.27 \text{ JK}^{-1} \text{ mol}^{-1}$
85. Which of the following expressions gives the relationship between  $\Delta S_{\text{universe}}$  and free energy change?
- a)  $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$   
 b)  $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{syst}}$   
 c)  $\Delta S_{\text{universe}} = \frac{-\Delta G}{T} + \Delta H$   
 d)  $\Delta S_{\text{universe}} = \frac{\Delta G}{T}$
86. The standard free energy change for a gaseous reaction at  $27^\circ\text{C}$  is X kcal. If equilibrium constant for a reaction is 100 and R is  $2 \text{ cal K}^{-1} \text{ mol}^{-1}$  Then X is
- a) -2.7636      b) -2.6736  
 c) +2.6746      d) +2.7636
87. Which of the following equation represents standard heat of formation of methane?
- a)  $\text{C}(\text{diamond}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$   
 b)  $\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$   
 c)  $\text{C}(\text{diamond}) + 4\text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g})$   
 d)  $\text{C}(\text{graphite}) + 4\text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g})$
88. In a closed vessel, the following equilibrium exists at  $25^\circ\text{C}$ :
- $\text{H}_2\text{O}(\text{l}) \dots \text{H}_2\text{O}(\text{g})$
- Which statement is correct?
- a)  $\Delta H > 0$       b)  $\Delta S > 0$   
 c)  $H - T \Delta S = 0$       d)  $\Delta H - T \Delta S > 0$
89. For a reaction to occur spontaneously
- a)  $\Delta S$  must be negative  
 b)  $(\Delta H - T \Delta S)$  must be negative  
 c)  $(\Delta H + T \Delta S)$  must be negative  
 d)  $\Delta H$  must be negative.

### Answer Key

Q.No.	Ans	Q.No.	Ans	Q.No.	Ans
1.	d)	2.	d)	3.	a)
4.	a)	5.	b)	6.	d)
7.	b)	8.	d)	9.	c)
10.	c)	11.	a)	12.	c)
13.	a)	14.	d)	15.	c)
16.	c)	17.	a)	18.	c)
19.	c)	20.	b)	21.	b)
22.	b)	23.	d)	24.	a)
25.	c)	26.	a)	27.	b)
28.	c)	29.	c)	30.	b)
31.	b)	32.	b)	33.	c)
34.	d)	35.	b)	36.	b)
37.	c)	38.	b)	39.	d)
40.	c)	41.	c)	42.	c)
43.	a)	44.	c)	45.	c)
46.	a)	47.	a)	48.	d)
49.	b)	50.	d)	51.	c)
52.	c)	53.	d)	54.	c)
55.	c)	56.	d)	57.	c)
58.	b)	59.	a)	60.	b)
61.	b)	62.	b)	63.	a)
64.	d)	65.	c)	66.	a)
67.	d)	68.	b)	69.	a)
70.	b)	71.	b)	72.	a)
73.	a)	74.	a)	75.	d)
76.	d)	77.	b)	78.	c)
79.	a)	80.	a)	81.	a)
82.	a)	83.	a)	84.	b)
85.	d)	86.	b)	87.	b)
88.	d)	89.	b)		



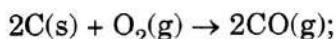


## EXPLANATIONS

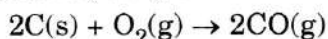
1. Freezing of water involves decrease in randomness.

2. All statements are true except (d) which is wrong. Renewable sources of energy are plant, wood, falling water, vegetable refuse etc.

3. We have to aim at



Multiply equation (i) by 2 and subtract equation (ii) from it, we get



$$2 \times (-394) - (-596) \text{ kJ} = -788 + 596 = -192 \text{ kJ}$$

This value is for the above equation, the half of this value will be heat of formation of CO

$$\text{i.e., } \Delta H = -109.5 \text{ kJ}$$

4.  $\Delta H = H_P - H_R$

$$= (2 \times 188 + 0) - 2 \times 286$$

$$= 376 - 572 = -196 \text{ kJ/mole.}$$

6. Entropy criteria of spontaneity is,  $\Delta S_{\text{Total}} > 0$ .

7.  $dE = Q - W = Q - pdV$

In this case work is done on the gas, hence W is negative.

$$-W = 2(10 - 5) = 10 \text{ litre atm}$$

$$= 242 \text{ cal} \quad \dots (\because 1 \text{ litre atm} = 24.2 \text{ cal})$$

$$\therefore dE = 100 - (-242) = 342 \text{ cal}$$

9.  $\Delta H^\circ = \Sigma \Delta H_f^\circ(\text{Product}) - \Sigma \Delta H_f^\circ(\text{reactant})$

Hence from the given data :

$$-Y = 2 \times \Delta H_f^\circ(\text{CO}_2) - [2 \times \Delta H_f^\circ(\text{CO}) + \Delta H_f^\circ(\text{O}_2)]$$

$$\text{or } -Y = 2(-X) - 2 \times \Delta H_f^\circ(\text{CO}_2) \quad \dots [\because \Delta H_f^\circ(\text{O}_2) = 0]$$

$$\text{or } 2 \times \Delta H_f^\circ(\text{CO}_2) = Y - 2X$$

$$\text{or } \Delta H_f^\circ(\text{CO}_2) = \frac{Y - 2X}{2}$$

10. Multiply equations (i) and (ii) by 2, equation (iii) by 4 and adding, get the final equation.

11.  $3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$

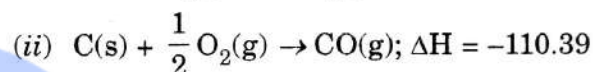
$$\begin{aligned} \Delta H_{\text{reaction}} &= \Delta H_f(\text{C}_6\text{H}_6) - 3\Delta H_f(\text{C}_2\text{H}_2) \\ &= 85 - 3(230) = -605 \text{ kJ mol}^{-1} \text{ benzene} \end{aligned}$$

13. Gibbs equation is,

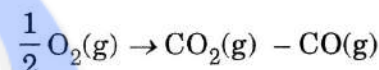
$$\Delta G = \Delta H - T\Delta S, \quad \text{where } \Delta G = 0,$$

The reaction is in equilibrium; when  $\Delta G > 0$ , and the reaction does not take place, and when  $\Delta G < 0$ , the reaction is spontaneous.

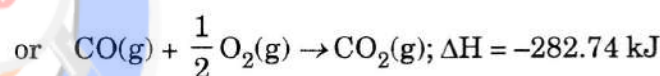
17. Given



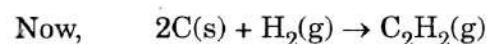
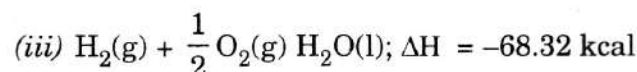
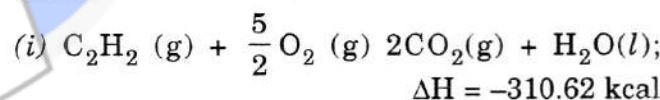
Subtracting equation (ii) from (i), we get



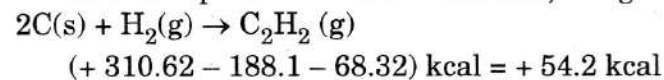
$$\Delta H = -393.13 - (-110.39) = -282.74 \text{ kJ}$$



18. The heat of combustion should be taken negative  
Given



Reverse equation (i), multiply equation (ii) by 2 and sum up all the three reactions, we get



19.  $3\text{H}_2\text{O(l)} \rightarrow 3\text{H}_2\text{O(g)}; \Delta n = 3$

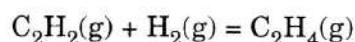
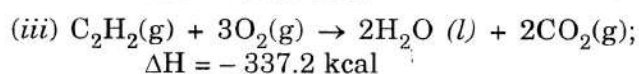
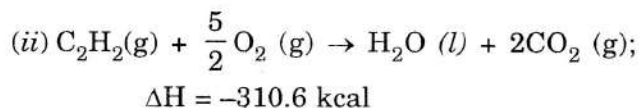
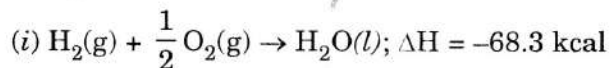
$$\Delta E = \Delta H - \Delta nRT$$

$$= 30 - 3 \times \frac{2}{1000} \times 500 = 27.0 \text{ kcal}$$

20.  $\Delta G = \Delta H - T\Delta S$   
 $= -46.11 \text{ kJ} - 298 \times 0.099 \text{ kJ mol}^{-1}$   
 $= -46.11 \text{ kJ} + 29.5 \text{ kJ} = -16.61 \text{ kJ}$

21.  $\Delta H_{\text{neut}}$  of strong acid/strong base is same.

22. The equation involving the reactions can be written as



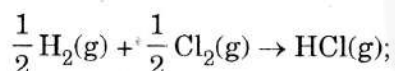
Subtracting equation (iii) from the sum of equation (i) and (ii); we get

$\Delta H = (-310.6 - 68.3) - (-337.2) = -41.7 \text{ kcal}$

Heat of reaction for the hydrogenation of acetylene at constant volume,

$\Delta E = \Delta H - \Delta nRT$   
 $= -41.7 - [(-1) \times 2 \times (273+25) \times 10^{-3}]$   
 $= 41.7 + 0.596 = 41.10 \text{ kcal.}$

23. Required equation is,



Bond breaking :

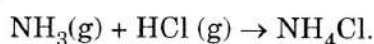
$\Delta H_1(\text{endothermic, +ve}) = \frac{104}{2} + \frac{58}{2} = 81 \text{ kcal}$

$\left(\frac{1}{2} \text{ mole of reactants}\right)$

Bond formation :  $\Delta H_2$  (exothermic, -ve)  
 $= -103 \text{ kcal (for 1 mole HCl)}$

Now  $\Delta H = \Delta H_1 + \Delta H_2 = (81 - 103) \text{ kcal}$   
 $= -22 \text{ kcal}$

24. 20 ml ammonia gas will neutralize with 20 ml hydrogen chloride gas and form ammonium chloride. So, at same temperature and pressure, the volume of gaseous mixture will be 20 ml



25. It is average of bond dissociation energies of two O-H bonds.

26. 1 mol of steam has volume =  $\frac{1 \times 0.082 \times 373}{1}$   
 $= 30.6 \text{ L}$

Work done =  $-30.6 \times 1 \times 101.3 \text{ J}$   
 $= -3099 \approx -3100 \text{ J.}$

27. Required equation is,  $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g});$   
 $\Delta H_f = -17.89 \text{ kcal mol}^{-1}$

Bond breaking :  $\Delta H_1$  positive  $\text{C}(\text{s}) \rightarrow \text{C}(\text{g});$

$+170.9 \text{ kcal mol}^{-1} \left[ \frac{1}{2} \text{H}_2 \rightarrow \text{H}; +52 \text{ kcal mol}^{-1} \right]$

Now,  $\Delta H_1 = +170.9 \text{ kcal mol}^{-1}$   
 $+4 \times 42 \text{ kcal mol}^{-1}$   
 $= 378.9 \text{ kcal mol}^{-1}$

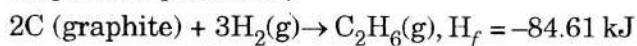
$\therefore \Delta H_f = \Delta H_1 + \Delta H_2$

or  $-17.89 \text{ kcal mol}^{-1} = 378.9 \text{ kcal mol}^{-1} + \Delta H_2$

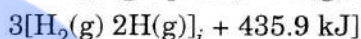
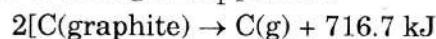
$\therefore \Delta H_2 = -396.79 \text{ kJ mol}^{-1}$

$\therefore \text{Average energy} = \frac{-396.7}{4} = -99.2 \text{ kJ mol}^{-1}$

28. Required equation is,

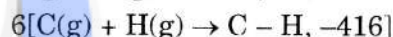
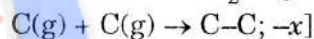


Bond breaking :  $\Delta H_1$  positive



$\Delta H_1 = 2 \times 716.7 \text{ kJ} + 3 \times 435.9 \text{ kJ}$

Bond formation :  $\Delta H_2$  negative



$\therefore \Delta H_2 = -x + 6(-416)$

From Hess's Law :

$\Delta H_f = \Delta H_1 + \Delta H_2 - 84.67 \text{ kJ}$

$= 2 \times 716.7 + 3 \times 435.9 + (-x - 2496)$

$\text{kJ}$

or  $-84.64 = 2741.1 - x - 2496$

or  $x = 245.1 + 84.65 = 329.65$

29.  $C_p = \frac{dH}{dT}$  for one mole of ideal gas.

32. Weight of carbon in 10 kg coal

$= 10 \times \frac{80}{100} = 8 \text{ kg} = 8,000 \text{ g}$

Weight of C converted into  $\text{CO}_2$

$= 8,000 \times \frac{60}{100} = 4,800 \text{ g}$

Weight of C converted into CO

$= 8,000 \times \frac{40}{100} = 3,200 \text{ g}$

Now, 12 (1 mole) of C on combustion into  $\text{CO}_2$  liberates = 394 kJ

$\therefore 4,800 \text{ g of C on combustion liberates}$

$= \frac{394 \text{ kJ} \times 4,800}{12} = 157600 \text{ kJ}$

Also, 12 g (1 mole) of C on combustion into CO liberates = 111 kJ

$$\therefore 3200 \text{ g of C on combustion into CO liberates} \\ = \frac{111 \times 3,200}{12} \text{ kJ} = 29,600 \text{ kJ}$$

$$\text{Total heat liberated} = 157600 \text{ kJ} + 29600 \text{ kJ} \\ = \mathbf{187,200 \text{ kJ}}$$

33. In this case 12 g carbon liberates = 394 kJ heat

$$\therefore 8,000 \text{ g carbon will liberate} = \frac{394 \text{ kJ} \times 8,000}{12} \\ = 262,666.67 \text{ kJ}$$

Heat loss by inefficient oven

$$= (262,666.67 - 187,200) \text{ kJ} \\ = 47546.67 \text{ kJ}$$

$$\text{Loss in heating value} = \frac{75,466.67 \times 100}{262,666.67} \\ = 30.25\%$$

35. 1 mol of  $\text{H}_2\text{SO}_4$  gives 2 mol of  $\text{H}^+$ . Thus, combination of 2 mol of  $\text{H}^+$  ions and 2 mol  $\text{OH}^-$  liberate heat more than 57.1 kJ.

37. Total energy required per day

$$= 100 \times 20,000 \text{ kJ} \\ = 2 \times 10^6 \text{ kJ}$$

Now 809 kJ is produced by burning 16 g  $\text{CH}_4$

$\therefore 2 \times 10^6 \text{ kJ}$  is produced by burning

$$= \frac{16 \times 2 \times 10^6}{809} \text{ g CH}_4 \\ = \frac{16 \times 2 \times 10^3}{809} \text{ kg} = 39.555 \text{ kg.}$$

Gobar gas required to be produced per day

$$= \frac{39.555 \times 100}{80} \text{ kg} = 49.44 \text{ kg}$$

38. Change in internal energy per day,

$$\Delta E = E_2 - E_1 \\ = (12,000 - 9,500) \text{ kJ} = 2500 \text{ kJ}$$

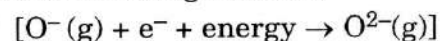
Now, 100 g sucrose = 1632 kJ

$$\therefore 1 \text{ kg or } 1000 \text{ g sucrose} = \frac{1632 \times 1000}{100} \\ = 16320 \text{ kJ}$$

$$\therefore \text{Number of days } 1 \text{ kg lost} = \frac{16320 \text{ kJ}}{2500 \text{ kJ day}^{-1}} \\ = 6.53 \text{ days}$$

39. Higher the bond dissociation energy, smaller is the size. Hence, C - E bond has 486 kJ/mole dissociation energy, so E has smallest size.

40. The process in option (c) refers to 2nd electron affinity of oxygen where, energy is required to add electron to negative ion.

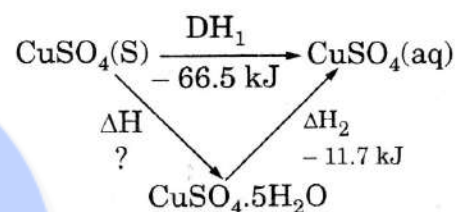


41.  $\Delta H_f^\circ$  is zero only for elements in their standard state.

$$\begin{aligned} 42. \quad \Delta G^\circ &= -2.303 RT \log K_p \\ &= -2.303 \times 8.31 \times 298 \log 1.8 \times 10^{-7} \\ &= -5.703 \log 1.8 \times 10^{-7} \\ &= -5703 (-6.7447) \\ &= 38,800 \text{ J mol}^{-1} \\ &= 38.80 \text{ kJ mol}^{-1} \end{aligned}$$

43. It is a process during which the volume of the system is kept constant.

44. The process of hydration may be expressed as :



According to Hess's law :

$$\begin{aligned} \Delta H_1 &= \Delta H + \Delta H_2 \\ \therefore \Delta H &= \Delta H_1 - \Delta H_2 \\ &= -66.5 - 11.7 \\ &= -78.2 \text{ kJ.} \end{aligned}$$

45. Gibbs-Helmoholtz equation is,

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

Now,  $\Delta S$  of the process can be +ve or -ve depending upon the reaction. Hence,  $\Delta G$  can be more or less than  $\Delta H$ .

46.  $\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporation}}$

47. After the melting of the solid, the entropy will increase with a much greater speed due to formation of vapour.

49. Since, the change occurs at constant volume, therefore the work done is zero and according to the first law of thermodynamics

$$Q = \Delta U + W$$

$$\text{or } Q = \Delta U = 500 \text{ J}$$

53. In the given combustion reaction automobile  $\Delta H$  is negative, it is a spontaneous reaction, hence  $\Delta G$  is negative and due to increase in number of moles of products the entropy change is positive.

54.  $2\text{CH}_4 + 4\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}; \Delta H = x \quad \dots(i)$   
 $2\text{CH}_3\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}; \Delta H = y \quad \dots(ii)$   
 Subtracting equation (i) from equation (ii), we get  
 $2\text{CO}_2 + 4\text{H}_2\text{O}; \Delta H = y \rightarrow \text{CH}_3\text{OH}; \Delta H = x - y$   
 $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{OH}; H = x - y = \text{negative}$   
 or  $x - y < 0$   
 or  $x < y$
55. Combustion process is always exothermic.
59.  $\frac{1}{2}\text{X}_2 + \frac{1}{2}\text{Y}_2 \rightarrow \text{X} - \text{Y}; \Delta H = -100 \text{ kJ}$   
 or  $100 \text{ kJ} = \frac{1}{2}\Delta H_{\text{X-X}} + \frac{1}{2}\Delta H_{\text{Y-Y}} - \Delta H_{\text{X-Y}}$   
 ... (if  $H_{\text{Y-Y}} = a$ )  
 or  $100 \text{ kJ} = \frac{1}{2}2a + \frac{1}{2}a - 2a$   
 or  $a = 200 \text{ kJ}$   
 $\therefore \Delta H_{\text{X-X}} = 2 \times 200 = 400 \text{ kJ mol}^{-1}$
64. Entropy change,  $\Delta S = \frac{\Delta H_f}{T} = \frac{2930}{300}$   
 $= 9.766 \text{ J mol}^{-1} \text{ K}^{-1}$
66. The process given in option (a) refers to decrease in number of gas moles. Hence, in such a case work will be done on the system, i.e. it will be positive.
68. Adding equations (i) and (ii), we get  
 $\text{Na(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}, \Delta H = -98 \text{ kcal.}$
69.  $\Delta H = \Delta E + \Delta n(g) RT$   
 where,  $\Delta n(g) = \text{total moles of gaseous product} - \text{total moles of gaseous reactants}$   
 $\Delta n = 2 - 3 = -1$   
 $\therefore \Delta H = \Delta E - RT.$
70.  $\Delta S = \left[ 50 - \frac{3}{2} \times 40 - \frac{1}{2} \times 60 \right] \text{JK}^{-1}$   
 Given:  $\Delta H = -20 \text{ kJ.}$   
 At equilibrium,  $T\Delta S = \Delta H$   
 or  $T = \frac{\Delta H}{\Delta S} = \frac{-20 \times 10^3}{-40} = 500 \text{ K}$
71. For spontaneity, the value of  $\Delta G = (\Delta H - T\Delta S)$  should  $< 0$ .  
 If  $\Delta S$  is -ve, the value of  $T\Delta S$  has to be less than  $\Delta H$   
 or value of  $\Delta S$  has to be less than  $\frac{\Delta H}{T}$  i.e.,  $\frac{x}{298}$ .
73. When  $H_R > H_P$ ,  $\Delta H$  is negative, hence exothermic.
75. Use relation,  $\Delta G = \Delta H - T\Delta S.$
77. Required reaction is,  
 $\text{K} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{KOH}; \Delta H_f$   
 Adding equations (i), (ii) and (iii), we get  
 $\Delta H_f = -68 - 48 + 14$
78.  $\text{S}_R + \text{O}_2 \rightarrow \text{SO}_2; \Delta H = 70960 \text{ cal} \quad \dots(i)$   
 $\text{S}_M + \text{O}_2 \rightarrow \text{SO}_2; \Delta H = 71030 \text{ cal} \quad \dots(ii)$   
 Subtract equation (ii) from equation (i), we get  
 $\text{S}_R - \text{S}_M; \Delta H = -70 \text{ cal}$
79. The mathematical form of first law of thermodynamics is  
 $\Delta Q = \Delta U + W$   
 or  $\Delta U = \Delta Q - W$
80. The enthalpy of formation of  $\text{OH}^-(\text{aq})$  refers to the enthalpy change during the formation of one mole of  $\text{OH}^-$  ions in solution from the constituent elements.
81. Find the enthalpy change for the reaction  
 $\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{SO}_2$   
 From the relation,  
 $\Delta H^\circ = \sum \Delta H^\circ_{(P)} - \sum \Delta H^\circ_{(R)}$   
 $= 2(-297) + (-393) - (117)$   
 $= -1104 \text{ kJ.}$
84.  $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{40.627 \times 1000}{373}$   
 $= 108.9 \text{ JK}^{-1} \text{ mol}^{-1}.$
85.  $\Delta S_{\text{universe}} = \frac{-\Delta G}{T}$
86. Apply,  $\Delta G^\circ = -2.303 RT \log K$   
 ... (use  $R = 2 \text{ Cal K}^{-1} \text{ mol}^{-1}$ )
87. According to the definition of heat of formation. Also graphite is more stable state of carbon than diamond.
89. For a reaction to be spontaneous the first energy change must be negative i.e.,  
 $\Delta G = \Delta H - T\Delta S = \text{negative}$