Thermodynamics

THERMODYNAMICS

Thermodynamics is a branch of science which deals with quantitative relation ship between heat and other form of energy.

Chemical thermodynamics : It is the branch of thermodynamics which deals with the study of processes in which chemical energy is involved.

Chemical thermodynamics is concerned with the following questions :

(i) When two or more substances are put together, will they react?

(ii) If they do react, what energy changes will be associated with the reaction?

(iii) If a reaction occurs, at what concentrations of the reactants and their products will equilibrium be established?

Limitations of thermodynamics :

(1) The law of thermodynamics apply only to the matter in bulk i.e., macroscopic system and not to individual atoms or molecules of the macroscopic system.

(2) Thermodynamics can only predict the feasibility or spontaneity of a process under a given set of conditions but does not tell anything about the rate at which the given process may proceed.

(3) It is not concerned with the total energy of the body but only with energy change.

TERMS USED IN THERMODYNAMICS

(1) **System** : A system is defined as a specific part of universe or specified portion of the matter which is under experimental investigation

(2) **Surrounding** : The rest part of the universe other than the system is called surrounding. We are never interested in surrounding. Our study is only restricted to system.

(3) **Boundary** : Any thing which sperates system and surrounding is called boundary. The boundary may be real or imaginary ; it may be rigid or non rigid ; it may be conductor or non conductor.

For example : A reaction is carried out in a beaker. The contents of beaker constitute the system, beaker serves as boundary and the anything which is out side the beaker is called surroundings.

Types of system : Systems can be classified in two ways :

(i) On the basis of exchange of energy and matter

(ii) On the basis of composition

(i) On the basis of exchange of energy and matter

(a) Open system : This type of system can exchange energy as well as matter with the surrounding. The boundary is not sealed and not insulated.

(b) **Closed system** : This type of systems can exchange energy, in the form of heat, work or radiations but not matter with its surroundings. The boundary between the system and its surroundings is sealed but not insulated.

(c) **Isolated system** : This type of system are perfectly insulated systems and can not interact in any way with its surrounding i.e. neither matter nor energy can be exchanged with the surrounding.

(ii) On the basis of composition -

(a) **Homogeneous system**: A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one phase only. eg. a pure single solid, liquid, gas, mixture of gases.

(b) **Heterogeneous system** : A system is said to be heterogeneous when it is not uniform throughout ie. it consists of two or more phases. eg. ice in contact with water, insoluble solids in contact with a liquid.

THERMODYNAMIC PROPERTIES

(a) **Extensive properties** : The properties of the system whose magnitude depends upon the quantity of matter present in the system are called extensive properties. e.g. volume, weight, energy, enthalpy, entropy, internal energy, mole etc.

(b) **Intensive properties** : The properties of the system which do not depend on the quantity of matter present in system or size of the system are called intensive properties.

These are the characteristic properties of the system only i.e. when the mass of the system is changed, these properties remain unchanged. For example melting points, boiling points, viscosity, refractive index, specific heat, surface tension, density, concentration etc.

Note : Extensive properties can change in intensive properties when divided to make per unit quantity. Ex. volume and weight are extensive property but mass of unit volume (density) is intensive property.

State of the system :

when the fundamental properties such as pressure, temperature, volume, number of moles & composition have definite values, the system is said to be in a any definite state, when there is any change in any one of these properties it is said that the system has undergone a change of state.

State functions/Thermodynamic function/State variable : Fundamental properties which determine the state of a system are referred to as state variables. The change in state properties depends only upon the initial and final state of the system but is independent of the manner in which the change has been brought about.

Path function : If change in fundamental properties depends upon initial and final state of the system as well as the manner in which the change has been brought about. e.g. Work, heat

Work :

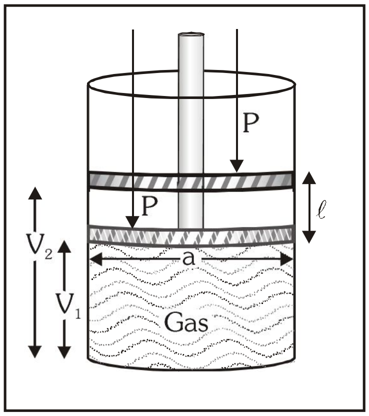
Product of force and displacement is known as work.

work (W) = force (F) × displacement (ℓ)

Consider a gas enclosed in a cylinder fitted with a frictionless piston. Suppose area of cross section of cylinder = a and pressure on the piston = P, Initial volume of the gas = V_1 and final volume of the gas = V_2

(By expansion) displacement of piston = ℓ

work done by the gas (in expansion) = W = F.ℓ



$$\because P = \frac{F}{a} \quad \therefore F = P \times a$$

$W = P \times a \times \ell$

(change in volume = $a \times \ell = V_2 - V_1$)

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

$W = P\Delta V$ (According to Physics)

In general $\boxed{W = -P_{\text{external}}\ \Delta V}$

(According to Chemistry)

- If system works then

  $V_2 > V_1 \Rightarrow$ work is –ve
- If work is done on the system then

  $V_1 > V_2 \Rightarrow$ work is + ve

Heat :

Heat may be defined as the quantity of energy which flows between a system and its surroundings on account of temperature difference.

- Heat always flows from high T to low T.
- Heat flowing into the systum q = +ve
- Heat flowing out of the systum q = – ve

Units of heat & work : Calorie It is defined as the quantity of heat required to raise the temperature of 1 g of water by 1°C (14.5 to 15.5°C)

$1\ \text{Nm} = 1\text{J} = 10^7\ \text{erg} = 0.239\ \text{cal}$

$1\ \text{cal} = 4.184\ \text{J} = 4.2\ \text{J}$

$1\ \text{L-atm} = 101.3\ \text{J} = 24.206\ \text{cal} = 101.3 \times 10^7\ \text{erg}$

1 L-atm > cal. > J. > erg

Internal energy [E] :

Total of all possible kinds of energy of a system is called its internal energy.

The exact value of this energy is not known as it includes all types of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational, the kinetic and potential energy of the nucleus and electrons within the individual molecules and the manner in which the molecules are linked together. The internal energy is denoted by E.

$E = E_{\text{trans.}} + E_{\text{rota.}} + E_{\text{vibra}} + E_{\text{bond}} + E_{\text{elec.}} + \dots\dots\dots.$

It is neither possible nor necessary to calculate the absolute value of internal energy of a system. Thermodynamics is concerned only with energy change which occurs when the system moves from one state to another.

Let ΔE be the difference of energy of the initial state (E_{in}) and the final stage (E_f) then $\Delta E = E_f - E_{in}$

In chemical reaction $\Delta E = E_{\text{Product}} - E_{\text{Reactant}}$

ΔE is + ve if $E_f > E_{in}$ & ΔE is – ve if $E_f < E_{in}$

Note : (1) Internal energy of 1 mole of mono atomic gas is $\frac{3}{2}$ RT

(2) Bomb calorimeter always gives the value of change in internal energy.

Charcteristics of I.E. :–

(1) Internal energy of a system is an extensive property.

(2) Internal energy is a state property.

(3) The change in Internal energy does not depend on the path by which the final state is reached.

(4) There is no change in internal energy a cyclic process.

Solved Examples

Ex.1 Classify the following into open, closed or isolated systems :

(i) Animals and plants

(ii) A referigerator or a fridge

(iii) A solar cooker

Sol. (i) Open system (ii) Closed system

(iii) Closed system

Ex.2 Which of the following are open, close or nearly isolated systems :

(i) Human beings

(ii) The Earth

(iii) Can of tomato soup

(iv) Ice-cube tray filled with water

(v) A satellite in a orbit

(vi) Coffee in a thermos flask and

(vii) Helium filled balloon.

Sol. Open : Human beings, Earth, Ice cube tray

Close : Can of Tomato soup, A satellite in an orbit, Helium filled balloon.

Isolated : Coffee in thermos flask.

Ex.3 Separate out the following into extensive and intensive.

Volume, Temperature, Pressure, Boiling point, Free energy.

Sol. Volume and free energy are extensive, others, are intensive.

Ex.4 Which of the following are state functions :

(i) Height of hill

(ii) Distance travelled in climbing the hill

(iii) Energy change in climbing the hill.

Sol. (i) and (iii)

THERMODYNAMIC PROCESSES

When a system changes from one state to another, the operation is called a thermodynamic process.

Thermodynamic processes are as follows.

(i) Isothermal process : Isothermal process are those processes in which

(a) Temperature remains const. i.e. $\Delta T = 0$

(b) Heat is exchanged with surroundings

(c) System is placed in a constant temperature bath i.e. thermostate.

(d) Change in Internal energy = 0 (only for ideal gases) i.e. $\Delta E = 0$

$$\left\{\begin{matrix}\Delta E = nCvdT & \\ \Delta E = 0 & (\because dT = 0)\end{matrix}\right\}$$

(ii) Isobaric process : Isobaric process are those processes in which

(a) Pressure remains const i.e. $\Delta P = 0$

(b) Volume & temperature are variable.

(c) System should be placed in an open vessel.

(iii) Isochoric process : Isochoric process are those processes in which

(a) volume remains constant i.e. $\Delta V = 0$

(b) pressure & temperature are variable

(c) Work, $W = -P\Delta V$, $\because \Delta V = 0$,

$\therefore W = 0$ (Zero)

(d) System should be placed in a closed vessel.

(iv) Adiabatic process : Adiabatic process are those processes in which

(a) No exchange of heat takes place ie. $q = 0$

(b) The temperature of the system varies.

(c) The system is thermally isolated this can be done by keeping the system in an insulated container.

(v) Cyclic process : When a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.

In cyclic process change in all state function will be zero. i.e. $\Delta E = 0$, $\Delta H = 0$, $\Delta P = 0$, $\Delta T = 0$

(vi) Reversible process :

(a) Process in which all changes occuring at any part of the system are exactly reversed when changes in variables are carrried out in opposite direction.

(b) Driving force should be infinitesimally greater than opposing force.

(c) Process takes place in infinitesimal small steps or in many steps and takes infinite time to complete the process.

(d) It is an ideal process.

(e) Work obtained is maximum.

(f) System is in virtual equilibrium at any state.

(vii) Irreversible process :

(a) Process in which direction of change cannot be reversed by small changes in variables.

(b) Process takes place in short time

(c) It takes finite time and in single step.

(d) All natural processes are irreversible

(e) System is in equilibrium only at initial and final state

(f) Driving force is greater than opposing force.

ZEROTH LAW OF THERMODYNAMICS

When a body A is in thermal equilibrium with a body B, and also separately with a body C, then B and C will be in thermal equilibrium with each other.

FIRST LAW OF THERMODYNAMICS

This law was given by Helmholtz and this law can be expressed as follows-

(i) Energy can neither be created nor be destroyed

(ii) The total energy of the universe is always a constant. i.e. the sum of energies of a system and its surrounding is always constant.

(iii) Whenever a particular form of energy disappears during a process, an equivalent amount of some other form of energy appears.

(iv) It is impossible to construct a perpetual motion machine which can operate in cycles and could produce work without any external help.

The mathematical form of first law of thermodynamics can be expressed as $\mathbf{\Delta E = q + W}$

here q is the energy given to system and W is the work done on the system. ΔE is change in internal energy.

Note : put the value of q and W with sign.

CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS

During isochoric process

At constant volume $V_1 = V_2$ i.e. $\Delta V = V_2 - V_1 = 0$

Hence $W = P\,\Delta V = P \times 0 = 0$ .... no work done at constant volume therefore

$q = \Delta E$ (At constant volume)

Thus during isochoric process, heat supplied to the system is equal to change in internal energy.

During an isothermal process

During an isothermal process the temperature of the system remains constant and hence $\Delta E = E_2 - E_1 = 0$

Therefore $q = -W$, Thus during an isothermal process, the total quantity of heat supplied to the system is equal to the work done by the system.

During an adiabatic process

During adiabatic process the system acts an isolated or insulated system and hence q = 0 in such cases. Therefore $\Delta E = W$

i.e., work done on the system is equal to increase in internal energy.

During Cyclic Process

$\Delta E = 0 \quad \Rightarrow \quad q = -W$

i.e., work done by the system is equal to heat absorbed by the system.

During Isobarric process

Let the energy given to system is q and work done by the system is W, then Internal energy $\Delta E = q_p - w$

Here, q_p = energy given to system at constant pressure

So $q_p = \Delta E + W$ ....(1)

$q_p = (E_2 - E_1) + P(V_2 - V_1)$

$q_p = (E_2 + PV_2) - (E_1 + PV_1)$

$q_p = H_2 - H_1$ $\{\because H = E + PV = \text{enthalpy}\}$

$q_p = \Delta H$

i.e. in isobaric process change in enthalpy is equal to heat absorbed by the system.

put the value of q_P in equation (1)

$\Delta H = \Delta E + P\Delta V$ ....(2)

We know that, Δ H = heat at constant pressure and Δ E = heat at constant volume.

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

or $q_p = q_v + P\Delta V$

or $q_P - q_V = P\Delta V$

i.e., difference between energy at constant pressure and energy at constant volume is equal to workdone

For gases : When temperature and pressure are remain constant then,

$PV_1 = n_1RT$ (n_1 = moles of reactant)

$PV_2 = n_2RT$ (n_2 = moles of product)

So $P(V_2 - V_1) = (n_2 - n_1)\,RT$

$P\Delta V = \Delta n_g RT$

(here Δn_g is only for gases not for solid and liquid)

put the value of PΔV in equation (2) –

or $\Delta H = \Delta E + \Delta n_g RT$ or $\boxed{\Delta H - \Delta E = \Delta n_g RT}$

(i) If $\Delta n_g = 0$; $\Delta H = \Delta E$,

(ii) If $\Delta n_g > 0$; $\Delta H > \Delta E$

(iii) If $\Delta n_g < 0$; $\Delta H < \Delta E$

Solved Examples

Ex.5 500 joule of heat was supplied to a system at constant volume. It resulted in the increase of temperature of the system from 20°C to 25°C. What is the change in internal energy of the system ?

Sol. $\Delta E = 500$ J

Ex.6 Neither q nor w is a state function, yet q + w is a state function. Explain why.

Sol. $q + w = \Delta E$ and ΔE is a state function.

Ex.7 The enthalpy change (ΔH) for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is – 92.38 KJ at 298 K. What is ΔU at 298K ?

Sol. $\Delta U = \Delta H - \Delta n_g RT = -92.38 - (-2) \times \frac{8.314}{1000} \times 298$

$= -87.42$ kJ

Ex.8 A thermally isolated gaseous system can exchange energy with the surroundings. What is the mode of transference of energy ?

Sol. Work

Ex.9 Can the absolute value of internal energy be determined ? Why or why not ?

Sol. No, because it is the sum of different types of energies, some of which cannot be determined.

Ex.10 Calculate the internal energy change in each of the following cases :

(i) A system absorbs 5 kJ of heat and does 1 kJ of work.

(ii) 5 kJ of work is done on the system and 1 kJ of heat is given out by the system.

Sol. (i) Here $q = +5$ kJ and $w = -1$ kJ

$\therefore$ According to first law of thermodynamics,

$\Delta E = q + w = 5 + (-1) = 4$ kJ

(ii) Here $w = +5$kJ and $q = -1$kJ

$\therefore$ According to first law of thermodynamics

$\Delta E = q + w = -1 + (+5) = 4$ kJ

i.e. the internal energy of the system increases by 4 kJ in each case.

Ex.11 The heat of combustion of napthalene $\{C_{10}H_8(s)\}$ at constant volume was measured to be – 5133 kJ mol^{-1} at 298K. Calculate the value of enthalpy change (Given R = 8.314 JK^{-1} mol^{-1}).

Sol. The combustion reaction of napthalene.

$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l)$,

$\Delta E = -5133$ KJ

$\Delta n_g = 10 - 12 = -2$ mol.

Now applying the relation.

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

$= -5133 \times 10^3 + (-2)(8.314)(298)$

$= -5133000\text{J} - 4955.14\text{ J} = -5137955.14$ joule

HEAT CAPACITY [C]

The amount of heat required to raise the temperature of a system by 1° C is called heat capacity of system. it is an extensive property.

Molar heat capacity : Amount of heat required to raise the temperature of 1 mole substance by 1°C.

Molar heat capacity = heat capacity/mole. It is an intensive property

Specific heat capacity : Amount of heat reuired to raise the temperature of 1 gm. of substance by 1°C.

Specific heat capacity = heat capacity/1g of substance. It is an intensive property.

Calorie : Amount of heat required to raise the temperature of 1g H_2O by 1°C (14.5°C to 15.5°C)

$\because$ Amount of heat required to raise the temperature. by dT°C = dq

$\therefore$ Amount of heat required to raise the temperature.

by $1°\text{C} = \frac{dq}{dt} = C$ J/K

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

If heat supplied at constant pressure

$$C_P = \left(\frac{dq}{dT}\right)_P = \frac{dH}{dT} \qquad \text{..........} (1)$$

If heat supplied at constant Volume

$$C_V = \left(\frac{dq}{dT}\right)_V = \frac{dE}{dT} \qquad \text{..........} (2)$$

from equation (1) and (2)

$dH = C_P dT$ (J/K), $dE = C_V dT$ (J/K)

from n mole

$dH = nC_P dT$ (J/mole K) .... (3)

$dE = nC_V dT$ (J/mole K) .... (4)

for m g

$dH = mC_P dT$ (J/g K), $dE = C_V dT$ (J/g K)

Relationship between C_P and C_V →

(i) as we know that

$\Delta H = \Delta E + P\Delta V$ (Now putting the Values of ΔH and ΔE from equation 3 and 4)

$nC_P dT = nC_v dT + P\Delta V$

or $nC_P dT - nC_V dT = P\Delta V$

$ndT\,(C_P - C_V) = P\Delta V$

if n=1 and dT = 1°C

$$\boxed{C_P - C_V = P\Delta V}$$

That is the difference between C_P and C_V is equal to workdone when 1 mole substance is heated through 1°C.

(ii) As we know that $H = E + PV$

ideal gas equation $PV = nRT$

(if n=1), $PV = RT$ $\Rightarrow H = E + RT$

Now diffrentiate to above equation with repect to T

$$\frac{dH}{dT} = \frac{dE}{dT} + R.\frac{dT}{dT} \quad \text{or} \quad \frac{dH}{dT} = \frac{dE}{dT} + R$$

or $C_P = C_V + R$

$C_P - C_V = R$ (This called mayer's relation)

(iii) $\frac{C_P}{C_V} = \gamma$ (Poissionous ratio)

Note:

(1) Heat capacity is an extensive property but molar heat capacity and specific heat capacity are intensive property.

(2) During the phase transition the heat capacity of the system is infinite.

during the phase transation temperature and pressure are constant.

$$\therefore \text{ heat capacity } C = \frac{dq}{dT} = \frac{dq}{0} = \infty$$

Solved Examples

Ex.12 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 mol of water at a temperature of 290 K. Calculate final temperataure of water. Specific heat of water = 4.184 J g^{-1} K^{-1}

Sol. Work done for an irreversible expansion at constant pressure

$W = -P(V_2 - V_1)$

$W = -3 \times (5-3) = -3 \times 2$ litre atm

$= -6 \times 101.3$ joule $= -607.8$ joule

Now this work is used up in heating water

$\therefore W = q_p = 607.8$ joule

$W = C_p \times m(dT)$

$607.8 = 4.184 \times 10 \times 18 \times dT$

$dT = 0.80$

$T_2 - T_1 = 0.80$

$T_2 = 290 + 0.80 = 290.80$ K

WORK DONE DURING DIFFERENT PROCESS

(A) In irreversible process : $W = -P_{external}\,\Delta V$

(B) In reversible process : $W = -\int_{V_1}^{V_2} PdV$

(i) During reversible isothermal process :

$$W = -\int_{V_1}^{V_2} PdV$$

$\because$ $PV = nRT$ $\therefore$

$$P = \frac{nRT}{V} \Rightarrow W = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$\because$ In isothermal process nRT = const

$$\therefore \quad W = -nRT\int_{V_1}^{V_2} \frac{1}{V} dV = -nRT$$

$$\left[\log_e V\right]_{V_1}^{V_2} = -nRT\left[\log_e V_2 - \log_e V_1\right]$$

$$= -nRT \log_e \frac{V_2}{V_1}$$

$$\boxed{W = -2.303\, nRT \log_{10} \frac{V_2}{V_1}}$$

$\because$ State equation of isothermal process is $P_1V_1 = P_2V_2$

$$\boxed{W = -2.303\, nRT \log_{10} \frac{P_2}{P_1}}$$

(ii) During reversible adiabatic process :

Work of expansion in adiabatic reversible process $W = -\int_{V_1}^{V_2} PdV$

For adiabatic process

$PV^{\gamma} = P_1V_1^{\gamma} = P_2V_2^{\gamma}$ = constant (K) or

$$P = \frac{K}{V^{\gamma}}$$

$$\therefore \quad W = -\int_{V_1}^{V_2} \frac{KdV}{V^{\gamma}} = -K\int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

$$= \frac{-1}{1-\gamma}\left(KV_2^{1-\gamma} - KV_1^{1-\gamma}\right)$$

But $P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$

$$\therefore \; W = \frac{-1}{1-\gamma}\left(P_2V_2^{\gamma}.V_2^{1-\gamma} - P_1V_1^{\gamma}.V_1^{1-\gamma}\right)$$

$$= \frac{-1}{1-\gamma}(P_2V_2 - P_1V_1) = \frac{-1}{1-\gamma}(nRT_2 - nRT_1)$$

or $\boxed{W = \frac{-nR(T_2 - T_1)}{1-\gamma}}$ ....(1)

here $\gamma = \frac{C_P}{C_V}$

C_P and C_V are heat capacities at constant pressure and volume respectively.

from mayer's relation $C_P - C_V = R$

$\because \quad \frac{C_P}{C_V} = \gamma \qquad \therefore C_p = C_V \times \gamma$

$\therefore \quad C_V \times \gamma - C_V = R$

or $\quad C_V(\gamma - 1) = R$

or $\quad -C_V(1-\gamma) = R$

or $\quad C_V = -\frac{R}{1-\gamma}$

so $\boxed{W = nC_V\,(T_2 - T_1)}$ ....(1)

for adiabatic process :- $\boxed{PV^{\gamma} = \text{constant}}$

$\boxed{TV^{\gamma-1} = \text{constant}}$ $\qquad$ $\boxed{T^{\gamma}P^{1-\gamma} = \text{constant}}$

Solved Examples

Ex.13 A gas occupies 2 litre at S.T.P. It is provided 300 joule heat so that its volume becomes 2.5 litre at 1 atm. Calculate change in its internal energy.

Sol. Given $V_1 = 2$ litre, $V_2 = 2.5$ litre , q = + 300J, $P_{external} = 1$ atm.

$\therefore \quad \Delta E = q + W$

$W = -P_{external}\,\Delta V = -P_{external}\,(V_2 - V_1)$

$= -1$ atm × (2.5–2) litre = –0.5 litre atm.

$W = -0.5 \times 101.3$ J = –50.65J

$\therefore \quad \Delta E = q + W = 300 + (-50.65) = 249.35$ J

Ex.14 Calculate the work done during the process when one mole of gas is allowed to expand freely into vacuum.

Sol. Given - Gas expands in vaccum i.e., $P_{ext} = 0$

$\Rightarrow \quad W = -P_{ext}\,\Delta V$

$\therefore \quad W = 0$

Ex.15 Two litre of N_2 at 0°C and 5 atm are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming the gas to be ideal calculate work of expansion ?

Sol. Given $P_1 = 5$ atm, $V_1 = 2$ litre, $P_2 = 1$ atm, $V_2 = ?$

We know that - if T is constant then $P_1V_1 = P_2V_2$

$$\Rightarrow \quad V_2 = \frac{P_1V_1}{P_2} = \frac{5\times 2}{1} = 10 \text{ litre}$$

$W = -P_{ext}\,\Delta V = -1(V_2 - V_1) = -1(10 - 2)$

$= -8$ litre atm $= -8 \times 101.3 = -810.4$ joule

Ex.16 Calculate the amount of work done in each of the following cases :

(i) One mole of an ideal gas contained in a bulb of 10 litre capacity at 1 atm is allowed to enter into an evacuated bulb of 100 litre capacity.

(ii) One mole of a gas is allowed to expands from a volume of 1 litre to a volume of 5 litres against the constant external pressure of 1 atm (1 litre atm = 101.3 J)

Sol. (i) $W = -P_{ext} \times \Delta V$

As expansion takes place into the evacuated bulb, i.e. against vacuum, $P_{ext} = 0$. Hence $W = 0$.

(ii) $\Delta V = V_2 - V_1 = 5 - 1 = 4$ litres , P = 1 atm

$\therefore \quad W = -P\Delta V = -1 \times 4$ litre atm

$= -4$ litre atm $= -4 \times 101.3$ J

$= -405.2$ J

Alternatively, using the SI units directly

P = 1 atm = 101325 Pa ,

$\Delta V = 4L = 4 \times 10^{-3}\ m^3$

$\therefore \quad W = -P \times \Delta V = -101325 \times 4 \times 10^{-3}$ J

$= -405.3$ J

The negative sign implies that the work is done by the system.

Ex.17 Calculate the work done during isothermal reversible expansion of one mol of an ideal gas from 10 atm to 1 atm at 300K.

Sol. Number of moles of ideal gas (n) = 1,

Inital pressure (P_1) = 10 atm,

Final pressure (P_2) = 1 atm

Constant absolute temp (T) = 300 K,

Gas constant (R) = 2 cal/mol.

$\therefore$ Work done for isothermal reversible expansion of an ideal gas

$$W = -2.303\ nRT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 1 \times 2 \times 300 \times \log_{10} \frac{10}{1}$$

$= -1381.8$ calories

Ex.18 A 5 litre cylinder contained 10 moles of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atomsphere pressure is 1.0 atm. Calculate the work done by the gas.Assuming gas to be ideal.

Sol. $V_{initial} = 5$ litre, T = 27°C = 27 + 273 = 300K.

$$V_{final} = \frac{nRT}{P} = \frac{10 \times 0.0821 \times 300}{1} = 246.3 \text{ litre}$$

$\Delta V = V_{final} - V_{initial} = 246.3 - 5 = 241.3$ litre

$W_{exp} = -P\Delta V = -1 \times 241.3$ litre × atm.

$= -24443.69J = -24.4$ kJ

i.e. work done by gas is 24.4 kJ

SPONTANEOUS PROCESS

A process which under some given conditions may either take place by itself or take place on initiation is called as spontaneous process. For example

(i) Heat flows from a hot reservoir to cold reservoir

(ii) Electricity flows from high potential to low potential

(iii) Water flows from higher side to lower side

Spontaneous processes proceed spontaneously only in one direction (from high energy to low energy side) till the state of equilibrium is attained and then they are irreversible.

A spontaneous process is accompained by decrease of internal energy or enthalpy. It indicates that only exothermic reactions are spontaneous. But melting of ice and evaporation of water are endothermic process which also proceed spontaneously. It means, there is some other factor in addition to enthalpy change (Δ H) which explain the spontaneous nature of the system. This factor is entropy which is included in 2nd law of thermodynamics.

The first law of thermodynamics has certain limitations.

(i) It puts no restriction on the direction of flow of heat.

(ii) It is not in position to tell that heat energy can not be completely converted into work.

ENTROPY (S)

Entropy is thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.Entropy is represented by symbol 'S'. It is difficult to define the exact entropy of a system.It is more convenient to define the change of entropy during a change of state.

$\Delta S = S_2 - S_1$

S_2 = Final entropy $\qquad S_1$ = Initial entropy

A spontaneous process is accompanied by an increase in entropy i.e. Δ S is positive.

At absolute zero, the entropy of pure crystal is zero.

The absolute entropy of a substance at 298 K and 1 atmospheric pressure is called the standard entropy (S^0) entropy is expressed in joules per kelvin.

The entropy of universe is continuously increasing.

At equilibrium entropy remains unchanged .

Entropy of gaseous system is greater than liquid systems and entropy of liquid systems is greater than entropy of solid systems.

If heat is absorbed Δ S is positive and if heat is evolved then ΔS is negative.

ΔS if +ve .... increase in entropy

ΔS if –ve .... decrease in entropy

The entropy change is represented as follows

$$\boxed{\Delta S = \frac{q_{rev.}}{T}}$$

q = quantity or heat supplied during reversible process.

T = Temperature on absolute scale

Entropy is an extensive property and state function.

Entropy change during phase transition :-

(1) for fusion $\boxed{\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}}}$

(2) for Vapourisation $\boxed{\Delta S_{Vap.} = \frac{\Delta H_{Vap.}}{T_{Vap.}}}$

(3) for Sublimation $\boxed{\Delta S_{Sub.} = \frac{\Delta H_{Sub.}}{T_{Sub.}}}$

Note :

for isothermal reversible process $W = -2.303\ nRT \log_{10}\frac{V_2}{V_1}$

$\because \quad q = -W \qquad \Rightarrow q = 2.303\ nRT \log_{10}\frac{V_2}{V_1}$

We know that $\Delta S = \frac{q_{rev.}}{T} = \frac{2.303nRT}{T}\log_{10}\frac{V_2}{V_1}$

$\Rightarrow \quad \boxed{\Delta S = 2.303\, nR \log_{10}\frac{V_2}{V_1}}$

Solved Examples

Ex.19 The enthalpy change for transition of liquid water to steam is 40.8 kJ mol^{-1} at 373K. Calculate Δ S for the process.

Sol. The entropy change for the vapourization of water is given by $\Delta S = \frac{\Delta H_{Vap.}}{T_{Vap.}}$

Given $\Delta H_{vap.} = 40.8$ kJ mol^{-1}

= 40.8 × 1000 J mol^{-1} and T = 373 K

$$\therefore \quad \Delta S = \frac{40.8 \times 1000\ Jmol^{-1}}{373K}$$

= 109.38 JK^{-1} mol^{-1}

Ex.20 Calculate the change in entropy for the fusion of 1 mole of ice (water). The malting point of water is 273 K and molar enthalpy of fusion for water = 6.0 kJ mol^{-1}.

Sol. $\Delta S_{fus} = \frac{\Delta H_{fus}}{T} = \frac{6000J\ mol^{-1}}{273K}$

= 21.97 JK^{-1} mol^{-1}

Ex.21 5 mol of an ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at an temperature of 27° C. Calculate the change in entropy.

Sol. For isothermal reversible process

$\Delta S = 2.303\ nR \log\frac{V_2}{V_1}$

$= 2.303 \times 5mol \times 8.314J/molK \log\frac{80}{8}$

$= 95.73\ JK^{-1}$

Ex.22 Calculate the entropy change in the melting of 1 kg of ice at 0° C in SI units. Heat of fusion of ice = 80 cal g^1.

Sol. $\Delta S_{fus.} = \frac{q_{fus.}}{T} = \frac{80 \times 1000}{273}\frac{cal}{K}$

$= \frac{8000}{273} \times 4.2JK^{-1}$

$= 1230JK^{-1}$

Ex.23 For each reaction, is the sign of ΔS (entropy) positive or negative ?

(a) $Ni(s) + 4CO(g) \longrightarrow Ni(CO)_4(g)$

(b) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O(s)$

(c) $H_2(g) + S(s) \longrightarrow H_2S(g)$

(d) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Sol. (a) Five molecules are organised into only one, so the disorder decreases and ΔS is negative.

(b) Seven molecules, three of which is are gases, become only two solid molecules thus $\Delta S < 0$.

(c) Two molecules, one of which is solid, form a gaseous molecule. Since only a heteronuclear gas results, disorder increases and ΔS is positive.

(d) Three gas molecules produce two gas molecules and disorder decreases, thus, $\Delta S < 0$.

SECOND LAW OF THERMODYNAMICS

It is not possible to construct a machine that functions in cycles and conveys heat from colder body to hotter body unless work is done on the machine by outside agency.

"Work can always be converted into heat but conversion of heat into work does not take place under all conditions ".

OR

"It is not possible to convert heat energy completely into work with compensation."

OR

"Whenever a spontaneous process takes place, it is accompained by an increase in the total entropy of the universe".

- It suggests direction of a given process.
- It is impossible to obtain work by putting a body below to the lowest temperature of the system.
- It is impossible to take heat from hot reserviour and convert it in work without transferring a part of it to cold reserviour (sink) [given by S-carnot]
- Heat cannot be passed from cold body to hot body without applying any external work.

[given by R - Clausius]

GIBBS FREE ENERGY AND SPONTANEITY

For the spontaneity of a reaction both ΔH and ΔS should be considered simultaneously. The function that takes both enthalpy and entropy into account is called free energy. It is denoted by symbol G, the meaning of which is Gibb's free energy, represented as follows -

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

Where ΔG = Change in free energy, ΔH = Change in enthalpy, ΔS = change in entropy

If ΔG is negative then spontaneous changes occur with decrease in free energy (The reaction occurs spontaneously in forward direction).

If ΔG is +ve then the reaction does not take place. But it means that the reaction is spontaneous in backward direction.

If $\Delta G = 0$, the system is in equilibrium.

Free energy of reaction changes with temperature.

The decrease in free energy is a measure of the maximum useful work that can be obtained from a reaction. In other words, it is the energy per mole of the reaction which will be liberated.

Example :- $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

for this reaction $\Delta H = -ve$ and $\Delta S = -ve$

So, at low temperature reaction will occur spontaneously but not at high temperature.

- The decrease in free energy is equal to useful work.
- Standard free energies of formation of all elementary and stable substances are taken as zero.

Ex. $Cl_2(g)$, $Br_2(\ell)$, $I_2(s)$, Carbon (graphite), Sulphur (Rhombic), Phosphorus(white).

Standard free energy change and equilibrium constant

$\Delta G^0 = -RT \ln K$ or $\Delta G^0 = -2.303\ RT \log_{10} K$

The above equation is known as **Vant Hoff reaction isotherm**.

If in the cell reaction E^0 is known , the free energy can be given by relationship.

$$\Delta G^0 = -n \times F \times E^0$$

Where n = moles of electrons involved

F = 1 Faraday = 96500 coulombs

E^0 = Standard cell potential

ΔG^0 = Standard change in free energy

Solved Examples

Ex.24 One mole of ice is converted into water at 273 K. The entropies of H_2O (s) and H_2O (I) are 38.20 and 60.01 J mol^{-1} K^{-1} respectively .The enthalpy change for the converstion would be.

Sol. At 273 K ice and water are in equilibrium with each other and at equilibrium $\Delta G = 0$

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

$\therefore \quad \Delta H = T\Delta S = 273 \times (60.01 - 38.20)$

$= 5954.13 \text{ J mol}^{-1}$

Ex.25 For the vaporisation of water :

$H_2O\text{ (l)} \rightleftharpoons H_2O\text{ (g)}$ [1 atm. pressrue]

Given : $\Delta S = 120 \text{ JK}^{-1}$ and $\Delta H = +45.0$ kJ.

Evaluate the temperature at which liquid water and water vapours are in equlibrium at 1 atm. pressure –

Sol. We known that : at equilibrium $\Delta G = 0$

$\because \quad \Delta G = \Delta H - T\Delta S \qquad \therefore \qquad T\Delta S = \Delta H$

$$\Rightarrow \quad T = \frac{\Delta H}{\Delta S} = \frac{45.0 \times 10^3 \text{ J}}{120 \text{JK}^{-1}} = 375 \text{ K}$$

Ex.26 For a certain reaction the change in enthalpy and change in entropy are 40.63 kJ mol^{-1} and 100 JK^{-1}. What is the value of ΔG at 27° C and indicate whether the reaction is possible or not ?

Sol. We know that : $\Delta G = \Delta H - T\Delta S$

Given $\quad T = 27 + 273 = 300$ K ,

$\Delta H = 40.63 \times 10^3 \text{ J mol}^{-1}$, $= 40630 \text{ J mol}^{-1}$,

$\Delta S = 100 \text{ JK}^{-1}$

$\Delta G = 40630 - 300 \times 100 = 40630 - 30000$

$= + 10630$ J

Positive value of ΔG indicates that the reaction is not possible.

Ex.27 Which of the following statement is incorrect.

(i) Entropy is a measure of disorder.

(ii) Entropy is not a state function.

(iii) Entropy is expressed in the units of J/k/mol.

(iv) The spontaneous process always accompanies the decrease in free energy.

Sol. (ii) Entropy is not a state function

Ex.28 For the equilibrium $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, $K_p = 1.8 \times 10^{-7}$. What is $\Delta G°$ for the reaction ?

Sol. $\Delta G = -2.303 \text{ RT log } K_P$

$= -2.303 \times 8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1} \times 298\text{K} \times \log 1.8 \times 10^{-7}$

$= 38.484 \text{ kJ mol}^{-1}$

Ex.29 Four mol of an ideal gas expand isothermally from 1 litre to 10 litres at 300 K. Calculated the change in free energy of the gas ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

Ans. For isothermal reversible process

$$\Delta H = 0 \text{ and } \Delta S = 2.303nR \log \frac{V_2}{V_1}$$

$$\Rightarrow \Delta G = \Delta H - T\Delta S = -2.303nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 4 \times 8.314 \times 300 \log \frac{10}{1} = -22976.5 \text{ J}$$

THIRD LAW OF THERMODYNAMICS

The entropy of all pure crystals is taken as zero at the absolute zero of temperature.

Exception :- Crystals of glassy solids, mixture of isotopes of chlorine, H_2O, N_2O, NO, CO, CO_2 etc.

JOULE THOMSON EXPANSION

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-thomson expansion.

- Joule thomson coefficient (μ) :

$$\mu = \frac{dT}{dP}$$

Where dT and dP are difference in temperature and pressure respectively.

- If $\mu = +ve \rightarrow$ Gas will cool on expansion.
- If $\mu = -ve \rightarrow$ Gas will warm on expansion.

for ideal gas $\mu = 0$

Inversion temperature : Every gas has a definite value of temperature. When the sign of μ changes from negative to positive. This temperature is termed inversion temperature.

- Most of the gases have inversion temperature near about room temperature and thus cool at room temperature when expansion is done.
- The value of inversion temperature has been calculated by using vander wall's equation.

$$T_i = \frac{2a}{Rb}$$

Where, a and b are Vander Wall's constants.

THERMOCHEMICAL EQUATION

It is a balanced chemical reaction which not only indicate physical state of reactants and products but also energy change during chemical reaction.

$C(s) + O_2(g) \longrightarrow CO_2(g)$;

$\Delta H = -393.5$ kJ/mol.

- If no condition is given then value of ΔH is considerd as standard condition.
- If equation is multiplied by coefficient then value of ΔH is also multiplied by that coefiicient.
- If equation is reversed then the value of ΔH remains same only sign changes.

HEAT OF A REACTION

It is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. Heat of a reaction always depends on the physical states of reactants and products.

Heat of reaction can be expressed at constant volume or at constant pressure. For example

(i) $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} + 44.0$ kcal
$\Delta H = -44$ kcal

(ii) $C_2H_{4(g)} + 3O_{2(g)} \rightleftharpoons 2CO_{2(g)} + 2H_2O_{(\ell)}$
$\Delta E = -335.8$ kcal

(The reaction (ii) is carried out at constant volume.)

(iii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$
$\Delta H = 94.3$ k cal

Factors which influence the heat of reaction :-

(i) Physical state of reactants and products :-

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$;

$\Delta H = -286$ kJ/mol

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$;

$\Delta H = -242$ kJ/mole

(ii) Allotropic forms of the element :-

$C(s) + O_2(g) \rightarrow CO_2(g)$;

$\Delta H = -393.5$ kJ/mole (graphite)

$C(s) + O_2(g) \rightarrow CO_2(g)$;

$\Delta H = -395.4$ kJ/mole (diamond)

(iii) Temperature : Relation between heat of reaction and temperature is given by the Kirchoff's equation

$(\Delta H_2 - \Delta H_1) = \Delta C_P (T_2 - T_1)$ at constant P.

and

$(\Delta E_2 - \Delta E_1) = \Delta C_V (T_2 - T_1)$ at constant V.

ΔH_1 and $\Delta H_2 \rightarrow$

Heat of reaction at temperature T_1 & T_2.

$$\Delta C_P = \underset{\text{(product)}}{C_P} - \underset{\text{(Reactant)}}{C_R}$$

(iv) Concentration of solution

(v) Condition of constant pressure and volume

$q_P = \Delta H$ and $q_V = \Delta E$

(vi) Quantity of reactants

$\Delta H \propto$ Quantity of reactants.

DIFFERENT TYPE OF HEAT OF REACTION

A. Heat of formation (ΔH_f) : The amount of heat absorbed or evolved when 1 mole of the substance is directly obtained from its consituent elements is called heat of formation.

C (graphite) $+ O_2(g) \rightarrow CO_2(g)$

$\Delta H_f = -393.5$ kJ/mol.

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

(This reaction not shows the heat of formation)

Standard heat of formation

= enthalphy of products – enthalpy of reactants.

$$\Delta H_f^\circ = \Sigma H_P^\circ - \Sigma H_R^\circ$$

Note : The heat of formation of all the elements in their standard states are arbitrarily assumed to be zero.

Solved Examples

Ex.30 ΔH_f^0 for Al_2O_3 is – 1670 KJ. Calculate the enthalpy change for the reaction $4Al + 3O_2 \xrightarrow{\quad} 2Al_2O_3$

Sol. Given $2Al + \frac{3}{2}O_2 \xrightarrow{\quad} Al_2O_3$;

$\Delta H = -\ 1670$ kJ

Multiplying it by 2

then $4Al + 3O_2 \xrightarrow{\quad} 2Al_2O_3$;

$\Delta H = 2 \times (-\ 1670) = -\ 3340$ kJ

Ex.31 Standard heat of formation of carbon mono oxide at 298 K is –110.5 kJ. Calculate the standard heat of formation of carbon mono oxide at constant volume and 298 K.

Sol. Heat of formation of CO (g) is represented in the form of following thermochemical equation :

$C\ (s) + \frac{1}{2}O_2\ (g) \xrightarrow{\quad} CO\ (g)$,

$\Delta H = -\ 110.5$ kJ

Δn for this equation = Number of gaseous moles of product – Number of gaseous mole of reactant

$\Delta n_g = 1 - \frac{1}{2} = +\frac{1}{2}$, $R = 8.314 \times 10^{-3}$ kJ/K/mol.,

T = 298 K

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

ΔE = Standard heat of reaction at constant volume = ?

Thus, $-110.5 = \Delta E + (+\frac{1}{2}) \times 8.314 \times 10^{-3} \times 298$

$\Delta E = (-\ 110.5 - \frac{1}{2} \times 8.314 \times 10^{-3} \times 298)$kJ/mol.

= (–110.5 – 1.238)kJ/mol.= – 111.738 kJ/mol.

Ex.32 Find the heat of formation of ethyl alcohol from following data :

$C\ (s) + O_2\ (g) \xrightarrow{\quad} CO_2\ (g)$,

$\Delta H = -\ 94$ kcal

$H_2\ (g) + \frac{1}{2}O_2\ (g) \xrightarrow{\quad} H_2O\ (\ell)$,

$\Delta H = -\ 68$ kcal

$C_2H_5OH\ (\ell) + 3O_2\ (g) \xrightarrow{\quad} 2CO_2\ (g) + 3H_2O\ (\ell)$,

$\Delta H = -\ 327$ kcal

Sol. On the basis of definition of heat of formation, the following thermochemical equation is written for which ΔH_f is to be calculated : $2C\ (s) + 3H_2\ (g) + \frac{1}{2}O_2\ (g) \xrightarrow{\quad} C_2H_5OH(\ell)$, ΔH_f = ?

Given data may be written as follows because thermochemical equation act as algebraic equations

(i) $2C\ (s) + 2O_2\ (g) \xrightarrow{\quad} 2CO_2\ (g)$

$\Delta H = -\ 188$ kcal

(ii) $3H_2\ (g) + \frac{3}{2}O_2\ (g) \xrightarrow{\quad} 3H_2O\ (\ell)$;

$\Delta H = -\ 204$ kcal

(iii) $2CO_2\ (g) + 3H_2O\ (\ell) \xrightarrow{\quad} C_2H_5OH\ (\ell) + 3O_2\ (g)$

$\Delta H = +\ 327$ kcal

On addition

$2C\ (s) + 3H_2\ (g) + \frac{1}{2}O_2\ (g) \xrightarrow{\quad} C_2H_5OH\ (\ell)$,

$\Delta H_f = -\ 65$ kcal/mol.

Ex.33 Find ΔH_f^0 of Fe_2O_3 (s) if the standard heat of reaction $Fe_2O_3\ (s) + 3CO\ (g) \xrightarrow{\quad} 2Fe\ (s) + 3CO_2\ (g)$ is –6.6 kcal. Given ΔH_f^0 CO (g) = –26.4 kcal. ΔH_f^0 CO_2 (g) = –94 kcal.

Ans. For following thermochemical equation

$Fe_2O_3\ (s) + 3CO\ (g) \xrightarrow{\quad} 2Fe\ (s) + 3CO_2\ (g)$,

$\Delta H = -6.6$ kcal

Thus,

$\Delta H_{\text{of reaction}} = [\Sigma\Delta H_f^0 \text{ of product} - \Sigma\Delta H_f^0 \text{ of reactant}]$

$= [(2 \times \Delta H_f^0 \text{ of Fe (s)} + 3\ \Delta H_f^0 \text{ of } CO_2\ (g) - (\Delta H_f^0 \text{ of } Fe_2O_3\ (s) + 3 \times \Delta H_f^0 \text{ of CO (g))}]$

$-6.6 = [(2 \times 0) + (3 \times -94) - (\Delta H_f^0 \text{ of } Fe_2O_3\ (s) + 3 \times -26.4)]$ kcal

$-6.6 = [0 - 282 - \Delta H_f^0 \text{ of } Fe_2O_3\ (s) + 79.2]$

$\therefore\ \Delta H_f^0 \text{ of } Fe_2O_3\ (s) = -\ 196.2$ kcal / mol

Ex.34 Calculate the heat of formation of KCl from the following data :

(i) $KOH\ (aq) + HCl\ (aq) \longrightarrow KCl\ (aq) + H_2O(\ell)$, $\Delta H = -57.3\ kJ\ mol^{-1}$

(ii) $H_2\ (g) + \frac{1}{2} O_2\ (g) \longrightarrow H_2O\ (\ell)$,

$\Delta H = -286.2\ kJ\ mol^{-1}$

(iii) $\frac{1}{2} H_2\ (g) + \frac{1}{2} Cl_2\ (g) + aq \longrightarrow HCl\ (aq)$,

$\Delta H = -164.4\ kJ\ mol^{-1}$

(iv) $K\ (s) + \frac{1}{2} O_2\ (g) + \frac{1}{2} H_2\ (g) + aq \longrightarrow KOH\ (aq)$,

$\Delta H = -487.4\ kJ\ mol^{-1}$

(v) $KCl\ (s) + aq \longrightarrow KCl\ (aq)$,

$\Delta H = +18.4\ kJ\ mol^{-1}$

Sol. Desired equation is :-

$K\ (s) + \frac{1}{2} Cl_2\ (g) \longrightarrow KCl\ (s)$,

$\Delta H = ?$ ...... (vi)

In order to get this thermochemical equation we follow the following two steps :

Step 1. Adding Equation (iii) and (iv) and subtracting Equation (v), we have

$K\ (s) + \frac{1}{2} Cl_2\ (g) + H_2\ (g) + \frac{1}{2} O_2\ (g) \longrightarrow$

$KCl\ (s) + HCl\ (aq) + KOH\ (aq) - KCl\ (aq)$

$\Delta H = -487.4 + (-164.4) - (18.4)$

$= -670.2\ kJ\ mol^{-1}$ ...... (vii)

Step 2. To cancel out the terms of this equation which do not appear in the required equation (vi). Adding Equation (i) to Equation (vi) and subtract Equation (ii) from their sum. This gives

$K\ (s) + \frac{1}{2} Cl_2\ (g) \longrightarrow KCl\ (s)$;

$\Delta H = -670.2 - 57.3 - (-286.2)$

$= -441.3\ kJ\ mol^{-1}$

Ex.35 Standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(\ell)$ are –75, –393.5, –286kJ respectively. Find out the change in enthalpy for the reaction.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$

Sol. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$

$\Delta H_{\text{of reaction}} = [\Sigma \Delta H_f^0 \text{ of product} - \Sigma \Delta H_f^0 \text{ of reactant}]$

$\Delta H° = [\ (-393.5) + 2(-286)\ ] - [\ (-75) + 2(0)\ ]$

$\Delta H° = (-965.5) - (-75) = -890.5\ kJ$

B. HEAT OF COMBUSTION : Heat evolved during the complete combustion of 1 mole substance is called heat of combustion.

(i) $C + O_2 \rightarrow CO_2$; $\Delta H = -393.5\ kJ/mol$

ΔH show heat of combustion of C and heat of formation of CO_2

(ii) $C + \frac{1}{2} O_2 \rightarrow CO$

equation (ii) does not show the heat of combustion because this is not complete combustion

Calorific Value or Fuel value : The amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised.

Maximum value of calorific value = Maximum efficiency or best fuel

$$\text{Calorific value} = \frac{\text{Heat of combustion}}{\text{Molecular weight of compound}}$$

Solved Examples

Ex.36 Find out the calorific value of Glucose $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; $\Delta H = -2900\ kJ/mole$

Sol. ∵ Heat evolved from 1 mole glucose = 2900 kJ

or Heat evolved from 180 gram glucose = 2900 kJ

∴ Heat evolved from 1 gram glucose = $\frac{2900}{180}$

= 16.11 kJ

Note : Hydrogen has the highest calorific value. However, it is not used as domestic or industrial fuel due to some technical problems.

Ex.37 The heat of formation of CO_2 and H_2O is –97 kcal and –68 kcal. The heat of combustion of benzene is –783 kcal. Calculate the heat of formation of benzene ?

Sol. Given :

(i) $C_6H_6\,(\ell) + \frac{15}{2}O_2\,(g) \longrightarrow 6CO_2\,(g) + 3H_2O\,(\ell)$; $\Delta H = -\,783$ kcal.

(ii) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta H = -\,97$ kcal.

(iii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(g)$; $\Delta H = -\,68$ kcal.

Hence :

$6CO_2\,(g) + 3H_2O\,(\ell) \longrightarrow C_6H_6\,(\ell) + \frac{15}{2}O_2\,(g)$;
$\Delta H = +\,783$ kcal.

$6C\,(s) + 6O_2\,(g) \longrightarrow 6CO_2\,(g)$;
$\Delta H = -\,582$ kcal.

$3H_2\,(g) + \frac{3}{2}O_2\,(g) \longrightarrow 3H_2O\,(g)$;
$\Delta H = -\,204$ kcal.

Adding, we get ;

$6C\,(s) + 3H_2\,(g) \longrightarrow C_6H_6(\ell)$;
$\Delta H = -\,3$ kcal.

Hence heat of formation of benzene is –3kcal

Ex.38 When 2 moles of C_2H_6 (g) are completely burnt, 3129 kJ of heat is liberated, calculate the heat of formation of C_2H_6 (g). ΔH_f for CO_2 and H_2O (ℓ) are – 395 and – 286 kJ mol^{-1} respectively.

Sol. $2C_2H_6\,(g) + 7O_2\,(g) \longrightarrow 4CO_2\,(g) + 6H_2O\,(\ell)$;
$\Delta H = -\,3129$ kJ

$$\Delta H_{\text{reaction}} = \Sigma\Delta H_{\text{products}} - \Sigma\Delta H_{\text{reactants}}$$

$$-\,3129 = [4 \times \Delta_f H_{CO_2} + 6 \times \Delta_f H_{H_2O}] - [2 \times \Delta_f H_{C_2H_6}]$$

$$= [4 \times (-\,395 + 6 \times (-286)] - [2 \times \Delta_f H_{C_2H_6}]$$

$$2\Delta_f H_{C_2H_6} = -\,167 \text{ kJ [for elements } \Delta H = 0]$$

$$\Delta_f H_{C_2H_6} = -\,83.5 \text{ kJ}$$

Ex.39 Calculate the enthalpy of combustion of ethylene (g) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of CO_2, H_2O and C_2H_4 are – 393.7, –241.8 + 52.3 kJ per mole respectively.

Sol. Given :

(i) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$
$\Delta H = -\,393.7$ kJ mol^{-1}

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

(iii) $2C\,(s) + 2H_2\,(g) \longrightarrow C_2H_4\,(g)$,
$\Delta H = +\,52.3$ kJ mol^{-1}

Objective reaction :

$C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g)$,
$\Delta H = ?$

2 × Eq. (i) + 2 × Eq. (ii) – Eq. (iii) gives

$$\begin{array}{lcl} 2C\,(s) + 2O_2\,(g) & \longrightarrow & 2CO_2\,(g) \\ +\,O_2\,(g) + 2H_2\,(g) & \longrightarrow & 2H_2O\,(g) \\ -2C\,(s) - 2H_2\,(g) & \longrightarrow & -\,C_2H_4\,(g) \\ \hline 3O_2\,(g) & \longrightarrow & 2CO_2\,(g) + 2H_2O\,(g) - C_2H_4\,(g) \end{array}$$

or $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g)$

$$\Delta H = 2(-393.7) + 2\,(-241.8) - (52.3)$$
$$= -\,1323.3 \text{ kJ mol}^{-1}$$

Alternative Method :

We aim at :

$C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g)$

We are given : $\Delta H_{f(CO_2)} = -\,393.7$ kJ mol^{-1},

$\Delta H_{f(H_2O)} = -\,241.8$ kJ mol^{-1}, $\Delta H_{f(C_2H_4)} = +\,52.3$ kJ mol^{-1}

$\Delta H_{\text{Reaction}}$ = (Sum of ΔH_f^0 values of Products) – (Sum of ΔH_f^0 values of Reactants)

$$= [2 \times \Delta H^0_{f(CO_2)} + 2 \times \Delta H^0_{f(H_2O)}] - [\Delta H^0_{f(C_2H_4)} + 3 \times \Delta H^0_{f(O_2)}]$$

$$= [2 \times (-393.7) + 2 \times (-241.8)] - [(52.3) + 0]$$

(∵ ΔH_f^0 for elementary substance = 0)

$$= [-787.4 - 483.6] - 52.3 = -1323.3 \text{ kJ mol}^{-1}$$

Ex.40 A cylinder of cooking gas is assumed to contain 11.2 kg of butane. The thermo chemical equation for the combustion of butane is :

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(\ell)$$

; $\Delta H = -2658$ kJ

If a family needs 15000 kJ of energy per day for cooking, how long would the cylinder last ?

Sol. Molecular mass of butane is = 58 g mol^{-1}

58 g of butane on combustion gives 2658 kJ of heat

$\therefore$ 11.2 kg of butane on combustion gives

$$= \frac{2658 \times 11.2 \times 1000}{58} \text{ kJ of heat}$$

The daily requirement of energy = 15000 kJ

$\therefore$ The cylinder would last

$$= \frac{2658 \times 11.2 \times 1000}{58 \times 15000} \text{ days} \quad \approx 34 \text{ days}$$

C. Heat of Hydrogenation :- Heat changes during the complete hydrogenation of 1 mole of unsaturated organic compound is called heat of hydrogenation.

(i) $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

$\Delta H = x$

(ii) $CH \equiv CH + H_2 \rightarrow CH_2 = CH_2$

$\Delta H = y$

Reaction (ii) will not show the heat of hydrogenation.

D. Heat of neutralisation :- The heat of neutralisation is defined as the heat evolved or decrease in enthalpy when 1 gram equivalent of an acid is neutralised by 1 gram equivalent of a base in dilute solution.

Heat of neutralisation of a strong acid against a strong base is always nearly the same, i.e., 13.7 k cal or 57.1 kJ.

Solved Examples

Ex.41 200 cm^3 of 0.1 M H_2SO_4 is mixed with 150 cm^3 of 0.2M KOH. Find the value of evolved heat.

Sol. 200 cm^3 of 0.1 M $H_2SO_4 = \frac{0.1 \times 200}{1000}$

= 0.02 mole H_2SO_4

150 cm^3 of 0.2 M KOH = $\frac{0.2 \times 150}{1000}$

= 0.03 mole KOH

0.02 mole $H_2SO_4 = 2 \times 0.02$ mole H^+

= 0.04 mole H^+

and 0.3 mole KOH $\equiv$ 0.03 mole OH^-

0.03 mole OH^- ions would react with 0.03 mole H^+ ions to form 0.03 mole H_2O.

$\therefore$ The heat liberated = 57.1 × 0.03 = 1.7 kJ

E. Heat of solution :- The amount of heat evolved or absorbed when 1 mole solute is dissolved in excess of solvent is called heat of solution.

KCl (s) + aq $\rightarrow$ KCl (aq.)

$\Delta H = 4.4$ kcal

$H_2SO_4 (\ell) + aq \rightarrow H_2SO_4(aq.)$

$\Delta H = -20.2$ kcal

F. Heat of Hydration :- The change in heat content when one mole of anhydrous or partially hydrated salt combines with required number of moles of water to form a specific hydrated substance.

$CuSO_4 (s) + 5H_2O (\ell) \rightarrow CuSO_4.5H_2O (s)$;

$\Delta H = -18.7$ kcal

G. Heat of fusion :- The heat required to convert 1 mole substance at its melting point into liquid is called heat of fusion.

$H_2O (s) \rightarrow H_2O (\ell)$;

$\Delta H = 6$ kJ

H. Heat of Vapourisation :- The heat required to convert 1 mole liquid at its boiling point into vapour is called heat of vapourisation.

$H_2O(\ell) \rightarrow H_2O(g)$;

$\Delta H = 40.6$ kJ

I. Heat of sublimation :- The heat required to convert 1 mole substance (a solid) at a particular temperature into vapour is called heat of sublimation.

J. Lattice Energy :- The amount of energy released when one mole of the compound is formed by the interaction of constituent gaseous cations and gaseous anions.

$A^+(g) + B^-(g) \rightarrow A^+B^- +$ Energy

(1 mole) (Latice energy)

Note : Lattice energy can be calculated with the help of Born-Haber cycle.

LAW OF THERMO CHEMISTRY

(a) Lavosier and Laplace's law :- Enthalpy of decomposition of a compound is numerically equals to the formation of that compound and only sign changes.

(b) Hess's Law :- The total amount of heat evolved or absorbed in a chemical reaction is the same whether the reaction is carried out in one or several steps by one or more methods.

It also does not depend upon the manner in which the chemical reaction is carried out.

Ex. Single step reaction

$A \rightarrow B\ ;\ \Delta H$

Multi step reaction to produce B from A is given

$$A \xrightarrow{\Delta H_1} C \xrightarrow{\Delta H_2} D \xrightarrow{\Delta H_3} E \xrightarrow{\Delta H_4} B$$

According to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$