

THERMOCHEMISTRY

It involves a study of interrelation of various kinds of energy accompanying physical or chemical changes. Initially it meant for studies accompanying heat changes (*thermos* heat, *dynamics* flow) and interrelate heat energy with work. Now the term in broader sense involves all kinds of energy changes accompanying the process.

Terminology of Thermodynamics:

System: A specified part of universe selected for the study of effect of certain properties such as P, T , etc

Surroundings: The adjacent part of universe outside the real or imaginary boundaries of system.

Type of System:

- 1 Homogeneous system:** A system is supposed to homogeneous if it uniform throughout, *i.e.*, all the substances present in it have only one phase.
- 2. Heterogeneous system:** Not uniform throughout, *i.e.*, it has more than one phase.

Classification of system may also be made as;

- 1. Open system:** A system which can exchange matter as well as energy with surroundings *e.g.*, liquid kept in a beaker
- 2. Closed system:** A system which can exchange only energy with surroundings *e.g.*, liquid in a sealed tube.
- 3. Isolated system:** Neither exchange of matter nor exchange of energy is possible surroundings.

State functions: The measurable properties of a system which depend only upon the state of system known as state variables, *e.g.*, P, V, T , composition; energy etc.

The cyclic rule: For 1 mole of an ideal gas

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$$

or
$$\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_P = -1$$

State of system : The state of the system at a time signify for the fact that the variable factors, *e.g.*, P, V, T , etc.(which completely define the state of system) are known.

Properties of system : The thermodynamics properties of a system are known.

Properties of system : The thermodynamic properties of a system are divided as:

- 1. Intensive properties:** Mass independent properties, *e.g.*, temperature, pressure, viscosity, density, refractive index, surface tension, chemical potential etc.
- 2. Extensive properties:** Mass dependent properties, *e.g.*, mass, volume, energy, heat enthalpy, entropy.

NOTE: An extensive property becomes intensive by specifying a unit amount of matter, *e.g.*, mass and volume are extensive but density = M/V is intensive property.

Thermodynamics process: The operations, by which the changes from one state to other are made, are known as thermodynamics process. All thermodynamics properties satisfy

$$\Delta U = q + w$$

$$H = U + PV$$

$$S = \frac{q_{rev}}{T}$$

1 Reversible process: A reversible or quasistatic process is one in which all changes occurring at any part of the process are exactly reversed, when it is carried out in opposite direction. A reversible process involves.

- (a) A slow change during investigations.
- (b) Driving force is infinitesimally greater than the opposing forces and *vice-versa*.
- (c) The process may take place in either direction.
- (d) Maximum work is obtained.

2. Irreversible process: A process whose direction cannot be reversed by small changes in variables is irreversible process. It involves

- (a) A fast change during investigation.
- (b) Driving force is much different than opposing force.
- (c) The unidirectional process.
- (d) Net work somewhat lesser than maximum work, is obtained.

Heat and temperature:

- 1. Heat is a measure of quantity of energy transferred from one body to other as result of temperature difference between them.
- 2. Temperature is a measure of intensity of energy, i.e., how much energetic each individual particle is.

Work: Work is expressed as the product of two factors, i.e., $W = \text{intensity factor} \times \text{capacity factor}$

Intensity factor is measure of force against which work is done. Capacity factor is the extent for which is done.

i.e., Mechanical work = force \times displacement = $F \times d$

Gravitational work = gravitational force \times height = $mg \times h$

Electrical work = pot. difference \times quantity of current = $E \times Q$

Work of expansion = pressure \times change in volume = $P \times \Delta V$

A -ve sign is given for work done by the system.

A +ve sign is given for work done on the system.

The general expression for all types of PV work can be written as

$$W = -P\Delta V$$

For expansion: $\Delta V = V_2 - V_1 = +ve$ ($\because V_2 > V_1$)

$$\therefore W = -ve$$

For compression: $\Delta V = V_2 - V_1 = -ve$ ($\because V_2 < V_1$)

$$\therefore W = +ve$$

Unit of work: $W = \text{dyne cm or erg}$ in C.G.S.
 $= \text{newton m or joule}$ in M.K.S.
 $= \text{calorie}$

$$1 \text{ cal} = 4.184 \times 10^7 \text{ erg} = 4.184 \text{ J}$$

Internal energy : It is sum total energy of the system at the constant volume. Each substance is associated with a definite amount of energy involving the energy depending upon the chemical nature of substance and the conditions of P, V, T . It includes many types of energy such as translational, vibrational, rotational, coulombic, potential energy etc. Therefore, exact magnitude of internal energy cannot be determined. Furthermore, it is a state function and denoted by U and is independent of path. In thermodynamics we deal with the change in internal energy of two states,

$$\Delta U = U_2 - U_1$$

ENTHALPY: It is sum total energy of the system at the constant pressure (Generally).

Heat enthalpy or heat content: Enthalpy ' H ' is also a state function and independent of path. It is expressed as

$$H = U + PV$$

Link U , in thermodynamics we deal with change in heat enthalpy ΔH ;

$$\Delta H = H_2 - H_1$$

Relation in between ΔH and ΔU : The two are related by

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

$$\text{at constant volume } \Delta H = \Delta U \quad (\because \Delta V = 0)$$

First law of thermodynamics: According to this law, mass and energy of an isolated system remains constant. The law is expressed mathematically as

$$dq = (dU) + (-dW) \quad \dots (1)$$

(For an infinitesimal change)

where, dU = Change in internal energy

dq = Heat supplied to system

$-dW$ = Work done by the system

$$\text{Also} \quad q = \Delta U + (-W) \quad \dots (2)$$

$$\text{or} \quad \Delta U = q + W \quad (\text{For finite change})$$

Some useful formulae based upon I law.

1. Isothermal process: A process in which temperature of the system remains constant through the studies

$$\because \Delta T = 0 \quad \therefore \Delta U = 0$$

$$\therefore \text{By Eq. (2)} \quad q = -W$$

i.e., heat given to a system is used in work done by the system.

2. Adiabatic process: A process during which no exchange of heat takes place in between system and surroundings.

$$\because \quad q = 0$$

$$\therefore \text{By Eq. (2)} \quad +\Delta U = W$$

$$\text{or} \quad -\Delta U = -W$$

i.e., work is done by the system on the cost of its internal energy.

3. Cyclic process: A process in which initial state of system is regained after a series of operations.

$$\therefore \quad \Delta U = 0$$

$$\therefore \text{By Eq. (2)} \quad q = -W$$

4. Isochoric process: A process in which volume of the system remains constant throughout the investigations

$$\because \quad \Delta V = 0$$

$$\therefore \text{By Eq. (2)} \quad q_v = \Delta U$$

i.e., heat given to a system under constant volume is used up in increasing internal energy.

5. Isobaric process: A process in which pressure of the system remains constant throughout the investigations.

$$\because \quad \Delta P = 0$$

Consider a system showing increase in volume from V_1 to V_2 at a constant pressure P , during absorption of heat q . The expansion work or work done by the system is $W = -p\Delta V$

$$\text{Thus by Eq. (2)} \quad q_p = \Delta U - (-P\Delta V)$$

$$= U_2 - U_1 - [P(V_2 - V_1)]$$

$$= (U_2 + PV_2) - (U_1 + PV_1)$$

$$= H_2 - H_1 \quad (\because H = U + PV)$$

$$q_p = \Delta H$$

i.e., heat given to a system under constant P is used up in increasing heat enthalpy of system. Work done in isobaric process = $dU - dq$

$$= nC_v \cdot dT - nC_p \cdot dT$$

$$= -RdT$$

$$= -nR(T_{final} - T_{initial})$$

6. **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

$$w = -P(V_2 - V_1) \quad \dots (3)$$

or
$$W_{irr} = -P(V_2 - V_1) \quad \dots (4)$$

Also
$$\Delta U = \Delta H = 0$$

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

7. **Work done in isothermal reversible process:** Consider a system under isothermal condition, showing reversible expansion of an ideal gas by a volume dV , then.

$$\because \Delta U = 0$$

$$\therefore dq = -dW = +PdV \quad (\because dW = -pdW)$$

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

The total work during expansion of gas from V_1 to V_2

$$\int dW = \int_{V_1}^{V_2} -PdV = \int_{V_1}^{V_2} -\frac{nRT}{V} \cdot dV$$

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

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

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

8. **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,

$$(\because dq = 0)$$

$$+dU = dW$$

$$\because dU = nC_v dT$$

or
$$+C_v \cdot n \times dT = dW$$

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

$$dW = +C_v \times n \times dT$$

$$C_p - C_v = R$$

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

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

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

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

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

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

Where γ is Poisson's ratio $= \frac{C_p}{C_v} \quad \dots (8)$

Also
$$\Delta H = nC_p (T_2 - T_1) \quad \dots (9)$$

If final temperature is not known:

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

Some important results of adiabatic expansions

1. $PV^\gamma = \text{constant} \quad \dots (11)$

2. $T^\gamma P^{1-\gamma} = \text{constant} \quad \dots (12)$

3. $V^{\gamma-1} T = \text{constant} \quad \dots (13)$

Overview

Thermo chemistry deals with the transfer of heat between a chemical system and its surroundings when a change of phase or a chemical reaction takes place within the system. In general, a chemical reaction can be either exothermic or endothermic. In the former case, heat is released to the surroundings when the reactants at a given temperature and pressure are converted to the products at the same temperature and pressure, and in the latter heat is absorbed by the system, from the surroundings.

Sign conventions:

If the heat is absorbed by the system ($q > 0$) then the reaction is said to be endothermic and

ΔE or ΔH value is given a positive sign. If the heat is evolved ($q < 0$) the reaction is said exothermic, and ΔE or ΔH values are given negative sign.

Standard States:

In the computation of heat of reactions it is a convention to assume that the heat of formation of elements in their standard states is zero. The standard state is taken as 1 atm pressure and a constant temperature.

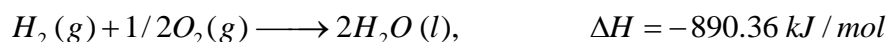
Standard states for various forms of matter are summarized below :

STATE	STANDARD STATE
Gas	Ideal gas at 1 atm and the given temperature
Liquid	Pure liquid at 1 atm and the given temperature
Solid	Stable crystalline form at 1 atm and given T (e.g. graphite form of carbon, rhombic form of sulphur)

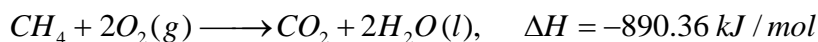
A standard state the heat of reactions is denoted by ΔE^o or ΔH^o at given temperature.

Various Types of Enthalpies of Reactions

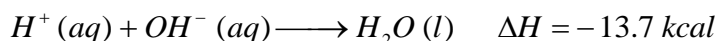
- (i) **Enthalpy of formation:** Enthalpy change when one mole of a given compound is formed from its elements.



- (ii) **Enthalpy of combustion:** Enthalpy change when one mole of a substance is burnt in oxygen



- (iii) **Enthalpy of neutralization:** Enthalpy change when one equivalent of an acid is neutralized by a base in dilute solution. This is constant and its values are -13.7 kcal for neutralization of any strong acid by a base since in dilute solutions they complete dissociate into ions.



For weak acids and bases, heat of neutralization is different because they are not dissociated completely and during dissociation some heat is absorbed. So total heat evolved during neutralization will be less.

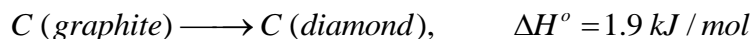


Heat of ionization in this reaction is equal to $(-2.9 + 13.7) \text{ kcal} = 10.8 \text{ kcal}$

- (iv) **Enthalpy of hydration:** Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite no. of mole of water to form a specific hydrate. For example, the hydration of anhydrous copper sulphates is represented by



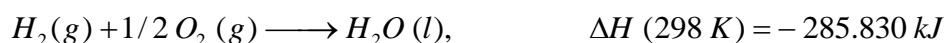
(v) **Enthalpy of transition:** Enthalpy change when one mole of a substance is transformed from one allotropic form to another allotropic form,



Laws of Thermo chemistry

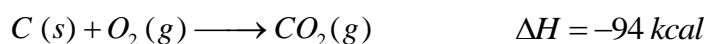
For some reactions it is not convenient to measure the heat change in the laboratory. So conventional procedure based on the principle of conservation of energy has been suggested which can be stated as follow:

- The heat of formation of any compound is equal in magnitude and of opposite sign to the heat of dissociation of that compound at the given temperature and pressure. For example, enthalpy of formation of liquid water from its elements hydrogen and oxygen is $-285.830 \text{ kJ mol}^{-1}$ and the enthalpy of dissociation is $285.830 \text{ kJ mol}^{-1}$, thus the process can be represented by

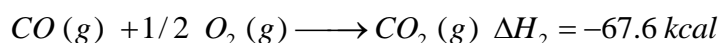


- The total enthalpy change of a reaction is the same, regardless of whether the reaction is completed in one step or in several steps. (Hess's Law of constant heat summation.) It has been experimentally verified and is also a consequence of the law of conservation of energy which are difficult for practical calorimetric measurements.

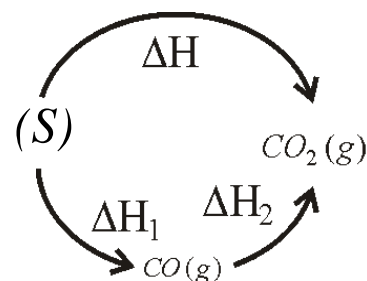
For example: Carbon is converted into CO_2 in 1 step



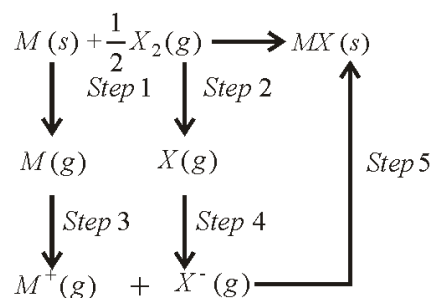
Or in two steps



According to Hess's law: $\Delta H = \Delta H_1 + \Delta H_2 = -26.4 - 67.6$



Lattice Energy of an Ionic Crystal (Born-Haber Cycle)



The change in enthalpy that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions.

Step 1: Conversion of metal to gaseous atoms.



Step 2: Dissociation of X_2 molecules to X atoms



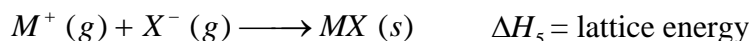
Step 3: Conversion of gaseous metal atom to metal ions by losing electron



Step 4: X (g) atoms gain an electron to form M^- ions



Step 5: $M^+(g)$ and $X^-(g)$ get together and form the crystal lattice



Applying Hess's law we get

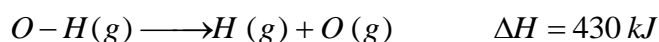
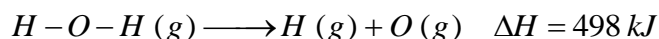
$$\Delta H_1 + 1/2 \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = \Delta H_f (MX)$$

On putting the various known values, we can calculate the lattice energy.

$$\Delta H = +26.10 \text{ kcal} \quad \dots (3)$$

BOND ENERGIES

Whenever a chemical bond is formed energy is released. Conversely, energy is required to rupture a chemical bond. The energy required to break a particular bond in a gaseous molecule is referred to as bond-dissociation energy.



In such case, bond energy is expressed as the average of the bond dissociation energies of various similar bonds.

$$\Delta H_{O-H} = (498 + 430) / 2 = 464 \text{ kJ mol}^{-1}$$

Hence, bond energy may be defined as the average amount of energy required to break one mole bonds of that type in gaseous molecules.

Thus, the values given in bond energy data can help us in:

- (i) Calculating standard enthalpy of reactions
- (ii) Calculation of bond energies of some specific bond in the molecule

Variation of Heat of Reaction with Temperature

The heat of reaction depends on the temperature, The relation between the two is known as Kirchoff's equation.

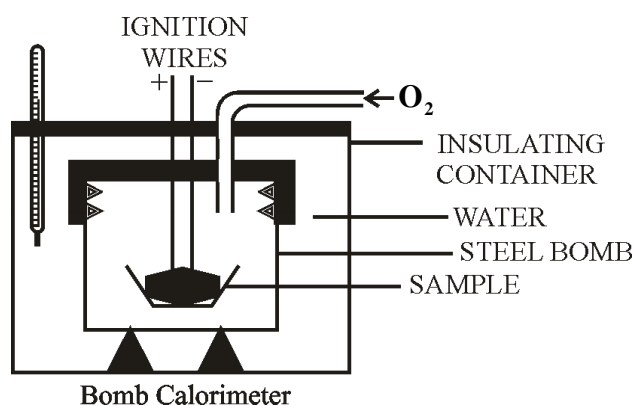
$$(i) \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

$$(ii) \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

ΔC_p = Molar heat capacity of products – molar heat capacity of reactants (at constant pressure) ΔC_v = molar heat capacity of products- molar heat capacity of reactants (at constant volume)

Bomb Calorimeter

The calorimeter used for determining enthalpies of combustion known as the bomb calorimeter is shown as Figs.



This apparatus was devised by **Berthelot** (1881) to measure the heat of combustion of organic compounds. A modified form of the apparatus shown in Figure shown consists of a sealed combustion chamber, called a bomb, containing a weighed quantity of the substance in a dish along with oxygen under about 20 atm pressure. The bomb is lowered contained in an insulated copper vessel. This vessel is provided with a stirrer and a thermometer reading up to 1/1000th of a degree. It is also surrounded by an outer jacket to ensure complete insulation from the atmosphere. The temperature of water is noted before the substance is ignited by electric current. After combustion, the rise in temperature of the system is noted on the thermometer and heat of combustion can calculate from the heat gained by water and the calorimeter. By knowing the heat capacity of calorimeter and also the rise in temperature, the heat of combustion can be calculated by using the expression

$$\text{Heat exchange} = Z \times \Delta T$$

Z-Heat capacity of calorimeter system ΔT – rise in temperature

Heat changes at constant volumes are expressed in ΔE and Heat changes at constant pressure are expressed in ΔH Also, $\Delta H = \Delta E + \Delta nRT$ Δn = gaseous product moles- gaseous reactant moles.

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

$$\Delta S = \sum S_{\text{Products}} - \sum S_{\text{Reactants}} \quad \dots (1)$$

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

$$= 2.303 nR \log_{10} \frac{V_2}{V_1} \quad \dots (2)$$

$$= 2.303 nR \log_{10} \frac{P_1}{P_2} \quad \dots (3)$$

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

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

$$\Delta S = \frac{\Delta H_{\text{rev}}}{T} \quad \dots (4)$$

i.e., entropy change if fusion:

$$\Delta S_f = \frac{\Delta H_f}{T} \quad \dots (5)$$

where T is freezing point

and entropy change of vaporization:

$$\Delta S_v = \frac{\Delta H_v}{T} \quad \dots (6)$$

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 state, $A \longrightarrow B$

$$\Delta S^\circ = S_B^\circ - S_A^\circ \quad \dots (7)$$

5. Entropy, S, is related to thermodynamic probability, W by the relation:

$$S = k \log_e W$$

$$\text{or} \quad S = 2.303 k \log_{10} W \quad \dots (8)$$

where k is Boltzmann's constant.

6. At absolute zero temperature, a solid is supposed to have highly ordered state, *i.e.*, $W = 1$ and hence $S = 0$, *i.e.*, $\lim_{T \rightarrow 0} S = 0$; This is zeroth law of thermodynamics

Free energy F or G : Free energy (F or G) is also a state function and is measure of maximum work done. It is expressed as

$$G = H - TS \quad \dots (9)$$

$$\text{or} \quad \Delta G = \Delta H - T \Delta S \quad \text{at constant T} \quad \dots (10)$$

Standard free energy change (ΔG°):

$$1. \quad \Delta G^\circ = -2.303 RT \log_{10} K \quad \dots (11)$$

$$2. \quad \text{At equilibrium } \Delta G = 0.$$

3. The decrease in free energy ($-\Delta G$) is given as:

$$-\Delta G = W_{net} = 2.303 nRT \log_{10} \frac{V_2}{V_1} \quad \dots (12)$$

$$4. \quad \Delta G_f^\circ \text{ for free elements state} = 0.$$

$$5. \quad \Delta G_f^\circ = G_{products}^\circ - G_{Reactants}^\circ \quad \dots (13)$$

Conditions for spontaneity of reaction: For a spontaneous change $\Delta G = -ve$. Thus, following results can also be evaluated for spontaneous process.

ΔH	ΔS	$\Delta H - T\Delta S$	Nature
$-ve$	$+ve$	$\therefore \Delta G = -ve$	Spontaneous
$+ve$	$-ve$	$\therefore \Delta G = +ve$	None spontaneous
$+ve$	$+ve$	If $\Delta H < T\Delta S$; $\Delta G = -ve$	Spontaneous
$-ve$	$-ve$	$\Delta G = -ve$	Spontaneous
		If $\Delta H > T\Delta S$	
		<i>i.e., T is low</i>	
		$\Delta G = +ve$	None Spontaneous
		If $\Delta H < T\Delta S$	
		<i>i.e., T is high</i>	

Gibb's Helmholtz equations: It interrelates ΔG and ΔH at constant pressure:

$$\Delta G = \Delta H + T \left[\frac{\delta(\Delta G)}{\delta T} \right]_P \quad \dots (14)$$

$$\text{or} \quad \frac{\Delta G - \Delta H}{T} = \left[\frac{\delta(\Delta G)}{\delta T} \right]_P \quad \dots (15)$$

$$\text{or} \quad -\Delta S = \left[\frac{\delta(\Delta G)}{dT} \right]_P \quad \dots (16)$$

$$\Delta S = nF \left[\frac{\delta E_{cell}}{\delta T} \right]_P \quad (\because \Delta G = -nEF) \quad \dots (17)$$

Thus, temperature coefficient of the emf of a cell is

$$\left[\frac{\delta E_{cell}}{dT} \right]_P = \frac{\Delta S}{nF} \quad \dots (18)$$

Temperature dependence of vapour state or the Clapeyron – Clausius equation.

Variation of the vapour pressure for the liquid \rightleftharpoons gas equilibrium is given by Clapeyron – Clausius equation.

$$\log P = -\frac{\Delta H_v}{2.303R} \left(\frac{1}{T} \right) + K \quad \dots (19)$$

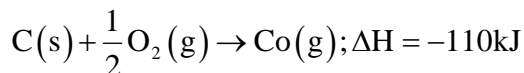
Eq. (36) is, represent the equation of a straight line. Hence the plot of $\log P$ vs $\frac{1}{T}$ yields a straight line with slope = $-\frac{\Delta H_v}{2303R}$ and intercepts = K . This enables the evaluation of ΔH_v , the **latent heat of vaporization**.

If vapour pressure P_1 and P_2 at temperature T_1 and T_2 are known then by Eq. (19).

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots (20)$$

SOLVED EXAMPLE

Problem 1 From the following data of ΔH of the following reaction,



and $\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(\text{g}); \Delta H = 132 \text{ kJ}$,

Calculate the mole composition of the mixture of steam and oxygen on being passed over cock at 1373 K, keeping the reaction temperature constant.

Solution

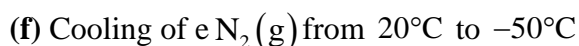
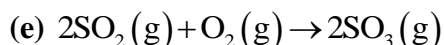
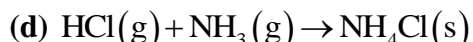
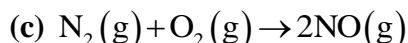
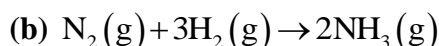
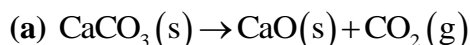
From the question we see that the first reaction is exothermic and the second one is endothermic. Thus, if a mixture of oxygen and steam (H_2O) is passed over cock and at the same time, the temperature does not change, the composition should be such that ΔH of both the reactions are numerically equal.

In the first reaction, consumption of $1/2$ mole of O_2 evolves 110 kJ of energy, while in the second reaction, for 1 mole of steam (H_2O), 132 kJ of energy is absorbed .

$$\therefore \text{mole of } \text{O}_2 \text{ needed to evolve } 132 \text{ kJ} = \frac{0.5}{110} \times 132 = 0.6$$

\therefore mole ratio of O_2 and steam (H_2O) = 0.6 : 1.

Problem 3 Predict whether the entropy change of the system in each of the following processes is positive or negative.



Solution

Gaseous substances generally possess more entropy than solids. So whenever the products contain more moles of a gas than reactants, the entropy change is probably positive. And hence, ΔS is

(a) positive

(b) negative

(c) small, the sign of ΔS is impossible to predict

(d) negative

(e) negative

(f) negative

[Note: For a given substance at a given temperature, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$]

Problem 4 K_a for CH_3COOH at 25°C is 1.74×10^{-5} . At 50°C , K_a is 1.633×10^{-5} . What are ΔH° and ΔS° for the ionisation of CH_3COOH ?

Solution

$$(\Delta G^\circ)_{298} = -2.303RT \log K$$

$$= -2.303 \times 8.314 \times 298 \times \log(1.754 \times 10^{-5})$$

$$(\Delta G^\circ)_{323} = -2.303 \times 8.31 \times 323 \times \log(1.633 \times 10^{-5})$$

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

$$27194 = \Delta H^\circ - 298\Delta S^\circ$$

$$29606 = \Delta H^\circ - 323 - 323\Delta S^\circ$$

$$\therefore \Delta H^\circ = -1.55 \text{ kJ/mol}$$

$$\Delta S^\circ = 96.44 \text{ J/mol.K}$$

Problem 5 A certain reaction is nonspontaneous at 298 K. The entropy change during the reaction is 121 J/K. Is the reaction endothermic or exothermic? What is the minimum value of ΔH for the reaction?

Solution Given that $\Delta G = +ve$ for nonspontaneous process.

As $\Delta G = \Delta H - T\Delta S$ and $\Delta S = +121 \text{ J/K}$

ΔH has to be positive, that is, the reaction is endothermic.

To calculate the minimum value of ΔH , $\Delta G = 0$.

$$\therefore \Delta H = T\Delta S$$

or $\Delta H = 298 \times 121 \text{ J}$

$$\Delta H = 36.06 \text{ kJ.}$$

Problem 8 Determine whether or not, it is possible for sodium to reduce aluminium oxide to aluminium at 298 K. Also calculate equilibrium constant. Given that G_f° of Al_2O_3 at $298 \text{ K} = -1582 \text{ kJ mol}^{-1}$; G_f° of $\text{Na}_2\text{O}(s)$ at $298 \text{ K} = -377 \text{ kJ mol}^{-1}$

Solution The given reaction is

$$\text{Al}_2\text{O}_3(s) + 6\text{Na}(s) \longrightarrow 3\text{Na}_2\text{O}(s) + 2\text{Al}(s)$$

Hence, $\Delta G^\circ = 3 \times G_f^\circ(\text{Na}_2\text{O}) - G_f^\circ(\text{Al}_2\text{O}_3)$

$$(G^\circ \text{ for Na and Al} = 0)$$

$$= 3 \times (-377) - (-1582)$$

$$= +451 \text{ kJ mol}^{-1}$$

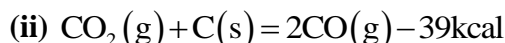
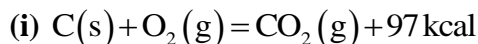
The reaction cannot occur since ΔG° is positive, $\Delta G^\circ = -2.303RT \log_{10} K$

$$451 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log_{10} K$$

$$\therefore \log K = -79.04$$

$$K = 9.1 \times 10^{-80}$$

Problem 9 For the given heat of reaction

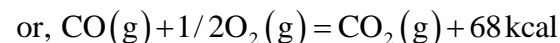
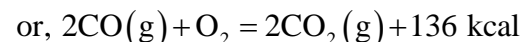
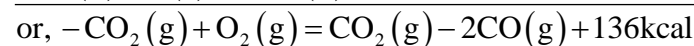
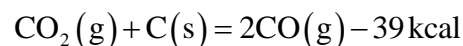
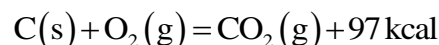


the heat of combustion of CO (g) is:

- (a) 68 kcal (b) -68 kcal (c) +48kcal (d) None

Solution

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



Required value = 68 kcal

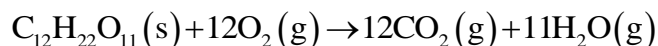
\therefore (a)

Problem 10 The heat of combustion of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{S})$ at constant volume is $-1348.9 \text{ kcal mol}^{-1}$ at 25°C , then the heat of reaction at constant pressure, when steam is produced, is

- (a) -1342.344 kcal (b) $+1342.344 \text{ kcal}$ (c) $+1250 \text{ kcal}$ (d) None

Solution

The combustion equation of sucrose is



Here

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

$$\Delta n = 12 + 11 - 12 = 11$$

As we Known

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

ΔE = heat of reaction at constant volume

Here, $\Delta E = -1348.9 \text{ kcal}$

$$R = 2.0 \text{ cal, } T = 25 + 273 = 298\text{K}$$

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

$$= -1348900 + 6556 \text{ cal} = -1342.344 \text{ kcal}$$

EXERCISE

- The difference between heats of reaction at constant pressure and constant volume of the following reaction, would be $2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \longrightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$ at 25°C in kJ mol^{-1} is
 (a) -7.43 (b) $+3.72$ (c) -3.72 (d) $+7.43$
- One mole of ice is converted into water at 273 K . The entropies of $\text{H}_2\text{O}(s)$ and $\text{H}_2\text{O}(l)$ are 38.20 and $60.01\text{ J mol}^{-1}\text{ K}^{-1}$ respectively. The enthalpy change for the conversion is:
 (a) 59.54 J mol^{-1} (b) 5954 J mol^{-1} (c) 595.4 J mol^{-1} (d) 320.6 J mol^{-1}
- For the combustion reaction at 298 K
 $2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow 2\text{Ag}_2\text{O}(s)$
 Which of the following relation will be true?
 (a) $\Delta H = \Delta U$
 (b) $\Delta H > \Delta U$
 (c) $\Delta H < \Delta U$
 (d) ΔH and ΔU bear no relation with each other
- For which of the following equations, will ΔH be equal to ΔU ?
 (a) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$ (b) $\text{H}_2(g) + \text{I}_2(g) \longrightarrow 2\text{HI}(g)$
 (c) $2\text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$ (d) $4\text{NO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{N}_2\text{O}_5(g)$
- The bond enthalpies of $\text{H}-\text{H}$, $\text{Cl}-\text{Cl}$ and $\text{H}-\text{Cl}$ are 435 , 243 and 431 kJ mol^{-1} , respectively. The enthalpy of formation of $\text{HCl}(g)$ will be
 (a) 92 kJ mol^{-1} (b) -92 kJ mol^{-1} (c) 247 kJ mol^{-1} (d) 770 kJ mol^{-1}
- The molar enthalpies of combustion of $\text{C}_2\text{H}_2(g)$, $\text{C}(\text{graphite})$ and $\text{H}_2(g)$ are -1300 , -394 and -286 kJ mol^{-1} , respectively. The standard enthalpy for formation of $\text{C}_2\text{H}_2(g)$ would be
 (a) -226 kJ mol^{-1} (b) -626 kJ mol^{-1} (c) 226 kJ mol^{-1} (d) 626 kJ mol^{-1}
- The ΔH_f° for $\text{CO}_2(g)$, $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ are -393.5 , -110.5 and $-241.8\text{ kJ mol}^{-1}$ respectively. The standard enthalpy change (in kJ mol^{-1}) for the reaction $\text{CO}_2(g) + \text{H}_2(g) \longrightarrow \text{CO}(g) + \text{H}_2\text{O}(g)$ would be
 (a) 524.1 (b) 41.2 (c) -262.5 (d) -41.2
- Equal volumes of 1 M HCl and $1\text{ M H}_2\text{SO}_4$ are neutralised completely by dil NaOH solution and $x\text{ kcal}$ and $y\text{ kcal}$ heat are liberated respectively. Which of the following relationship between x and y will be true?
 (a) $x = y$ (b) $x = \frac{y}{2}$ (c) $x = 2y$ (d) $x = \frac{1}{2y}$

9. Heat capacity of H_2 at constant P and T is
 (a) $3 \text{ cal mol}^{-1} \text{ K}^{-1}$ (b) $5 \text{ cal mol}^{-1} \text{ K}^{-1}$ (c) $7 \text{ cal mol}^{-1} \text{ K}^{-1}$ (d) ∞
10. The heats of neutralisation of four acids A, B, C, D are -13.7 , -9.4 , -11.2 and -12.4 kcal respectively when they are neutralized by a common base. The acidic character obeys the order
 (a) $A > B > C > D$ (b) $A > D > C > B$ (c) $D > C > B > A$ (d) $D > B > C > A$
11. The dissociation energy of CH_4 and C_2H_6 are respectively 360 and 620 kcal/mol . The bond energy of C–C bond would be
 (a) 260 kcal/mol (b) 180 kcal/mol (c) 130 kcal/mol (d) 80 kcal/mol
12. A system is provided 50 J of heat and work done on the system is 10 J . The change in internal energy during the process is
 (a) 40 J (b) 60 J (c) 80 J (d) 50 J
13. The ΔG in the process of melting of ice at -15°C would be
 (a) ΔG is $-ve$ (b) ΔG is $+ve$ (c) $\Delta G = 0$ (d) All of these
14. Temperature of 1 mole of a gas is increased by 1° at constant pressure. The work done is
 (a) R (b) 2R (c) R/2 (d) 3R
15. Heat of neutralisation of NaOH and HCl is $-57.46 \text{ kJ/equivalent}$. The heat of ionization of water (kJ/mol) will be
 (a) -57.46 (b) $+57.46$ (c) -114.92 (d) $+114.92$
16. On standard conditions ΔH and ΔS for a particular reaction are $-1.17 \times 10^3 \text{ J/mole}$ and -105 J/mol K respectively. This reaction will be
 (a) Exothermic and spontaneous (b) exothermic and non-spontaneous
 (c) Spontaneous and reversible (d) spontaneous and non-reversible
17. At 0°C $\Delta_{\text{fus}}H^\circ = 6 \text{ kJ mole}^{-1}$, change of entropy for freezing 1mole ice will be
 (a) ∞ (b) 0 (c) $21.98 \text{ J mole}^{-1} \text{ K}$ (d) 13.6 J
18. $\Delta_C H_{C_2H_6}^\circ$ and $\Delta_C H_{C_2H_2}^\circ$ are $-341.1 \text{ kcal mole}^{-1}$ and $-310.0 \text{ kcal mole}^{-1}$ respectively then
 (a) ethane is better welding gas having more magnitude of $\Delta_C H^\circ$.
 (b) ethyne is better welding gas having more value of $\Delta_C H^\circ$.
 (c) ethyne is better welding gas having more magnitude of $\Delta_C H^\circ/\text{unit weight}$.
 (d) ethane is better welding gas as here oxidation state of C is -3 .
19. For $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) + 44 \text{ kcal}$; $\Delta_f H^\circ$ and $\Delta_f H_{HCl(g)}^\circ$ are
 (a) $-44 \text{ kcal mole}^{-1}$; $-22 \text{ kcal mole}^{-1}$ (b) $-44 \text{ kcal mole}^{-1}$; $-44 \text{ kcal mole}^{-1}$
 (c) $-22 \text{ kcal mole}^{-1}$; $-22 \text{ kcal mole}^{-1}$ (d) $-22 \text{ kcal mole}^{-1}$; $+22 \text{ kcal mole}^{-1}$
20. Heats of combustion of $CH_4(g)$, $C_2H_4(g)$ and $C_2H_6(g)$ are -890 , -1411 and -1560 kJ/mole ; most favourable fuel gas combination will be as
 (a) 1: 3: 6 (b) 3: 1: 6 (c) 6: 3: 1 (d) 8: 1: 1

21. On adding 0.5 L each of NaOH and HCl rise in temperature has found as 4°C , on adding 1 L of each rise in temperature must be
 (a) 1°C (b) 2°C (c) 3°C (d) 4°C
22. All spontaneous changes in the universe result into
 (a) increase in entropy of the system (b) decrease in entropy of the system
 (c) increase in entropy of the surroundings (d) increase in entropy of universe
23. Universal gas constant 'R' can be defined as; at constant pressure
 (a) mechanical work associated with 1 mole gas in order to increases temperature by 1°C .
 (b) mechanical work associated with 1 mole gas when expands by 1 L at 278 K.
 (c) mechanical work associated with 1 L gas at STP when at expands by 1 L.
 (d) mechanical work done by 1 mole gas when it expands by 22.4 L at STP.
24. $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g}); \Delta_f H^{\circ} = -110\text{kJ}$
 $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}); \Delta_f H^{\circ} = 132\text{kJ}$
 Composition of steam and O_2 when it passed over coke keeping temperature 1273 K will be
 (a) 1 : 2 (b) 5 : 3 (c) 4 : 5 (d) 1 : 1
25. For the reaction $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \Delta H^{\circ} = -67650\text{cal}$ at 25°C . Calculate ΔH° at 100°C , given that the required molar heat capacities are as follows
 $C_p(\text{CO}, \text{g}) = 6.97\text{cal}^{\circ}\text{C}^{-1}$, $C_p(\text{CO}_2, \text{g}) = 8.97\text{cal}^{\circ}\text{C}^{-1}$, $C_p(\text{O}_2, \text{g}) = 7.00\text{cal}^{\circ}\text{C}^{-1}$
 (a) -54.6 cal (b) -67650.4 cal
 (c) -67684.4 cal (d) -67762.5 cal
26. The enthalpy of vaporization of water at 100°C is 40.63 kJ mol^{-1} . The value ΔU° for this process would be
 (a) 37.53 kJ mol^{-1} (b) 39.08 kJ mol^{-1} (c) 42.19 kJ mol^{-1} (d) 43.73 kJ mol^{-1}
27. The S—S bond energy is if $\Delta H_f^{\circ}(E_t - S - E_t) = -147\text{ kJ/mol}$; $\Delta H_f^{\circ}(E_t - S - S - E_t) = -202\text{ kJ mol}$ and $\Delta H_f^{\circ}S(\text{g}) = +223\text{ kJ/mol}$:
 (a) 168 kJ (b) 126 kJ (c) 278 kJ (d) 572 kJ
28. The enthalpy of combustion of $\text{H}_2(\text{g})$ at 298 K to give $\text{H}_2\text{O}(\text{g})$ is -249 kJ mol^{-1} and bond enthalpies of H—H and O = O are 433 kJ mol^{-1} and 492 kJ mol^{-1} , respectively. The bond enthalpy of O—H would be
 (a) 464 kJ mol^{-1} (b) -464 kJ mol^{-1} (c) 232 kJ mol^{-1} (d) -232 kJ mol^{-1}
29. For a monatomic gas, the value of the ratio of $C_{p,m}$ and $C_{v,m}$ is
 (a) $5/3$ (b) $7/5$
 (c) $9/7$ (d) $9/11$

30. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2 . At equilibrium when the flask is heated at $100^\circ C$, the brown colour deepens and on cooling it becomes less coloured. The change in enthalpy, ΔH for this system will be

- (a) Negative (b) Positive (c) Zero (d) Undefined

ANSWER KEY

1. (a)	2. (b)	3. (c)	4. (b)	5. (b)
6. (c)	7. (b)	8. (b)	9. (d)	10. (b)
11.(d)	12. (b)	13. (b)	14. (a)	15. (b)
16. (b)	17. (c)	18. (c)	19. (a)	20. (d)
21. (d)	22. (d)	23. (a)	24. (b)	25. (d)
26. (a)	27. (c)	28. (a)	29. (a)	30. (b)