CHEMISTRY

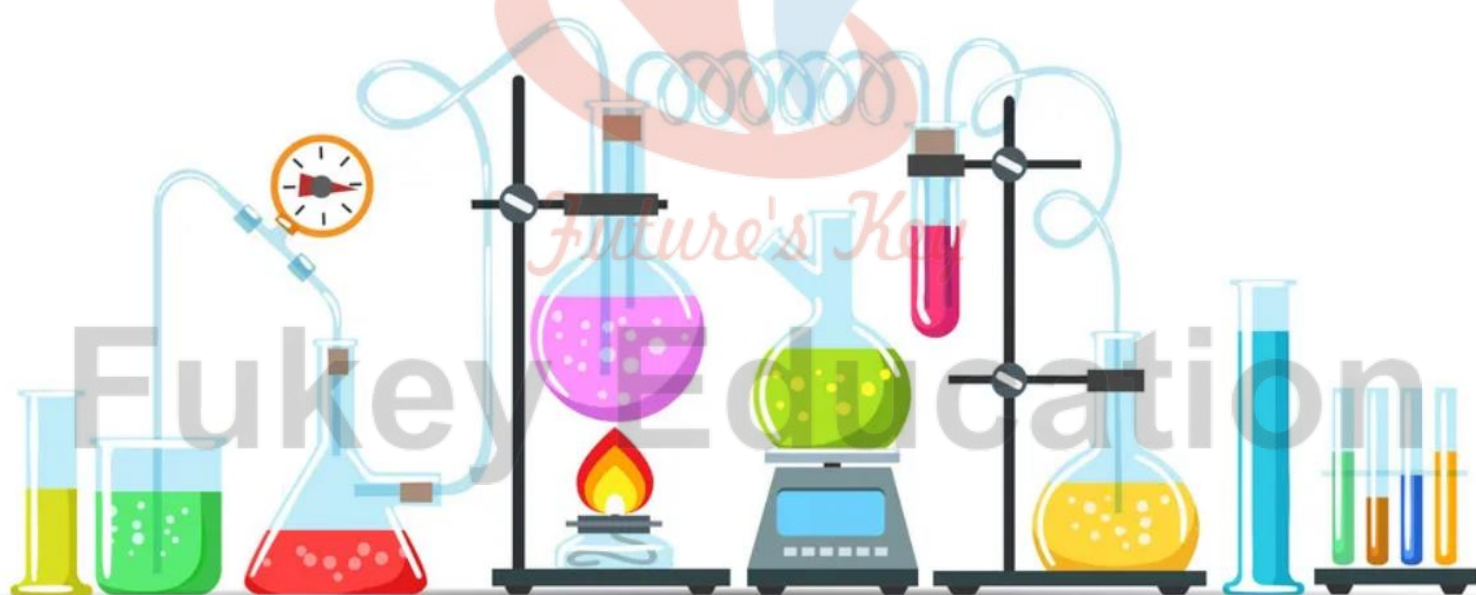## CHAPTER 5: THERMODYNAMICS

THERMODYNAMICS

Introduction

Chemical thermodynamics deals with the relationship between various form of energy in a process. Thermodynamics deals with macroscopic properties. This chapter introduces a major subsidiary thermodynamic property, the Gibbs free energy which lets us express the spontaneity of a process in terms of the properties of the system. This chapter helps to explain why gases expand or diffuse.

System and Surrounding

1. **System:** A specific portion of universe under study which is seperated from rest of the universe with a boundary is called system.

2. **Surroundings:** Rest of the universe which might be in a position to exchange energy and matter with the system is known as surrounding.

Types of System:

1. **Open system:** System can be open if it can exchange both energy and matter with surroundings.

2. **Closed system:** System can be closed if it can exchange energy but not matter with surroundings.

3. **Isolated system:** System can be isolated if it can neither exchange energy nor matter with surroundings.

Extensive Properties

The properties which depend upon mass of the substance is known as extensive properties i.e., mass, volume, internal energy, enthalpy etc.

Intensive Properties

The properties which are independent of mass of the substance is known as intensive properties i.e., temperature, pressure, density, refractive index.

Thermodynamic State of a System

(1)

A state is the condition of a system as specified by its physical properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

State Functions

The thermodynamic parameters which depends only on initial and final states of system is known as state function. i.e., internal energy(E), Enthalpy (H), entropy (S), Gibb's free energy (G).

Path Functions

The thermodynamic parameters where value does not depend merely on initial and final state but depends upon the path followed is known as path function. i.e., heat (q), work done (W).

Thermodynamic Process

The sequence followed to change one thermodynamic state of a system into another is called thermodynamic process. The types of thermodynamic processes are:

1. **Isothermal process:** It is the process in which temperature is kept constant means temperature of initial and final state of system along with entire path of process is same.

2. **Isobaric process:** It is the process in which pressure is kept constant for entire process.

3. **Isochoric process:** It is the process in which volume is kept constant.

4. **Adiabatic process:** The process in which heat transaction across boundary is not allowed.

5. **Reversible process and Irreversible process:** In thermodynamics, a process is said to be reversible when energy change in each step of the process can be reversed by changing the variables such as pressure, volume or temperature acting on them. In such a process, the driving and opposing forces differ infinitesimally and the process can be reversed completely by increasing the opposing force by an infinitesimally small amount.

   Any process which does not take place in the above mentioned manner is said to be an irreversible process. In an irreversible process the driving and opposing force differ by a large amount.

6. **Cyclic process:** It is the process which run in close loop means process in which initial and final states are identical.

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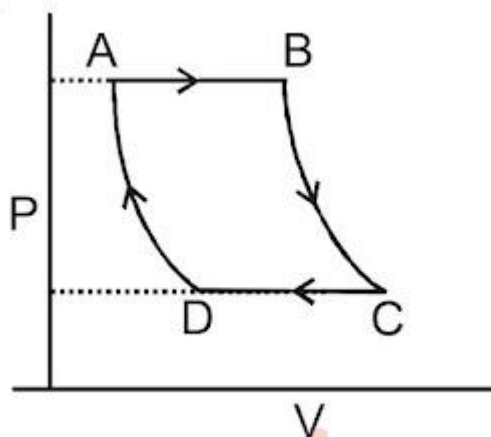
Internal Energy

Every substance is associated with definite amount of energy that is called internal energy. It is an extensive property and a state function. Internal energy of ideal gases is a function of temperature only.

Pressure-Volume Work

It is the work done when the gas expands or contracts against the external pressure. Consider a cylinder containing one mole of an ideal gas fitted with a frictionless and weightless piston having an area of cross-section A. The total volume of the gas is Vi and the initial pressure of the gas inside P.
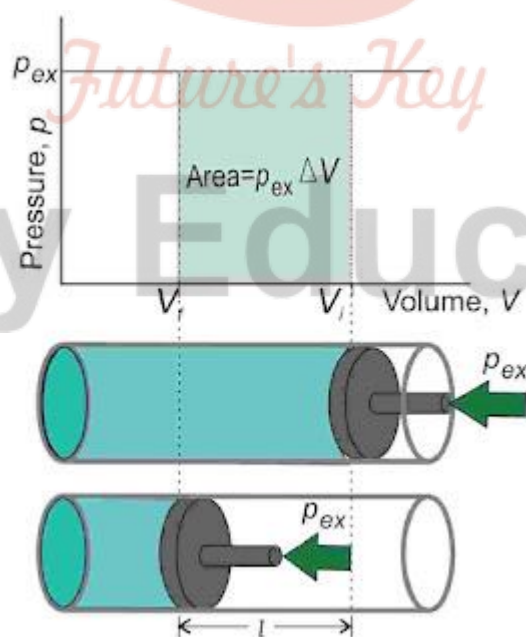
Let the external pressure acting on the piston is Pex. If the external pressure Pex is slightly greater than P piston moves downward till the pressure inside the cylinder becomes equal to

(3)

Pex. Let this change be achieved in a single step and the final volume be Vf. During this compression, suppose the piston moves a very small distance Δl. Thus, the work done on the gas is given by,

$$\omega = -\int_{V_i}^{V_f} P_{ex} dv$$

Heat

The change in internal energy of a system can be brought about by the transfer of heat from the surroundings to the system or vice-versa. This exchange of energy between the system and surroundings is possible as a result of the temperature difference between them. This energy called heat is represented by Q.

First Law of Thermodynamics

First law of thermodynamics states the law of conservation of energy in a different manner. According to this law, whenever a quantity of one kind of energy disappears an equivalent amount of energy appears in some other form.

According to first law of thermodynamics,

ΔU = q + W

Where, Q = Heat change

W = Work done

ΔU = Change in internal energy

Enthalpy (H)

The total heat content of a system at constant pressure is known as its enthalpy. Mathematically it is the sum of internal energy and pressure-volume energy

ΔH = ΔU + PΔV

It is an extensive property and a state function. Increase in enthalpy H is equal to heat absorbed at constant pressure.

Heat Capacity

Heat capacity is amount of heat require to raise the temperature of a system by unity. It is represented as "C". It is an extensive property and temperature dependent.

Types of heat capacity

1. Specific heat: For 1 gram system the heat loose or gained by system to bring one unit change in temperature is called specific heat denoted by 's'. specific heat is the intensive property.

$$S = \frac{C}{m}$$

2. Molar heat capacity: It is heat capacity for a system having 1 mole of material. It is represented as Cm. It is an intensive property.

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

3. Heat capacity at constant volume: Heat capacity of a system in isochoric condition is called heat capacity at constant volume, it is represented as C_v means molar heat capacity at constant volume.

$$C_v = \frac{dU}{dT}$$

4. Heat capacity at constant pressure: Heat capacity of a system in isobaric condition. It is represented by C_p means molar heat capacity at constant pressure.

$$C_p = \frac{dH}{dT}$$

Relation between Cp and Cv

We know that,

$\Delta H = \Delta U + P\Delta V$ .....(i)

As per ideal gas equation

$P\Delta V = R\Delta T$ .....(ii)

From (i) and (ii)

$\Delta H = \Delta U + R\Delta T$

(5)

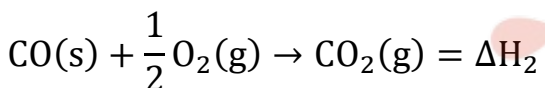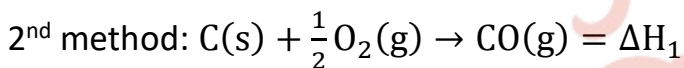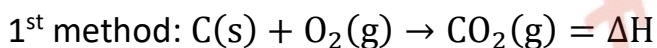**Website - www.fukeyeducation.com, Email :- fukeyeducation@gmail.com**

$$\frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + R$$

$C_p = C_v + R$

$C_p - C_v = R$

Hess's Law

According to Hess's law, If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

1st method: $C(s) + O_2(g) \rightarrow CO_2(g) = \Delta H$

2nd method: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) = \Delta H_1$

$$CO(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) = \Delta H_2$$

According to Hess's law,

$\Delta H = \Delta H_1 + \Delta H_2$

Application of Hess's Law

1. Calculation of enthalpy of formation.

2. Determination of standard enthalpies of reactions.

Bond Dissociation Energy

The energy required to break one mole bond of a particular type in gaseous molecule is known as bond dissociation energy. For example, we consider the dissociation of water,

$H - OH(g) \rightarrow H(g) + OH(g) = \Delta H = 498 \text{ kJ/mol}$

Entropy

Entropy is a measure of degree of randomness or disorder in a system. Entropy is an extensive property and a state function.. Its value depends upon the amount of substance present in the system.

Second Law of Thermodynamics

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This states that the entropy of the universe always increases in every spontaneous (natural) change.

Free Energy (G)

Gibb's free energy is defined as,

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

H is enthalpy, S is entropy and T is the temperature on Kelvin scale.
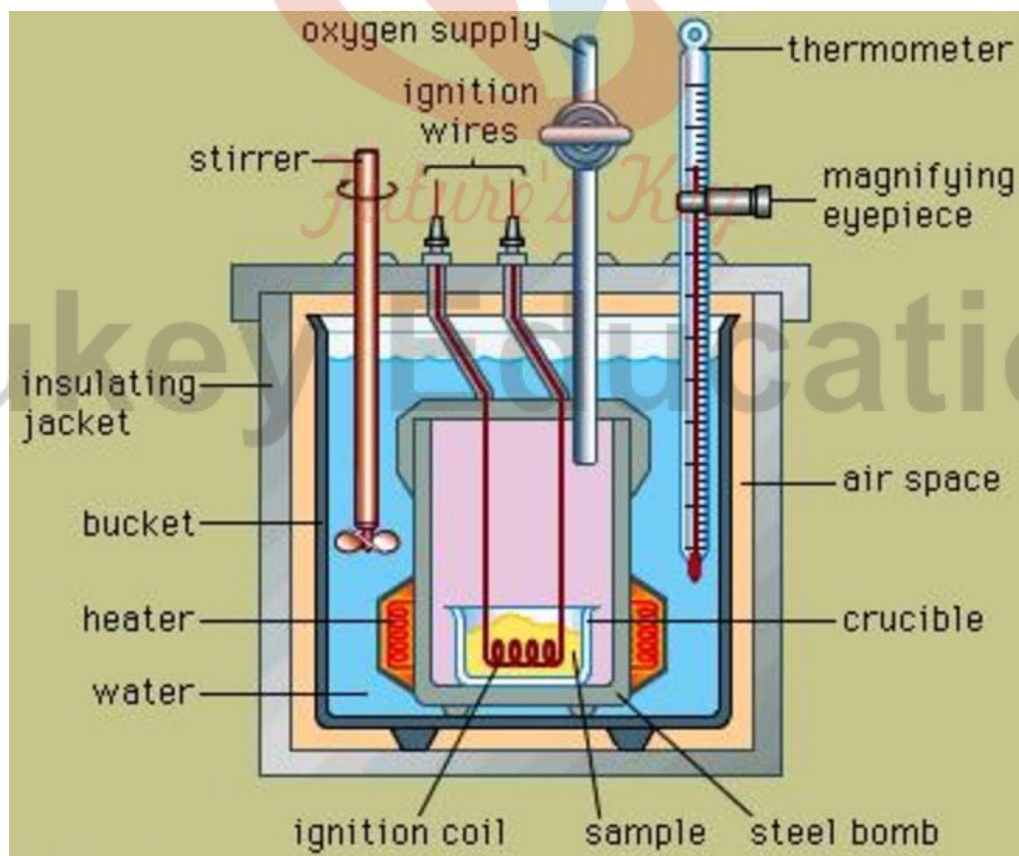
Measurement Of Change In Internal Energy and Enthalpy

The experimental technique of measuring energy changes accompanying any chemical or physical process is called calorimetry.

These measurements are generally carried out under 2 condition

1) at constant volume (ΔU or qv)

2) at constant pressure (ΔH or qp)

Measurements of ΔU

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Internal energy change is measured experimentally using an apparatus called Bomb calorimeter.

It consists of a strong steel vessel which can stand high pressure. It is surrounded by a bigger vessel which contains water and is insulated. A thermometer and a stirrer are suspended in it.

Procedure

1) A known mass of compound is taken in the platinum cup.Oxygen under high pressure is introduced into the bomb. A current is passed through the filament immersed in the compound. Combustion of the compound takes place. The increase in the temperature of water is noted. From this, the heat capacity of the apparatus can be calculated.

2) The experiment is repeated as in step 1.As the reaction is carried out in a closed vessel, therefore, heat evolved is the heat of combustion at constant volume and hence is equal to internal energy change.

The value of ΔU can be calculated using the formula

$\Delta U = (Q \times \Delta t \times M) / m$
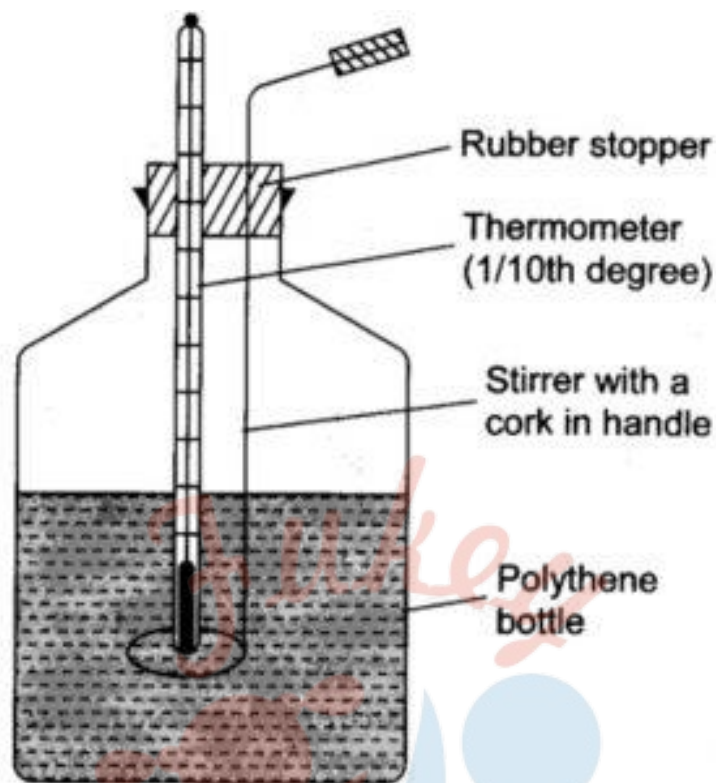
where Q =heat capacity of the calorimeter

Δt = rise in temperature

m= mass of the substance taken

M =molecular mass of the substance

Measurement of ΔH

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Rubber stopper

Thermometer
(1/10th degree)

Stirrer with a
cork in handle

Polythene
bottle

Taking the example of heat of neutralisation of an acid with a base or vice versa, it can be determined using a simple calorimeter consisting of a polythene bottle fitted with a cork having two holes , one for the thermometer and the other for the stirrer.

Thermometer

Cardboard or
Styrofoam lid

Nested
Styrofoam cups

Exothermic
reaction
occurs in
solution.
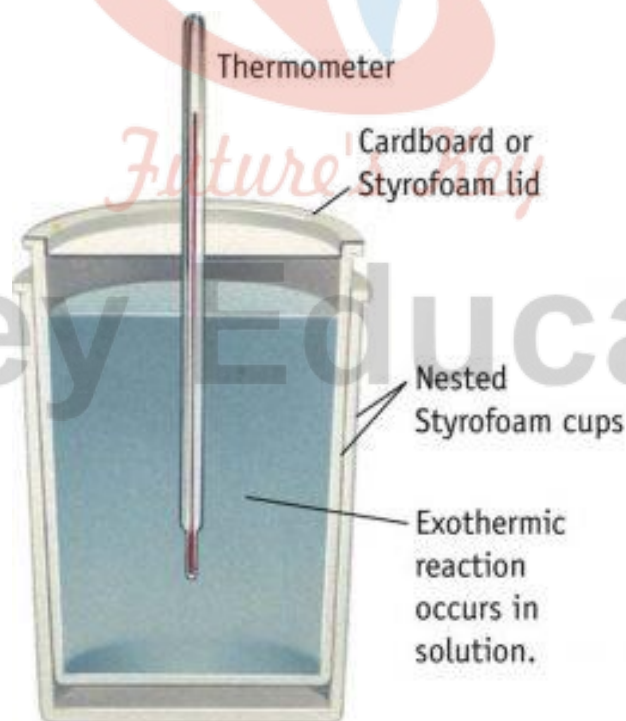
Instead of polythene bottle , a foamed polystyrene cup with a cover is also sometimes used .It is called coffee cup calorimeter.

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Taking the example of neutralisation of HCl with NaOH.

1) A known volume of HCL of known concentration ($100cm^3$ of 0.5 N) is taken in one beaker and an equal volume of NaOH of the same concentration ($100cm^3$ of 0.5 N) is taken in another beaker.

2) Both the beakers are kept in water bath till the solution attain the same temperature.

3) HCl solution kept in the first beaker is transferred into the polythene bottle. Immediately NaOH solution kept in the second beaker is added into the polythene bottle. Stirring is done to mix HCl and NaOH. The highest temperature attained is noted.

Suppose the initial temperature of the acid and the base = t_1 ° C

Final temperature of the solution after mixing = t_2 ° C

Rise in temperature= ($t_2 - t_1$) °C

Total mass of the solution = 200 g

Heat produced = mass × specific heat × rise in temperature

Heat produced by neutralisation of 1000 cc of 1 N HCl

This give the heat of neutralisation per equivalent.

Heat of neutralisation of a strong acid by a strong base is always equal to 57.1 kJ equi-1 or 57.1 kJ mol-1 of H+ or OH– ions.

Measurement of ΔH or qp reaction for any reaction

For any reaction occurring in solution, the heat change accompanying the reaction at constant pressure i.e. enthalpy change can be measured by using the calorimeter.

The reaction is allowed to take place in the polythene bottle.

If the reaction is exothermic, temperature will rise and if the reaction is endothermic, temperature will fall.

For exothermic reaction, ΔH is negative whereas for endothermic reaction, ΔH is positive.

For the measurement of q_p or ΔH ,the reaction may be carried out in a vessel with conducting walls.

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This vessel may be placed in an insulated outer vessel containing water and fitted with a stirrer and a thermometer. The Rise or fall in temperature may be recorded and the result calculated.
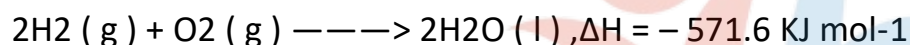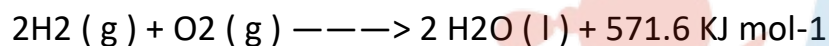
Thermochemical Equation

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

Fractional coefficients may be used in writing a thermochemical equation.

H2 (g) + ½ O_2 (g) ———> H_2O (l) + 285.8 KJ mol-1

H2 (g) + ½ O_2 (g) ———> H_2O (l) ΔH = – 285.8 KJ mol-1
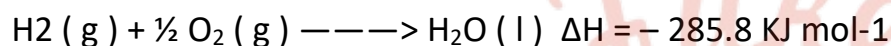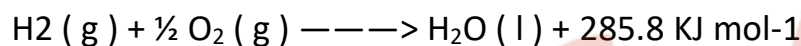
285.8 KJ mol-1 of heat is produced when 1 mole of hydrogen reacts with 0.5 mole of Oxygen. If the quantities of reactants are doubled, the heat produced will also be doubled.

2H2 (g) + O2 (g) ———> 2 H2O (l) + 571.6 KJ mol-1

2H2 (g) + O2 (g) ———> 2H2O (l) ,ΔH = – 571.6 KJ mol-1

Conventions about thermochemical equation

1)For exothermic reaction, ΔH is negative whereas for endothermic reaction, ΔH is positive.

2)ΔH values are for the standard state of the substance (298 K and 1 bar pressure)

3) The coefficients of different substances represents the number of moles reacted and formed for the heat change represented in the equation.

4) The physical state of the different substances must be mentioned as the heat evolved or absorbed depends upon the physical state.

5) If the coefficient of the substances are multiplied or divided by some number , the value of ΔH is multiplied or divide by the same number.

6) If the reaction is reversed ,the sign of ΔH changes but the magnitude remains the same.

Heat of reaction or Enthalpy of reaction or Enthalpy change of reaction

The amount of heat evolved or absorbed in a chemical reaction when the number of moles of reactants as represented by the chemical equation have completely reacted, is called the heat of reaction or enthalpy of reaction or enthalpy change of reaction.

(11)

It is represented by Δr H.

For example

CH4 (g) + O_2 (g) ———> CO_2 (g) + 2 H_2O (l) ΔH = − 890.4 KJ mol-1

C (s) + H_2O (g) ——> CO (g) + H_2 (g) ΔH = 131 Kj mol-1
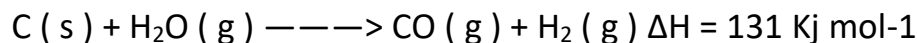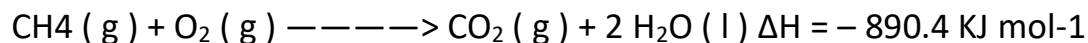
1 mole of methane combines completely with 2 moles of Oxygen gas, 890.4 KJ of heat is produced.

1 mole of solid carbon react completely with one mole of steam ,131.4 KJ of heat is absorbed.

Enthalpy of reaction, ΔH = Sum of enthalpies of products – Sum of enthalpies of reactants

ΔH = $\sum a_i$ H (products) – $\sum b_i$ H (reactants)

where symbol ∑ represent summation, ai and bi represents the coefficient of the products and reactants.

If the reaction is reversed , the sign of ΔH changes

H_2 (g) + ½ O_2 (g) ——> H_2O (l) ΔH = − 285.8 KJ mol-1

H_2O (l) ——>H_2 (g) + ½ O_2 (g) ΔH = 285.8 KJ mol-1
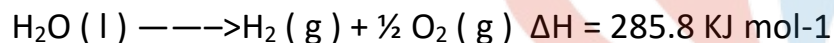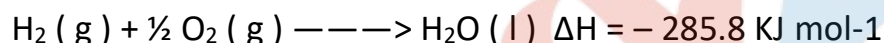
Factors on which the heat of reaction depends

1) Quantities of the reactants involved

If the quantities of reactants are doubled, the heat of reaction is also doubled.

2)Physical state of the reactants and products

The physical state of the reactants and products affects the heat of reaction.

When hydrogen and oxygen gas combine to form liquid water, the heat of reaction is different than when they combine to form water in the gaseous state.

H_2 (g) + ½ O_2 (g) ———> H_2O (l) ΔH = − 285.8 KJ mol^{-1}

H_2 (g) + ½ O_2 (g) ———> H_2O (g) ΔH = − 241.8 KJ mol^{-1}
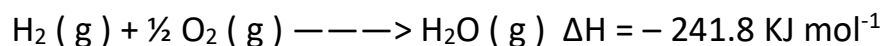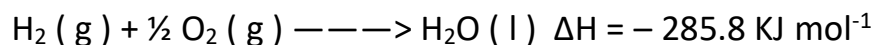
It is essential to write the symbols s, l, g or aq to indicate whether a particular substance is a solid ,liquid ,gaseous or an aqueous solution.

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3)Allotropic modification

For elements like Sulphur and carbon which exist in different allotropic modification, the heat of reaction is different in different allotropic form is involved in the reaction.

C (diamond) + O_2 (g) ——––> CO_2 (g) , ΔH = -395.4 KJ mol^{-1}

C (graphite) + O_2 (g) ——––> CO_2 (g) , ΔH = -395.4 KJ mol^{-1}
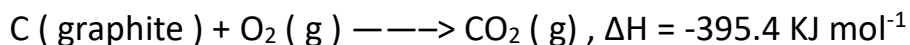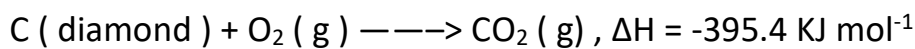
4)Concentration of solution

Heat changes occurs when a solute is dissolved in a solvent to form a solution or when solution is diluted.

Therefore, if the solutions are involved in a reaction, their concentration affect the heat of reaction.

5)Temperature

The heat of reaction depends upon the temperature at which the reactants and products are taken. The values are usually reported at 298 K.

6)Conditions of constant pressure or constant volume

Whether the reaction take place at constant pressure or at constant volume.

Standard enthalpy of reaction

The enthalpy change of a reaction depends upon the condition under which the reaction is carried out. Hence it is essential to specify some standard conditions.

The standard enthalpy of a reaction is the enthalpy change accompanying the reaction when all the reactants and products are taken in their standard state.

A substance is said to be in standard state when it is in the purest and most stable form at 1 bar pressure and the specified temperature.

This temperature is usually taken as to 298 K.

Standard state of pure ethanol at 298 k is pure liquid ethanol at 298 K and 1 bar pressure.

in terms of S.I. unit, 1 atm=101.325 KPa whereas 1 bar = 10^5 Pa .

The enthalpy change of a reaction in the standard state is represented by the symbol $\Delta H°$

(13)

Bond Enthalpy

Bond energy is the amount of energy released when 1 mole of bonds are formed from the isolated atoms in the gaseous state or the amount of energy required to dissociate one mole of bonds present between the atoms in the gaseous molecules.

It is represented by $\Delta_b H$ or $\Delta_{bond} H$.

For diatomic molecules like H_2, O_2, N_2, Cl_2, HCl, HF etc. the bond energies are equal to their dissociation energies. These may also be called as their enthalpy of atomisation.

For polyatomic molecules ,the bond energy of a particular bond is not the same when present in different types of compounds.

The bond energy of a particular type of bond is not same even in the same compound.

For Ex: In CH4 the bond energy for first, second ,third and fourth C-H bonds are not equal: their values being 427, 439, 452 and 347 KJ mol-1

$\Delta_a H° = 427 + 439 + 452 + 347$

$\Delta_a H° = 1665$ KJ mol^{-1}

To calculate bond energy, an average is taken.

ΔC-H = 1665 / 4 = 416 KJ mol^{-1}

Bond energy usually means bond dissociation energy. It is always taken as positive because it is the energy required and not the energy released. It is the energy for one mole of a particular type of bonds and not for 1 mole of the substance.

Bond dissociation energies are obtained at 0 K by spectroscopic method whereas bond enthalpy are calculated by considering combustions from heat capacities and pΔV terms.

Bond enthalpy helps to calculate the enthalpy of formation of atoms.

For polyatomic molecules ,the bond enthalpy of a particular bond is found from the values of the enthalpies of formation.

Bond enthalpy of heteronuclear diatomic molecules can be obtained directly from the experiments or may be calculated from the bond enthalpies of homonuclear diatomic molecules.

Spontaneous and Non-spontaneous Process

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

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

A spontaneous process is simply a process which is feasible.

The rate of the process may vary from extremely slow to extremely fast.

Examples of processes which take place by themselves :

1) Dissolution of common salt in water

2) Evaporation of water in an open vessel

3) Flow of heat from hot end to cold end or from a hot body to a cold body

4) Flow of water down a hill

5) Combination of nitric oxide and oxygen to form Nitrogen dioxide

$2NO\ (\ g\ ) + O_2\ (\ g\ )\ ———–> 2NO_2\ (\ g\ )$
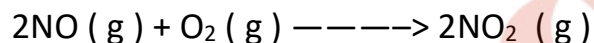
Examples of processes which take place on initiation

1) Lightning of candle involving burning of wax

2) Heating of calcium carbonates to give calcium oxide and carbon dioxide

$CaCO_3\ (\ s\ )\ ————–> CaO\ (\ s\ ) + CO_2\ (\ g\ )$
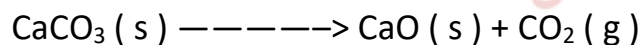
3) Combination of hydrogen and oxygen to form water when initiated by passing an electric spark

$H_2\ (\ g\ ) + ½\ O_2\ (\ g\ )\ ———> H_2O\ (\ g\ )$
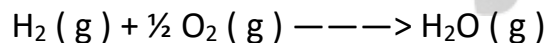
A process which can neither take place by itself nor by initiation is called a non spontaneous process.

For Example

1) Flow of water up a hill

2) Flow of heat from cold body to a hot body

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3) Diffusion of gas from low pressure to a high pressure

4) Dissolution of sand in water

The force which is responsible for the spontaneity of a process is called a driving force

Nature of driving force

In order to acquire maximum stability, every system tends to have minimum energy.

Tendency for minimum energy

For example

1) A stone lying at height has a tendency to fall down so as to have minimum potential energy

2) Water flows down a hill to have minimum energy

3) A wound watch spring has tendency to unbind itself to decrease its energy to minimum

4) Heat flows from hot body to cold body so that heat content of the hot body becomes minimum

All the processes are spontaneous because they have tendency to acquire minimum energy.

Consider the following exothermic reaction, all of which are spontaneous :

1) H_2 (g) + ½ O_2 (g) ————> H_2O (l) $\Delta rH° = -285.8$ KJ mol^{-1}

2) N_2 (g) + 3H_2 (g) ————> 2NH_3 (g) $\Delta rH° = -92.2$ KJ mol^{-1}

3) C (s) + O_2 (g) ————> CO_2 (g) $\Delta rH° = -285.8$ KJ mol^{-1}
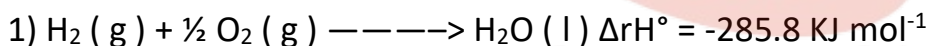
All these reactions are accompanied by evolution of heat. The heat content of the products is less than those of the reactants. These reactions are spontaneous because they are accompanied by decrease of energy.

A tendency to attain minimum energy i.e. a negative value of enthalpy change, might be responsible for a process or a reaction to be spontaneous or feasible.

limitation of the criteria for minimum energy

1) A number of reactions are known which are endothermic i.e. for which ΔH is positive but still they are spontaneous.

1) Evaporation of water or melting of ice

It takes place by absorption of heat from the surrounding.

H_2O (l) ——— -> H_2O (g) $\Delta_{vap} H° = 40.8$ KJ mol^{-1}

H_2O (s) ——— -> H_2O (l) $\Delta fus H° = 6$ KJ mol^{-1}
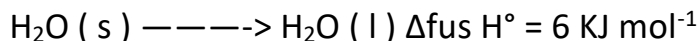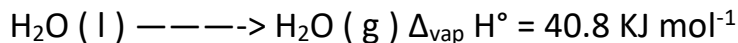
2) Dissolution of salts like NH_4Cl , KCl

NH4Cl (s) + aq ——-> NH_4^+ (aq) + Cl^- (aq) $\Delta_r H° = 15.1$ KJ mol^{-1}
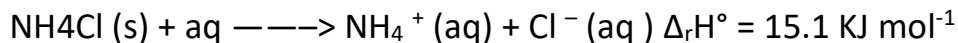
3) Decomposition of calcium carbonate on heating

$CaCO_3$ (s) ————> CaO (s) + CO_2 (g) $\Delta_r H° = 177.8$ KJ mol^{-1}
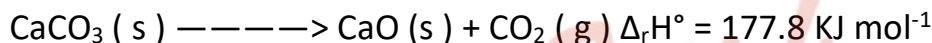
4) Decomposition of N2O5 at room temperature

$2N_2O_5$ (g) ————> $4NO_2$ (g) + O2 (g) $\Delta_r H° = 219$ KJ mol^{-1}
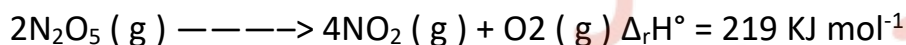
5) Decomposition of mercuric oxide on heating

2HgO (s) ————> 2Hg (l) + O2 (g) $\Delta r H° = 90.8$ KJ mol^{-1}
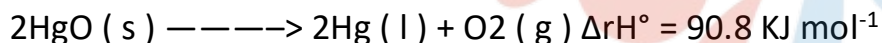
2) A number of reactions are known for which ΔH is zero but still they are spontaneous

Reaction between acetic acid and ethyl alcohol

CH_3COOH (l) + C_2H_5OH (l) ———> $CH_3COOC_2H_5$ (l) + H_2O (l)
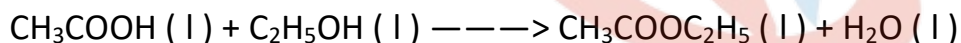
2) Expansion of an ideal gas into vacuum

3) Even those reactions for which ΔH is negative, rarely proceed to completion even though ΔH remains negative throughout.

4) Reversible reactions also occur.

H_2 (g) + I_2 (g) ——>2HI (g)

2HI (g) ———-> H_2 (g) + I_2 (g)
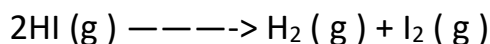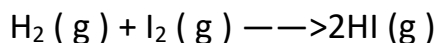
The energy factor or enthalpy factor cannot be the sole criterion for predicting the spontaneity or the feasibility of a process.

Tendency for maximum randomness

Suppose the two gases are enclosed in bulbs A and B connected to each other by a tube and kept separated by a stopcock. If the stock cock is opened the two gases mix completely. The gases

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which were confined to bulbs A and B separately are no longer in order. A disorder has come in or the randomness of the system has increased.

A spontaneous process for which ΔH = 0 is the spreading of a drop of ink in a beaker filled with water.

Second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness.

For example:

1) Evaporation of water take place because the gaseous water molecules are more random than the liquid water molecules. The process is spontaneous because it is accompanied by increase of randomness. Melting of ice is a spontaneous process because liquid state is more random than the solid state.

2) Dissolution of Ammonium Chloride is spontaneous because in the solid, the ions are fixed but when they go into the aqueous solution, they are free to move about.

3) Decomposition of solid calcium carbonate is spontaneous because CO_2 produced is more random than the solid $CaCO_3$.

4) Decomposition of N_2O_5 is spontaneous because 2 moles of gaseous N_2O_5 give 5 moles of gaseous product .

5) Decomposition of solid Mercury oxide is spontaneous because the liquid Mercury and gaseous oxygen formed are more random than solid HgO.

The overall tendency for a process to occur depends upon the resultant of the following two tendencies :

1) Tendency for minimum energy

2) Tendency for maximum randomness

The resultant of the above 2 tendencies which gives the overall tendency for a process to occur is called the driving force of the process.

For example :

E represents the tendency for minimum energy

R represents the tendency for maximum randomness.

D represent the overall tendency

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1) Evaporation of water

$H_2O \, (\, l \,)$ ———-> $H_2O \, (\, g \,)$ $\Delta H = 44$ kJ mol^{-1}
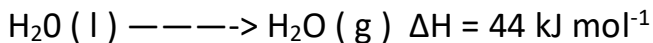
E opposes(process being endothermic), R favours (because gas is more random than liquid).Since the process is known to be spontaneous hence R must be greater than E.

2)Dissolution of NH_4Cl in water

$NH_4Cl \, (\, s \,) + aq$ ———-> $NH_4^+ \, (aq \,) + Cl^- \, (aq)$ $\Delta H = 15.1$ kJ mol^{-1}
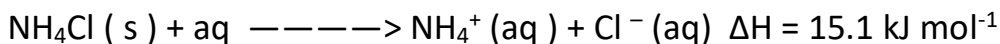
In this process E opposes and R favour. Here again , the spontaneity of the process is explained by suggesting that R > E.

Summary

1. **System:** A part of universe which is under investigation.

2. **Surroundings:** The rest of the universe which is not a part of the system.

3. **State of the system:** The conditions of existence of a system when its macroscopic properties have definite values.

4. **State functions:** The thermodynamic quantities which depend only on the initial and final state of the system.

5. **Energy:** Energy is exchanged between the system and the surroundings as heat if they are at different temperatures.

6. The properties of the system whose value is independent of the amount of substance are called intensive properties. e.g., temperature, pressure, viscosity, surface tension, dielectric constant, specific heat capacity.

7. The properties of the system whose value depends upon the amount of substance present in the system are called extensive properties. e.g., mass, volume, surface area, energy, enthalpy, entropy, free energy, heat capacity.

8. Work is also a mode of transference of energy between system and the surroundings. Work done by the system on the surroundings is given by pΔV.

9. **Internal energy (U):** The energy associated with the system at a particular conditions of temperature and pressure.

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10. **Enthalpy (H):** It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called heat content (H = E + pV).

11. **Hess's law:** The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

12. **Bond enthalpy:** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.

13. **Entropy (S):** It is a measure of randomness or disorder of the system. Thus, the order is Gas > Liquid > Solid.

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Class : 11th Chemistry
Chapter- 6: Thermodynamics

$\Delta_r H = \sum a_i H_{products} - \sum_i b_i H_{reactants}$

(a) Standard Enthalpy of reactions is the enthalpy change for a reaction when all the participating substances are in their standard states.
(b) Enthalpy changes during phase transformations: Standard enthalpy of fusion / molar enthalpy of fusion, $\Delta_{fus} H^\theta$ is the enthalpy change that accompanies melting of one mole of a solid substance in standard state. Standard enthalpy of vaporization or molar enthalpy of vaporization. $\Delta_{vap} H^\theta$ is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure.
(c) Standard molar enthalpy of formation $\Delta_r H^\theta$ is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation.

In calorimetry, the process is carried out in a vessel called calorimeter, immersed in a known volume of a liquid.
(a) U measurements: The energy changes are measured at constant volume. No work is done.
(b) H measurements: In exothermic reaction, heat is evolved, so q_p and rH will be negative. In endothermic reaction, heat is absorbed, so q_p and rH will be positive.

Enthalpy Change $\triangle_r H$ -Reaction Enthalpy

Measurement of ΔU and ΔH

Enthalpy of Solutions is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent.

Lattice Enthalpy is the enthalpy change when one mole of an ionic compound dissociates into its ions in gaseous state

Enthalpy of atomization $\Delta_a H^\theta$ is the enthalpy change on breaking one mole of bonds completely to obtain atoms in gas phase

Entropy
$\Delta S_{Total} = \Delta S_{systems} + \Delta S_{surroundings}$
$\Delta = \dfrac{q_{rev}}{T}$

Standard Enthalpy of combution $\Delta_c H^\theta$ is the enthalpy change per mole of a substance when it undergoes combustion and all reactants and products are in standard state.

Thermodynamics

Gibb's Energy
$*\Delta G = \Delta H - T\Delta S$
ΔG is <0, process is spontaneous.
$* \Delta G$ is >0, process is non-spontaneous

Heat Capacity
$q = C \times m \times \Delta T = C\Delta T$

Applications

$Work = P_{ex.A.l} = -Pex (V_f - V_l) = \int_{V_i}^{V_f} P_{ex}\ dV$

Reversible Process: The process which can be reversed at any moment by an infinitesimal change.
Irreversible Process: Processes other than reversible process.
At constant temperature $W_{rev} = 2.303\ nRT \log \dfrac{V_t}{V_i}$
For adiabatic change, $q=0$, $\Delta U = W_{ad}$

$\triangle_r H^\circ$
Σ **bond enthalpies reactants** $- \Sigma$ **bond enthalpies products**

$\triangle_r G_\theta = -RT\ ln k$

Enthaply, H
ΔH is negative: Exothermic reactions. ΔH is positive: Endothermic reactions

Terms

• Systems and surroundings: A system refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.
• Types of System:
1. Open System: There is exchange of energy and matter between system and surroundings.
2. Closed System: There is no exchange of matter but exchange of energy is possible.
3. Isolated System: There is no exchange of energy or matter between the system and surroundings.
4. State of system : is described by its measurable or macroscopic properties.
5. Internal Energy: as a state function: It is the sum of chemical, electrical, mechanical or any other type of energy.
6. (a) Work: Adiabatic process is in which there is no transfer of heat between system and surroundings.

(b) Heat is change in internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. q is positive: Heat is transferred from surroundings to system. q is negative: Heat is transferred from system to surroundings.
(c) General Case First law of Thermodynamics: $\Delta U = q+w$ the energy of an isolated system is constant.

A spontaneous process is an irreversible process which may be reversed by some external agency

Relationship between C_p and C_v For An Ideal Gas
$C_p - C_v = R$

Hess's Law of Constant Heat summation

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of standard enthalplies of international reactions into which the overall reactions may be divided at the same temperature.

$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 ....$

$A \xrightarrow{\Delta_r H_1} C$
$\Delta_r H_1 \downarrow \quad \uparrow \Delta_r H_3$
$B \xrightarrow{\Delta_r H_2} D$

Extensive Property property which does not depend on the quantity or size of matter present in the system. Temperature density, pressure.

Important Questions

Multiple Choice questions-

Question 1. Hesss law is an application of

(a) 1st law of Thermodynamics

(b) 2nd law of Thermodynamics

(c) Entropy change

(d) $\Delta H = \Delta U + P\Delta V$.

Question 2. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. Wirr at 300 K is:

(a) -15.921 kJ

(b) -11.224 kJ

(c) -110.83 kJ

(d) None of these

Question 3. At absolute zero the entropy of a perfect crystal is zero. This statement corresponds to which law of thermodynamics?

(a) Zeroth Law

(b) First Law

(c) Second Law

(d) Third Law

Question 4. Which of the following has the highest entropy?

(a) Mercury

(b) Hydrogen

(c) Water

(d) Graphite

Question 5. An ideal gas is taken through the cycle A → B → C → A as shown in figure. If the net heat supplied to the gas in cycle is 5 J, the work done by the gas in the process C → A.
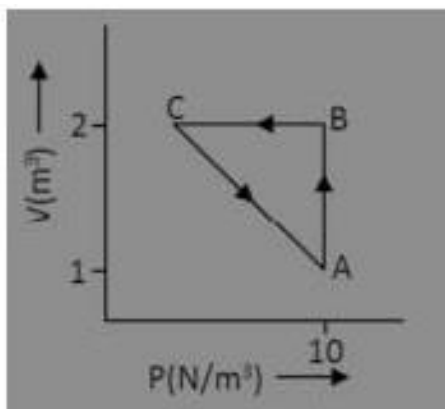
(a) -5 J

(b) -15 J

(c) -10 J

(d) -20 J

Question 6. One mole of which of the following has the highest entropy?

(a) Liquid Nitrogen

(b) Hydrogen Gas

(c) Mercury

(d) Diamond

Question 7. An ideal gas is taken around the cycle ABCA as shown in P-V diagram The next work done by the gas during the cycle is equal to:
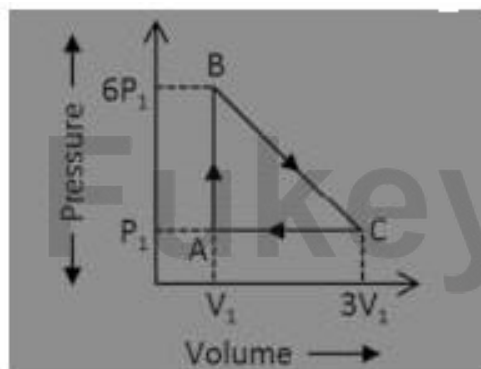
(a) $12P_1V_1$

(b) $6P_1V_1$

(c) $5P_1V_1$

(d) P_1V_1

Question 8. Third law of thermodynamics provides a method to evaluate which property?

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(a) Absolute Energy

(b) Absolute Enthalpy

(c) Absolute Entropy

(d) Absolute Free Energy

Question 9. Which of the following is/are a reason that water is a desirable heat sink for use in calorimeters?

I) Waters heat specific capacity is very precisely known.

II) Water is readily available.

III) Water has an unusually large specific heat capacity.

(a) I only

(b) I and II

(c) I, II and III

(d) II only

Question 10. In a chemical reaction the bond energy of reactants is more than the bond energy of the products. Therefore, the reaction is

(a) Exothermic

(b) Athermic

(c) Endothermic

(d) Endergonic

Question 11. In a reversible process the system absorbs 600 kJ heat and performs 250 kJ work on the surroundings. What is the increase in the internal energy of the system?

(a) 850 kJ

(b) 600 kJ

(c) 350 kJ

(d) 250 kJ

Question 12. Which of the following neutralization reactions is most exothermic?

(a) HCl and NaOH

(b) HCN and NaOH

(c) HCl and NH_4OH

(d) CH_3COOH and NH_4OH

Question 13. A student runs a reaction in a closed system. In the course of the reaction, 64.7 kJ of heat is released to the surroundings and 14.3 kJ of work is done on the system. What is the change in internal energy (ΔU) of the reaction?

(a) -79.0 kJ

(b) 50.4 kJ

(c) 79.0 kJ

(d) -50.4 kJ

Question 14. Identify the correct statement from the following in a chemical reaction.

(a) The entropy always increases

(b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction

(c) The enthalpy always decreases

(d) Both the enthalpy and the entropy remain constant

Question 15. 2 mole of an ideal gas at 27° C expands isothermally and reversibly from a volume of 4 litters to 40 litre. The work done (in kJ) is:

(a) w = -28.72 kJ

(b) w = -11.488 kJ

(c) w = -5.736 kJ

(d) w = -4.988 kJ

Very Short:

1. Under what conditions the heat evolved or absorbed is equal to the internal energy change?

2. What is the sign of AH for endothermic reactions and why?

3. What is the relationship between the standard enthalpy of formation and the enthalpy of a compound?

4. Why enthalpy of neutralization of HF is greater than 57.1 kJ mol^{-1}?

5. What are the specific heat capacity and molar heat capacity for water?

6. Why enthalpy of neutralization is less if either the acid or the base or both are weak?

7. What do you mean by a system?

Short Questions:

1. Ice is lighter than water, but the entropy of ice is less than that of water. Explain.

2. Define spontaneity or-feasibility of a process.

3. Enthalpy of neutralization of CH_3COOH and NaOH is 55.9 kJ. What is the value of ΔH for ionization of CH_3COOH?

4. When 1 gm of liquid naphthalene (C10H8) solidifies, 150 J of heat is evolved. What is the enthalpy of fusion of $C_{10}H_8$?

5. Why most of the exothermic processes (reactions) are spontaneous?

6. What is meant by the term state function? Give examples.

Long Questions:

1. Define
    (i) Standard enthalpy of formation.
    (ii) Standard enthalpy of combustion
    (iii) Enthalpy of atomization
    (iv) Enthalpy of solution
    (v) Lattice enthalpy
    (vi) Thermochemical equation.

2. For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, $K_c = 1.8 \times 10^{-7}$. What is ΔG° for the reaction? (R = 8.314 $JK^{-1} mol^{-1}$).

3. Calculate the equilibrium constant, K, for the following reaction at 400 K?

    $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

    Given that $\Delta_rH° = 80.0$ kJ mol^{-1} and $\Delta_rS° = 120$ $JK^{-1} mol^{-1}$.

4. Calculate the standard entropy change for the reaction $X \rightleftharpoons Y$ if the value of ΔH° = 28.40 kJ and equilibrium constant is 1.8×10^{-7} at 298 K and $\Delta_rG° = 38.484$ kJ.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

    Assertion (A): Combustion of all organic compounds is an exothermic reaction.

    Reason (R) : The enthalpies of all elements in their standard state are zero.

    (i) Both A and R are true and R is the correct explanation of A.

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(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A is false but R is true

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Assertion (A) : Spontaneous process is an irreversible process and may be

reversed by some external agency.

Reason (R) : Decrease in enthalpy is a contributory factor for spontaneity.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A is false but R is true.

Case Study Based Question:

1. This law was presented by Hess in 1840. According to the law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change is always the same.

Thus, the total enthalpy change of a chemical reaction depends on the initial and final stages only.
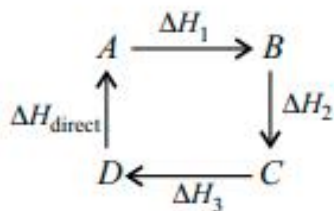
Total enthalpy change from A to D,

$\Delta H_{total} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta H_{total} + \Delta H_{direct} = 0$
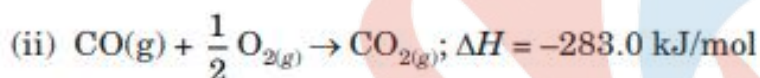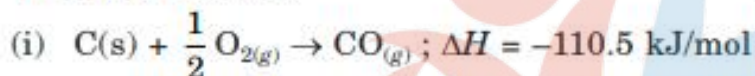
i.e., $\Delta H_{total} = -\Delta H_{direct}$

For example, formation of CO_2 from C in two different manners involves a total heat change of -393.5 kJ/ mol

Single step process :

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -393.5$ kJ/mol

Two step process :

(i) $C(s) + \dfrac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$; $\Delta H = -110.5$ kJ/mol

(ii) $CO(g) + \dfrac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -283.0$ kJ/mol
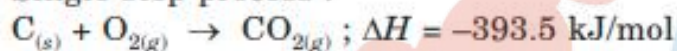
$\Delta H_{Total} = -110.5 + (-283.0) = -393.5$ kJ/mol

(1) In which of the enlisted cases, Hess's law is not applicable?

  (a) Determination of lattice energy

  (b) Determination of resonance energy

  (c) Determination of enthalpy of transformation of one allotropic form to another

  (d) Determination of entropy

(2) Use the bond energy data and calculate the enthalpy change for

$$C_{(g)} + 2H_{(g)} + 2Cl_{(g)} \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-Cl$$
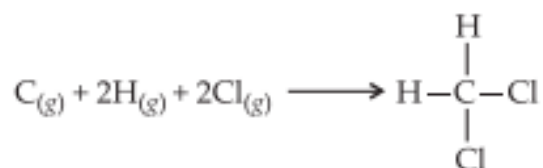
The Bond energies of $C-H$ and $C-Cl$ are 413 and 328 kJ mol^{-1} respectively.

  (a) – 1465 kJ/mol

  (b) 1465 kJ/mol

(c) – 1482 kJ/mol

(d) 1482 kJ/mol

(3) A hypothetical reaction, A 2B, proceeds through the following sequence of steps:

$$A \longrightarrow C; \Delta H = q_1$$
$$C \longrightarrow D; \Delta H = q_2$$
$$\frac{1}{2}D \longrightarrow B; \Delta H = q_3$$
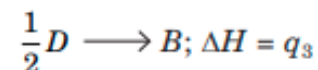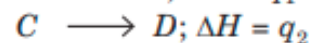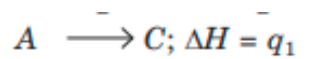
The heat of reaction is

(a) $q_1 - q_2 + 2q_3$

(b) $q_1 + q_2 - 2q_3$

(c) $q_1 + q_2 + 2q_3$

(d) $q_1 - 2q_2 + 2q_3$

2. The enthalpy of a system is defined as the sum of the internal energy of the system and the energy that arises due to its pressure and volume. Mathematically, the enthalpy is defined by the equation,

H = U + PV

Enthalpy change (ΔH) of a system is the heat absorbed or evolved by the system at constant pressure.

ΔH = qp, ΔH = ΔU + PΔV

(1) Which of the following is not correct about enthalpy?

(a) It is an extensive property

(b) It is not a state function

(c) Its absolute value cannot be determined

(d) Enthalpy of a compound is equal to the enthalpy of formation of that compound.

(2) Lattice enthalpies are determined by:

(a) Born-Haber cycle

(b) Hess's law

(c) lattice cycle

(d) None of these

(3) In which of the following thermochemical changes ΔH is always negative?

(a) Enthalpy of solution

(b) Enthalpy of hydrogenation

(c) Enthalpy of reaction

(d) Enthalpy of transition

Answer Key:

MCQ

1. (d) 1st law of Thermodynamics

2. (b) -11.224 kJ

3. (d) Third Law

4. (b) Hydrogen

5. (a) -5 J

6. (b) Hydrogen Gas

7. (c) $5P_1V_1$

8. (c) Absolute Entropy

9. (c) I, II and III

10. (c) Endothermic

11. (c) 350 kJ

12. (a) HCl and NaOH

13. (d) -50.4 kJ

14. (b) The change in entropy along with suitable change in enthalpy decides the fate of a reaction

15. (b) w = -11.488 k

Very Short Answer:

1. At constant volume.

2. AH is positive as $\Delta H = H_p - H_r$ and $H_r < H_p$.

3. They are equal.

4. This is due to the high hydration energy of fluoride ions.

5. Specific heat capacity for $H_2O = 4.18$ JK^{-1} g^{-1}

Molar heat capacity for $H_2O = 4.18 \times 18 = 75.24$ JK^{-1} mol^{-1}.

6. A part of the heat is used up for dissociation of the weak acid or weak base or both

7. A specified part of the universe that is under thermodynamic observation is called a system.

Short Answer:

Ans: 1. Water is the liquid form while ice is its solid form. Molecular motion in ice is restricted than in water, i.e., a disorder in ice is restricted than water, i.e., a disorder in ice is less than in water.

Ans: 2. Spontaneity or feasibility of a process means its inherent tendency to occur on its own in a particular direction under a given set of conditions.

Ans: 3. The heat of neutralization of strong acid and strong base + ΔH of ionization of CH_3COOH
= Enthalpy of neutralization of CH_3COOH and NaOH
∴ − 57.1 kJ + ΔH of ionization of CH3COOH = − 55.9 kJ
∴ ΔH of ionization of $CH_3COOH = (- 55.9 + 57.1)$ kJ
= 1.2 kJ.

Ans: 4. ΔHsolidifcation $= − 150 \times 128 = − 19200$ J $= − 19.2$ kJ

[∵ M.wt.of $C_{10}H_8 = 128$]

Ans: 5. $\Delta G = \Delta H - T\Delta S$; For exothermic reactions,

ΔH is -ve For a spontaneous process ΔG is to be -ve.

Thus decrease in enthalpy (- AH) contributes significantly to the driving force (To make ΔG negative).

Ans: 6. A state function is a thermodynamic property that depends upon the state of the system and is independent of the path followed to bring about the change. Internal energy

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change (ΔU), enthalpy change (ΔH) entropy change (ΔS), and free energy change (ΔG) are examples.

Long Answer:

Ans: 1. Standard enthalpy of formation: The heat change accompanying the formation of 1 mole df a substance from its elements in their most stable state of aggregation is called its standard enthalpy of formation.

$$H_2(g) + \frac{1}{2} O_2(g) \; H_2O(l); \; \Delta_f He = 285.8 \text{ kJ mol}^{-1}$$
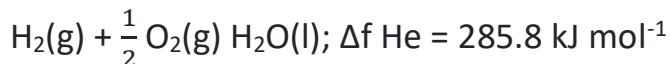
(ii) Standard enthalpy of combustion: It is the heat change accompanying the complete combustion or burning of one mole of a substance in its standard state in excess of air or oxygen.

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(1); \; \Delta H\theta = - 2658.0 \text{ kJ mol}^{-1}.$$
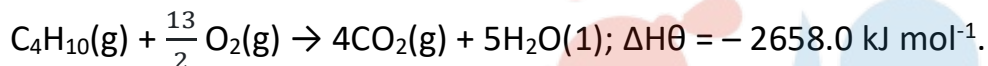
(iii) Enthalpy of atomization: It is defined as the enthalpy change accompanying the breaking of one mole of a substance completely into its atoms in the gas phase.

$$H_2(g) \rightarrow 2H(g) \; \Delta_c He = 435.0 \text{ kJ mol}^{-1}$$

(iv) Enthalpy of solution: It is defined as the heat change when one mole of a substance dissolves in a specified amount of the solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving 2 moles of the substance in an infinite amount of the solvent.

(v) Lattice Enthalpy: The lattice enthalpy of an ionic compound is the enthalpy change that occurs when one mole of an ionic compound dissociates into its ions in a gaseous state.

$$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g); \; \Delta_{lattice} H^0 = + 788 \text{ kJ mol}^{-1}$$
1 mole
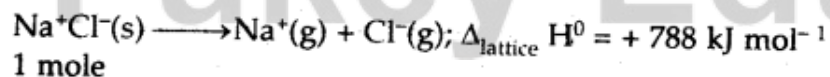
(vi) Thermochemical Equation: A balanced chemical equation together with the value of its A^H is called a thermochemical equation.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); \; \Delta_r H^0 = - 1367 \text{ kJ mol}^{-1}$$
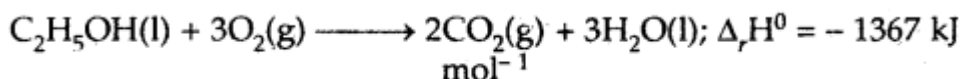
The above equation describes the combustion of liquid ethanol. The negative sign indicates that tills are an exothermic reaction. We specify the physical state along with the allotropic state of

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the substance in a thermochemical equation.

Ans: 2.

$$K_P = K_C(RT)^{\Delta n}$$
$$\Delta n = n_p - n_r = 2 - 1 = 1.$$
$$T = 298 \text{ K}, R = 8.314 \text{ JK}^{-1} \text{mol}^{-1} [Given]$$
$$\therefore \quad K_p = 1.8 \times 10^{-7} \times 8.314 \times 298 = 4.46 \times 10^{-4}$$
Now
$$\Delta_r G^0 = -2.303 \text{ RT log } K_p$$
$$= -2.303 \times 8.314 \times 298 \times \log(4.46 \times 10^{-4})$$
$$= 19111.86 \text{ J mol}^{-1} = 19.12 \text{ kJ mol}^{-1}.$$

Ans: 3.

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$
$$= 80.0 - 400 \times 0.12 = 32.0 \text{ kJ}$$
$$\Delta_r G^0 = -2.303 \text{ RT log } K$$
$$32.0 = -2.303 \times 0.0831 \times 400 \log K$$

or
$$\log K = -4.1782 = \bar{5}.8218$$

or
$$K = \text{Antilog } \bar{5}.8218 = 6.634 \times 10^{-5}.$$

Ans: 4.

$$\Delta_r G^0 = -2.303 \text{ RT log } K = 38484 \text{ J (given)}$$
$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$
$$\Delta_r S^0 = \frac{\Delta_r H^0 - \Delta_r G^0}{T} = \frac{28400 - 38484}{298}$$

$$= -33.8 \text{ JK}^{-1} \text{ mol}^{-1}$$

Assertion Reason Answer:

1. (ii) Both A and R are true but R is not the correct explanation of A.

2. (ii) Both A and R are true but R is not the correct explanation of A.

Case Study Answer:

1. **Answer:**

(1) (d) Determination of entropy

(2) (c) – 1482 kJ/mol

(3) (c) $q_1 + q_2 + 2q_3$

2. Answer:

(1) (b) It is not a state function

(2) (a) Born-Haber cycle

(3) (b) Enthalpy of hydrogenation

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