

COURSE : B.Sc I
PAPER : I
TOPIC : THERMODYNAMICS

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Thermodynamics and Energetics

Thermodynamics

Thermodynamics is the study of transfer of heat and other forms of energy into or out of system due to physical or chemical transformation

Thermodynamics is concerned only with the energy changes accompanying a given process (physical or chemical) and not with the total energy of the body.

The study of thermodynamics is based on three general laws, called first, second and third law of thermodynamics. All these laws are based on human experiences and although there is no formal proof so far for these laws.

Basic concepts of thermodynamics

Chemical Energetics

The branch of chemistry which deals with energy changes during various physical processes and chemical reactions is called chemical energetics.

Thermodynamic scale of temperature

To understand hotness or coldness of matter, we need to define a temperature scale. In Celsius scale, we are familiar with reference points— ice point (0° C) and the steam point (100° C) for water. This scale has 100 divisions and each division is referred to 1° C. In SI unit system, Kelvin is an internationally accepted scale. It is based on the absolute zero of temperature and **the triple point of water**. (Triple point of water is a temperature at which all the phases ..i.e., ice, liquid water and vapour coexist and in equilibrium). One kelvin is $\frac{1}{273.16}$ of the triple point temperature of water (273.16 K). This scale is called thermodynamic temperature scale.

Zerth Law of Thermodynamics

When two objects, at different temperatures are brought in thermal contact with each other, they exchange heat till they reach a state of thermal equilibrium and after that no further exchange of energy takes place. At this point, temperatures of both the objects are the same and the reading on the thermometer should be constant and the calibration mark will give the temperature of the object. These ideas are expressed in the form of law of temperature or thermal equilibrium, also known as zeroth law of thermodynamics.

System

A specific part of the matter which is under investigation and is isolated from the rest of the universe is called *system*.

Surroundings

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

For example, we wish to investigate the properties of Benzene. Here Benzene is the system. For studying the properties, we must take it in a container, say a beaker. The walls of the container are called boundaries. The other part of the universe that can interact with the system is called surroundings.

Types of Systems

- (i) A system which cannot exchange matter and energy with surroundings is called isolated system. Thermally well insulated and sealed to inflow of matter can be considered as an isolated system. A perfectly isolated system does not exist.
- (ii) A system is said to be closed system if it can exchange energy (heat or work) but not matter e.g., ice in a closed beaker.
- (iii) A system is said to be open system if it can exchange energy (heat or work) as well as matter with the surroundings. e.g., water in an open beaker takes energy from the surroundings and evaporates so that water vapours pass into surroundings.

State of Macroscopic System (State Functions)

The state of a thermodynamic system is described by its measurable or macroscopic properties. The thermodynamic parameters which depend only upon the initial and final states of the system and are independent of how the change is accomplished are called state functions. Examples of state functions are internal energy (E), enthalpy (H), entropy (S), free energy (G), pressure (P), temperature (T), volume (V) etc. Work and heat are not state functions because their values do not depend merely on the initial and final states but depend upon the path followed.

Energy of a System

The energy of the system is equal to the energy of all its components. In a system containing pure substance, the energy is equal to the sum of the energies of all the molecules, atoms or ions. The energy of a molecular system is equal to the translation energy, vibrational energy, rotational energy, bond energy, electronic energy.

Internal Energy or Intrinsic Energy is the total energy stored in a substance by virtue of its chemical nature.

$$E = E_t + E_v + E_r + E_e + E_n + E_{PE}$$

Internal energy is a state function i.e., depends only upon the state of the system and is independent of the method by which state had been attained.

Change in internal energy is the difference between the internal energies of the product, E_2 or E_P and that of reactants, E_1 or E_R .

$$E = E_2 \text{ (or } E_P) - E_1 \text{ (or } E_R)$$

Thermodynamic Process

The operation by which a thermodynamic system changes from one state to another is called thermodynamic process.

Isothermal Process: A process in which although heat enters or leaves the system yet temperature of the system remains constant throughout the process is called **isothermal process**.

Adiabatic Process: A process during which no heat enters or leaves the system during any step of the process is called **adiabatic process**.

Isochoric Process: A process during which volume of the system remains constant

throughout the reaction is known as **isochoric process**.

Cyclic Process: A process during which system comes to its initial state through a number of different processes is called **cyclic process**.

Reversible Process: A process in which change is carried out so slowly that the system and surroundings are always in equilibrium is known as **reversible process**.

Irreversible Process: When a process is completed in a single step and cannot be reversed, it is called an **irreversible process**. In such process, the system is in equilibrium with the surroundings in the initial and final state. Natural processes are irreversible.

Thermodynamic Equilibrium

It is an equilibrium that involves following:

- (i) Mechanical equilibrium
- (ii) Thermal equilibrium and
- (iii) Chemical equilibrium

Work

Work is a mode of energy transfer from or to a system with reference to the surroundings. Work is said to have been done whenever the point of application of a force is displaced in the direction of the force.

In thermodynamics, two types of works are mainly used.

Electrical work where reaction takes place between ions. Here generalized force is the EMF and the generalized displacement is the quantity of electricity flowing through the circuit. This,

Electric work done = EMF × Quantity of electricity

Mechanical (Pressure-Volume) work. As the name indicates pressure-volume type of work is performed when a system changes its volume in the presence of external pressure.

Work is usually represented by **W** and its units are **kg m² s⁻²**.

Heat

Heat is the energy exchange between the system and the surroundings as a result of difference of temperature between them. It is usually represented by **Q**.

Heat is usually measured in calories. A calorie is defined as the quantity of heat required to raise the temperature of one gram of water through 1°C. In SI system, its unit is **Joules**.

First Law of Thermodynamics

The first law of thermodynamics is identical to the law of conservation of energy. It states that **energy can neither be created nor destroyed although it can be converted from one form to another**.

The law can also be stated in the following ways:

(i) The total energy of an isolated system remains constant throughout although it can undergo a change from one form to another.

(ii) Whenever a quantity of some form of energy disappears, an exactly equivalent amount of some other form of energy must be produced.

(iii) It is impossible to construct a perpetual motion machine i.e., a machine which would produce work continuously without consuming energy (Helmholtz, 1847).

(iv) There is an exact equivalence between heat and mechanical work, i.e., for every 4.184 joules of work done, 1 calorie of heat is produced and vice versa (Joule, 1840).

Mathematical Representation of First Law of Thermodynamics

The Relation between Internal Energy, Work and Heat

The change in internal energy, E (i.e., $E_P - E_R$) accompanying a process, performing work, W and involving absorption of heat (Q) i.e., when the work is done by the system, is given by the relation

$$E = Q - W \quad \dots(1)$$

In case work is done on the system, then $E = Q + W$

Special Forms of the First Law of Thermodynamics

Under special conditions, the equation of first law of thermodynamics can be modified as:

(a) For Thermal reversible process,

$$E = 0$$

$$Q = -W$$

Since $W = -2.303 nRT \log \frac{V_2}{V_1}$

$$Q = 2.303 nRT \log \frac{V_2}{V_1} \quad \dots(A)$$

(b) For Cyclic process resulting to original state, i.e., for a process involving isothermal expansion of an ideal gas

$$E = 0$$

$$Q = W \quad \dots(B)$$

(c) For Isochoric process, no work of expansion is done, i.e.,

$W = 0$, equation (1) becomes

$$E = Q_v \quad \dots(C)$$

Where subscript v denotes that volume is held constant.

(d) For adiabatic process, when no heat is gained or lost to the surroundings, $Q = 0$

$$E = - W_Q \quad \dots(D)$$

Where subscript Q stands for constant heat.

(e) (i) When a gas expands against external pressure P, the work done by it is given by equation

$$W = - P \Delta V \quad \dots(E)$$

Where $\Delta V = V_2 - V_1$.

(ii) When a gas is compressed, work is done on the system and is given by

$$W = P \Delta V \quad \dots(F)$$

(iii) When a gas expands in vacuum, work done by it is zero since $P = 0$, therefore, $W = 0$.

(iv) In case of expansion of gas, maximum work is done if the process is isothermal and reversible.

5.14 Enthalpy (H)

The enthalpy is the Greek work (en = in, thalpos = heat). Formerly, it was called the heat content. It is defined as the total heat content of a system at constant pressure is known as enthalpy. Mathematically, it is the sum of internal energy and the pressure – volume energy.

$$H = E + PV \quad \dots(G)$$

Where E = internal energy of the system

PV = pressure volume work

Enthalpy is also a state function and its absolute value cannot be determined.

5.15 Change in Enthalpy (ΔH)

In a chemical reaction carried at constant pressure is the heat that is exchanged between the system and the surroundings. It is denoted by ΔH and is in fact the difference of the enthalpies of the products and reactants.

$$\Delta H = H_P + H_R \quad \dots(H)$$

Where H_P = Enthalpy of the products

H_R = Enthalpy of the reactants

Relation between Internal Energy (E) and Change in Enthalpy (ΔH)

The relation between internal energy (E) and change in enthalpy (ΔH) is given by the following equation

$$\Delta H = \Delta E + P \Delta V \quad \dots(I)$$

Using gas law, we know that

$$P \Delta V = nRT$$

Or $P(V_B - V_A) = n_g RT \quad \dots(J)$

Here, n_g refer to the number of moles gaseous products minus the number of moles of gaseous reactants.

Above equations are useful for calculating ΔH and ΔE and vice versa.

Heat Capacity and Specific Heat Capacity

The quantity of heat needed to raise the temperature of a substance by one degree Celsius (or one Kelvin) is known as Heat Capacity (C).

Heat capacity is directly proportional to the amount of substance.

Changing the temperature of a gaseous substance from t_1 to t_2 requires heat equal to $q = C_V \Delta T$ where $\Delta T = t_2 - t_1$

The specific heat or molar heat capacity of a substance is its heat capacity for one mole of the substance.

For finding out the heat q required to raise the temperature of a sample, the equation is

$$q = c \times m \times \Delta T$$

where c is the specific heat capacity of the substance

m is the mass of the substance and

ΔT is the temperature change.

5.18 Measurement of ΔE and ΔH

By using experimental technique called **calorimetry**, we can determine the energy changes associated with chemical and physical processes. Whenever a system absorbs or release energy in the form of heat, temperature changes takes place. These changes in temperature can be measured. Energy changes are made under two different

(i) at constant volume and

(ii) at constant pressure.

At constant volume,

$$\Delta E = q_v$$

i.e., heat absorbed gives the increase in internal energy.

At constant pressure, heat absorbed is equal to increase in enthalpy, i.e.,

$$\Delta H = q_p$$

for chemical reactions heat absorbed at constant volume is measured in a bomb calorimeter (See figure).

Figure should be here

5.19 Exothermic Reactions

If in a chemical reaction carried out at constant pressure, a certain amount of heat energy is **released** from the system to the surroundings at a give temperature, the

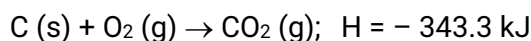
reaction is known as **exothermic reaction**.

Since heat energy has been released from the system to the surroundings, the enthalpy of the product becomes less than the enthalpy of the reactants.

$$H_p < H_R \quad \text{or} \quad H = H_p - H_R = -ve$$

Thus, in an exothermic chemical reaction, the heat evolved during the reaction is given by +ve sign, while H is given by -ve sign.

For example,

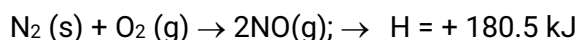


5.20 Endothermic Reactions

If in a chemical reaction carried out at constant pressure, a certain amount of heat energy is absorbed from the system to the surroundings at a give temperature, the reaction is known as **endothermic reaction**.

$$H_p > H_R \quad \text{or} \quad H = H_p - H_R = +ve$$

For example,



5.21 Thermochemical Equations

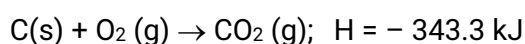
A chemical equation which gives the heat change (evolved or absorbed) during the reaction is called **thermochemical equation**. A thermochemical equation can be written in two ways.

(a) By writing the heat evolved or heat absorbed as a term in the equation.

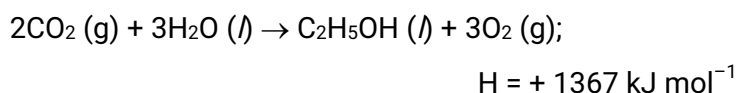
For example,



(b) By writing H notation i.e., writing $H = -ve$ for exothermic and $H = +ve$ for endothermic reactions.



For endothermic reaction, the equation can be written as



5.22 Conventions for Writing the Thermochemical Equation

(i) For exothermic reactions, H is negative and for endothermic reactions, H is positive.

(ii) Unless otherwise mentioned, H values are given for Standard State of a substance, i.e., when reactions occur at 298 K and standard pressure.

(iii) The coefficient of the substances of the chemical equations indicate the number of moles of each substance involved in the reaction (fraction may be used), and the H values given corresponds to these quantities of material.

(iv) For indicating the physical state of each substance in a chemical equation, designation such as (g), (s), (l) and (aq) are given along with the chemical formulae of reactants and products.

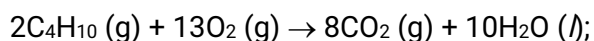
(v) In case the coefficients in the chemical equation are multiplied or divided by a factor, the ΔH values must also be multiplied or divided by the same factor.

(vi) When a chemical equation is reversed, the sign but not the magnitude of the ΔH value is changed. In other words, a reaction that is endothermic in one direction will be exothermic in the reverse direction.

5.23 Standard Enthalpy of Combustion (Heat of Combustion)

Combustion reactions are exothermic in nature. It is defined as the enthalpy per mole of a substance, all the reactants and products being in their standard state at the specific temperature. It may also be stated as the amount of heat evolved when one mole of the substance is completely burnt in air or oxygen. The reaction is exothermic, hence ΔH value is negative.

Cooking gas in cylinder contains Butane (C_4H_{10}). One mole of this gas on combustion gives 2658 kJ of heat.

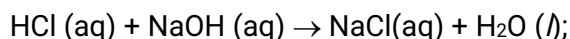


$$\Delta H = - 2658.0 \text{ kJ mol}^{-1}$$

5.24 Enthalpy of Neutralization (Heat of Neutralization)

It is the amount of heat evolved (i.e., change in enthalpy) when one gram equivalent of acid (or base) is neutralized by one equivalent of a base (or acid) in fairly dilute solution.

When one gram equivalent of HCl in dilute solutions is neutralized by NaOH solution, the enthalpy ΔH change is -57.1 kJ



$$\Delta H = - 57.1 \text{ kJ}$$

It has been observed that the enthalpy of neutralization of a strong acid against a strong base is always constant (13.7 kcal or 57 kJ mole^{-1}).

In fact strong acids and base are completely dissociated in aqueous solutions and enthalpy of neutralization is nothing except enthalpy of formation of H_2O formed by the combination of H^+ ions of the acid with OH^- ions of the base.

However, if either the acid or the base is weak, the enthalpy of neutralization is less than -57.1 kJ and is also different for different reactions.

5.25 Enthalpy Changes during Phase Transformation

(Enthalpy of Fusion)

It is defined as the enthalpy change that accompanies the conversion of one mole of a solid substance into the liquid state at its melting point.

For example, when one mole of ice melts at 273 K , the enthalpy of fusion is 6 kJ , indicating that it is an endothermic change.



5.26 Enthalpy Changes during Phase Transformations

(Enthalpy of Evaporation)

It is defined as the enthalpy change that accompanies the conversion of one mole of a liquid substance into the gas state at its boiling point.

The enthalpy change accompanying the vaporization of one mole of water (liquid) into gas (water vapour) at its boiling point 100°C is 40.5 kJ.



5.27 Enthalpy Changed during Phase Transformation

(Enthalpy of Sublimation)

It is defined as the enthalpy change that accompanies the conversion of one mole of a solid substance directly into its gaseous state at a temperature below its melting point.

For example, the enthalpy of sublimation of iodine is 621.39 kJ

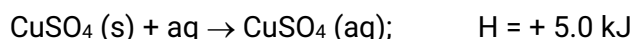


5.28 Enthalpy Changes during Phase Transformations

(Enthalpy of Solutions)

The enthalpy changes accompanying the dissolution of one-mole of a substance in such a large excess of solvent so that further addition of solvent does not produce any enthalpy change is called enthalpy of solution.

For example, dissolution of anhydrous copper sulphate



5.29 Hess's Law of Constant Heat Summation

The law states that the total heat change (H) accompanying a chemical reaction is the same whether the reaction takes place in one or more steps. It means that the heat of a reaction depends only on the initial reactant and the final products and not on the intermediate products that may be formed. Hess's law of heat summation may be represented as

$$\text{H} = \text{H}_a + \text{H}_b + \text{H}_c + \dots\dots\dots$$

Where a, b, c, refer to balanced thermochemical equations that can be summed to give the equation for the desired reaction.

5.30 Enthalpy of Formation

It may be given as the enthalpy change that accompanies the formation of one mole of a substance from its elements.

Normally it is measured under standard conditions of temperature (298 K) and

pressure (760 mm of Hg). It is known as standard enthalpy of formation and is denoted as H_f° .

For example,



Here H_f° is the same as the enthalpy of reaction H . But in certain reactions the two value may not be the same.

By convention, the standard enthalpy of formation H_f° of an element in its standard state is taken as zero.

5.31 Bond Enthalpies

The bond energy is the amount of energy necessary to break bonds in one mole of a gaseous covalent substance to form products in the gaseous state. for example, the bond energy of H-H bond in H_2 molecule is 435 kJ mol^{-1} .

The value of H (change in enthalpy) in terms of bond energy may be calculated as

$$H = \sum \text{Bond energy of reactants} - \sum \text{bond energy of products}$$

Remember that this relationship is approximate and is valid when all substances (reactants and products) in the reaction are in gaseous state.

5.32 Calorific Value of Food Stuff

It is the energy released in the combustion of one gram of the substance (food or fuel). It is expressed in kilo calories per gram i.e., kcal g^{-1} .

5.33 Spontaneous Change or Reaction

The term spontaneous means the **feasibility of a process**. When a system undergoes a physical or chemical change either of its own or under slight initiation of temperature, pressure or concentration, such change is called **spontaneous change**.

(a) Process where no limitation is needed

Water keeps on evaporating from river, sea or open vessels.

(b) Process where some limitations are required

Once a reaction between H_2 and O_2 is initiated by passing electric spark through it, then it occur itself spontaneously even at room temperature.

5.34 Cause of Spontaneity

There are two main reasons or factors of spontaneity of a process.

These are

- (i) tendency to have minimum energy.
- (ii) tendency to have maximum randomness

(i) Tendency to have minim energy is the factor responsible for spontaneous nature of change. Most of the spontaneous changes are exothermic i.e., there is a release of

energy from the system to the surrounding during the change. H has $-ve$ sign.

(ii) Tendency to have maximum randomness. Although the most spontaneous changes are of exothermic nature but there are many changes which are accompanied by the absorption of energy. H has $+ve$ sign.

Thus, it is clear that tendency to have minimum energy cannot be the only criterion for the spontaneous change to take place.

During the evaporation of water there is a change in physical state from liquid to the gas. The products formed have a greater randomness or free movement as compared to the reactants. The energy absorbed is used to increase the randomness or free movement of the species. Thus tendency to have maximum randomness is another factor responsible for the spontaneous nature of a change.

5.35 Entropy

The entropy of a system is the property which measures its randomness or disorder. It is always denoted by S . The change in entropy is indicated by ΔS . For a process carried out reversibly under equilibrium conditions, the entropy change is given by

$$S = \frac{q}{T} = \frac{\Delta E + P\Delta V}{T} \quad [\because q = \Delta E + P\Delta V]$$

The change in entropy

$$\Delta S = S_{(\text{product})} - S_{(\text{reaction})}$$

Unit of Entropy is calories per degree per mole or Joules per Kelvin per mole ($\text{JK}^{-1} \text{mol}^{-1}$)

5.36 Free Energy

It may be defined as the maximum amount of energy available to a system during a process that can be converted into useful work. It is denoted by the symbol G and is given by

$$G = H - TS$$

Where H is the enthalpy of the system. S is the entropy and T is the absolute temperature.

If a process is carried out at constant temperature, the change in free energy is denoted as ΔG and is given by

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

This equation is called **Gibb's Helmholtz equation** and is useful for indicating the feasibility of a spontaneous change or reaction.

Illustration 7

(a) Calculate the energy needed to raise the temperature of 10.0 g of iron from 25° to 500° if specific heat capacity of iron is $0.45 \text{ J } (^\circ\text{C})^{-1} \text{ g}^{-1}$.

(b) What mass of gold (of specific heat capacity of $0.13 \text{ J } (^\circ\text{C})^{-1} \text{ g}^{-1}$) can be heated through the same temperature difference when supplied with the same amount of energy as in (a)?

Solution

(a) Mass of iron, $m = 10.0 \text{ g}$

Temperature difference, $t = 500 - 25 = 475^\circ\text{C}$

Specific heat capacity of iron, $c = 0.45 \text{ J}(\text{°C}^{-1}) \text{ g}^{-1}$

Energy needed = $m \times c \times t$

$$= 10 \times 0.45 \times 475 = 2.1 \times 10^3 \text{ J}$$

(b) Specific heat capacity of gold, $c = 0.13 \text{ J}(\text{°C}^{-1}) \text{ g}^{-1}$

Energy needed = $m \times c \times t$

$$2.1 \times 10^3 = m \times 0.13 \times 475$$

$$m = \frac{2.1 \times 10^3}{0.13 \times 475} = 34 \text{ g}$$

Illustration 8

Standard vaporization enthalpy of benzene at its boiling point is 30.8 kJ mol^{-1} ; for how long would a 100 W electric heater have to operate in order to vaporize a 100 g sample of benzene at its boiling temperature? $\left(\text{power} = \frac{\text{energy}}{\text{time}}, 1 \text{ W} = 1 \text{ Js}^{-1} \right)$

Solution

Standard vaporization enthalpy of benzene

= 30.8 kJ/mol (given)

Power of heater = 100 W

Molar mass of $\text{C}_6\text{H}_6 = 72 + 6 = 78 \text{ amu}$

Heat required to vaporize 78 g of $\text{C}_6\text{H}_6 = 30.8 \times 1000 \text{ J}$

Heat required to vaporize 100 g of C_6H_6

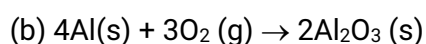
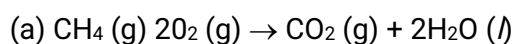
$$= \frac{30.8 \times 1000 \times 100}{78} = 39900 \text{ J}$$

100 J heat is given in 1 s

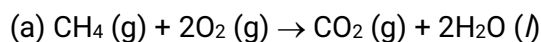
$$39900 \text{ J heat is given in } \frac{39900 \times 1}{100} = 399 \text{ s} = 6.6 \text{ min.}$$

Illustration 9

Use the standard enthalpies of formation and calculate the enthalpy changes accompanying the following reactions:

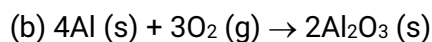


Solution

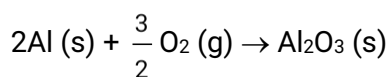


1 g of CH₄ on combustion liberates -55.6 kJ

16 g (1 mole) CH₄ liberates -55.6 × 16 = 889.6 or 890 kJ



The equation can be written as



Heat evolved in the combustion of 2 × 27 = 54 g of Al

$$= -1675.5 \text{ kJ}$$

Heat evolved in the combustion of 4 × 27 = 108 g of Al

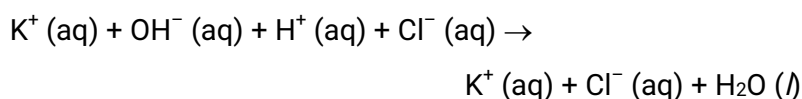
$$= -1675.5 \times 2 \text{ kJ} = -3351.0 \text{ kJ}$$

Illustration 10

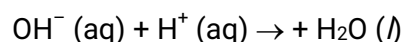
Acetic acid (ethanoic acid) and hydrochloric acid reacts with KOH solution. the enthalpy of neutralization of ethanoic acid is - 55.8 kJ mol⁻¹ while that of hydrochloric acid is - 55.8 kJ mol⁻¹. Can you think of how are these different?

Solution

The enthalpies of neutralization of ethanoic acid and hydrochloric acid are different. It is so because both hydrochloric acid and KOH are strong and are completely ionized in aqueous solutions of their own. No energy is needed for their ionization. The cations of the base and anions of the acids cancel out from both side of the reaction equation. The neutralization involves the combination of H⁺ ions of the acid and OH⁻ ions of the base aqueous solution, as is shown in the equation below



By cancelling the common ions, we get



Ethanoic acid is a weak which is not completely ionized in aqueous solution. KOH is strong, it has to be ionized fully to complete the neutralization reaction. For this purpose, some energy is needed. This is why, enthalpies of neutralization of ethanoic acid is -55.8 kJ and hydrochloric acid is - 57.3 kJ.

Illustration 11

Specific heat of Li(s), Na(s), K(s), Rb(s) and Cs(s) at 398K are 3.57, 1.24, 0.756, 0.363 and 0.242 Jg⁻¹K⁻¹, respectively. Compute the molar heat capacity of these elements and identify any periodic trend, if there is trend, use it to predict molar heat capacity of Fr.

Solution

Molar heat capacity = sp. Heat \times molar mass

$$\begin{aligned}\text{Molar heat capacity of Li(s)} &= 3.57 \times 6.919 \\ &= 24.8 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Molar heat capacity of Na (s)} &= 1.24 \times 22.99 \\ &= 28.3 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Molar heat capacity of K(s)} &= 0.756 \times 39.012 \\ &= 29.6 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Molar heat capacity of Rb(s)} &= 0.363 \times 85.47 \\ &= 31.0 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Molar heat capacity of Cs(s)} &= 0.242 \times 132.90 \\ &= 32.2 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Molar heat capacity of Fr will be $33.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

Illustration 12

Calculate the enthalpy change when 2.38 g of carbon monoxide (CO) vaporize at its normal boiling point.

Solution

Molar mass of CO = 12 + 16 = 28 amu

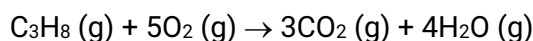
$$H_{\text{vap}} \text{ of CO} = 6.04 \text{ kJ mol}^{-1}$$

For 28 g of CO enthalpy change is 6.04

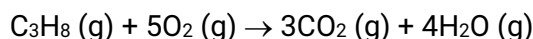
$$\begin{aligned}\text{For 2.38 g of CO enthalpy change will be } &\frac{6.04 \times 2.38}{28} \text{ kJ} \\ &= 0.5134 \text{ kJ} = + 513.4 \text{ J}\end{aligned}$$

Illustration 13

Propane has the structure $\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_3$. Use the average bond enthalpies from the table 5.3 a to estimate the change in enthalpy, ΔH , for the following reaction:



Solution

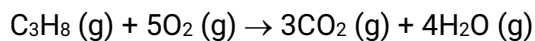


$$\begin{aligned}\Delta H &= [3(-393.5) + 4(-241.8)] - [-103.2] \\ &= -(-1180.5 - 967.2) + 103.2 \\ &= -2147.7 + 103.2 = -2044.5 = -2.05 \times 10^3 \text{ kJ/mol}\end{aligned}$$

Illustration 14

In the above reaction (Problem 13), if the standard enthalpy change $\Delta H = -2.05 \times 10^3$ kJ/mol and bond energies of C-C, C-H, C = O and O - H remains the same, calculate the energy of oxygen-oxygen bond in O_2 molecules and compare the calculated value with the value given in the table.

Solution



$$C_3H_8 = 3(414) + 8(436) = 1242 + 3488 = 4730$$

$$5O_2 = 10x$$

$$3CO_2 = 3 \times 414 + 3 \times 2 \times (464) = 1242 + 2784 = 4026$$

$$4H_2O = 4 \times 2 \times (436) + 4(464) = 3488 + 1856 = 5344$$

As per equation

$$4026 + 5344 - 4730 - 10x = -2.05 \times 10^3$$

$$4640 - 10x = -2050$$

$$-10x = -2050 - 4640 = -6690$$

$$x = 669 \text{ kJ/mol.}$$

Energy of oxygen bond is 669 kJ/mol.

Energetic

Illustration 8.4

How much heat is evolved when:

- (i) 500 ml of 0.2 M HCl is mixed with 250 ml of 0.3 M NaOH.
 (ii) 0.15 Moles of H₂SO₄ are neutralized by 0.3 moles of NaOH.
 (iii) 100 ml 0.5 M HNO₂ is mixed with 200 ml of 1.0 M KOH.

Solution

To solve such problems we have to bear in mind:

(i) That 1 mole of an acid or base = x equivalents of it where x is the number of H⁺ ions per mole of the acid or OH⁻ ions per mole of the base furnished in the solution on dissociation.

For example $x = 1$ in case of HCl, HNO₃, NaOH, KOH, NH₂OH, CH₃COOH

$x = 2$ in case of H₂SO₄, H₂C₂O₄, Ca(OH)₂, Ba(OH)₂

$x = 3$ in case of H₂PO₄.

(ii) V mol of M molar solution

$$= V \times M \text{ millimoles or } \frac{V \times M}{1000} \text{ moles}$$

Keeping this in mind let us first calculate the equivalent of the acid and base taken in each case of the problem.

1st Case: 500 ml of 0.2 M HCl

$$= \frac{500 \times 0.2}{1000} = 0.1 \text{ mole of HCl} = 0.1 \text{ equivalents}$$

250 ml of 0.3 M NaOH

$$= \frac{250 \times 0.3}{1000} = 0.075 \text{ mole of NaOH} = 0.075 \text{ equivalent}$$

Obviously, in this case 0.075 eq. of HCl will be neutralized by 0.075 eq. of NaOH and (0.1 - 0.075) = 0.025 eq. of HCl which is in excess will remain un-neutralized in solution.

Since heat of neutralization = 57.3 kJ or 57300 J eq⁻¹

Heat evolved in this case = 57300 × 0.075 = 4298 J

2nd Case: 0.15 mol of H₂SO₄ = 0.15 × 2 = 0.3 eq. of H₂SO₄.

0.3 mol of NaOH = 0.3 × 1 = 0.3 eq. of NaOH

Since equal moles of the acid and base are mixed, there will be complete neutralization in this case.

Heat evolved for neutralization of 0.3 eq. of acid = 57300 × 0.3

$$= 17190 \text{ J}$$

3rd Case: 100 ml of 0.5 M HNO₃

$$= \frac{100 \times 0.5}{1000} = 0.05 \text{ mol or } (0.05 \times 1) = 0.05 \text{ eq. of HNO}_3$$

200 ml of 1.0 M KOH

$$= \frac{200 \times 1.0}{1000} = 0.2 \text{ mol or } (0.2 \times 1) = 0.2 \text{ eq. of NaOH}$$

In this case NaOH being in excess, only 0.05 eq. of both will be neutralized.

$$\begin{aligned} \text{Heat evolved when 0.55 eq. acid is neutralized} &= 57300 \times 0.05 \\ &= 2865 \text{ J} \end{aligned}$$

Illustration 8.5

Calculate the rise in temperature in the (i), (ii) and (iii) cases given above assuming that the water equivalent of the Calorimeter (Container, thermometer and stirrer) = 10 g K⁻¹ (specific heat of water is 4.18 JK⁻¹)

Solution

Water equivalent of 10g K⁻¹ means that for every one degree Kelvin rise of temperature heat absorbed by the calorimeter (container, thermometer and stirrer) absorb the same quantity of heat as 10 g of water for calculations of rise in temperature, we use the following formula, assuming that density of solution = 1g/ml so that volume of solution = mass of solution.

Heat evolved = (Total mass of solution taken + water equivalent)

(sq. heat). T Thus, in case (i), (500 + 250 + 10) (4.18) T = 4298

Whence T, rise in temperature = $\frac{4298}{760 \times 4.18} = 1.35 \text{ K}$ and in case (iii), (100 + 200 + 10)

(4.18) T = 2865.

Rise in temperature in this case, $T = \frac{2865}{310 \times 4.18} = 2.21 \text{ K}$

Similarly, in case (iv), (600 + 1000 + 10) (4.18) T = 5730.

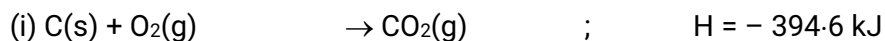
Rise in temperature in this case = $\frac{5730}{1610 \times 4.18} = 0.85 \text{ K}$

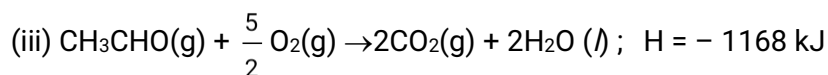
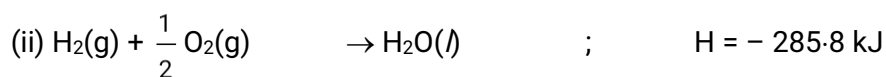
Illustration 8.6

Heat of formation of CO₂(g) and H₂O under standard conditions is 394.6 and 285.8 kJ per mole. If the standard heat of combustion of acetaldehyde be 1168 kJ per mole, find its heat of formation.

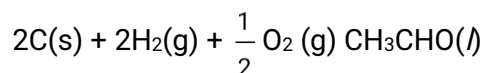
Solution

From the given data

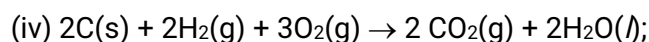




We are required to find out the H value for the reaction

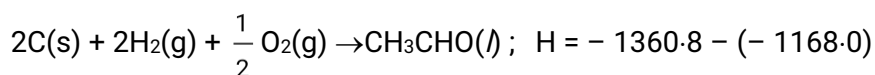


To obtain this equation multiply (i) and (ii) by 2 and add



$$\text{H} = 2(-394.6 - 285.8) = - 1360.8 \text{ kJ}$$

Subtracting (iii) from (iv) and rearranging



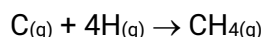
$$= - 192.8 \text{ kJ}$$

Illustration 8.7

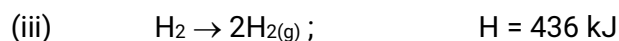
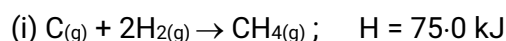
Calculate the enthalpy of C – H bond. Given that enthalpy of formation of methane is $-75.0 \text{ kJ mol}^{-1}$ and bond energy of $\text{C}(\text{g}) - \text{C}(\text{g}) = 718.6 \text{ kJ mol}^{-1}$ and that of hydrogen = $436.0 \text{ kJ mol}^{-1}$.

Solution

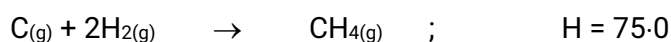
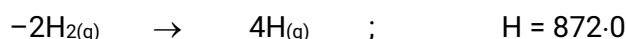
For this purpose, we need the enthalpy change for the reaction



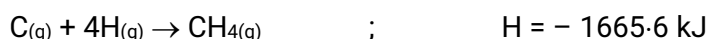
We write the thermochemical equations representing formation of methane, dissociation of $\text{C}(\text{g}) \rightarrow \text{C}(\text{g})$ and of $\text{H}_2(\text{g}) \rightarrow 2\text{H}$ as



In order to obtain the desired reaction, viz, $\text{C}(\text{g}) + 4\text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g})$ which involves the formation of four C-H bonds, we multiply (ii) by (-1) and (iii) by (-2) and (i) by 1 as



On adding the three equations and rearranging , we get



Assuming them to be identical, the average energy for forming one C-H bond = $-1665.6 \div 4 = -416.4$ kJ.

Hence, by definition bond energy of C-H = 416.41 kJ

Illustration 8.9

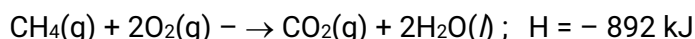
How much gobar gas will be needed to meet the requirement of 250 families of a village each requiring on an average 25000 kJ of energy per day, if gobar gas contains 80% of methane by weight. Heat of combustion of methane is 892 kJ mol.

Solution

Consumption of energy per family = 25000 kJ per day.

Total daily consumption of energy of the village of 250 families
= $25000 \times 250 = 6250000$ kJ.

From the combustion reaction of methane



Mass of methane required to generate 890 kJ of energy = 16 g

Methane required to generate 6250000 kJ of energy

$$= \frac{16 \times 6250000}{892} = 1,12,00,000 \text{ g} = 11200 \text{ kJ}$$

Since gobar gas contains 80% methane

$$\text{Requirement of gobar gas for the village} = \frac{11200 \times 100}{80} = 14000 \text{ kg}$$

Illustration 9

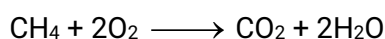
A gas mixture of 3.67 L of ethylene and methane on complete combustion at 25°C produces 6.11 L of CO₂. Find out the amount of heat evolved on burning 1 L of the gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol⁻¹ at 25°C.

Solution

Let volume of C₂H₄ and CH₄ be a and b litre respectively at 25°C.

$$a + b = 3.67 \text{ L} \quad \dots(1)$$

Also, $\text{C}_2\text{H}_4 + 3\text{O}_2 \longrightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$



Volume of CO₂ produced by a litre C₂H₄ = b

$$2a + b = 6.11 \quad \dots(2)$$

By equation (1) and (2)

$$a = 2.44 \text{ L}$$

$$b = 1.23 \text{ L}$$

Volume of CH₄ in 1 L mixture at 25°C

$$= \frac{2.44}{3.67} \times 1 = 0.6648 \text{ L}$$

And, volume of CH₄ in 1 L mixture at 25°C

$$= \frac{1.23}{3.67} \times 1 = 0.3352 \text{ L}$$

Now, volume of 1 mole C₂H₄ at 0°C = 22.2 L

$$\text{Volume of 1 mole C}_2\text{H}_4 \text{ at } 25^\circ\text{C} = \frac{22.4 \times 298}{273}$$

$$= 24.45 \text{ L}$$

Similarly,

$$\text{Volume of 1 mole CH}_4 \text{ at } 25^\circ\text{C} = \frac{22.4 \times 298}{273}$$

$$= 24.45 \text{ L}$$

∴ 24.45 L C₂H₄ produces = + 1423 kJ at 25°C

$$0.6648 \text{ L C}_2\text{H}_4 \text{ produces} = \frac{+1423 \times 0.6648}{24.45}$$

$$= + 38.69 \text{ kJ}$$

Similarly,

24.45 L CH₄ produces = + 891 kJ at 25°C

$$0.3352 \text{ L CH}_4 \text{ produces} = \frac{+891 \times 0.3352}{24.45}$$

$$= + 12.22 \text{ kJ}$$

Thus, total heat produced = 38.69 + 12.22

$$= 50.91 \text{ kJ}$$

Illustration 21

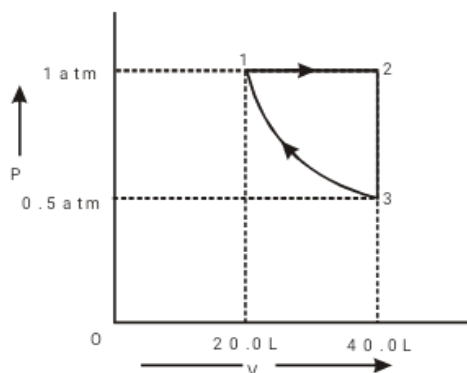
Two moles of a perfect gas undergo the following processes:

- a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L)
- a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L)
- a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)

- (i) Sketch with labels each of processes on the same P-V diagram.
- (ii) Calculate the total work (w) and the total heat change (Q) involved in the above processes.
- (iii) What will be the values of U , H and S for the overall process?

Solution

(I) P-V diagram



(i) In reversible isobaric expansion pressure is constant (i.e., 1.0 atm) and volume is increased from 20.0 L to 40.0 L (from state 1 to 2). So work done

$$\begin{aligned} w_1 &= -P(V_2 - V_1) \\ &= -1 \times (40 - 20) \\ &= -20 \text{ L-atm} \end{aligned}$$

(ii) In reversible isochoric change of state (from '2' to 3), volume is constant (40 litres) while pressure is decreased from 1 atm to 0.5 atm. Hence in this change work done (w_2) = 0

(iii) In reversible isothermal compression volume and pressure both are change. Thus system is reached at state '1' (Change takes place from 3 to 1). Hence in this change work done

$$\begin{aligned} w_3 &= -2.303 nRT \log_{10} \frac{V_2}{V_1} \\ &= -2.303 \times 2 \times 0.0821 \times 298 \log_{10} \frac{20}{40} \\ &= -2.303 \times 2 \times 0.0821 \times 298 \times -0.3010 \text{ L-atm} \\ &= 33.92 \text{ L-atm} \end{aligned}$$

(II) Total work (w) = $w_1 + w_2 + w_3$

$$= -20 + 0 + 33.92 = 13.92 \text{ L-atm}$$

$$= 13.92 \times \frac{8.314}{0.0821} \text{ J} = 1.409 \times 10^3 \text{ J}$$

$$(III) \quad U = 0, \quad S = 0 \text{ and } H = 0$$

(for cyclic process)

Illustration 23

100 mL of a liquid contained in an insulated container at a pressure of 1 bar. The pressure is steeply increases to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the H and U .

Solution

$$U = q = W$$

For adiabatic process $q = 0$; hence $U = W$

$$\text{And } W = -p(\Delta V) = -P(V_2 - V_1)$$

$$\text{So, } U = -100(99 - 100) = -100(-1)$$

$$\text{Hence, } U = 100 \text{ bar mL}$$

$$\text{Now } H = U + (PV)$$

Here U already calculated above and

$$PV = (P_2V_2 - P_1V_1)$$

$$\text{So, } H = 100 + (100 \times 99 - 1 \times 100) = 9900 \text{ bar mL}$$