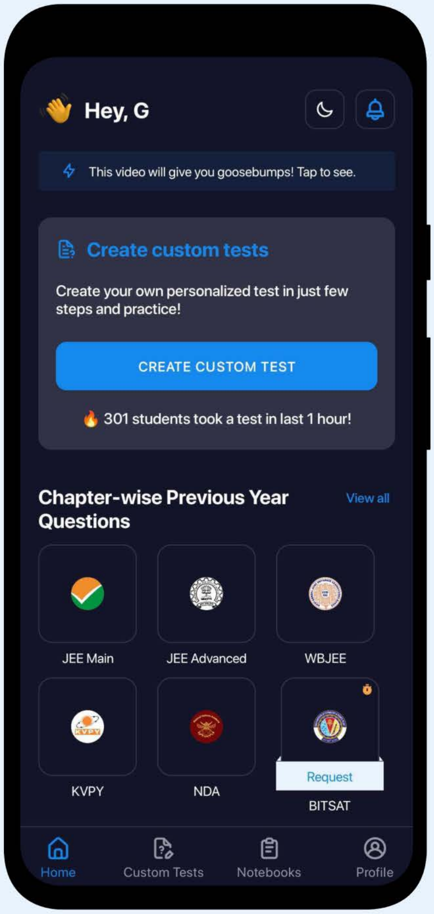


THERMOCHEMISTRY

THERMODYNAMICS

Introduction

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

All chemical reactions are normally accompanied by energy changes. These energy changes take place because energy is needed to break chemical bonds, and energy is released when new bonds are formed. In the process of chemical reaction, rearrangement of atoms in reactants take place, to give products.

Important Thermodynamic Terms

Some common terms, which are frequently used in the discussion of energetics need to be known.

System

'A specified part of the universe which is under investigation is called the system'. The system is separated from the rest of the universe by a definite (real or imaginary) boundary.

Types of Systems

Systems are of various types depending upon the exchange of mass and energy and the constituent between the system and the surroundings.

Isolated system

A system, which can neither exchange mass nor energy with surroundings, is called an isolated system. They are also called insulated systems. Hot coffee (in contact with its vapour) in a closed and insulated thermos is an example of isolated system. Since the vessel is closed, matter can neither enter nor leave the vessel. Moreover, as the vessel is well insulated, heat can neither leave the system nor enter from the surroundings.

Closed system

A system, which can exchange energy but not mass with the surroundings is called a closed system. For example, boiling water in a closed steel vessel is an example of a closed system. The energy can be gained or lost (through the steel walls) but not matter. Similarly, all reactions carried out in a closed container are examples of closed systems.

Open system

A system, which can exchange matter as well as energy with the surroundings is called an open system. All reactions carried out in open containers are examples of open system. Evaporation of water in a beaker or hot coffee in a cup represents an open system. Here vapour of water or coffee (matter) can leave the system and escape into atmosphere. The heat energy required for this purpose is absorbed from the surroundings. All physical and chemical processes taking place in open in our daily life are open systems because they are continuously exchanging matter and energy with the surroundings.

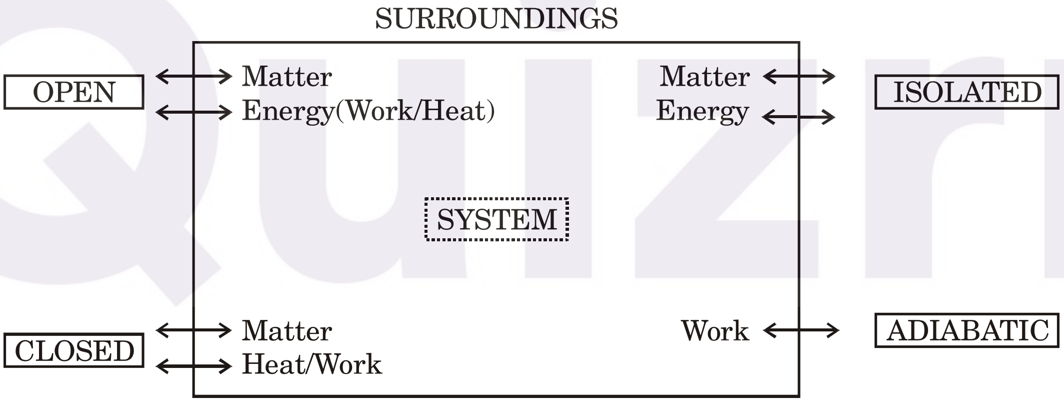
- A system is said to be macroscopic when it consists of a large number of molecules, atoms or ions. Properties associated with a macroscopic system are called macroscopic properties; pressure, volume, temperature, mass, composition, surface area etc. are macroscopic properties.
- A system is homogeneous when it is completely uniform throughout–a system with one phase, pure gas, pure liquid or pure solid. A system is heterogeneous when it is not uniform throughout–a system with two or more phases.
  - gaseous mixture is always one-phase system
  - every solid is in different phase.

$$2NH_3(g) \rightleftharpoons 3H_2(g) + N_2(g)$$

one-phase system

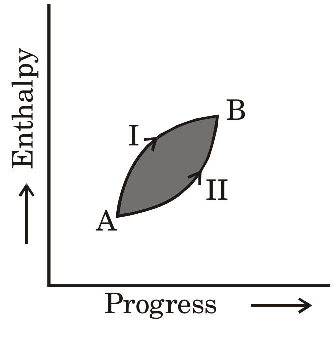
$$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2(g)$$

three-phase system



Different type of systems

State Functions



We use the term state function to describe any property of a system that does not depend on how the system gets to the state exhibiting that property. The change in the state function depends on the initial and final values and not on the manner or path adopted to bring about that change. We move A to B by path I as well as by path II. If heat content (enthalpy) is a state function then

$$\Delta H_1 = \Delta H_2 = H_B - H_A$$

Internal energy, entropy, free energies, etc., are state functions or state of a system.

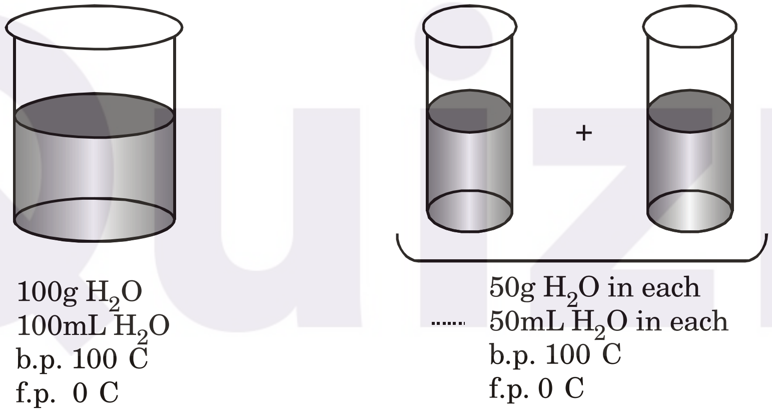
State Variables

When there is any change in the macroscopic property, state of the system also changes, hence macroscopic properties are also called state variables. For an ideal gas PV = RT (R is gas constant and P, V and T are state variables.) If P and T are known, then V can be calculated. The two variables, generally specified, are temperature and pressure–called independent variables. The third variable generally volume is called dependent variable.

- Thermodynamic state of a system consisting of a single gaseous substance may be completely defined by specifying any two of the three variables–temperature, pressure and volume.
- A system in a state of thermodynamic equilibrium is one in which the macroscopic properties do not change with time.

Extensive and Intensive Properties

Those variables whose values on division remain the same in any part of the system are called intensive variables, e.g., temperature, pressure, concentration (molarity, normally), density, dipole moment, viscosity, refractive index, pH, surface tension, molar volume, gas constant, specific heat capacity, vapour pressure, specific gravity, emf of a dry cell, etc.



Those variables whose values in any part of the divided systems are different from the entire system are called extensive variables, e.g., volume, energy, heat capacity, enthalpy, entropy, free energy, length and mass.

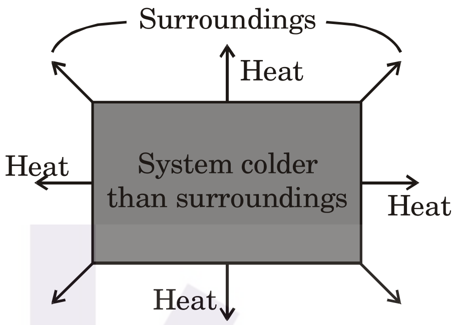
mass changes on division – an extensive property
volume changes on division – an extensive property
b.p. and f.p. are same even on division – intensive properties

Energy Terms in Thermodynamics

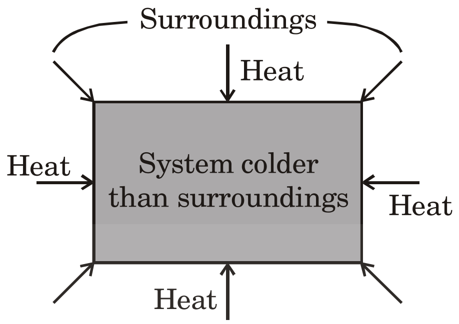
Every system has a definite amount of energy. It can exchange energy (lose or gain) with the surroundings in a variety of ways. In chemical systems the two important modes of transference of energy between the system and the surroundings are heat and work.

Heat (Q)

Energy exchanged between the system and the surroundings when they are at different temperatures is commonly known as heat. If a system is at a higher temperature than the surroundings, then there is a flow of heat (or energy) from system to surroundings, causing a decline of the systems temperature and an increase in the surrounding temperature. These process continue till the fall in temperature of the system and rise in temperature of the surroundings, become equal.



(a) Temprature of system decreases



(b) Temprature of system increases

Work (W)

Work is another mode of transference of energy. Work is said to be done if the point of application of force undergoes displacement in the direction of the force. If the system loses energy, we say that the work is done by the system. Alternatively, if the system gains energy, we say that work is done on the system.

For example, if a gas, enclosed in a cylinder with a piston, has a higher pressure than the surroundings, the piston will move upward until the pressure inside and outside become equal. The gas expands against a constant external pressure 'P' and its volume changes by an amount equal to ΔV. The energy transfer that takes in this case is called work. At this step the work is done by the system on the surroundings. This is given as :

Work done by the system = $P\Delta V$.

Alternatively, if the system is at lower pressure, piston will be pushed down until the pressure of the system becomes equal to that of the surroundings. In this case work is done on the system by the surroundings.

Obviously, if there is no change in volume, i.e.,

$\Delta V = 0$, no work is done by the system, i.e. work = 0.

In addition to these two modes, radiant energy and electrical energy are also modes of transference of energy between the system and the surroundings.

Units of heat and work

The heat changes are measured in calories (cal), kilo calories (kcal), joules (J) or kilojoules (kJ). These are related as :

1 cal = 4.184 J

1 kcal = 4.184 kJ

The S.I. unit of heat is joule or kilojoule

Work is measured in terms of ergs or joules.

1 Joule = 10^7 ergs

1 calorie = 4.184 $\quad 10^7$ ergs

The S.I. unit of work is joule.

Sign Conventions for Heat and Work

The signs of ‘w’ and ‘q’ are related to the internal energy change. When ‘w’ or ‘q’ is positive, it means that energy has been supplied to the system as work or as heat. The internal energy of the system in such a case increases. On the other hand, if ‘w’ or ‘q’ is negative, it means that energy has left the system as work or heat. The internal energy of the system decreases. The signs of ‘q’ and ‘w’ are :

Heat absorbed by the system = q positive

Heat evolved by the system = q negative

Work done on the system = w positive

Work done by the system = w negative

Internal Energy

Every substance possesses a definite amount of energy which depends upon factors such as composition of the substance, temperature and pressure. This is called intrinsic or internal energy (E).

$E = E_T + E_R + E_V + E_B + E_E$ ....

where E_T = Translational energy, E_R = Rotational energy, E_V = Vibrational energy, E_B = Bonding energy and E_E = Electronic energy.

Internal energy of a system is state function and its absolute value can not be calculated but its change can be determined. When the system undergoes a change in its state, the internal energy change is given by

$\Delta E = E_2 - E_1$

where E_1 = Internal energy in the initial state and E_2 = Internal energy in the final state.

In a chemical reaction, $\Delta E = E_P - E_R$

where E_P = Internal energy of products and E_R = Internal energy of reactants.

Enthalpy (H)

Heat content of a system at constant pressure is called enthalpy. It is related with internal energy by the equation,

$$H = E + PV.$$

Every substance has a definite value of enthalpy in a particular state. It is also a state function like internal energy. The change in enthalpy accompanying a process can be determined as

$$\Delta H = H_2 - H_1$$

where H_1 = Enthalpy of a substance in the initial state and H_2 = Enthalpy of a substance in the final state.

In the case of a chemical reaction, $\Delta H = H_P - H_R$

where H_P = Enthalpy of products and H_R = Enthalpy of reactants.

Relation Between ΔH and ΔE

Let us consider a chemical reaction, $X \longrightarrow Y$

then at constant pressure (P), the enthalpy change would be given as $\Delta H = H_y - H_x$

we know that, $H = E + PV$

Let E_x and V_x be the internal energy and volume of the reactants and E_y and V_y be the respective values of products. Then

$$H_x = E_x + PV_x \ \& \ H_y = E_y + PV_y$$

$$\Delta H = (E_y + PV_y) - (E_x + PV_x)$$

$$\Delta H = (E_y - E_x) + P(V_y - V_x)$$

$$\Delta H = \Delta E + P\Delta V \quad \text{...(i)}$$

Thermodynamic Equilibrium

A system in which the macroscopic properties do not undergo any change with time is said to be in **thermodynamic equilibrium.**

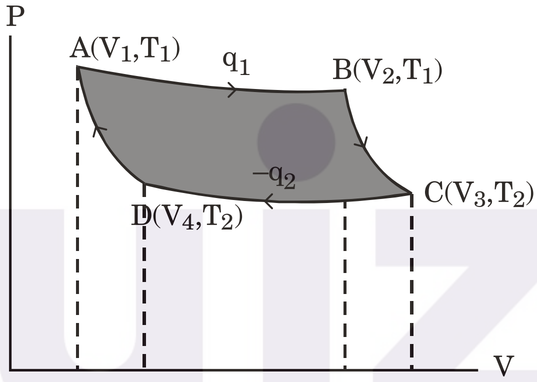
- If there is no flow of heat from one portion of the system to another then system is said to be in **thermal equilibrium.** This is only possible if temperature remains constant throughout in all parts of the system.
- These are expressed by **zeroth law of thermodynamics.**
- Two objects at different temperatures in thermal contact with each other tend to move towards the same temperature.
- Two objects in thermal equilibrium with the third one are in thermal equilibrium with each other.

- If no mechanical work is done by one part of the system on another part of the system then system is said to be in **mechanical equilibrium.** This is only possible if pressure remains same throughout in all parts of the system.
- If composition of the various phases in the system remains the same throughout then system is said to be in **chemical equilibrium.**

Process

The operation by which a system changes from one state to another is called a process. A process is accompanied by change in energy (and matter also if system is open).

- If a process is taking place at constant temperature, it is said to be **isothermal** (iso-same, therm-heat, temperature) process.
- If a process is taking place at constant pressure, it is said to be **isobaric** process.
- If a process is taking place at constant volume, it is said to be **isochoric** process.
- If no heat enters or leaves the system during any step of the process, it is said to be adiabatic process.



In this types of processes, temperature changes because the system is not in a position to exchange heat with the surroundings. If there is any type of expansion (due to increase in volume), it is done at the expense of internal energy which therefore decreases hence temperature may fall. If there is any type of contraction, internal energy is released, which therefore, increases and temperature may increase.

Process	**Temperature**	**Volume**	**Heat exchange**	**Type**
A to B	T_1 constant	$V_2 > V_1$	$+ q_1$	isothermal expansion
B to C	$T_2 < T_1$	$V_3 > V_1$	0	adiabatic expansion, temperature falls
C to D	T_2 constant	$V_4 < V_3$	$- q_1$	isothermal compression
D to A	$T_2 < T_1$	$V_1 < V_4$	0	adiabatic compression temperature increases

In the above example system has undergone a series of changes and ultimately comes back to the initial state. Such type of process is called **cyclic** process.

- If a process is carried out in such a way that the system remains virtually in a state of equilibrium, it is saidto be quasi-static (or reversible) process. The overall change in a state function is zero when the system returns to its original condition.

Example 1

Assuming ideal behaviour, calculate the work done when 1.6 mole of water evaporates at 373 K against the atmospheric pressure of 760 mm of Hg.

Solution :

Volume of 1.6 mole of water at 373 K in gaseous state

$$= \frac{nRT}{P} = \frac{1.6 \times 0.082 \times 373}{1} = 48.93$$

Volume of 1 mol = 18 g of liquid water (density = 1 g ml^{-1})

$$= 18 \quad 1.6 \quad 10^{-3} \text{ L} = 0.0288 \text{ L}$$

Now work done (W) $= -P(V_2 - V_1)$

$$= -1(48.93 - 0.0288) = -48.90 \text{ atm L}$$

$$= -48.90 \quad 101.325 \text{ J} = -4954.8 \text{ J}$$

Example 2

A system absorbs 470 J of heat and does work equivalent to 200 J on its surroundings. Calculate the change in internal energy.

Solution :

Heat absorbed by the system = 470 J or q = 470 J

Work done by the system = 200 J or w = – 200 J

According to first law of thermodynamics

$\Delta E = q + w$

$\Delta E = 470 - 200 = 270$ J

Example 3

A gas absorbs 120 J of heat and expands against the external pressure of 1.10 atm from a volume of 0.5 L to 2.0 L. What is the change in internal energy ? (1 L atm = 101.3 J)

Solution :

Work of expansion, $w = P\Delta V$

$\Delta V = 2.0 - 0.5 = 1.5$ L, P = 836 mm of Hg

$$P\Delta V = 1.10 \quad 1.5$$

$$= 1.650 \text{ L atm}$$

$$= 1.650 \quad 101.3 \text{ (1 L atm = 101.3 J)}$$

$$= 167.1 \text{ J}$$

Since work is done by the system $w = -167.1$ J

Heat absorbed by the system = 120 J or $q = +120$ J

Now, $\Delta E = q + w$

$$= 120 \text{ J} + (-167.1) = -47.1 \text{ J}$$

Enthalpy Changes

Generally, the amount of heat, q that a system absorbs or evolves as it changes is not a state function; it varies with the method the process has adopted. If the change occurs in such a way that the only work done is to affect a change in volume of the system at constant pressure, then q reflects a change in a state function of the system called enthalpy, H defined by equation

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

We cannot determine the enthalpy of a system but we can measure change in enthalpy as the system changes.

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

$$\Delta H = \Delta E - (-P\Delta V)$$

$$\Delta H = \Delta E - W$$

$$\Delta E = \Delta H + W$$

where $W = -P\Delta V = -P(V_2 - V_1)$

Like E, H is also a state function as its change, ΔH, is independent of the path adopted.

- Enthalpy of the element (in gaseous, liquid, solid or combined as H_2) is zero

  If $PV = nRT$ for n moles of an ideal gas

  $P(V + \Delta V) = (n + \Delta n_g)RT$ for $(n + \Delta n_g)$ moles of an ideal gas

  $\therefore \quad PV + P\Delta V = nRT + \Delta n_g RT$

  $\therefore \quad P\Delta V = \Delta n_g RT$

  $\therefore \quad \Delta H = \Delta E + \Delta n_g RT = q$

ΔH is also called heat of reaction at constant pressure and ΔE the heat of reaction at constant volume, Δn_g = coefficient of gaseous products – coefficient of gaseous reactants

At constant volume (V = constant)

$$\Delta V = 0$$

$$\therefore \quad P\,\Delta V = \Delta n_g RT = 0$$

$$\therefore \quad \Delta H = \Delta E = q$$

Under standard states when temperature is 298 K and pressure is 1 atm and all the species present are at unit activity.

$$\Delta H = \Delta E + \Delta n_g RT$$

Better way to specify standard states is to write temperature also

$$\Delta H_{298K} = \Delta H_{298\ K} + \Delta n_g R\ (298\ K)$$

and ΔH , etc., is to specify the temperature other than 298 K but at 1 atm and all the species at unit activity.

Heat Capacity

Heat capacity gives a measure of the quantity of heat absorbed by a system. It is defined as the amount of heat required to rise the temperature of the system through 1 C. If the quantity of heat required is to raise the temperature of unit mass of the substance through 1 C then it the specific heat of the substance. Whereas when the whole mass of the substance is considered, it is the heat capacity.

If 'q' is the heat required by the system to raise its temperature from T_1 to T_2, mathematically the heat capacity C of the system is given by the expression :

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

The value of 'C' is considered over a small temperature range as heat capacity varies with temperature. If δq is the heat required to raise the temperature of the system from T to T + dT, then

$$C = \frac{\delta q}{dT}$$

Heat capacity is path function and so the conditions such as constant volume or constant pressure have to be be specified to define the path for calculating the heat capacity of a system.

The heat capacity at constant volume is represented by C_v and that at constant pressure is represented by C_p.

Significance of C_v and C_p

For infinitesimally small changes, the expression for the first law can be written as $dE = \delta q + \delta w = \delta q - PdV$

$$\delta q = dE + PdV$$

At constant volume; At constant pressure;

or $dV = 0$ $dV \neq 0$

$$\delta q_{(v)} = dE$$

Now, $C_v = \frac{\delta q(v)}{dT}$ Also $H = E + PV$

$\therefore$ $dH = dE + PdV$

or $C_v = \frac{dE}{dT}$ or $\left(\frac{\partial E}{\partial T}\right)_v$ or $dE = dH - PdV$

Substituting in (i)

$$\delta\, q_{(p)} = dH - PdV + PdV = dH$$

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

Thus, heat capacity at constant volume represents the rate of increase of internal energy of the system with temperature, while the heat capacity at constant pressure represents the rate of increase of enthalpy of the system with temperature.

Molar heat capacities

The heat capacities of 1 mole of a gaseous system at constant volume and at constant pressure are called molar heat capacities.

Relationship between C_p and C_v

When the temperature of 1 mol of ideal gas is to be raised through one degree (1 K) the gas is heated at constant volume. The gas under this condition does no external work and the heat supplied increases the internal energy of the gas. When the gas is heated at constant pressure, there will be an increase in its volume. The gas will expand and do some external work. Extra heat must be supplied to the gas to enable it to perform this external work. Thus, heat capacity at constant pressure (C_p) is larger than that at constant volume (C_v). The difference between the two i.e., ($C_p - C_v$), gives the work done by

1 mol of the gas in expansion when it is heated through one degree. This represents the work done per mol per degree rise in temperature, i.e., R the universal gas constant. Thus,

$$C_p - C_v = R$$

The above conclusion can be arrived mathematically as follows :

$$C_p - C_v = \frac{dH}{dT} - \frac{dE}{dT} \quad .... \text{(i)}$$

Also $H = E + PV$

For an ideal gas, $PV = RT$

Therefore $H = E + RT$

Differentiation with respect to T $\frac{dH}{dT} = \frac{dE}{dT} + R.1$

or $$\frac{dH}{dT} - \frac{dE}{dT} = R \qquad \text{........ (ii)}$$

Comparing (i) and (ii) $C_p - C_v = R$ for 1 mole of ideal gas

The above relation is also called Meyer's relationship. It can also be written as $C_p - C_v = R = 1.99$ cal K^{-1} mol^{-1} = 8.314 JK^{-1} mol^{-1}.

The Ratio C_p/C_v

The ratio of molar heat capacities at constant pressure to that at constant volume is represented by γ. The value of γ gives information about the atomicity of gases.

$$\frac{C_p}{C_v} = \gamma$$

For monoatomic gases $\gamma = 1.67$

For diatomic gases $\gamma = 1.40$

For triatomic gases $\gamma = 1.30$

Example 4

A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against constant external pressure of 3.0 atm. The work of expansion is used to heat 10.0 mol of water at temperature 290 K. Calculate final temperature of water. (Specific heat of water = 4.184 JK^{-1} g^{-1})

Solution :

$W = - P(V_2 - V_1)$

$= - 3 \quad (5 - 3) = - 6$ L atm $= - 6 \quad 101.25$ J $= 6.07 \quad 10^2$ J

Now, $Q = m. C.\Delta T$

$$\Delta T = \frac{Q}{mC} = \frac{6.027 \times 10^2 \text{ J}}{10 \quad 18(g) \quad 4.184\,(J\,g^{-1}\,K^{-1})} = 0.8\,K$$

Final temperature = $T + \Delta T = 290 + 0.8 = 290.8$ K

PRESSURE–VOLUME WORK

Isothermal Expansion

No heat flows out of or into the system in an isothermal expansion, so that temperature remains constant throughout the process of expansion. Since for an ideal gas, the internal energy (ΔE), depends only on temperature, the internal energy of the gas remains constant.

i.e. $\Delta E = 0$

From Ist law of thermodynamics,

$$\Delta E = q + w$$

For isothermal process,

$$\Delta E = 0, \text{ hence } q = -w$$

In the case of isothermal expansion, work is done by the system at the cost of heat absorbed. The magnitude of 'q' or 'w' depends on the manner in which the process of expansion is carried out i.e. reversibly or irreversibly.

ΔH can be calculated as follows

We know, $\Delta H = \Delta E + \Delta n_g RT$

For isothermal process, $\Delta E = 0$ & $\Delta T = 0$ thus, $\Delta H = 0$

Work done in irreversible isothermal process

Suppose an ideal gas expands against external pressure P and its volume changes by an amount dV then work done W can be given by

$$W = -PdV$$

(a) **Free expansion** : $W = 0$, Since $P = 0$

(b) Expansion or compression against external pressure P

For a finite change V_1 to V_2,

Total work done on the system W is derived by

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

or $$W_{irr} = -P(V_2 - V_1) \quad ...(3)$$

Also $$\Delta U = \Delta H = 0 \quad ...(4)$$

If $V_2 > V_1$ then W_{irr} is – ve, i.e., expansion work or work done by the system.

The total work done during expansion of gas from V_1 to V_2

$$\int dW = \int_{v1}^{v2} -P\,dV = \int_{v1}^{v2} -\frac{nRT}{V}.dV$$

$$W_{rev} = -nRT\log_e\frac{V_2}{V_1} = -2.303\ nRT\log_{10}\frac{V_2}{V_1} \quad ...(5)$$

$(\therefore\ P \propto 1/V)$

Also $$W_{rev} = -2.303\ nRT\log_{10}\frac{P_1}{P_2} \quad ...(6)$$

Adiabatic Expansion

From first law of thermodynamics, $\Delta E = q + w$

In an adiabatic expansion, $q = 0$, $\therefore \Delta E = w$

The molar heat capacity at constant volume of an ideal gas is given by $C_v = \left(\frac{dE}{dT}\right)_v$

or $dE = C_v.\ dT$

and for finite changes, $\Delta E = C_v \quad \Delta T = w \quad ...(x)$

The value of ΔT depends upon the nature of process (i.e. reversible or irreversible).

Work done in adiabatic reversible process

Consider a system under adiabatic conditions, showing reversible expansion of an ideal gas by a volume dV, then from I law of thermodynamics,

($\because$ dq = 0)

$$+ dU = dW$$

$\therefore$
$$dU = nC_v\ dT$$

or
$$+ C_v.n \quad dT = dW$$

This equation reveals on further treatment within temperature limits of T_1 and T_2, reveals

$$dW = C_v \quad n \quad dT$$

$$C_p - C_v = R$$

$$\frac{C_p}{C_v} - \frac{C_v}{C_v} = \frac{R}{C_v}$$

$$C_v = \frac{R}{(\gamma - 1)}$$

Therefore,
$$dW = + \frac{R}{(\gamma - 1)} \times n \times dT$$

$$dW = \frac{nR}{\gamma - 1}.dT$$

on integration
$$\int dW = \frac{nR}{\gamma - 1}\int_{T_1}^{T_2} dT$$

$$w_{rev} = \frac{nR}{\gamma - 1}[T_2 - T_1] \quad ...(7)$$

if $T_2 > T_1$ then W_{rev} = + ve, i.e., work done on the system

if $T_2 < T_1$ then W_{rev} = – ve, i.e., work done by the system

$$\text{where } \gamma \text{ is Poisson's ratio} = \frac{C_p}{C_v} \qquad ...(8)$$

Also $$\Delta H = nC_p (T_2 - T_1) \qquad ...(9)$$

If final temperature is now known :

$$w = -\, nC_v T_1 \left[1 - \left(\frac{P_2}{P_1}\right)^{R/C_p}\right] \qquad ...(10)$$

Some important results of adiabatic expansions

1. PV^{γ} = constant ...(11)
2. $T^{\gamma}\ P^{1-\gamma}$ = constant ...(12)
3. $V^{\gamma-1}\ T$ = constant ...(13)

Work done in adiabatic irreversible expansion or compression

(a) Expansion against vacuum or free expansion

$$w = 0$$

(b) Expansion or compression against external pressure :

$$w = -\,P_{ext} \times R\left[\frac{P_1T_2 - P_2T_1}{P_1P_2}\right] \qquad ...(14)$$

Example 5

An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T. The other portion is a perfect vacuum. If a hole is opened between two portions, calculate :

(a) the change in internal energy

(b) the change in temperature of gas.

Solution :

The system being thermally insulated and thus q = 0. The gas expands through hole in other portion to show free expansion, i.e.

$$w = -\int P\Delta V = 0 \text{ (Since } P = 0)$$

Also from I law of thermodynamics

$$q = \Delta U + w$$

Since, $q = 0;\ w = 0 \quad \therefore\ \Delta U = 0$

Also Internal energy $U = \frac{3}{2}RT$. Since, internal energy remains same

($\therefore\ \Delta U = 0$) and thus temperature will also remain constant.

Example 6

2.8 g of N_2 gas at 300 K and 20 atm was allowed to expand isothermally against a constant external pressure of 1 atm. Calculate ΔU, q and W for the gas.

Solution :

Initially for N_2

$$20 \quad V_1 = \frac{2.8}{28} \times 0.0821 \times 300$$

$$\therefore \quad V_1 = 0.123 \text{ litre}$$

Finally for N_2

$$1 \quad V_2 = \frac{2.8}{28} \times 0.0821 \times 300$$

$$\therefore \quad V_2 = 2.463 \text{ litre}$$

$\therefore \quad W = -P \quad \Delta V$ [$\therefore$ work is done against constant P $\therefore$ irreversible]

$$= -1 \quad (2.463 - 0.123)$$

$$= -2.340 \text{ litre atm}$$

$$= -\frac{2.340 \times 1.987}{0.0821} \text{ calorie}$$

$$= -\frac{2.340 \times 1.987 \times 4.184}{0.0821} J$$

$$W = -236.95 \text{ J}$$

Now $\quad q = \Delta U - W$

$q = 0 + 236.95 \quad$ ($\therefore\ \Delta U = 0$ for isothermal process)

$q = 0\ 236.95$ Joule

SECOND LAW OF THERMODYNAMICS

Spontaneous Process

In any system, a spontaneous process is one which occurs in its own without the help of external energy. The natural changes that occur around us result for such processes. For example, flow of heat from a body to a cold one, flow of water downhill, and the expansion of a gas from high pressure to low pressure. Besides being spontaneous, these processes are also unidirectional i.e., they occur own in one direction only. A spontaneous process cannot be reversed without the aid of external work or energy. The work has to be done to move uphill or to compress a gas.

Many common chemical reactions are spontaneous and occur in one direction although finally a state of equilibrium is reached. Everything in nature have a tendency to move towards a state of lowest energy, at which point equilibrium exists. The heat energy which is given out during an exothermic reaction shows that there is a lowering in chemical energy on proceeding from the reactants to the products. From this, we may conclude that a reduction in enthalpy provides the necessary driving force for a reaction to occur. However, many endothermic reactions also proceed on their own and so it looks as though a negative enthalpy change is not a reliable criterion to judge the spontaneity of chemical reactions.

The first law of thermodynamics does not state whether a reaction is spontaneous or not and in which direction it will occur. For example, let us take a metal bar, which is heated at one end. Assuming no loss of heat from the bar, when heat passes from the hot end to the cold end, the decrease in thermal energy at the hot end is equal to the increase at the cold end. This satisfies the requirements of the law. From experience, we know that heat will not flow, on its own from the cold end to the hot end. However, the I law does not exclude the occurrence of such non-spontaneous processes, but only tells us that an energy decrease in one part of the system is equal to an increase in another part.

Statement of the II Law

Second law of thermodynamics is concerned with the direction and spontaneity of processes. There are many ways of formulating the law based on our experience of the direction or manner in which natural processes occur. Clausius stated the law as “The transference of heat from a cold to a hot body cannot be achieved without the performance of work.”

Because natural or spontaneous processes occur over a period of time, they must be thermodynamically irreversible. Another way of formulating the second law is ‘Any process occurring on its own is thermodynamically irreversible’.

The basic concept of the second law of thermodynamics is that all spontaneous processes are unidirectional and thermodynamically irreversible.

Entropy

Entropy (S) is a state function and is a measure of degree of disorder or randomness of system. More is the disorder in system, higher is its entropy. It is normally expressed in terms of change in entropy.

1. For a reaction entropy change (ΔS) is given by

$$\Delta S = \Sigma S_{\text{Products}} - \Sigma S_{\text{Reactants}} \qquad \text{...(18)}$$

2. $\Delta S = \frac{q_{rev}}{T} = \frac{W_{rev}}{T} = \frac{nRT \log_e \frac{V_2}{V_1}}{T} = nR \log_e \frac{V_2}{V_1}$

$$= 2.303\ nR \log_{10} \frac{V_2}{V_1} \qquad \text{...(19)}$$

$$= 2.303\ nR \log_{10} \frac{P_1}{P_2} \qquad \text{...(20)}$$

where, q_{rev} is the heat supplied to a system at temperature T (K) under reversible conditions.

3. At constant P, $q_{rev} = \Delta H_{rev}$

$$\Delta S = \frac{\Delta H_{rev}}{T} \qquad \text{...(21)}$$

i.e., entropy change of fusion :

$$\Delta S_f = \frac{\Delta H_f}{T} \qquad \text{...(22)}$$

where T is freezing point

and entropy change of vaporization :

$$\Delta S_v = \frac{\Delta H_v}{T} \qquad \text{...(23)}$$

where T is boiling point

4. Entropy of one mole of a substance in pure state at one atmosphere and 25 C is termed as standard entropy, S .

For a reaction in standard, A $\longrightarrow$ B

$$\Delta S^\circ = S_B^\circ - S_A^\circ \qquad \text{...(24)}$$

5. At absolute zero temperature, a solid is supposed to have highly ordered state,

$$S = 0, \text{ i.e, } \lim_{T \to 0} S = 0.$$

Meaning of Entropy

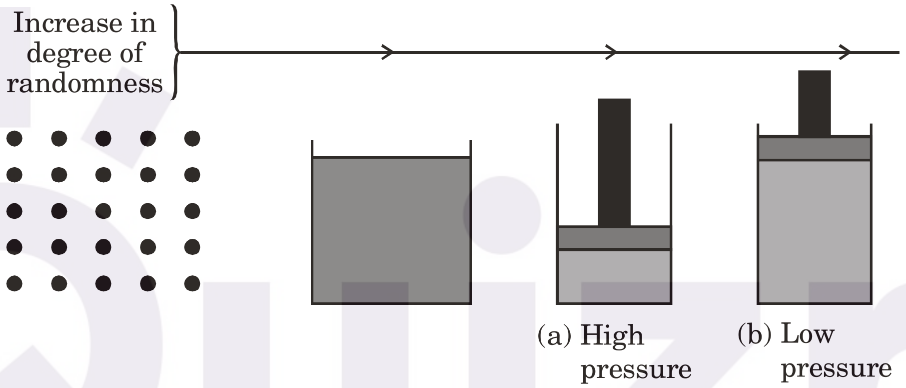
Although the concept of entropy was first applied to the performance of heat engines, pictorial representations of entropy can be obtained from two sources and lead to the following conclusions,

(a) Entropy is the degree of disorder or randomness of a system.

(b) Change in entropy is the capacity for spontaneous change in a system.

Entropy is a measure of disorderness of a system

To illustrate the meaning of disorder or randomness, consider a substance which changes state.



(1) Solid (2) Liquid (3) Gas

In the gaseous state and low pressure, the molecules are free to move about unrestricted. If the pressure is increased, the same number of molecules now occupy a smaller volume. The chances of finding a molecule within a given volume are greater under these conditions than when it was at lower pressure. Hence, the molecules are more ordered (or less randomly distributed) at higher pressure. Added to this, the force of intermolecular attraction increases as the pressure increases and this too has a restricting effect on the molecules.

In the liquid state, the molecules are much closer together than in the gaseous state, because the volume containing the same number of molecules is much smaller. The molecules in the liquid state are more highly ordered than a gas at high pressure. Also in the liquid state, the forces of intermolecular attraction are greater, causing a still more highly ordered state.

In this solid state, the atoms, molecules or ions that form the crystal are usually held in fixed crystal lattices, which can only vibrate and rotate. Hence in a solid, the atoms, molecules or ions have little or no choice as to where they shall be i.e., they are highly ordered or have a very small freedom.

This gradual decreases in the measure of disorder of the molecules is identified with entropy changes, being high for a gas and low for a solid.

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

For a spontaneous process ΔS_{total} must be positive, i.e.,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

When an isolated system is in equilibrium, the entropy is maximum. The mathematical condition for entropy (S) to be maximum is that the change in entropy (ΔS) is zero, i.e.,

$\Delta S = 0$ (at equilibrium for an isolated system)

In exothermic reactions, heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive. In some exothermic reactions, entropy of the system may also decrease due to conversion of a gas into a solid product. However, if reaction is highly exothermic and increase in entropy of the surroundings is very high, the total entropy change will be spontaneous. Let us take oxidation of magnesium which is highly exothermic. Conversion of oxygen into oxide results in decrease of entropy.

$$2Mg\ (s) + O_2\ (g) \rightarrow 2MgO\ (s)$$

$$\Delta_r S = -\ 217\ JK^{-1}\ mol^{-1}$$

$$\Delta_r H = -\ 1202\ kJ\ mol^{-1}$$

Heat released will increase the entropy of the surroundings and therefore

$$\Delta S^{\circ}_{surr} = -\frac{\left(-1202 \times 10^3\ Jmol^{-1}\right)}{298\ K} = +\ 4.03 \times 10^3\ JK^{-1}mol^{-1}$$

$$\Delta S_{total} = -\ 217\ JK^{-1}\ mol^{-1} + 4.03 \quad 10^3\ JK^{-1}\ mol^{-1} = +\ 3.81 \quad 103\ JK^{-1}\ mol^{-1}$$

Since ΔS_{total} is positive, reaction will be spontaneous.

In endothermic reactions, reactants on conversion into products go to higher energy state and temperature of the system falls. As a consequence, heat flows from surroundings into the system, the entropy of the surroundings decreases. If the disorder of the system rises sufficiently high and overall entropy increase is positive, the reaction will be spontaneous.

Entropy Change during Phase Transformations

Phase changes occur at constant temperature at a given pressure and process is reversible.

For example

$H_2O\ (s) \rightarrow H_2O\ (l);\ \Delta_{fus}H = 6.0\ kJmol^{-1}$

(takes place at 273 K at 1 bar)

$H_2O(l) \rightarrow H_2O\ (vap);\ \Delta_{vap}H = 40.79\ kJmol^{-1}$

(takes place at 373 K at 1 bar)

When solid melts, there is an equilibrium between the solid and the liquid at the freezing or melting point. The process involves latent heat which is equal to standard enthalpy of fusion, $\Delta_{fus}H$ at constant temperature and pressure. For water, $\Delta_{fus}H = 6.0\ kJmol^{-1}$.

$$\Delta_{fus}S = \frac{q_{rev}}{T} = \frac{\Delta_{fus}H^{\circ}}{T}$$

$$= \frac{6.0\ kjmol^{-1}}{273\,K} = \frac{6.0 \times 1000\ Jmol^{-1}}{273\ K} = 219.9\ mol^{-1}K^{-1}$$

Similarly, when a liquid is transformed into vapour at constant pressure and temperature.

$$\Delta_{vap}S = \frac{\Delta_{vap}H^{\circ}}{T}, \text{ (T is boiling point)}$$

Standard enthalpy of vaporization for water is 40.79 $kJmol^{-1}$

$$\Delta_{vap}S = \frac{\Delta_{vap}H^{\circ}}{T} = \frac{40.79\ kJmol^{-1}}{373\ K} = \frac{40.79 \times 1000\ Jmol^{-1}}{373\ K}$$

$$= 109.356\ JK^{-1}\ mol^{-1}$$

Example 7

The enthalpy of vaporization of benzene (C_6H_6) is 308 kJ mol^{-1} at its boiling point (80.1 C). Calculate the entropy change in going from (i) liquid to vapour and (ii) vapour to liquid at 80.1 C.

Solution :

Vaporization of a liquid is an endothermic process and therefore enthalpy of vaporization, $\Delta_{vap}H$ is positive. Contrary to this, condensation (i.e., from vapour to liquid) is exothermic process and therefore enthalpy of condensation is negative but magnitude of enthalpy in both the case is equal. That is,

$$\Delta_{vap}H = \Delta_{condens}H$$

For vaporization of benzene,

$$\Delta_{vap}S = \frac{\Delta_{vap}H^{\circ}}{T}$$

$$= \frac{30.8\ kJmol^{-1}}{353\ K} = \frac{30.8 \times 1000\ Jmol^{-1}}{353\ K} = 87.3\ JK^{-1}\ mol^{-1}$$

For condensation of benzene,

$$\Delta_{condens}S = \frac{-\Delta_{vap}H^{\circ}}{353\ K} = -87.3\ JK^{-1}\ mol^{-1}$$

Absolute Entropy

The entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached. This is third law of thermodynamics.

Molar entropy, the entropy per unit amount of a substance, is denoted by S_m. Standard molar entropy, the entropy per unit amount of substance in its standard state at the specified temperature is denoted by S_m°. The standard entropy of a substance or ion is also called absolute entropy. The definition of the entropy given by equation earlier helps in determination of entropy. The unit of molar entropy is $JK^{-1}mol^{-1}$.

Entropy Change for a Reaction

Entropy change for a chemical reaction (when reactants change completely into products) is calculated with the help of data given for standard molar entropies at a given temperature. From the sign of the entropy of a reaction, we can give qualitative information about the reaction. However, for quantitative work, we require standard entropy change, $\Delta_r S$ for a reaction and it can be determined by subtracting the standard entropies of reactants from the standard entropies of products. Thus,

$$\Delta_r S_m^\circ = \Sigma v_p S_m^\circ \text{(products)} - \Sigma v_r S_m^\circ \text{ (reactants)} \text{ (} v_p \text{ and } v_R \text{ are stoichiometric coefficients)}$$

For example, in a general reaction :

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r S_m^\circ = [c S_m^\circ \text{ (C)} + d S_m^\circ \text{ (D)}] - [a S_m^\circ \text{ (A)} + b S_m^\circ \text{ (B)}]$$

For oxidation of iron, $4Fe(s) + 3O_2\ (g) \rightarrow 2Fe_2O_3\ (s)$, we can write

$$\Delta_r S_m^\circ = 2 S_m^\circ\ [Fe_2O_3] - [4 \quad S_m^\circ\ (Fe) + 3 \quad S_m^\circ\ (O_2)]$$

$$= \{2 \quad 87.4 - (4 \quad 27.3 + 3 \quad 205.0)\}\ JK^{-1}mol^{-1}$$

$$= -\ 549.4\ JK^{-1}\ mol^{-1}$$

As expected, there is a large decrease in entropy during the reaction, mostly because the highly dispersed oxygen gas reacts to form the compact solid Fe_2O_3. Now, we would like to understand that inspite of the negative entropy of the reaction, why is the reaction spontaneous. As already emphasized, $\Delta S_{total} = (\Delta S_{System} + \Delta S_{Surrounding})$ only decides the spontaneity of a reaction. In this case, heat evolved during the reaction increases the entropy of the surroundings.

For calculating entropy changes in the surroundings, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H$. At temperature T, the entropy change of the surroundings is

$$\Delta S_{(surrounding)} = -\frac{\Delta_r H^\circ}{T} = \frac{q}{T}$$

In equation (above), because $-\Delta_r H$ is positive and so $\Delta_r S$ (surroundings) is also positive, corresponding to an increase from its initial value.

$$\Delta^{\circ}_{(\text{surrounding})} = \frac{-\left(-1648 \times 10^{3}\ \text{Jmol}^{-1}\right)}{298\ \text{K}} \quad (\Delta_r H \text{ for the reaction is } -1648 \quad 10^{3}\ \text{J mol}^{-1})$$

$$= 5530\ \text{JK}^{-1}\ \text{mol}^{-1}$$

This high increases in entropy of the surroundings is due to release of energy (heat) into surroundings. Thus, total entropy change for the oxidation of iron,

$$\begin{aligned} \Delta_r S^{\circ}_{m\ (\text{total})} &= \Delta_r S_{\ (\text{surroundings})} + \Delta_r S_{\ (\text{system})} \\ &= -\Delta_r H / T + \Delta_r S_{\ (\text{system})} \\ &= (+\ 5530\ \text{JK}^{-1}\text{mol}^{-1}) + (-\ 549.4\ \text{JK}^{-1}\text{mol}^{-1}) \\ &= 4980.6\ \text{JKmol}^{-1} \end{aligned}$$

This overall increase in the entropy makes the oxidation of iron $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ spontaneous.

Free Energies

Gibbs free energy G, is defined as $G = H - TS$

where H is the enthalpy, T is the temperature in Kelvin scale, S is the entropy. TS is the part of system's energy that is already disordered and H – TS (= G) is the part of the system's energy and that is still ordered hence, free (available) to cause spontaneous change by becoming disordered.

- G is also a state function hence, change in free energy (ΔG) for a process is independent of path
- $$\Delta G = \Delta H - T\Delta S$$

Also

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

$$= \Delta S - \frac{\Delta H}{T}$$

Since,

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$$

(we write ΔS_{system} simply as ΔS)

$$T\ \Delta S_{\text{total}} = T\Delta S - \Delta H$$

or

$$-T\Delta S_{\ \text{total}} = \Delta H - T\ \Delta S$$

$$-T\ \Delta\ S_{\text{total}} = \Delta G$$

Thus, ΔG and ΔS_{total} have opposite signs (T is always positive); hence sign of ΔG can also be used to predict feasibility of a reaction at constant temperature and pressure. For a reaction to be

$$\begin{aligned}\text{spontaneous if } \Delta S &> 0 \text{ then } \Delta G < 0\\ \text{nonspontaneous if } \Delta S &< 0 \text{ then } \Delta G > 0\\ \text{in equilibrium if } \Delta S &= 0 \text{ then } \Delta G = 0\end{aligned}$$

- $$\begin{aligned}\Delta G &= \Delta H - T\Delta S\\ &= \Delta E + P\Delta V - T\Delta S \qquad \left(\because \Delta S = \frac{q}{T}\right)\\ &= \Delta E - q + P\Delta V \qquad \Delta E = q - W \text{ by first law}\\ \Delta G &= -W + P\,\Delta V\\ -\Delta G &= W - P\,\Delta V = W_{net}\\ -\Delta G &= W_{net} = 2.303\, n\, RT \log\frac{V_2}{V_1}\end{aligned}$$

Thus, decrease in G, (– ΔG), is equal to net work done = (total work – mechanical work)

Table : Signs of Enthalpy, Entropy and Free Energy Changes and Reaction Spontaneity at Constant Temperature and Pressure

ΔH	**ΔS**	**ΔG = ΔH – TΔS**	**Reaction Spontaneity**
Exothermic	+	–	Spontaneous at all temperatures
	–	–	Spontaneous at low temperatures
		+	Non-spontaneous at high temperatures
Endothermic	+	+	Non-spontaneous at low temperatures
+	–		Spontaneous at high temperatures
	–	+	Non-spontaneous at all temperatures
TΔS = ΔH			Equilibrium

For a reaction in which a compound in its standard state is formed from its elements in their standard states, the free energy change is the standard free energy of formation, ΔG_f

$\Delta G_f = 0$ for the elements,

$$\begin{aligned}\Delta G_f &= (\Delta G_{products} - \Delta G_{reactants})\\ &= \Delta H - T\,\Delta S\end{aligned}$$

- ΔG is an extensive property,
- ΔG changes sign when a process is reversed.

Energy and Electromotive Force (EMF) of a cell

Using $\Delta G = \Delta G + 2.303\ RT \log Q$

$$\Delta G = -\ nFE_{cell}$$

$$\Delta G = -\ nFE\ _{cell}$$

We have $-\ nFE_{cell} = -\ nFE\ _{cell} + 2.303\ RT \log Q$

$$E_{cell} = E\ _{cell} - \frac{2.303\ RT}{nF}\log Q$$

This is called **Nernst equation** for emf of a cell.

E_{cell} is the emf of a cell in a given state, E cell is the standard emf, n the number of electrons exchanged, F the faraday of electricity, R gas constant and T the temperature. At 298 K

$$\frac{2.303\ RT}{F} = \frac{2.303 \times 8.314 \times 298}{96500}$$

$$= 0.0591\ V$$

$$\therefore \quad E_{cell} = E\ _{cell} - \frac{0.0591}{n}\log Q$$

When equilibrium is attained, $E_{cell} = 0$ and $Q = K$

$$\therefore \quad E\ _{cell} = \frac{00591}{n}\log K$$

Example 8

Determine whether or not it is possible for sodium to reduce aluminium oxide to aluminium at 298 K.

$\Delta G\ _f$ (298 K)/kJ mol^{-1} $Al_2O_3(s) = -\ 1582$

$Na_2O(s) = -\ 377$, element = 0

Solution :

The reaction is

$$Al_2O_3(s) + 6Na(s) \longrightarrow 3Na_2O(s) + 2Al(s)$$

hence, $\Delta G = 3\Delta G\ _f(Na_2O) - \Delta G\ _f(Al_2O_3)$

$= 3 \quad (-\ 377) - (-\ 1582) = +\ 451$ kJ mol^{-1}

Evidently the reaction cannot occur since ΔG (298 K) is positive.

Example 9

Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs

$$\textbf{S(rhombic)} \longrightarrow \textbf{S(monoclinic)}$$

If ΔH = 276.144 J at 298 K and 1 atm and ΔG = 75.312 J

(a) Calculate ΔS at 298 K

(b) Assume that ΔH and ΔS do not vary significantly with temperature, calculate T_{eq}, the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

Solution :

(a) Since $\Delta G = \Delta H - T\,\Delta\,S$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$= \frac{276.144 - 75.312}{298} = 0.674 \text{ J K}^{-1}$$

(b) Under equilibrium condition $\Delta G = 0$

$$\therefore \quad \Delta H - T_{eq}\Delta S = 0$$

$$\therefore \quad T_{eq} = \frac{\Delta H}{\Delta S} = \frac{276.144}{0.674}$$

$$= 409.7 \text{ K}$$

Example 10

Assume ΔH and ΔS to be independent of temperature, at what temperature will the reaction given below become spontaneous ?

$$\mathbf{N_2(g) + O_2(g) \longrightarrow 2NO(g)}$$

	$N_2(g)$	$O_2(g)$	2NO(g)
S /JK^{-1}mol^{-1}	**191.4**	**204.9**	**210.5**

ΔH = 180.8 kJ mol^{-1}

Solution :

$$\Delta S = 2S_{NO} - S_{N_2} - S_{O_2}$$

$$= 2 \quad 210.5 - 191.4 - 204.9$$

$$= 24.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore \quad \Delta G = \Delta H - T\,\Delta S$$

$$\Delta G = 180.8 - (T \quad 24.7 \quad 10^{-3}) \text{kJ mol}^{-1}$$

For spontaneity, $\Delta G \; < 0$ and this occurs when

$$T \;\; \Delta S \;\; > \Delta H$$

$$T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T > \frac{180.8 \quad 10^3}{24.7} = 7320 \text{ K}$$

The reaction becomes spontaneous above a temperature of 7320 K.

Example 11

The enthalpy change for the transition of liquid water to steam is 41 kJ mol^{-1} at 100 C. Calculate the entropy change for the process.

Solution :

$$H_2O(l) \longrightarrow H_2O(vap.)$$

The equation for entropy change is $\Delta S = \frac{L}{T} = \frac{\Delta H_{vap}}{T}$

$$= \frac{41 \times 1000}{(273 + 100)} = \frac{41000}{373} = 110 \text{ J mol}^{-1} \text{ K}^{-1}$$

Note that ΔS is greater than zero as there is an increase in disorder (randomness) in the system.

Example 12

3 moles of N_2(g) originally at 1 atm pressure are mixed isothermally with 5 moles of H_2(g) also at 1 atm pressure to yield a mixture whose total pressure is 1 atm. Assuming ideal behaviour, calculate entropy of mixing.

Solution :

Total pressure of mixture = 1 atm

$$\text{Final pressure of } N_2 = \frac{3}{5+3}(1) = 0.375 \text{ atm}$$

Final pressure of $H_2 = 1 - 0.375 = 0.625$ atm

For N_2, entropy change

$$\Delta S_{N_2} = -\,nR\,\ln\frac{P_2}{P_1} = -\,2.303 \quad 3 \quad 8.314 \quad \log\left(\frac{0.325}{1}\right) = 28.03 \text{ J/K}$$

For H_2, entropy change

$$\Delta S_{H_2} = -\ nR\ \ln\frac{P_2}{P_1} = -5 \quad 8.314 \quad 2.303\ \log\frac{0.675}{1} = 16.34\ J/K$$

Total entropy change due to mixing = $\Delta S_{N_2} + \Delta S_{H_2}$ = 44.37 J/K

Example 13

Calculate the entropy change when 1 kg of water is heated from 27 C to 200 C forming super heated steam under constant pressure. Given specific heat of water = 4180 J/kg-K and specific heat of steam = 1670 + 0.49T J/kg-K and latent heat of vaporization = 23 10^5 J/kg.

Solution :

$$\Delta S = 2.303\ m \quad C_p \quad \log\frac{T_2}{T_1}\ \text{[where m in kg and } C_p \text{ in J/kg]}$$

Entropy change for heating water from 27 to 100 C

$$\Delta S = 2.303\frac{1000}{18}\times\frac{4180\times 18}{1000}\log\frac{373}{300}$$

$$= 910.55\ J$$

Entropy change for heating 1 kg H_2O to 1 kg steam at 100 C

$$\Delta S = \frac{\Delta H_v}{T} = \frac{23\times 10^5}{373} = 6166.21J$$

Entropy change for heating 1 kg steam from 373 to 473 K, m in kg.

$$\Delta S = \int_{373}^{473}\frac{nC_p\,.dT}{T} = m\int_{373}^{473}\frac{(1670+0.49T)\,dT}{T}$$

$$= m\int_{373}^{473}\frac{1670\,dT}{T} + m\int_{373}^{473}0.49\ dT$$

$$= m\times 1670\times 2.303\,[\log T]_{373}^{473} + m\times 0.49[T]_{373}^{473}$$

$$= 1 \quad 1670 \quad 2.303\ \log\frac{473}{373} + 1 \quad 0.49 \quad 100$$

$$= 396.73 + 49 = 445.73\ J$$

$\therefore$ Total entropy change = 910.55 + 6166.21 + 445.73

= 7522.50 J

Example 14

Titanium metal is extensively used in aerospace industry because the metal imparts strength to structures but does not unduly add to their masses. The metal is produced by the reduction of $TiCl_4$(l) which in turn is produced from mineral rutile TiO_2(s). Can the following reaction for production of $TiCl_4$(l) be carried out at 25 C ?

$$TiO_2(s) + 2Cl_2(g) \longrightarrow TiCl_4(l) + O_2(g)$$

Given that H_f° for TiO_2(s), $TiCl_4$(l), Cl_2 (g) and O_2 (g) are – 944.7, – 804.2, 0.0, 0.0 kJ mol^{-1}. Also S for TiO_2 (g), $TiCl_4$(l), Cl_2(g) and O_2(g) are 50.3, 252.3, 233.0, 205.1 J mol^{-1} K^{-1} respectively.

Solution :

ΔH for reaction

$$= \left[H^{\circ}_{TiCl_4}(l) + H^{\circ}_{O_2}(g) - H^{\circ}_{TiO_2} - H^{\circ}_{Cl_2} \times 2\right]$$

$$= [-\ 804.2 + 0.0 - (-\ 944.7) - 0.0]$$

$$= 140.5 \text{ kJ}$$

Also, ΔS for reaction

$$= \left[S^{\circ}_{TiCl_4}(l) + S^{\circ}_{O_2}(g) - S^{\circ}_{TiO_2}(s) - S^{\circ}_{Cl_2}(g) \times 2\right]$$

$$= [252.3 + 205.1 - 50.3 - 2 \quad 233.0]$$

$$= -\ 58.9 \text{ J}$$

$$= -.0589 \text{ kJ}$$

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

$$= 140.5 - 298.15 \quad (-\ 0.0589)$$

$$= 158.06 \text{ kJ}$$

Example 15

A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mole of water of temperature 290 K. Calculate final temperature of water. Specific heat of water = 4.184 J g^{-1} K^{-1}.

Solution :

Since work is done against constant P and thus, irreversible

$$\Delta V = 5 - 3 = 2 \text{ dm}^3 = 2 \text{ litre; } P = 3 \text{ atm}$$

$$\therefore \quad W = -\ P.\ \Delta V = -\ 3 \quad 2 \text{ litre atm}$$

$$= -\ \frac{6 \times 4.184 \times 1.987}{0.0821} \text{ joule} = -\ 607.57 \text{ joule}$$

Now this work is used up in heating water

$\therefore \quad W = n \quad C \quad \Delta T$

$607.57 = 10 \quad 4.184 \quad 18 \quad \Delta T$

$\therefore \quad \Delta T = 0.81$

$\therefore$ Final temperature $= T_1 + \Delta T$

$\therefore \quad = 290 + 0.81$

$= 290.81\ \text{K}$

Example 16

1 mole of an ideal gas undergoes reversible isothermal expansion from an initial volume V_1 to a final volume 10 V_1 and does 10 kJ of work. The initial pressure was 1 10^7 Pa.

(a) Calculate V_1.

(b) If there were 2 mole of gas, what must its temperature have been ?

Solution :

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

(a) Where W is work done by the system under isothermal reversible conditions, note that work done by the system is negative.

$$-10 \quad 10^3 = -2.303 \quad 1 \quad 8.314 \quad T \log \frac{P_1}{P_2} \qquad \text{...(i)}$$

Also $\quad P_1V_1 = P_2V_2$ at constant temperature

$$1 \quad 10^7 \quad V_1 = P_2 \quad 10V_1$$

$$\therefore \quad P_2 = \frac{1 \quad 10^7}{10} = 10^6\ \text{Pa}$$

$\therefore$ By Eq. (i)

$$-10 \quad 10^3 = -2.303 \quad 1 \quad 8.314 \quad T \log \frac{10^7}{10^6}$$

$\therefore \quad T = 522.27$ K

Now, using $\quad PV = nRT$ for 1 mole of gas;

$P = 1 \quad 10^7\ \text{Pa} = 10^7\ \text{Nm}^{-2}$

$1 \quad 10^7 \quad V_1 = 1 \quad 8.314 \quad 522.27$

$V = 4.34 \quad 10^{-4}\ \text{m}^3$

(b) If 2 mole of gas have been used, the temperature would have been

$$\frac{522.27}{2} = 261.13\ \text{K}$$

Example 17

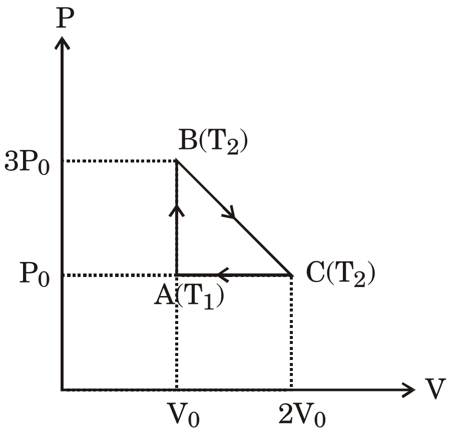
One mole of an ideal monoatomic gas is taken round cyclic process ABCA as shown in figure. Calculate :

(a) The work done by the gas

(b) The heat rejected by the gas in the path CA the heat adsorbed by the gas in the path AB

(c) The net heat absorbed by the gas in the path BC

(d) The maximum temperature attained by the gas during the cycle.



Solution :

Path AB is isochoric ($w_1 = 0$), path BC is isothermal ($w_2 = -$ ve), path CA is isobaric ($w_3 = +$ ve)

Total work done by gas (w) = $w_1 + w_2 + w_3$

$$= 0 + 2.303\ nRT \log \frac{V_B}{V_C} + P(V_C - V_A)$$

$$= 0\ 2.303\ P_B V_B \log \frac{V_B}{V_C} + P_C(V_C - V_A)$$

$$= 2.303 \quad 3P_0 \quad V_0 \log \frac{V_0}{2V_0} + P_0(2V_0 - V_0)$$

$$= -2P_0V_0 + P_0V_0$$

$$= -P_0V_0$$

Also $w_2 = -2\,P_0V_0$ and $w_3 = P_0V_0$

Also For the path AB, i.e., isochloric

$$q_1 = n \quad C_v \quad (T_B - T_A) = 1 \times \frac{3}{2} R\left[\frac{P_B V_B - P_A V_A}{R}\right]$$

$$= \frac{3}{2}[3P_0V_0 - P_0V_0]$$

$$= +3\,P_0V_0$$

For the path CA, i.e., isochoric :

$$q_3 = n \quad C_p\,(T_A - T_B) = 1 \quad \frac{5}{2}\ R\left[\frac{P_A V_A - P_B V_B}{R}\right]$$

$$= \frac{5}{2}\ [P_0V_0 - 2P_0V_0]$$

$$q_3 = -\frac{5}{2}\ P_0V_0$$

$$\text{Also net heat absorbed} = 3P_0V_0 - \frac{5}{2}\ P_0V_0 = \frac{P_0V_0}{2}$$

$$\therefore \quad q_{net} = \frac{P_0V_0}{2}$$

$$\text{Also} \quad \frac{P_0V_0}{T_1} = \frac{3P_0V_0}{T_2}$$

$$\therefore \quad T_2 = 3T_1 = \frac{3P_0V_0}{R}$$

Example 18

Consider a class room of dimensions 5   10   3 dm^3 at temperature 20 C and pressure 1 atm. There are 50 peoples in the room, each losing energy at the rate of 150 watt. Assuming that the walls, ceiling, floor and furniture perfectly insulated and none of them absorbing heat, how much time will be needed for rising the temperature of air in the room to body temperature, i.e., 37 C ? For air $C_p = \frac{7}{2}$ R. Loss of air to the outside as the temperature rises may be neglected.

Solution :

$$\text{Volume of air in the room} = 5 \quad 10 \quad 3$$

$$= 150\ m^3$$

$$= 150 \quad 106\ cm^3$$

$$\therefore \quad \text{Mole of air} = n = \frac{PV}{RT}$$

$$= \frac{1 \quad 150 \quad 10^6}{10^3 \times 0.0821 \times 293}$$

$$= 6.236 \quad 10^3$$

Also, $\left(\frac{\delta H}{\delta T}\right)_p = C_p = \frac{\Delta H}{\Delta T}$ (for 1 mole)

$\therefore$ $\Delta H = n.C_p.\Delta T$ (for n mole)

$$= 6.236 \quad 10^3 \quad \frac{7}{2} \quad 8.314 \quad (310 - 293)$$

$$= 3.085 \quad 10^6 \text{ J}$$

Thus, heat needed to heat the room to 37 C = 3.085 10^6 J

Also, heat released by 50 peoples = 150 50 J/sec

= 7500 J/sec

7500 J heat is provided in 1 sec

$\therefore$ 3.085 10^6 J heat will be provided in $\frac{1 \times 3.085 \times 10^6}{7500}$

= 411.3 second

Example 19

An aeroplane weighing 63,000 kg flies up from sea level to a height of 8000 metre. Its engine run with pure normal octane (C_8H_{18}) has a 30% efficiency. Calculate the fuel cost of the flight, if octane sells at Rs. 3/- per litre. Given density of octane = 0.705g mL^{-1}**, heat of combustion of octane = 1300 kcal mol^{-1}. (g = 981 cm/sec^2)**

Solution :

Weight of the plane = 6.3 10^7 g

Height of the plane = 8 10^5 cm

$\therefore$ Work required to lift it to this height

= mgh

$$= 6.3 \quad 10^7 \quad 981 \quad 8 \quad 10^5 \text{ erg}$$

$$= 4.9442 \quad 10^{16} \text{ erg}$$

$$= \frac{4.9442 \times 10^{16}}{4.18 \times 10^7} \text{cal}$$

$$= 1.1828 \quad 10^9 \text{ cal}$$

$\therefore$ Efficiency of fuel is 30%

$\therefore$ Work obtained by 1 mole fuel $= \dfrac{1300 \times 30}{100}$ kcal

$\therefore$ $\dfrac{1300 \times 30}{100}$ kcal work is obtained by 1 mole fuel

$\therefore$ $1.1828 \quad 10^6$ kcal work is obtained $= \dfrac{1.1828 \times 10^6 \times 100}{30 \times 1300} \times 3.033 \times 10^3$ mol

$= 3.033 \quad 10^3 \quad 114$ g

$= 3.46 \quad 10^5$ g

$\therefore$ Volume of fuel $= \dfrac{3.46 \times 10^5}{d} = \dfrac{3.46 \times 10^5}{0.705}$

$= 4.908 \quad 10^5$ mL $= 4.908 \quad 10^2$ litre

$\therefore$ Cost of fuel $= 490.8 \quad 3 = 1472.4$ Rs.

THERMOCHEMISTRY

It is a branch of physical chemistry that deals with energy changes accompanying chemical transformations. It is also known as "Chemical Energetics". It is based on the first law of thermodynamics.

Physicochemical changes are classified as endothermic, accompanied by adsorption of heat and exothermic, accompanied by the evolution of heat. For example,

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g);\ \Delta H = -57.8\ \text{kcal}$$

$$H_2O(g) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g);\ \Delta H = 57.8\ \text{kcal}$$

For exothermic reactions **($q < 0$)**

At constant pressure, $\Delta H = (H_P - H_R) = -\text{ ve } (\therefore H_P < H_R)$

At constant volume, $\Delta E = (E_P - E_R) = -\text{ ve } (\therefore E_P < E_R)$

For endothermic reaction, **($q > 0$)**

At constant pressure, $\Delta H = (H_P - H_R) = +\text{ ve } (\therefore H_P > H_R)$

At constant volume, $\Delta E = (E_P - E_R) = +\text{ ve } (\therefore E_P > E_R)$

Like any other transfer of heat, the heat of a chemical reaction depends upon the conditions that hold during the process by which it is carried out.

Condition I

If the volume of the system is kept constant, no work is done on the system and the first law of thermodynamics reduces to

$$\Delta E = qv$$

This condition is excellently approximated when the reaction is carried out in a bomb calorimeter, where the volume remains constant.

Condition II

During the course of an experiment under ordinary bench-top conditions, the pressure is kept constant. Many calorimeters operate at this constant atmospheric pressure. Then, we have

$$\Delta H = q_P$$

The heat of reaction measured at constant pressure is exactly equal to the change in enthalpy of the reaction system.

It is often necessary to use data obtained with bomb calorimeter which give ΔE in order to calculate ΔH.

We know that, $\Delta H = \Delta E + \Delta(PV)$

If all the reactants and products are liquids or solids, the PV values change only slightly during the reaction, provided the pressure is low (say 1 atm). In such cases, $q_P \cong q_v$.

For reactions in which gases are involved, the values of $\Delta(PV)$ depends on the change inj the number of moles of gas as a result of reaction.

$\therefore \quad \Delta(PV) = \Delta n_g(RT)$

$\therefore \quad \Delta H = \Delta E + \Delta n_g RT$

Constant pressure processes are much common in chemistry. Therefore, usually when ever we speak of heat of reaction, it implies enthalpy change at constant pressure.

Heat of Reaction

It is defined as the "amount of heat evoled or absorbed when the reacting species, as represented by a balanced chemical equation have completely reacted."

$$A + B \longrightarrow C + D, \Delta H = q$$

$$\begin{aligned}\Delta H &= H_{\text{Products}} - H_{\text{Reactants}} \\ &= (H_C + H_D) - (H_A + H_B)\end{aligned}$$

- If $H_{\text{Products}} = H_{\text{Reactants}}$, $\Delta H = 0$
- If $H_{\text{Products}} > H_{\text{Reactants}}$, $\Delta H = +$ ve, reaction is said to be endothrmic
- If $H_{\text{Products}} < H_{\text{Reactants}}$, $\Delta H = -$ ve, reaction is said to be exothermic.
- Enthalpy of every element in any state = Zero.

Physical States of the Reactants and Products

Since an appreciable change is involved in changing a substance from one state of matter to another, it is important that a state symbol is attached to all the formulae given in an equation, e.g.,

(1) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \qquad \Delta H = -285.9 \text{ kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g), \qquad \Delta H = -241.8 \text{ kJ mol}^{-1}$

The difference between two ΔH values arises due to difference in physical state of water.

Thus, $H_2O(l) \longrightarrow H_2O(g), \qquad \Delta H = 44.1 \text{ kJ mol}^{-1}$
It reprsents molar enthalpy of vaporisation of water.

(2) $C\text{ (graphite)} + O_2\text{ (g)} \longrightarrow CO_2(g), \quad \Delta H = -393.5 \text{ kJ mol}^{-1}$

$C\text{ (diamond)} + O_2\text{ (g)} \longrightarrow CO_2(g), \quad \Delta H = -380.4 \text{ kJ mol}^{-1}$
The difference between two ΔH values arises due to different allotropes of carbon.

Thus $\quad C\text{(diamond)} \longrightarrow C\text{ (graphite)}, \quad \Delta H = 13.1 \text{ kJ mol}^{-1}$
It represents molar enthalpy of transition of carbon.

Enthalpies of Solution

Enthalpies of solution differ depending on whether the substances react together in dry state or in solution. For example,

$$H_2S(g) + I_2(g) \longrightarrow 2HI(\text{solution}) + S(s); \qquad \Delta H = -17.2 \text{ kcal}$$

$$H_2S(g) + I_2(\text{solution}) \longrightarrow 2HI\ (\text{solution}) + S(s); \qquad \Delta H = -21.93 \text{ kcal}$$

Temperature

Enthalply of reaction also depends on temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature.

Relation between ΔH or ΔE and temperature are given by Kirchoff's equation.

$$(\Delta H_2 - \Delta H_1) = \Delta C_P\ (T_2 - T_1)$$

$$(\Delta E_2 - \Delta E_1) = \Delta C_V\ (T_2 - T_1)$$

The above relations may be derived as follows :

For a reaction at constant pressure, $\Delta H = H_P - H_R$

Differentiating it w.r.t. T at constant P, we get

$$\left(\frac{d\Delta H}{dT}\right)_P = \left(\frac{dH_P}{dT}\right)_P - \left(\frac{dH_R}{dT}\right)_P = (C_P)_P - (C_P)_R = \Delta C_P$$

or $\quad d(\Delta H) = \Delta C_P dT$

Integrating this equation within appropriate limits, we get

$$\int_{T_1}^{T_2} d(\Delta H) = \Delta C_P \int_{T_1}^{T_2} dT$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_P\ (T_2 - T_1)$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{(T_2 - T_1)} = \Delta C_P \qquad \text{...(1)}$$

This equation is used to find heat of reaction at a temperature when it is known at another temperature.

Similarly, $\dfrac{\Delta E_{T_2} - \Delta E_{T_1}}{(T_2 - T_1)} = \Delta C_v$ ...(2)

In the limits as $(T_2 - T_1) \longrightarrow 0$, equation (1) yields the differential form $\frac{d(\Delta H)}{dT} = \Delta C_P$

This shows that the rate of change of the enthalpy of a reaction is equal to the difference in heat capacities of products and reactants.

Since actually the heat capacities themselves vary with temperature, it is sufficiently accurate to use the average value of the heat capacity over the range of temperature considered.

Example 20

For Ag, $\overline{C}_P$ (JK^{-1} mol^{-1}) is given by 23.43 + 0.00628 T. Calculate ΔH if 3 mol of silver are raised from 25 C to its melting point 961 C under 1 atm pressure.

Solution :

At constant P for 1 mole

$$\Delta H = \int_{T_1}^{T_2} C_P dT = \int_{T_1}^{T_2} (23.43 + 0.00628T)dT$$

$$\Delta H = 23.43\ (T_2 - T_1) + \frac{1}{2}\ (0.00628(T_2^2 - T_1^2)\ \ Jmol^{-1}.$$

Since, $T_1 = 273.15 + 25 = 298.15$ K and $T_2 = 273.15 + 961 = 1234.15$ K

$(T_2 - T_1) = 936$ K

$\Delta H = 23.43(936) + ½(0.00628)\ [(1234.15)^2 - (298.15)^2] = 21930 + 4500$

$= 26430$ J/mol

For 3 mol, $\Delta H = 3(26430)$ J $= 79290$ J

Types of Heat (enthalpy) of Reactions

The heat or enthalpy changes taking place during the chemical reactions are expressed in different ways depending upon the nature of the reaction. The various types of enthalpies of reactions are :

(1) Heat or Enthalpy of Formation

The heat evolved or absorbed when 1 mole of a substance is formed from its elements is called heat of formation. It is denoted by ΔH_f.

For example, heat of formation of carbon dioxide and methane may be expressed as :

$$C(s) + 2H_2(g) \longrightarrow CH_4\ (g)\ \ \Delta H_f = -\ 74.8\ kJ$$

These equations should always be written for one mole as per the definition of the substance to be formed. If for balancing, we require the coefficient 2,. 3 ... etc., in the equation then ΔH_f values should also be multiplied by the same number as discussed earlier.

Standard heat of formation

The heat of formation ΔH_f depends upon the condition of temperature, pressure and physical state (gas, liquid or solid) of the reactants and the products. Therefore the heat change accompanying the formation of one mole of a compound from its elements when all the substances are in their standard states (1 atm pressure and 298 K), is called the standard heat of formation. It is expressed as $\Delta H_{f\cdot}$

Since no heat changes are involved in the formation of elements form themselves in their standard states, the standard enthalpy of formation of all elements is zero.

For example, the standard enthalpy of formation ($\Delta H_{f\cdot}$) for $H_2O_{(l)}$ is – 286 kJ mol^{-1} i.e., when one mole of liquid water is formed from its elements $H_{2(g)}$ and $O_{2(g)}$ at 298 K and 1 atm pressure, then 286 kJ mol^{-1} of heat is released. The negative value of $\Delta H_{f\cdot}$ indicates the formation of a stable compound.

Standard heat of reaction from standard heats of formation

The knowledge of standard heats of formation of various substances can be used to calculate the heats of reactions under standard conditions. The standard heat of any reaction (ΔH) is equal to the difference between the $\Delta H_{f\cdot}$ of all the reactants i.e.,

ΔH = Sum of the standard heats – Sum of the standard heats of formation of products of formation of reactants

i.e., $\Delta H = \Sigma\Delta H_{f\ (\text{products})} - \Sigma\Delta H_{f\ (\text{reactants})}$

For a reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H = \Sigma\Delta H_{f\ (\text{products})} - \Sigma\Delta H_{f\ (\text{reactants})}$$

$$= [c\Delta H_f(C) + d\Delta H_f(D)] - [a\Delta H_f(A) + b\Delta H_f(B)]$$

The heat of formation of all elements in their standard state is zero. On this basis, it is evident that the heat of formation of a compound is the heat of the compound.

$$\text{Elements} \longrightarrow \text{Compound}$$

Heat of formation = H_f (compound) – H_f (elements)

Example 21

The heat change for the reaction,

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ is – 92.2 kJ. Calculate the heat of formation of ammonia.

Solution :

The heat of formation of ammonia is the heat change for the formation of 1 mole of ammonia from its elements, i.e.,

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \quad \Delta H_f = ?$$

The heat change for the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

is $\Delta H = -92.2$ kJ. This equation corresponds to formation of two moles of ammonia. Thus,

$$\Delta H_f = \frac{-92.2}{2} = -46.1 \text{ kJ mol}^{-1}$$

Example 22

Calculate the heat change for the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

The heat of formation of $CH_{4(g)}$ and H_2O are – 74.8 $kJmol^{-1}$, – 393.5 $kJmol^{-1}$ and – 285.8 kJ mol^{-1} respectively.

Solution :

ΔH for the reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

is : $\Delta H = \Delta H^\circ_{f\,(products)} - \Delta H^\circ_{f\,(reactants)}$

$$\left\{\Delta H^\circ_f[CO_2(g)] + 2\Delta H^\circ_f[H_2O(l)]\right\} - \left\{\Delta H^\circ_f[CH_4(g)] + 2\Delta H^\circ_f[O_2(g)]\right\}$$

$$\Delta H^\circ_f[CO_2(g)] = -393.5 \text{ kJmol}^{-1},\ \Delta H^\circ_f[H_2O(l)] = -285.8 \text{ kJmol}^{-1}$$

$$\Delta H^\circ_f[CH_4(g)] = -74.8 \text{kJmol}^{-1},\ \Delta H^\circ_f[O_2(g)] = 0 \text{ (by convention)}$$

$$\Delta H = \{-393.5 + 2(-285.8)\} - \{-74.8 + 2 \quad 0)\}$$
$$= 965.1 + 74.8 = -890.3 \text{ kJmol}^{-1}$$

---

(2) Enthalpy of Combustion

The enthalpy of combustion of a compound is the enthalpy change at normal pressure and at constant temperature accompanying complete combustion of one mole of the compound. It is denoted by ΔH_c. Combustion here means the burning of the given compound to the highest oxides of the constituent elements in the presence of excess of oxygen.

For example, the enthalpy of combustion of benzene at 298 K is the enthalpy change of the reaction.

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l);\ \Delta H = -3268 \text{ kJ}$$

Example 23

The heats of combustion of CH_4 and C_2H_6 are – 890.3 and – 1559.7 kJ mol^{-1} respectively. Which of the two has greater efficiency of fuel per gram ?

Solution :

The fuel efficiency can be predicted from the amount of heat evolved for every gram of fuel consumed.

(i) The combustion of methane is as follows :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$\Delta H_c = 890.3 \text{ kJmol}^{-1}$

Molar mass of $CH_4 = 16$

$$\text{Heat produced per gram} = \frac{890.3}{16} = 55.64 \text{ kJ g}^{-1}$$

(ii) The combustion of ethane is as follows :

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$\Delta H_c = 1559.7 \text{ kJmol}^{-1}$

Molar mass of $C_2H_6 = 30$

$$\text{Heat produced per gram} = \frac{1559.7}{30} = 51.99 \text{ kJ g}^{-1}$$

Thus, methane has greater fuel efficiency than ethane.

Example 24

(a) A cylinder of gas supplied by a company is assumed to contain 14 kg of Butane. If a normal family requires 20,000 kJ of energy per day for cooking, how long will the cylinder last ?

(b) If the air supplied to the burner is insufficient, a portion of gas escapes without combustion. Assuming that 25% of the gas is wasted due to this inefficiency, how long will the cylinder last ? (Heat of combustion of butane = 2658 kJ/mol)

Solution :

(a) Molecular formula of butane = C_4H_{10}

Molecular mass of butane = $4 \quad 12 + 10 \quad 1 = 58$

Heat of combustion of butane = 2658 kJ mol^{-1}

1 mole of 58 g of butane on complete combustion given heat = 2658 kJ

14 10^3 g of butane on complete combustion gives heat = $\dfrac{(2658)\times(14)\times10^3}{58} = 641586$

The family needs 20,000 kJ of heat for cooking per day.

641586 kJ of heat will be used for cooking by a family in $\dfrac{641586}{20000} = 32$ days

The cylinder will last for 82 days.

(b) 25 per cent of the gas is wasted due to inefficiency. This means that only 75% of butane is combusted. Therefore,

the energy produced by 75% combustion of butane = $\dfrac{(641586)\times75}{100} = 481190$ kJ

∴ The number of days the cylinder will last = $\dfrac{481190}{20000} =$ 24 days

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Example 25

The enthalpy change involved in the oxidation of glucose is – 2880 kJ mol^{-1}. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose.

Solution :

ΔH_{comb} of Glucose ($C_6H_{12}O_6$) = – 2880 kJ mol^{-1}

Total energy available from 120 g of glucose = $\dfrac{2880\times120}{180} = 1920$ kJ

Energy available for muscular work = $\dfrac{1920\times25}{100} = 480$ kJ

Distance travelled = $\dfrac{480}{100} = 4.8$ km

Example 26

Calculate the enthalpy change of combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_{2(g)}$, $H_2O_{(l)}$ and propane$_{(g)}$ are – 393.5, – 285.8 and 20.42 kJmol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is – 33.0 kJ mol^{-1}.

Solution :

The required ΔH is

$$\underset{\text{cyclopropane}}{C_3H_6} + \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O;\ \Delta H = ?$$

The given equations are :

(i) $C + O_2 \longrightarrow CO_2;\ \Delta H_1 = -\ 393.5\ \text{kJ}$

(ii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O;\ \Delta H_2 = -\ 285.8\ \text{kJ}$

(iii) $3C + 3H_2 \longrightarrow CH_3CH = CH_2;\ \Delta H_3 = +\ 20.42\ \text{kJ}$

(iv) $\underset{\text{cyclopropane}}{C_3H_6} \longrightarrow CH_2 = CH–CH_3;\ \Delta H_4 = -\ 33.0\ \text{kJ}$

Multiply equation (i) and (ii) by 3 and add them. Now subtract equation (iii) and subsequently add equation (iv) from the resulting expression.

$$\Delta H = 3\Delta H_1 + 3\Delta H_2 - \Delta H_3 - \Delta H_4$$
$$= 3(-\ 393.5) + 3(-\ 285.8) - (20.42) + (-\ 33.0) = -\ 2091.32\ \text{kJ}$$

---

(3) Heat or Enthalpy of Neutralisation

The reaction in which an acid and a base react to give a salt and water is called neutralization reaction. Neutralization reactions are exothermic in nature. The heat change when one gram equivalent of an acid is completely neutralised by a base or vice versa in dilute solution, is called heat of neutralization.

Examples of heat of neutralization are :

Neutralization of HCl with NaOH

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O(l)\ \Delta H = -\ 57.1\ \text{kJ}$$

It is important to note that the term gram equivalent is used in the definition of heat of neutralization. This is because neutralization involves 1 mole of H^+ ions and 1 mole of OH^- ions to form 1 mole of water and 57.1 kJ of heat is liberated.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O(l)\ \Delta H = -\ 57.1\ \text{kJ}$$

Now, one gram equivalent of various acids on complete dissociation liberates one mole of H^+ ions. But one mole of the acid may produce more than one mole of H^+ ions in solution depending upon its basicity; for example 1 mol of H_2SO_4 gives 2 mol of H^+ ions and 1 mol of H_3PO_4 gives 3 mol of H^+ ions on complete dissociation. But 1 gram equivalent of both (H_2SO_4 or H_3PO_4) produces only 1 mol of H^+ ions.

Thus, it is more appropriate to use the term gram equivalent in the definition of enthalpy of neutralization.

The average enthalpy of nuetralization of any strong acid by a strong base is found to be – 57.7 kJ (– 13.7 kcal) irrespective of the nature of acid or the base. This suggests that the net chemical reaction in all neutralization reactions is the same, viz.,

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O(l) \ \Delta H = -57.1 \text{ kJ}$$

This is because strong acid and strong base are completely ionized in aqueous solutions. The aqueous solution of one gram equivalent of all strong acids contains the same number of H^+ ions. Similarly, aqueous solution of one gram equivalent of all strong bases also contains same number of OH^-. The neutralization reactions between strong acids and strong bases in aqueous solutions involve simply the combination of H^+ ions (from an acid) and OH^- ions (from a base) to form unionized water molecules.

Neutralization of weak acids and weak bases

The heat of neutralization of a weak acid or a weak base is less than – 57.1 kJ and is also different for different weak acids or bases.

For example for acetic the enthalpy of neutralization is – 54.9 kJ.

Example 27

100 ml of 1 N of an acid and 100 ml of 1 N of a base are mixed at 298 K. During the experiment, the temperature arose to 298.0067 K. Calculate the heat of neutralization.

Solution :

Heat capacity of solution = Mass of solution   Specific heat capacity

Total mass of solution = 100 + 100 = 200 ml

Heat capacity of solution = 200   4.2 = 840 JK^{-1}

Heat change in the reaction = Heat capacity   Rise in temperature

$= (840 \ JK^{-1}) \ (298.0067 - 298)K$

$= 840 \quad 0.0067 \ J = 5.63 \ J$

Now, one gram equivalent of acid = 1 N HCl in 1000 ml

100 ml of 1 N acid on neutralization gives heat = 5.63 J

1000 ml of 1 N acid on neutralization gives heat = $\frac{5.63}{100} \times 1000 = 56.3$ J

Heat of neutralization = – 56.3 J

Example 28

Whenever an acid is neutralized by a base, the net reaction is :

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O(l) + 57.1 \text{ kJ}$$

Calculate the heat evolved when 0.60 mol of HNO_3 solution is mixed with 0.30 mol of KOH solution

Solution :

According to the reacation

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O(l) + 57.1 \text{ kJ}$$

When 1 mole of H^+ ions and 1 mol of OH^- ions are neutralized to form 1 mol of water, 57.1 kJ of energy is released.

(a) Heat evolved on mixing 0.60 mol of HNO_3 with 0.30 mol of KOH solution.

Since HNO_3 and KOH are strong acid and bases,

0.60 mol of HNO_3 ≡ 0.60 mol of H^+ ions

0.30 mol of KOH ≡ 0.30 mol of OH^- ions

In this case, out of 0.60 mol of H^+ ions (from HNO_3) only 0.30 mol will be neutralised (equal to OH^- ions present) by the base. 0.3 mol of H^+ ions of HNO_3 will remain unreacted. The net reaction is :

$$H^+ \text{ (0.30 mol)} + OH^- \text{ (0.30 mol)} \longrightarrow H_2O \text{ (0.30 mol)}$$

Now, heat evolved during the formation of 1 mol of H_2O = 57.1 kJ

Heat evolved in the formation of 0.3 mol of H_2O = 57.1 0.3 = 17.13 kJ

---

(4) Enthalpy of solution (ΔH_{sol})

When a solute is dissolved in a solvent a solution is formed. During dissolution of a solute in any solvent, a certain amount of heat is either absorbed or evolved. Such heat changes under constant pressure conditions are known as the enthalpy of solution. The change in enthalpy when one mole of a solute is dissolved in a specific quantity of a solvent at a given temperature is called enthalpy of solution.

To avoid the amount of solvent, heat of solution is usually defined for an infinite dilute solution. Thus, heat of solution of infinite dilution is the heat change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further heat change.

For example, dissolution of sodium chloride

$$NaCl_{(s)} + aq \qquad NaCl_{(aq)} \qquad \Delta H = \Delta H_{sol} = +\ 5.0 \text{ kJ}$$

Here ‘aq’ represents aqueous meaning a large excess of water.

(5) Enthalpy of fusion (ΔH_{fus})

The enthalpy of fusion of a substance is defined as 'the change in enthalpy when one mole of a solid substance is melted at its melting temperature'. For example, the enthalpy change of the reaction,

$$\text{Ice } (273\text{ K}) \longrightarrow H_2O(l)\ (273\text{ K}) \qquad \Delta H = 6.0\text{kJ mol}^{-1}$$

(6) Enthalpy of Vaporisation (ΔH_{vap})

'The change in enthalpy when one mole of a liquid is converted into vapours at its boiling temperature is called enthalpy of vaporisation' (ΔH_{vap}).

Thus, the enthalpy change of the reaction

$$H_2O(I),\ 373\text{ K} \longrightarrow H_2O(v),\ 373\text{K} \qquad \Delta H = 40.7\text{ kJ mol}^{-1}$$

is the enthalpy of vaporisation of water.

Example 29

Determine the value of ΔH and ΔE for the reversible isothermal evaporation of 90.0 g of water at 100 C. Assume that water vapours behave as ideal gas and heat of evaporation of water is 540 cal g^{-1}.

($R = 2$ cal mol^{-1} K^{-1})

Solution :

$$90 \text{ g of water} = \frac{90}{18} = 5.0 \text{ mol}$$

Heat of evaporation of 1 g of water = 540 cal

Heat of evaporation of 90 g of water = 540 90 = 48600 Cal.

$\Delta H = 48600$ Cal

The evaporation of 5 mol of water is represented as

$$5H_2O(l) \longrightarrow 5H_2O(g)$$

$\Delta n = (5 - 0) = 5$

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

$= 48600 - (5)\ (2.0)\ (373) = 44870$ cal

---

(7) Enthalpy of Sublimation (ΔH_{sub})

Sublimation is a process in which a solid substance directly changes into its vapours at any temperature below its melting point. Enthalpy of sublimation is defined as follows :

The change in enthalpy when one mole of a solid substance is converted into its vapours without melting point at a temperature below its melting point is called the enthalpy of sublimation.

For example, when one mole of solid iodine is converted into its vapours at room temperature, heat equal to 62.4 kJ is absorbed. So, the enthalpy of sublimation of iodine is + 62.4 kJ mol^{-1}, i.e.,

$$I_2(s) \xrightarrow{\Delta} I_2(v) = 62.4 \text{ kJ mol}^{-1}$$

Compounds, which sublime on heating are camphor, dry ice, ammonium chloride etc.

The heat of sublimation is related to heat of fusion and heat of vaporization as :

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}}$$

Example 30

When 1 g of liquid naphthalene ($C_{10}H_8$) solidifies, 149 J of heat is evolved. Calculate the heat of fusion of naphthalene.

Solution :

The molecular mass of naphthalene is $C_{10}H_8 = 10 \quad 12 + 8 \quad 1 = 128$

Heat evolved when 1 g of naphthalene solidifies = 149 J

Heat evolved when 128 g of naphthalene solidifies = $149 \quad 128 = 19072$ J

If $C_{10}H_8(l) \longrightarrow C_{10}H_8(s) \qquad \Delta H = 19072 \text{ J}$

For the fusion reaction,

$$C_{10}H_8(s) \longrightarrow C_{10}H_8(l)$$

This reaction is the reverse of the above solidification reaction so that

$$\Delta H_{\text{fusion}} = -\Delta H_{\text{solidification}}$$

$$\Delta H_{\text{fusion}} = 19072 \text{ J or } = 19.072 \text{ kJ}$$

---

(8) Enthalpy of hydration

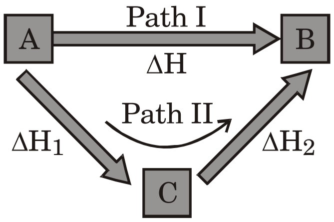
This is defined as the heat change (evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water to form the specific hydrated salt.

HESS'S LAW OF CONSTANT HEAT SUMMATION

This law states that 'the heat change in a particular reaction is the same whether it takes place in one step or several steps'.

For example, a reactant 'A' changes to a product 'B' in one step and the heat change during this process is ΔH. If the reaction is carried out in two steps where 'A' first changes to 'C' an intermediate stage and then 'C' changes to 'B' in the following step then let the heat change during the formation of 'A' to 'C' be ΔH_1 and that from 'C' to 'B' be ΔH_2. From Hess's law the heat change for the reaction is given as :

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



This means that the amount of heat evolved or absorbed in a chemical reaction depends only upon the energy of initial reactants and the final products. The heat change is independent of the path or the manner in which the change has taken place.

The formation of carbon dioxide from carbon and oxygen can be illustrated as follows. Carbon can be converted into carbon dioxide in two ways. Firstly solid carbon combines with sufficient amount of oxygen to form CO_2. The same reaction when carried in presence of lesser amount of oxygen gives carbon monoxide which then gets converted to CO_2 in step two in the presence of oxygen.

Path I : $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\ kJ$

Path II : $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H_1 = -110.5\ kJ$

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2 = -283.0\ kJ$

$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\ kJ$

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

Thus, one can conclude that thermochemical equations can be added, subtracted or multiplied like algebraic equations to obtain the desired equation.

Example 31

Calculate the standard heat of formation of carbon disulphide (l). Given that the standard heats of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are 393.3, – 293.72 and – 1108.76 kJ mol^{-1} respectively.

Solution :

The given data can be written in thermochemical equation form as :

$C(s) + O_2(g) \longrightarrow CO_2(g)\ \Delta H = -393.5\ kJ$ (i)

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -\ 293.72\ kJ\ (ii)$$

$$CS_2(I) + 3O_2(g) \longrightarrow CO_2(g) + SO_2(g) \quad \Delta H = -\ 1108.76\ kJ\ (iii)$$

The required equation is :

$$C(s) + 2S(g) \longrightarrow CS_2(l) \qquad \Delta H = ?$$

Multiplying equation (ii) by 2 and adding to equation (i) we get,

$$2S(s) + 2O_2(g) \longrightarrow 2SO_2(g) \qquad \Delta H = -\ 587.44\ kJ$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -\ 393.5\ kJ$$

$$2S(s) + C(s) + O_2(g) \longrightarrow 2SO_2(g) + CO_2(g)$$

$\Delta H = -\ 980.74$ kJ

Subtracting equation (iii) from the above equation we have,

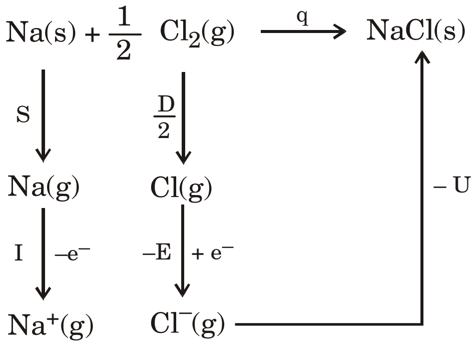
$$2S(s) + C(s) + O_2(g) \longrightarrow 2SO_2(g) + CO_2(g) \quad \Delta H = -\ 980.74\ kJ$$

$$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + SO_2(g) \qquad \Delta H = -\ 1108.76\ kJ$$

$$C(s) + 2S(g) \longrightarrow CS_2(l) \qquad \Delta H = -\ 128.02\ kJ$$

Born-Haber Cycle

This cycle is based on thermochemical changes taking place in the formation of a lattice. This cycle can be used to determine lattice energy which cannot be directly measured. It is defined as that energy released when one mole of the atomic compound (lattice) is formed from its isolated ions in the gaseous state under standard condition.



$$nA^{m+}(g) + mB^{n-}(g) \longrightarrow A_nB_m(s)$$

$\Delta H = -\ U$ (lattice energy)

Formation of NaCl(s) lattice involves thus,

$$S + I + \frac{D}{2} - E - U = q$$

hence, U can be calculated.

here, S = heat of sublimation of Na(s)

I = ionisation energy of Na(g)

D = dissociation energy of Cl_2

E = electron affinity of Cl(g)

U = lattice energy

q = heat of formation of NaCl(s)

If lattice is $MgX_2(s)$ then

$$S + (I_1 + I_2) + D - 2E - U = q$$

where, $(I_1 + I_2)$ = total ionisation energy to form $Mg^{2+}(g)$.

Bond Energy or Bond Enthalpy

In chemical reactions the formation of a chemical bond is accompanied by the release of energy. Conversely energy has to be supplied for the breaking of a bond.

Bond strengths are commonly described by their bond dissociation energy which is the energy required to break one mole of a bond of particular type. This is a definite quantity and is expressed in kJ mol^{-1}. For diatomic molecules the bond dissociation energy is same as bond energy, whereas in polyatomic molecules the bond energy is taken as the mean average of the various bond dissociation energies of the bonds of a given type.

The thermochemical data is useful in determining the bond energies of different bonds.

For example the bond energy of C-H bond in methane can be calculated form its heat of formation. The heat for formation of methane from carbon and hydrogen has been found to be–1663 kJ mol^{-1}.

$$C(s) + 4H(g) \longrightarrow CH_4(g) \ \Delta H = -1663 \text{ kJ}$$

Methane has four C-H bonds and the energy required to break all the four C-H bonds is 1663 kJ. Therefore the average C-H bond energy is $\frac{1663}{4} = 415.75$ or 416 kJ mol^{-1}.

Example 32

Compute the average S-F bond energy in SF_6. The values of standard enthalpy of formation of $SF_{6(g)}$, $S_{(g)}$, are, 100, 275 and 80 kJ mol^{-1} respectively.

Solution :

Consider the equation

$$SF_{6(g)} \longrightarrow S(g) + 6F(g)$$

$$\Delta H_{reaction} = 6\Delta H_f\,(F) + \Delta H_f(S) - \Delta H_f\,(SF_6)$$
$$= 6 \quad 80 + 275 - (-1100) = 1855 \text{ kJ}$$

$$\Delta H_{S-F} \text{ bond} = \frac{1855}{6} = 309.17 \text{ kJ mol}^{-1}$$

Example 33

The enthalpies of combustion of carbon and carbon monoxide in excess of oxygen at 298 K and constant pressure are – 393.5 kJ/mol and 283.0 kJ/mol respectively. Calculate the heat of formation of carbon monoxide at constant volume.

Solution :

Heat of formation of CO is written as

$C(s) + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)};$ $\Delta H = ?$

Now we have :

1. $C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)};$ $\Delta H_1 = -393.5$
2. $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)};$ $\Delta H_2 = -283$

Adding appropriately (i.e., 1 - 2), we get;

$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$

From Hess's Law : $\Delta H_f = \Delta H_1 - \Delta H_2$

$\Delta H_f = -393.5 - (-283) = -110.5$ kJ

Now calculation of the heat of formation at constant volume means that we have to calculate change in internal energy (i.e. ΔE). Proceeding in the following manner...

From First Law of Thermodynamics : $\Delta H = \Delta E + P\Delta V$

Now, $PV = nRT$

$\Rightarrow$ $P\Delta V = \Delta nRT$ (Δn = gaseous moles of products – gaseous moles of reactant)

$\Rightarrow$ $\Delta H = \Delta E + \Delta n\, RT$

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

$\Delta n = 1 - \frac{1}{2} = \frac{1}{2} T = 298$ K $\quad R = 8.314$ J/K/mol. $\quad H = -110.5$ kJ

$\Rightarrow$ $\Delta E = -110.5 - (\frac{1}{2} \quad 8.314 \quad 298 = -111.7$ kJ

Example 34

The heat of combustion of sucrose, $C_{12}H_{22}O_{11}$(s) at constant volume is – 1348.9 kcal mol^{-1} at 25 C, then the heat of reaction at constant pressure, when steam is produced, is

(A)	**– 1348.9 kcal**	**(B)**	**+ 1342.344 kcal**
(C)	**+ 1250 kcal**	**(D)**	**None**

Solution :

The combustion equation of sucrose is

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O\ (l)$$

Here,

Δn = sum of gaseous product moles – sum of gaseous reactant moles

$\Delta n = 12 + 11 - 12$

$\Delta n = 11$

As we know,

$\Delta H = \Delta E + \Delta n\, RT$, where ΔH = heat of reaction at constant pressure

ΔE = heat of reaction at constant volume

Here, $\Delta E = -1348.9$ kcal

$R = 2.0$ cal, $T = 25 + 273 = 298$ K

$\therefore \quad \Delta H = (-1348.9 \quad 1000) + 11 \quad 2 \quad 298$

$= -1348900 + 6556 = -1342344$ cal

$= -1342.344$ kcal

Hence, (A) is correct.

Example 35

In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Heats of combustion : CH_4 = 809 kJ/mol; C_4H_{10} = 2878 kJ/mol.

Solution :

In 1.0 hour, x lts of CH_4 required 6x lts of O_2

ΔH (combustion) of CH_4 = 809 kJ/mol

$\Rightarrow \quad \dfrac{809}{24.48}$ kJ/ lts at 1.0 atm and 25 C

ΔH (combustion) of C_4H_{10} = 2878 kJ/mol

$\Rightarrow \quad \dfrac{2878}{24.48}$ k/J lts at 1.0 atm and 25 C

x lts of CH_4 produces $\dfrac{809}{24.48}$ (x) kJ

Now this much energy has to be provided by burning of C_4H_{10}.

$$\Rightarrow \quad \frac{809}{24.48}\,(x) \text{ kJ will be provided by}$$

$$\left(\frac{809}{24.48}(x)\right) \times \left(\frac{24.48}{2878}\right) = (0.28\,x) \text{ lts of } C_4H_{10}$$

$C_4H_{10} + 13/2\ O_2 \rightarrow 4CO_2 + 5H_2O$

$\Rightarrow$ 1 mol $CH_4 \equiv 13/2$ mol O_2

$\Rightarrow$ (3   13/2) times of O_2 is required/mol

$\Rightarrow$ rate of O_2 per hour = (0.28 x)   (39/2) = (5.48 x) lts O_2

Example 36

Standard enthalpy of formation of $C_3H_7NO_2$(s), CO_2(g) and H_2O(l) are – 133.57, – 94.05 and – 68.32 kcal/mol respectively. Standard enthalpy of combustion of CH_4 at 25 C is – 212.8 kcal per mole. Calculate ΔH for the reaction : $2CH_4 + CO_2 + 1/2\ N_2 \rightarrow C_3H_7NO_2(s) + 1/2\ H_2$. Calculate ΔE for combustion of $C_3H_7NO_2$(s).

Solution :

$2CH_4 + CO_2 + 1/2N_2 \rightarrow C_3H_7NO_2$: $\Delta H = ?$

First find ΔH_f of CH_4

Given : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$: $\Delta H = -212.8$

Using the definition of ΔH, we have :

$\Delta H = [\Delta H_f(CO_2) + 2\Delta H_f(H_2O)] - \Delta H_f(CH_4)$ (note that $\Delta H_f\ O_2 = 0$)

$\Rightarrow -212.8 = [-94.05 + 2(-68.32)] - \Delta H_f\ (CH_4)$

$\Rightarrow \Delta H_f\ (CH_4) = -17.89$ kcal/mol

Now find the ΔH of the required equation using $\Delta H_f\ (CH_4)$

$\Delta H = [\Delta H_f\ (C_3H_7NO_2) - 0] - [2\quad \Delta H_f\ (CH_4) + \Delta H_f\ (CO_2) + 0]$

$\Rightarrow \Delta H = (-133.57) - 2(-17.89) - (-68.32) = -3.74$ kcal/mol

Now calculate ΔH(combustion) of $C_3H_7NO_2$.

$C_3H_7NO_2(s) + 15/4O_2 \rightarrow 3CO_2(g) + 1/2N_2(g) + 7/2H_2O(g)$

$\Delta H_{comb} = 3\Delta H_f\ (CO_2) + 0 + 7/2\Delta H_f\ (H_2O) - \Delta H_f\ C_3H_7NO_2 - 0$

$= 3(-94.05) + 7/2(-68.32) - (-133.57) = -387.70$ kca/mol

Find ΔE using $\Delta E = \Delta H - \Delta nRT$

$\Delta E = -387.70 - (-1/4)\quad 2\quad 10^{-3}(298) = -387.72$ kcal/mol

Example 37

Calculate the heat of reaction for the hydrogenation of acetylene to ethylene at constant volume at 25 C from the following data :

- **(i) Enthalpy of formation of water = – 285.8 kJ mol^{-1}**
- **(ii) Enthalpy of combustion of acetylene = – 1299.6 kJ mol^{-1}**
- **(ii) Enthalpy of combustion of ethylene = – 1410.8 kJ mol^{-1}**

Solution :

(i) $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O\ (l),\ \Delta H = -\ 285.8\ \text{kJ mol}^{-1}$

(ii) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O\ (l),\ \Delta H = -\ 1299.6\ \text{kJ mol}^{-1}$

(iii) $C_2H_4(g) + 3O_2\ (g) \longrightarrow 2CO_2(g) + 2H_2O\ (l),\ \Delta H = -\ 1410.8\ \text{kJ mol}^{-1}$

Eqn. (ii) + Eqn. (i) – Eqn. (iii), we get

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_4(g)$

$\Delta H = -\ 1299.6 - 285.8 + 1410.8$

$= -\ 174.6\ \text{kJ mol}^{-1}$

$\Delta E = -\ 174.6 - (-1)\ (8.314 \quad 10^{-3})\ (298)$

$= -\ 172.12\ \text{kJ mol}^{-1}$

Example 38

From the following data, calculate the bond enthalpies of C–C and C ≡ N bonds :

- **(i) Enthalpy of formation of CH_3CN = 87.86 kJ mol^{-1}**
- **(ii) Enthalpy of formation of C_2H_6 = – 83.68 kJ mol^{-1}**
- **(iii) Enthalpy of sublimation of graphite = 719.65 kJ mol^{-1}**
- **(iv) Enthalpy of dissociation of nitrogen = 945.58 kJ mol^{-1}**
- **(v) Enthalpy of dissociation of hydrogen = 435.14 kJ mol^{-1}**
- **(vi) C–H bond enthalpy = 414.22 kJ mol^{-1}**

Solution :

$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g), \qquad \Delta H = -\ 83.68\ \text{kJmol}^{-1}$

$\Delta H = [2\Delta H_{C(s)} \longrightarrow {}_{C(g)} + 3[\Delta H_{H-H}] - \Delta H_{C-C} + 6\Delta H_{C-H}]$

$-\ 83.68 = [2 \quad 719.65 + 3\ (435.14)] - [\Delta H_{C-C} + 6 \quad 414.22]$

On solving we get, $\Delta H_{C-C} = 343.08$ kJ mol^{-1}

$$2C(s) + \frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \longrightarrow CH_3CN(g),\ \Delta H = 87.86\ \text{kJ mol}^{-1}.$$

$$\Delta H = [2\Delta H_{C(S)} \longrightarrow {}_{C(g)} + \frac{3}{2}\ H_{H-H} + \frac{1}{2}\Delta H_{N=N}] - [\Delta H_{C-C} + 3\Delta H_{C-H} + \Delta H_{N\equiv N}]$$

$$87.86 = [12 \quad 719.65 + \frac{3}{2}\ (435.14) + \frac{1}{2}\ (945.58)] - [343.08 + 3(414.22 + \Delta H_{N\equiv N}]$$

On solving we get, $\Delta H_{N\equiv N} = 89.12$ kJ mol^{-1}.