CHAPTER 4

Energetics

Chapter Contents

First law of thermodynamics; Internal energy, work and heat, pressure–volume work; enthalpy, Hess's law; Heat of reaction, fusion and vapourization; Second law of thermodynamics; Entropy; Free energy; Criterion of spontaneity and Various levels of multiple-choice questions.

THERMODYNAMICS

Thermodynamics is the branch of science which deals with the quantitative relationships between different forms of energy. Or, It deals with the energy changes accompanying physical and chemical transformations.

Main objectives of Thermodynamics

Its main objectives are as follows:

- To decide the feasibility of a given transformation.
- To derive various energy changes and their inter relations.
- To derive laws like—Phase rule, Law of mass action etc.
- Presentation of experimental data in a correct manner.

Limitations

Its limitations are as follows:

- It is not applicable when substance is present in less amount.
- It gives no explanation of rate of reaction.
- It gives no explanation of system far from equation.
- It does not deal with internal structure of atoms and molecules.

Terms Related to Thermodynamics

System

It is the region or space to be investigated or the origin at which study of pressure, temperature etc., are to be made and which is isolated from rest of the universe with a bounding surface.

Surroundings

It is region apart from the system which might be in a position to exchange energy and mass with the system.

Homogeneous and Heterogeneous Systems

Homogeneous Systems

It is all over uniform that is made of one phase only.

Example, pure liquid or pure solid or pure gas present alone.

Heterogeneous Systems

It is non uniform as it consist of two or more phases. Example, ice and water, solid in contact with a liquid.

Type of Systems

Systems are divided into three parts:

(i) ***Open System:*** In such a system, both matter and energy can be exchanged with the surrounding.

Example, Boiling of water in a beaker,

Lime kiln or ice in an open beaker

Zinc granules reacting with dilute HCl to give hydrogen gas is also an example of open system as hydrogen gas escapes and the heat of reaction is transferred to the surroundings.

(ii) ***Closed System:*** In such a system, exchange of energy takes place only with the surroundings.

Example, Heating of liquid in a sealed tube or ice in a closed beaker.

(iii) ***Isolated System:*** In such a system, there is no exchange of matter or energy with the surroundings. Example, Liquid in a sealed thermous flask or ice in thermous flask.

Macroscopic system and Macroscopic Properties

A system is said to be macroscopic system when it has a large number of molecules, atoms or ions and the properties associated with it are called macroscopic properties.

Example, pressure, volume, temperature, position, density, colour, refractive index, viscosity and surface tension etc.

State Variables or Functions

The state of a system is fixed by its macroscopic properties if any of the macroscopic property is changed the state of a system also changes so these properties are called state variables.

These determine the state of a system. These are fundamental properties or thermodynamic parameters which depend only upon initial and final states.

Example, Pressure, temperature, volume, mass and composition are the most important state variables. Some other examples are enthalpy, free energy, internal energy, entropy, pressure, volume and number of moles.

REMEMBER

In case of a single gas composition is not one of the variables as it always remains 100%.

In a closed system having one or more components, mass is not a state variable.

Properties of System

All macroscopic properties of a system irrespective of the fact whether they are state variable or not are divided into two types:

1. ***Intensive Properties***

   Such properties remains same on any division in system that is, do not depend upon amount of substance present in the system.

   Example, Temperature, pressure, concentration, density, viscosity, surface tension, specific heat, refractive index, pH, EMF of dry cell, vapour pressure dipole moment etc.

2. ***Extensive Properties***

   Such properties depend upon amount of substance that is, their values are different in the divided system than in the entire system

   Example, Mass, volume, energy, work, internal energy, entropy, enthalpy, heat capacity, length.

- An extensive property can be made intensive by specifying it in unit amount of matter.

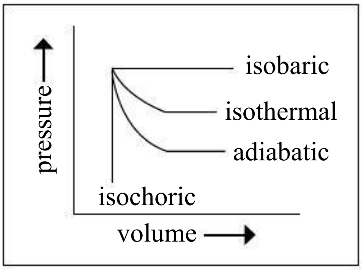
  Example, Density $\approx \left(\frac{\text{Mass}}{\text{Volume}}\right)$

Thermodynamic Process

It is the path along which a change of state occurs.
or
It is a path of change of a system from one equilibrium state or another which is usually accompanied by a change in energy or mass.

Types of Process

Processes are of the following types



1. Isothermal Process

Here temperature is kept constant during each step of the process. Example,

$\Delta T = 0, \Delta E = 0$

- It is achieved by using a thermostatic control.
- Heat can be absorbed or evolved here that is, can be exchange with the surroundings.

  Example, Freezing, melting, evaporation, condensation.

2. Isobaric Process

Here pressure is kept constant ($\Delta P = 0$) during each step of the process.

Example, Expansion of gas in an open system.

- Vaporization and heating of water up to its boiling point occurs at the same atmospheric pressure.

3. Isochoric Process

Here volume is kept constant. [$\Delta V = 0$] during each step of the process.

Example, Heating of substance in a closed vessel (system) or non-expanding chamber.

4. Adiabatic Process

Here no exchange of heat takes place between the system and the surroundings that is, $\Delta Q = 0$

- It is achieved by insulating the system or in closed insulated containers (thermos)

5. Cyclic Process

- Here the System undergoes a series of changes but finally comes back to initial state.
- $\Delta E = 0, \Delta H = 0$

Reversible or Quasi-Static Process

It is carried out in such a way that the system remains in a state of equilibrium. All changes occurring at any part of the process will be exactly reversed when change in carried out in the opposite direction.

- It involves slow changes during operation.
- This process may occur in any direction.
- It gives rise to maximum work.
- Here driving force and opposing force differ with each other by a small value.

Irreversible Process

Here direction of change can not be reversed by small changes in variables. All processes occurring naturally are reversible.

- It involves fast changes during operation.
- It is uni-directional process.
- It gives rise to net work that is $W_{rev.} > W_{irr.}$
- Here, driving and opposing forces differs by a large amount.

Polytropic Process

PV^m = constant is known as general or polytropic process.

If $m = 0$, the process is at constant pressure.

If $m = 1$, the process is at isothermal.

If $m = \infty$, the process is constant volume.

If $m = \gamma$, the process is at adiabatic.

The value of molar specific heat is given as

$$C_m = C_V \frac{(\gamma - m)}{1 - m}$$

Thermodynamic Equilibrium

A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium.

If a system is heterogeneous and it is in equilibrium the macroscopic properties in the various phases remain unchanged with time.

Types: It is of three types.

(i) Mechanical Equilibrium

Here no mechanical work is done by one of the system on another part of the system and it is possible if the pressure remains the same through out the system that is, there is no flow of matter from one part to another.

(ii) Thermal Equilibrium

There is no flow of heat from one part to another that is, temperature is constant.

(iii) Chemical Equilibrium

There is no change in composition of any part of the system with time.

HEAT AND WORK

Heat

Heat is the energy transfer due to difference in temperature. Heat is a form of energy which the system can exchange with the surroundings if they are at different temperatures. The heat flows from higher temperature to lower temperature.

Heat is expressed as ‘q’.

Heat absorbed by the system = +q

Heat evolved by the system = –q

Heat is expressed in calorie and the amount of heat required to raise the temperature of one gram of water by 1°C is equal to one calorie.

Now it is also expressed in joule as joule proved that there is a relation between mechanical work done (W) and heat produced (H) as

$$W \propto H$$

$$W = J H$$

Here J = mechanical equivalent of heat

J = 4.185 Joule

Work

It is the energy transfer due to difference in pressure that is, mode of energy transfer.

W = Intensity factor × Capacity factor

Here intensity factor is a measure of force responsible for work while capacity factor is a measure of extent for which work is done.

Types of work

(i) Mechanical Work (Pressure volume work)
= Force × Displacement

(ii) Electrical Work = Potential difference × charge flow
$V \times Q = EnF$

(iii) Expansion Work = $P \times \Delta V$
$= -P_{ext} . [V_2 - V_1]$
P = external pressure
ΔV = increase or decrease in volume.

(iv) Gravitational Work = mgh
Here m = mass of body,
g = acceleration due to gravity
h = height moved.

Units: dyne cm or erg (C.G.S.)
Newton meter (joule)

(i) If the gas expands, $[V_2 > V_1]$ and work is done by the system and W is negative.

(ii) If the gas contracts, $[V_2 < V_1]$ and work is done on the system and W is positive.

Different Types of Works and the Formulas

(i) Work done in reversible isothermal process

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

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

(ii) Work done in irreversible isothermal process

$$W = -\text{Pext.}\ (V_2 - V_1)$$

that is, $W = -P\,\Delta V$

Illustrations

1. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 20 to 60 litres.

Solution $W = -2.303\ nRT \log_{10} \dfrac{V_2}{V_1}$

$= -2.303 \times 2 \times 2 \times 298 \times \log_{10} \dfrac{60}{20}$

$= -1309.7$ Calories

2. Calculate the minimum work necessary to compress 64 g of O_2 from 10 to 5 litres at 300 K. How much heat is evolved in this process?

Solution $W = -2.303\ nRT \log_{10} \dfrac{V_2}{V_1}$

$W = -2.303 \times \dfrac{64}{32} \times 2 \times 300 \log \dfrac{5}{10}$

$= -831.8$ calories

$Q = W = 831.8$ calories

3. Calculate the work done by 10 g of an ideal gas of molecular weight 44 in expanding reversibly and isothermally from a volume of 5 to 10 litre at 300 K.

Solution $W = -2.303\ nRT \log_{10} \dfrac{V_2}{V_1}$

Number of moles of ideal gas $n = \dfrac{10\text{ g}}{44\text{ g mole}^{-1}}$

$= \dfrac{10}{44}$ mole

$R = 1.987$ cal deg^{-1} mole^{-1}

$T = 300$ K

$V_2/V_1 = 10/5 = 2$

On substituting the values, we get

$W = -2.303 \times \dfrac{10}{44} \times 1.987 \times 300 \times \log_{10} 2$

On solving

$W = -93.93$ cal

Internal Energy or Intrinsic Energy

The energy stored within a substance is called its internal energy. The absolute value of internal energy cannot be determined.

Or

It is the total energy of a substance depending upon its chemical nature, temperature, pressure, and volume, amount of substrate. It does not depend upon path in which the final state is achieved.

$$E = E_t + E_r + E_v + E_e + E_n + E_{P.E} + E_B$$

E_t = Transitional energy

E_r = Rotational energy

E_v = Vibrational energy

E_e = Electrical energy

E_n = Nuclear energy

$E_{P.E}$ = Potential energy

E_b = Bond energy

The exact measurement of it is not possible so it is determined as ΔE as follows:

$$\Delta E = \sum E_P - \sum E_R$$

$$\Delta E = E_f - E_i$$

Here E_f = final internal energy

Ei = Initial internal energy

Ep = Internal energy of products

Er = Internal energy of reactants

Facts about Internal Energy

- It is an extensive property.
- Internal energy is a state property.
- The change in the internal energy does not depend on the path by which the final state is reached.
- Internal energy for an ideal gas a function of temperature only so when temperature is kept constant ΔE is zero for an ideal gas.
- For a cyclic process ΔE is zero (E = state function) $E \alpha T$
- For an ideal gas it is totally kinetic energy as there is no molecular interaction.

- Internal energy for an ideal gas is a function of temperature only hence, when temperature is kept constant it is zero.
- At constant volume (Isochoric) $Q_V = \Delta E$
- In adiabatic expansion, gas cooled as ΔE decreases.
- For exothermic process, ΔE is negative as $E_R > E_P$ but For endothermic process ΔE is positive as $E_R < E_P$.
- It is determined by using a Bomb calorimeter.

$$\Delta E = \frac{Z \times \Delta T \times m}{w}$$

Z = Heat capacity of Bomb calorimeter

ΔT = Rise in temperature

w = Weight of substrate (amount)

m = Molar mass of substrate

Illustrations

4. Calculate the standard internal energy change for the following reaction at 25°C:

$2H_2O_2\,(l) \rightarrow 2H_2O\,(l) + O\,(g)$.

ΔH^o_f at 25°C for $H_2O_2\,(l) = -188$ kJ mol^{-1}

$H_2O\,(l) = -286$ kJ mole^{-1}

Solution $\Delta H^o = \sum\Delta H^o\,(\text{Products}) - \Delta S^o\,(\text{Reactants})$

$= 2\,(-286) + 0 - 2\,(-188)$

$= -572 + 376 = -196$ kJ

$\Delta n\,(g) = 1 - 0 = 1$

$\Delta H^o = \Delta E^o + \Delta n\,(g)\,RT$

$= -196 - 1 \times 8.314 \times 10^{-3} \times 298$

$= 198.4775$ kJ

5. Calculate standard internal energy change (E^o) for the reaction

$C\,(\text{graphite}) + H_2O\,(g) \rightarrow CO\,(g) + H_2\,(g)$

ΔH^o_f of $H_2O\,(g) = -241.8$ kJ mol^{-1}

ΔH^o_f of $CO\,(g) = -110.5$ kJ mol^{-1}

Solution $C\,(s) + H_2O\,(g) \rightarrow CO\,(g) + H_2\,(g)$

$\Delta H^o\text{reaction} = \sum\Delta H^o_f\,(\text{Products}) - \sum\Delta H^o_f\,(\text{Reactants})$

$= \Delta H^o_f\,(CO) + \Delta H^o_f\,(H_2) - [\Delta H^o_f\,(H_2O) + \Delta H^o_f\,(C)]$

$= 1 \times (-110.5) + (0) - [1 \times (-241.8) + 0]$

$= -110.5 + 241.8$

$= +131.3$ kJ

Δn = Moles of gaseous products–Moles of gaseous reactants

$= (1 + 1) - 1$

= 1 mol

$\Delta nRT = 1 \times 8.314 \times 298 = 2477.6$ J $= 2.48$ kJ

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

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

$= +131.3 - 2.48 = +128.82$ kJ

First Law or Law of Conservation of Energy

It was introduced by Helmholtz and according to it "Energy can neither be created nor destroyed but can be converted from one form to another or the total energy of universe is constant".

It can also be written as:

- Energy of an isolated system must remain constant, although it may be transformed from one form to another.
- Energy in one form, if it disappears will make its appearance in an exactly equivalent in another form.
- When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.
- It is never possible to construct a perpetual motion machine that could produce work without consuming any energy.

Thus if heat is supplied to a system it is never lost but it is partly converted into internal energy and partly in doing work in the system that is,

Heat supplied = Work done by the system

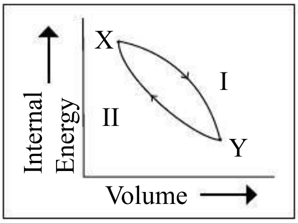
+

Increase in internal energy

So increase in internal energy

= Heat supplied – work done by the system

Mathematical Formulation of the First Law



If a system absorbs 'q' amount of heat and its state changes from X to Y and this heat is used up.

(i) On increasing the internal energy of the system

$\Delta E = E_Y - E_x$

(ii) In order to do some external work (W) on the surrounding by the system.

From first law we get the relation

$\Delta E = Q - W$ (that is, work done by the system)

$\delta E = \delta Q - \delta W$

(Work done by the system or in expansion)

or

$\Delta E = Q + W$ (that is, work done on the system)

$\delta E = \delta Q + \delta W$ or $\delta E = \delta Q + P\delta V$

(Work done on the system or in compression).

REMEMBER

+q = Heat absorbed by system

–q = Heat evolved by system

+W = Work done on the system

–W = Work done by the system

Some Useful Relations Based Upon First Law of Thermodynamics

For a Reversible Cycle: ΔE or $\delta E = 0$,

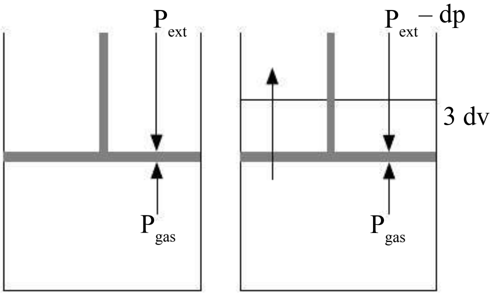
So $\delta W = \delta q$

$$Q = -W\text{max} = P\Delta V = 2.303nRT \log_{10} \frac{V_2}{V_1} \text{ or } \frac{P_1}{P_2}$$

For Isochoric Process: $\Delta E = Q$ ($\Delta V = 0$)

For Adiabatic Process: $\Delta E = W$ (as $q = 0$)

PRESSURE–VOLUME WORK



Pressure Volume and Work

Let us consider a cylinder fitted with a frictionless and weightless piston having an area of cross section as 'A'. If the external pressure (P) is applied on this piston and the value of P is slightly less than that of the internal pressure of the gas.

When the gas undergoes a little expansion and the piston is pushed out by a small distance dx the work done by the gas on the piston is given by as

dw = force × distance = pressure × area × distance

$dw = P.A.dx$

As $A.dx = dV$

$\boxed{dw = P.dV}$

$dw = P.dV$

When the volume of the gas changes from V_1–V_2, the total work done (W) can be given as

$W = P. \int .dV$

If we consider the external pressure (P) to be constant than

$W = P \int dV = P(V_2 - V_1) = P.\Delta V$

$\boxed{W = P.\Delta V}$

Isothermal irreversible expansion of an ideal gas

When a gas expands against a constant external pressure (P_{ext} = constant). There is considerable difference between the gas pressure (inside the cylinder) and the external pressure. The temperature does not change during the process.

$$W = -\int_{V_1}^{V_2} P_{ext}\, dV$$

$$= -P_{ext} \int_{V_1}^{V_2} dV$$

$$= -P_{ext}\,(V_2 - V_1)$$

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

Work done in Isothermal reversible expansion of an ideal gas

As a small amount of work done δW on reversible expansion of a gas through a small volume dV against an external pressure 'P' can be given as

$$\delta W = -PdV$$

So the total work done when the gas expands from initial volume V_1 to final volume V_2 is given as

$$\int dW = \int_{v_1}^{v_2} PdV$$

As according to ideal gas equation PV = nRT

$$P = \frac{nRT}{V}$$

So $\quad W_{rev.} = \int_{v_1} nRT\,dV$ (as temp. is constant)

So $\quad W_{rev} = -\,nRT\ \mathrm{In}\ \dfrac{V_2}{V_1} = -2.303\ nRT\ \log_{10}\dfrac{(V_2)}{(V_1)}$

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

Here negative sign indicates work of expansion and it is maximum and greater than work in the irreversible process.

As in such a case, temperature is kept constant and internal energy depends only on temperature so it internal energy is constant.

So $\quad \Delta E = 0$

$$\Delta E = q + W$$

$$q = -\,W$$

Hence, during isothermal expansion, work is done by the system at the expanse of heat absorbed.

Here ΔH can be found out as follows:

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

As, for isothermal process, $\Delta E = 0$, $\Delta T = 0$

So $\Delta H = 0$

Adiabatic Reversible Expansion of An Ideal Gas

As in an adiabatic change there is no transfer of heat that is, q = 0 or dq = 0

So $\quad \Delta E = -W$

$$dE = -dW$$

Suppose only mechanical work of expansion or contraction is made here so dW = PdV

As $\quad dE = C_V\,dT \;=\; nC_v dt$

So $\quad C_V\,dT = -PdV$

In a system of 1 mole of an ideal gas, for an adiabatic and reversible expansion from temperature T_1 to T_2 and volume V_1 to V_2, we get

$$C_V\,dT = \frac{-RT}{V}\,dV$$

or $\quad \dfrac{dV}{V} = \dfrac{-C_V}{R}\cdot\dfrac{dT}{T}$

or $\quad \int\dfrac{dV}{V} = \dfrac{-C_V}{R}\int\dfrac{dT}{T}$

$$\mathrm{In}\,\frac{V_2}{V_1} = \frac{-C_V}{R}\,\mathrm{In}\,\frac{T_2}{T_1} = \frac{C_V}{R}\,\mathrm{In}\,\frac{T_1}{T_2}$$

or $\quad \mathrm{In}\,\dfrac{V_2}{V_1} = \mathrm{In}\ (T_1/T_2)^{Cv/R}$

or $\quad (V_1T_1)^{Cv/R} = (V_2T_2)^{Cv/R} = K$

$$C_P - C_V = R$$

$$\mathrm{In}\,\frac{V_2}{V_1} = \frac{C_V}{C_P - C_V}\,\mathrm{In}\,\frac{T_1}{T_2}$$

or $\quad \dfrac{C_P - C_V}{C_V}\,\mathrm{In}\,\dfrac{V_2}{V_1} = \mathrm{In}\,\dfrac{T_1}{T_2}$

or $\quad (\gamma - 1)\,\mathrm{In}\,\dfrac{V_2}{V_1} = \mathrm{In}\,\dfrac{T_1}{T_2}$ (as $\gamma = C_P/C_V$)

$$\mathrm{In}\,(V_2/V_1)^{\gamma-1} = \mathrm{In}\,T_1/T_2$$

or $\quad (V_2/V_1)^{\gamma-1} = (T_1/T_2)$

or $\quad V_2^{\gamma-1}\,T_2 = V_1^{\gamma-1}\,T_1 = K$

On substituting T by $\dfrac{PV}{R}$ we get

$$\frac{PV}{R}\,V^{\gamma-1} = \text{Constant}$$

$$PV^{\gamma} = R \times \text{Constant} = \text{Constant}$$

Similarly

$$TV^{\gamma-1} = T\,(RT/P)^{\gamma-1} = \text{Constant}$$

$$T^{\gamma}\,P^{1-\gamma} = \text{Constant}$$

Irreversible Adiabatic Expansion

As In a free expansion the value of external pressure is zero so work done is zero.

that is, $\Delta E = W = 0$

$$\Delta T = 0,\ \Delta H = 0$$

During intermediate expansion the volume changes from V_1 to V_2 against external pressure (P_{ext}.)

$$W = -P_{ext}\,(V_2 - V_1) = -P_{ext}\,\frac{(RT_2 - RT_1)}{P_2\,P_1}$$

$$= -P_{ext}\,\frac{(T_2P_1 - T_1P_2)}{P_1\,P_2} \times R$$

$$W = C_V\,(T_2 - T_1) = -RP_{ext}\,\frac{(T_2P_1 - T_1P_2)}{P_1\,P_2}$$

Adiabatic Compression Work

$$W = -C_VT = -C_V\,(T_2 - T_1) = C_V\,(T_1 - T_2)$$

As T_1, T_2 are initial and final temperatures respectively

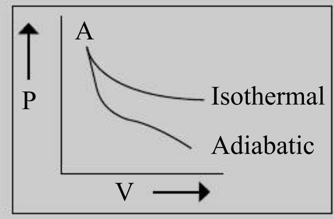
For 1 mole of gas $T = \dfrac{PV}{R}$

Hence adiabatic work is given as

$$W = C_V\,\frac{(P_1V_1 - P_2V_2)}{R \quad R} = \frac{C_V}{R}\,(P_1V_1 - P_2V_2)$$

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

REMEMBER



Illustrations

6. Calculate Q, W, ΔE and ΔH for the isothermal reversible expansion of 1 mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.

Solution As in isothermal process as temperature remains constant so both ΔE and ΔH are zero.

$$\Delta E = 0$$

$$\Delta H = 0$$

According to first law of thermodynamics,

$$\Delta E = W + Q$$

$$0 = W + Q$$

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

$$= -2.303 \times 1 \times 8.314 \times 273\ \log_{10}\frac{1}{0.1}$$

$$= 5227.169\ \text{J}$$

$$= 5.227\ \text{kJ}$$

7. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 litre to 5 litre. Calculate q, w, ΔE and ΔH for this process.

($R = 2$ cal K^{-1} mol^{-1}, $\log 2 = 0.30$, atomic weight of Ar = 40)

Solution $W = -2.303\ nRT\ \log_{10}\dfrac{V_2}{V_1}$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300\ \log_{10}\frac{5}{10}.$$

$$= 103.635\ \text{cal}$$

$$\Delta E = 0$$

$$q = \Delta E - W$$

$$q = -W = -103.635\ \text{cal}$$

8. A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant pressure of 3.0 atm. The work done during expansion is used to heat 10.0 mole of water of temperature 290.0 K. Calculate the final temperature of water (Specific heat of water = 4.184 JK^{-1} g^{-1}).

Solution

Work done = P × dV

$= 3.0 \times (5.0 - 3.0)$

$= 6.0$ litre-atm $= 6.0 \times 101.3$ J

$= 607.8$ J

Let ΔT be the change in temperature

Heat absorbed $= m \times s \times \Delta T$

$= 10.0 \times 18 \times 4.184 \times \Delta T$

$P \times dC = m \times s \times \Delta T$

or $\Delta T = \dfrac{P \times dV}{m \times s}$

$= \dfrac{607.8}{10.0 \times 18.0 \times 4.184}$

$= 0.807$

Final temperature $= 290 + 0.807 = 290.807$ K

9. Two moles of an ideal gas initially at 300 K and one atm are compressed reversibly to half the initial volume. Find q, W, ΔE and ΔH when the process is carried on isothermally.

Solution

$W = 2.303\, nRT \log_{10} \dfrac{V_2}{V_1}$

$T = 300$ K

$n = 1$

$R = 1.98$ cal deg^{-1} mole^{-1}

As $V_2 = ½ V_1$

$W = 2 \times 2.303 \times 1.98 \times 300 \log_{10} ½$

$= -1914.0$ cal

As the process is being carried on isothermally that is, no change of temperature.

$\Delta H = 0$ and $\Delta E = 0$

According to first law of thermodynamics,

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

$q = \Delta E + W$

$q = 0 + W$

$q = -1914$ cal

$W = -1914$ cal $\qquad \Delta E = 0, \Delta H = 0$

$q = -1914$ cal.

10. Find the value of Q, W and ΔE for the reversible adiabatic expansion of 1 mole of an ideal gas ($C_V = 3/2\ R$) from 5.00 to 25.00 litres at 27°C.

Solution

For adiabatic process Q = 0.

$\Delta E = W = C_V (T_2 - T_1)$ (for adiabatic)

$T_1 (V_1)^{R/Cv} = T_2 (V_2)^{R/Cv}$

$T_2 = T_1 (V_1/V_2)^{R/Cv}$

$= 300.0 (5/25)^{2R/3R}$

$= 300.0 (5/25)^{2/3}$

$T_2 = 102.6$ K

$\Delta E = W = 3/2\ R (T_2 - T_1)$

$= 1.500 \times 1.98 (102.6 - 300)$

$\Delta E = -588.4$ cal/mol.

11. One mole of an ideal gas which $C_V = 3/2\ R$ is heated at a constant pressure of 1 atm from 298 K to 373 K. Find ΔH and ΔU.

Solution

$C_V = \dfrac{3}{2} R$

$C_P = C_V + R = \dfrac{3}{2} R + R = \dfrac{5}{2} R$

Heat given at constant pressure = m. $C_{P.} \Delta T$

H or $q_P = 1 \times \dfrac{5}{2} R \times (373 - 298)$

$\Delta H = 1 \times \dfrac{5}{2} \times 1.987 \times 75 = 372.56$ cal

Now work done in the process $= -P\Delta V$

$W = -P (V_2 - V_1)$

$= -P \dfrac{(nRT_2}{P} - \dfrac{nRT_1)}{P}$

(As PV = nRT)

$= -nR (T_2 - T_1)$

$= -1 \times 1.987 \times (373 - 298)$

$= -1 \times 1.987 \times 75$

$= -149.025$ cal

According to first law of thermodynamics

$\Delta U = q + W$

$= 372.56 - 149.05$

$= 223.51$ cal.

12. Calculate q, W, ΔU and ΔH for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.

Solution

For isothermal reversible expansion:

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

$$= -2.303 \times 1 \times 8.314 \times 2.73 \log_{10} \frac{1.0}{0.1}$$

At constant temperature , for expansion $\Delta T = 0$, therefore $\Delta U = 0$

$$\Delta U = 1 \times C_V \times \Delta T = 0 \qquad \text{(for 1 mole)}$$

$$\Delta U = q + w$$

So $q = -W = 5227.2$ J

At constant temperature, $P_1V_1 = P_2V_3$ or PV is constant.

So $\Delta H = \Delta U + \Delta(PV)$

$\Delta H = 0$

Limitations of the First Law of Thermodynamics

- It fails to explain why heat cannot be completely converted into work.
  that is, W = J H
- If fails to tell the spontaneity of the process.
- It can establish the relation between +q and –W but it puts no restriction regarding the direction of flow of heat.
- This law fails to tell us under what conditions and to what extent it is possible to bring about conversion of one form of energy into the other.
- The first law fails to contradict the non-existence of a 100 per cent efficient heat engine or a refrigerator.
- It fails to explain the expansion of gases in vaccum when $\Delta E = 0$, $\Delta H = 0$, $W = 0$.
- It fails to explain the expansion of gases invacum when $\Delta E = 0$, $\Delta h = 0$ $w = 0$.

Heat Content or Enthalpy Change or Heat content (H)

If we deal a process in open vessel (at constant pressure), it becomes essential to use a new thermodynamic function heat enthalpy in place of internal energy. It is defined as “The amount of heat absorbed or evolved by a system at constant pressure”. Mathematically, it is the sum of internal energy pressure volume energy.

- It is not a state function.
- It is denoted by H at constant pressure.
- It is denoted by E at constant volume.
- Enthalpy of the elements in gaseous, liquid or solid or combined state is taken as zero.
  Example, C, O_2 , H_2 etc.

Relation Between ΔH and ΔE: Mathematically, enthalpy change is equal to the sum of internal energy(E)

And pressure volume energy which is given as,

$$H = E + PV$$

The change in enthalpy of a given system is given as:

$$\Delta H = H_2 - H_1$$

or $\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$

$\Delta H = (E_2 - E_1) + (P_2V_2 - P_1V_1)$

or $\Delta H = \Delta E + \Delta\ (PV)$

If ‘P’ is constant

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

or $\Delta H = Q$

Hence the change in enthalpy of the system ΔH may be defined as the amount of heat absorbed at constant pressure.

As $P\Delta V = \Delta n_g RT$

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

Here ΔH = change in enthalpy in constant pressure

ΔE = change in enthalpy in constant volume.

Δn_g = difference in the moles of gaseous reactants and product

Illustrations

13. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured of constant volume and at 27°C. Calculate heat of combustion of benzene at constant pressure at 27°C. (R = 8.314 J/mol/K).

Solution $C_6H_6\,(l) + 7\frac{1}{2}\,O_2\,(g) \rightarrow 6CO_2\,(g) + 3H_2O(l)$

$\Delta n = 6 - 7\frac{1}{2} = -3/2$

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

(ΔE per mole for benzene $= (327 \times 78)/7.8$

$= -327$ kJ)

$= -3270 \times 10^3 + (-3/2) \times 8.314 \times 300$

$= -32737413 = -3273.74$ kJ

14. Calculate the standard internal energy change for the following reaction at 25°C.

$2H_2O_2\,(l) \rightarrow 2H_2O\,(l) + O_2\,(g).$

ΔH^o_f at 25°C

$H_2O_2\,(l) = -188.0$ kJ mole^{-1}

$H_2O\,(l) = -286.0$ kJ mole^{-1}

($R = 8.314$ JK^{-1} mol^{-1})

Solution $2H_2O_2\,(l) \rightarrow 2H_2O\,(l) + O_2\,(g)$

$\Delta H^o = \Delta H^o_f\,(\text{products}) - \Delta H^o_f\,(\text{reactants})$

$= (2 \times 286 + 0.0) - (2 \times -188)$

$= -196$ kJ

$\Delta n = 3 - 2 = 1$

$\Delta E^o = \Delta H^o - \Delta nRT$

$= -196 \times 10^3 - 1 \times 8.314 \times 298$

$= -193.58$ kJ

Heat Capacity

The heat capacity of a system is defined as "The quantity of heat required for increasing the temperature of one mole of a system through 1°C". It is given as follows:

$$C = \frac{\delta q}{dT} \qquad \ldots..\ (1)$$

(i) Heat capacity at constant volume

According to first law of thermodynamics,

$$\delta q = dE + PdV \qquad \ldots..(2)$$

On substituting the value of δq in equation (2)

$$C = \frac{dE + PdV}{dT} \qquad \ldots\ldots(3)$$

If volume is constant then

$$C_V = (dE/dT)_V \qquad \ldots..\ (4)$$

Hence the heat capacity at constant volume of a given system may be defined as the rate of change of internal energy with temperature.

(ii) Heat capacity at constant pressure

If pressure is constant, equation (3) becomes as follows:

$$C_P = \frac{dE + PdV}{dT}$$

or $C_P = (\delta q/dT)_V$

Hence the heat capacity at constant pressure of a system may be defined as the rate of change of enthalpy with temperature.

- For one mole of a gas C_P and C_V are known as molar heat capacities and the difference between them is equal to the work done by one mole of gas in expansion on heating it through 1°C.

  At constant pressure work done by the gas

  $= P\Delta V$

  For one mole of gas $PV = RT$

  On increasing temperature by 1°C, the volume becomes $V + \Delta V$

  Hence $P\,(V + \Delta V) = R\,(T + 1)$

  or $P\Delta V = R$

  that is, $\boxed{C_P - C_V = P\Delta V = R}$

Thermochemistry

It deals with the heat changes during chemical reactions. It is called chemical energetics and based on first law of thermodynamics. It is called as chemical energetics and based on first law of thermodynamics.

Exothermic Reaction

- Heat is evolved here.
- ΔH is –ve as $H_R > H_P$
- $\Delta H = H_P - H_R = -ve$ (at constant pressure)

At constant volume,

$\Delta E = (E_P - E_R) = -ve$

that is. $E_R > E_P$

Endothermic Reaction

- Here heat is absorbed.
- ΔH or ΔE = +ve for endothermic
- $\Delta H = H_P - H_R = +ve$ (at constant pressure as)
- As $H_P > H_R$ or $E_P > E_R$
- At constant volume

  $\Delta E = (E_P - E_R) = +ve$

Heat or Enthalpy of Reaction

It is the change in enthalpy (amount of heat evolved or absorbed) when the number of gm-moles of the substance indicated by a chemical reaction have undergone complete reaction.

- It is determined by water and Bomb calorimeters. Mathematically, it is given as

  $= \sum H_P - \sum H_R$
- It can be express by $[\Delta H]_P$ or $[\Delta E]_V$ at constant pressure and volume respectively.

Example,

$$C_2H_4\,(g) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 2H_2O\,(l) + 335.8\text{ kcal}$$

Here 335.8 kcal heat is evolved or 335.8 kcal of internal energy of the system is decreased.

Factors Effecting Heat of Reaction

1. Nature or Physical State of Reactant and Products

Heat of reaction changes with the change of physical state of the reactants or the products.

Example,

$$\underset{(g)}{H_2} + \underset{(g)}{\tfrac{1}{2}O_2} \leftrightarrow \underset{(g)}{H_2O} \quad \Delta H = -57.8\text{ K.cal}$$

$$\underset{(g)}{H_2} + \underset{(g)}{\tfrac{1}{2}O_2} \leftrightarrow \underset{(l)}{H_2O} \quad \Delta H = -68.32\text{ K.cal}$$

that is, when steam condenses heat is evolved.

2. Allotropic Forms of the Element

$$C_{diamond} + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H = -94.3\text{ Kcal}$$

$$\underset{(amorphous)}{C} + O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -97.6\text{ Kcal}$$

that is, $\underset{(d)}{C} \rightarrow \underset{(amp.)}{C} \qquad \Delta H = 3.3\text{ Kcal}$

This Heat is called **Heat of Transition**.

3. Enthalpies of Solution

Heat of reaction changes when in one case dry substance react and in another case the solution state of the substance react.

Example,

$$\underset{(g)}{H_2S} + \underset{(g)}{I_2} \rightarrow 2HI + S\,; \quad \Delta H = -17.3\text{ Kcal}$$

$$\underset{(sol)}{H_2S} + \underset{(sol)}{I_2} \rightarrow 2HI + S\,; \quad \Delta H = -21.93\text{ Kcal}$$

4. Temperature

The effect of temperature on heat of reaction is given by Kirchoff equation as follows:

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P\, dT = \Delta C_P \int_{T_1}^{T_2} dT = \Delta C_P \Delta T$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_V\, dT = \Delta C_V \int_{T_1}^{T_2} dT = \Delta Cv\, \Delta T$$

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_V$$

For a Reaction at Constant Pressure or Constant Volume:

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

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

$\Delta H = \Delta E + \Delta(PV)$

* Δn = number of gaseous product – number of reactant molecules.

Illustrations

15. A sample of 0.16 g CH_4 was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and R = 8.314 J K^{-1} mol^{-1}.

Solution

Heat of combustion at constant volume,

ΔE = Heat capacity of calorimeter system × rise in

$$\text{temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

that is, $\Delta E = -885 \text{ kJ mol}^{-1}$

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

$\Delta n = 1 - 3 = -2$

$T = 27 + 273 = 300 \text{ K}$

$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

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

$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$

$= -885 - 4.988$

$= -889.988 \text{ kJ mol}^{-1}$

16. The molar heat of formation of NH_4NO_3 (s) is –367.54 kJ and those of N_2O (g), H_2O (l) are 81.46 and –285.8 kJ respectively at 298 K and 1 atm pressure. Find ΔH and ΔU of the reaction.

$NH_4NO_3 (s) \rightarrow N_2O (g) + 2H_2O (l)$

Solution

$NH_4NO_3 (s) \rightarrow N_2O (g) + 2H_2O(l);\ \ \Delta H = ?$

$\Delta H_{\text{Reaction}} = \Delta H_{\text{Products}} - \Delta H_{\text{Reactants}}$

$= \Delta HN_2O + \Delta HH_2O \times 2 - \Delta HNH_4NO_3$

$\Delta HN_2O = +81.46 \text{ kJ}$

$\Delta HH_2O = -285.8 \text{ kJ}$

$\Delta HNH_4NO_3 = -367.54 \text{ kJ}$

$\Delta H\text{Reaction} = +81.46 + 2(-285.8) - (-367.54)$

$\Delta H = -122.6 \text{ kJ}$

$\Delta H = \Delta U + \Delta nRT$

Here $\Delta n = 1 - 0 = 1$

$R = 8.314 \text{ J}$

$T = 298 \text{ K}$

$-122.6 \times 10^3 = \Delta U + 1 \times 8.314 \times 298$

$\Delta U = -125077$ Joule

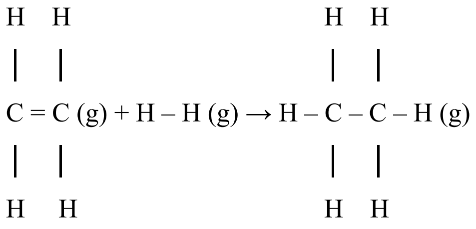
$= -125.077 \text{ kJ}$

17. Calculate the enthalpy of the following reaction:

$H_2C = CH_2 (g) + H_2 (g) \rightarrow CH_3 - CH_3 (g)$

The bond energies of C – H, C – C, C = C and H –H are 99, 83, 147 and 104 kcal respectively.

Solution



$$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ C = C \end{array} (g) + H - H (g) \rightarrow \begin{array}{c} H\ \ H \\ |\ \ \ | \\ H - C - C - H \\ |\ \ \ | \\ H\ \ H \end{array} (g)$$

$$\begin{array}{c} |\ \ \ | \\ H\ \ H \end{array}$$

$\Delta H = ?$

ΔH = Sum of bond energies of reactants

– Sum of the bond energies of products

$= [\Delta H_{C=C} + 4 \times \Delta H_{C-H} + \Delta H_{H-H}]$

$- [\Delta H_{C-C} + 6 \times \Delta H_{C-H}]$

$= (147 + 4 \times 99 + 104) - (83 + 6 \times 99)$

$= -30$ kcal.

Heat of Formation

The amount of heat evolved or absorbed or change in enthalpy when 1 mole of a substance is obtained from its constituents or free elements.

Example,

$N_2 + 3H_2 \leftrightarrow 2NH_3$; $\Delta H = -22$ Kcal

$N_2 + O_2 \leftrightarrow 2NO$; $\Delta H = +42$ Kcal

$H_2 + Cl_2 \leftrightarrow 2HCl$; $\Delta H = -44$ Kcal

- Heat of formation of NH_3 is –11 Kcal

  Heat of formation of NO is +21 Kcal.

  Heat of formation of HCl is –22 Kcal.
- Heat of formation at 25°C and 1 atm pressure is called standard heat of formation (ΔH^o).

State	Standard State
Solid	Stable crystalline form at a given temperature and 1at pressure.
Liquid	Pure liquid at a given temperature and 1at pressure
Gas	Idea gas at a given temperature and 1at pressure

$\Delta H^o = \sum H^o p - \sum H^o r$

Once the value of H^o at 25° C for any species has been assigned the value of H^o at other temperature

Can be find out by using kirchoff's equation as follows.

$$\int_{298}^{T} dH^{o} = \int_{298}^{T} C_p^{o}\, dT$$

$$H_t^{o} - H^{o}_{298} = \int_{298}^{T} C_p^{o}\, dT$$

$$H_t^{o} = H^{o}_{298} + \int_{298}^{T} C_p^{o}\, dT$$

- Standard heat of formation of free element is taken as zero.

  Example, In carbon—graphite form is taken as standard state and in sulphur, monoclinic form is standard state.
- Heat of formation may be +ve or –ve.

  If ΔH is –ve compound is exothermic.

  If ΔH is +ve compound is endothermic.
- Stability of exothermic compound is more than that of endothermic compound hence,greater the liberated energy greater is the stability of compound.

  Example, HF > HCl > HBr > HI

Illustrations

18. The molar heat of formation of NH_4NO_3 (s) is –367.5 kJ and those of N_2O (g) and H_2O (l) are +81.46 kJ and –285.78 kJ respectively at 25°C and 1 atmospheric pressure. Calculate ΔH and ΔE for the reaction.

$NH_4NO_3\ (s) \rightarrow N_2O\ (g) + 2H_2O\ (l)$

Solution $\Delta H^o = \Delta H^o_f\,(\text{products}) - \Delta H^o_f\,(\text{reactants})$

$= [\Delta H^o_f\ (N_2O) + 2 \times \Delta H^o_f\ (H_2O)] - [\Delta H^o_f\ (NH_4NO_3)]$

$= 81.46 + 2 \times (-285.78) - (-367.5)$

$= 81.46 - 571.56 + 367.5$

$= -122.56$ KJ

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

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

$\Delta n = 1$

$R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}

$T = 298$ K

$\Delta E = -122.56 - (1) \times (8.314 \times 10^{-3}) \times 298$

$= -122.56 - 2.477$

$= -125.037$ kJ

19. The standard heats of formation at 298 K for CCl_4 (g), H_2O (g), CO_2 (g) and HCl (g) are —25.5, –57.8, –94.1 and –22.1 kcal mol^{-1} respectively, Calculate $\Delta H^o_{298\,K}$ for the reaction

$CCl_4\ (g) + 2H_2O\ (g) \rightarrow CO_2\ (g) + 4HCl\ (g)$

Solution $\Delta H_{(\text{reaction})} = \sum$ Heat of formation of products

$- \sum$ Heat of formation of reactants

$= [\Delta H_f\ (CO_2) + 4\ \Delta H_f\ (HCl)] - [\Delta H_f\ (CCl_4) + 2\Delta H_f(H_2O)]$

$= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)]$

$= -41.4$ kcal.

20. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation of HCl (g).

Solution Reaction

$\frac{1}{2} H_2 (g) + \frac{1}{2} Cl_2 (g) \rightarrow HCl (g) \qquad \Delta H = ?$

$\Delta H = [\ \frac{1}{2} \Delta H_{H-H} + \frac{1}{2} \Delta H_{Cl-Cl}] - [\Delta H_{H-Cl}]$

$= \frac{1}{2} \times 104 + \frac{1}{2} \times 58 - 103$

$= -22$ kcal mol^{-1}

Heat of Combustion

- It is change in enthalpy when one mole of a substance is completely oxidized or combusted or burnt.
- ΔH is –ve here as heat in always evolved here that is, exothermic process.
- Heat of combustion is useful in calculating calorific value of food and fuels.
- It is also useful in confirming structure of organic molecules having C,H,O,N etc.
- Enthalpy change by combustion of 1 gm solid or 1 gm liquid or 1 cc gas is called calorific value.

$$C.V = \frac{\text{Heat of combustion}}{\text{Molecular wt.}}$$

$C + O_2 \rightarrow CO_2 \quad \Delta H = -94$ Kcal

$C.V = -\frac{94}{12} = -\ 7.83$ Kcal

$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$

$\Delta H = -1349$ Kcal

$C.V = -\frac{1349}{342} = 3.94$

$\Delta H(\text{heat of reaction}) = -\sum \Delta H^o_P - \sum H^o_R$

Illustrations

21. The standard molar heats of formation of ethane, carbon dioxide and liquid water are –21.1, –94.1 and –68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

Solution Reaction for combustion of ethane is as follows.

$2C_2H_6 (g) + 7O_2 (g) \rightarrow 4CO_2 (g) + 6H_2O (l)$

$\Delta H^o = ?$

This reaction involves 2 moles of C_2H_6;

Heat of combustion of ethane $= \frac{\Delta H^o}{2}$

$\Delta H^o = \Delta H^o_f (\text{products}) - \Delta H^o_f (\text{reactants})$

$= [4\ \Delta H^o_f (CO_2) + 6\ \Delta H^o_f (H_2O)] - [2\ \Delta H^o_f (C_2H_6) + 7\ \Delta H^o_f (O_2)]$

$= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7 \times 0]$

$= -376.4 - 409.8 + 42.2$

$= -744.0$ kcal

$\Delta H^o/2 =$ Heat of combustion of ethane

$= -\frac{744.0}{2}$

$= -372.0$ kcal

22. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Find the fuel value per cm^3 of the mixture. Heat of formation and densities are as follows:

$H_f (Al_2O_3) = -399$ kcal mol^{-1}

$H_f (Fe_2O_3) = -199$ kcal mol^{-1}

Density of Al = 2.7 g/cm^3

Density of Fe_2O_3 = 5.2 g/cm^3

Solution Reaction

$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe, \ \Delta H = ?$

$\Delta H = \Delta H_f (\text{products}) - \Delta H_f (\text{reactants})$

$= [\Delta H_f (Al_2O_3) + 2\ \Delta H_f (Fe)] - [2\ \Delta H_f (Al) + \Delta H_f (Fe_2O_3)]$

$= [-399 + 2 \times 0] - [2 \times 0 + (-199)]$

$= -399 + 199 = -200$ kcal

Atomic mass of Al = 27

Molecular mass of Fe_2O_3 = 160

Volume of reactants $= \frac{160}{5.2} + 2 \times \frac{27}{2.7}$

= 50.77 cm3

Fuel value per cm^3 $= \frac{200}{50.77} = 3.92$ kcal

23. Given the heats of formation of benzene (liquid), water and carbon dioxide gas at 298 K as 11.718, –68.32 and –94.052 Kcal. Calculate the heat of combustion of liquid benzene at 298 K.

Solution The reaction is as follows:

C_6H_6 (l) + 7 ½ O_2 (g) → $6CO_2$ (g) + $3H_2O$ (l)

The given data:

6C (s) + $3H_2$ (s) → C_6H_6 (l), ΔH = 11.718 Kcal …… (i)

H_2 (s) + ½ O_2 (g) → H_2O (l), ΔH = –68.32 Kcal …… (ii)

C (s) + O_2 (g) → CO_2 (g), ΔH = –94.052 Kcal …… (iii)

Multiply reaction (ii) by 3 and reaction (iii) by 6, and then add reaction (ii) and (iii)

$3H_2$ (s) + 3/2 O_2 (g) → $3H_2O$ (l), ΔH = –204.96 kcal

6C (s) + $6O_2$ (g) → $6CO_2$ (g), ΔH = –564.312 kcal

$3H_2$(g) + 6C(s) + 7 ½ O_2 (g) → $6CO_2$ (g) + $3H_2O$(l)

ΔH = –769.272 kcal … (iv)

Subtract reaction (i) from reaction (iv)

7½ O_2 (g) → C_6H_6 (l) + $6CO_2$ (g) + $3H_2O$ (l)

ΔH = –780.99 kcal

or C_6H_6 (l) + 7½ O_2 (g) → $6CO_2$ (g) + $3H_2O$ (l)

ΔH = –780.990 kcal

Therefore heat of combustion of benzene is— 780.99 kcal.

Heat of Neutralization

It is enthalpy change during neutralization of 1 gm mole of an acid and base. It is also heat of formation of water.

Example,

$H^+ Cl^- + Na^+ OH^- \rightarrow NaCl + H_2O$ +

13.7 Kcal/mole or 57.3 kJ/mole

$H^+ + OH^- \rightarrow H_2O$ + 13.7 Kcal

or 57.3 kJ/mole

ΔH = –13.7 Kcal or –57.3 kJ/mole

- It is always exothermic ΔH = –ve
- Heat of neutralization of strong acid and strong base is always 13.7 Kcal/mole or 57.3 kJ/mole
- It is independent of nature of strong acid or strong base.
- If one electrolyte is weak than ΔH will be less than –13.7 Kcal as some amount of heat will be absorbed in ionization of weak electrolyte.

Example,

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

+ 55.2 kJ/mole or 13.4 Kcal/mole

Example,

$HCl + NH_4OH \leftrightarrow NH_4Cl + H_2O$

ΔH = –12.3 K.cal

i.e., heat of ionization of CH_3COOH is 0.3 Kcal or 1.9 kJ/mole

- If both electrolytes are weak then

$CH_3COOH + NH_3 \rightarrow CH_3COONH_4 + H_2O$

+ 50.4 kJ/mole

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

ΔH = –11.9 K.cal

- In case of HF, ΔH is more due to more hydration of F^- ions.

Measurement

In laboratory it is measured by using polythene on polystyrene bottles as follows.

Here 10 ml of each of acid and alkali having same normality are taken in separate bottles and temperature is noted at regular intervals. When constant temperature is achieved, the alkali solution is added to the acid solution. The mixture is stirred and the highest temperature is noted.

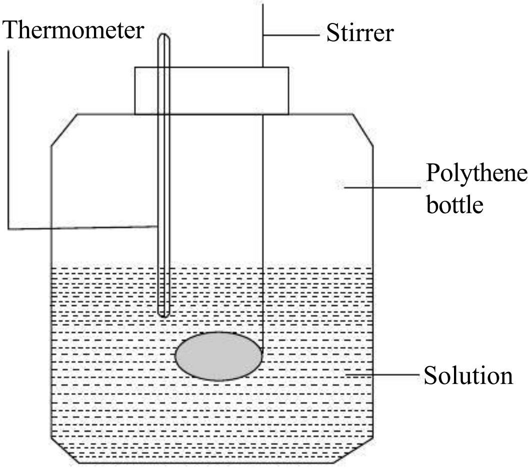
Suppose T_1 and T_2 are initial and final temperatures here then

Rise in temperature = $(T_2 - T_1)$ K

Here specific heat capacity of the solution is assumed to be the same as that of water while heat capacity can be ignored as it is quite less than that of solution.

$Q = ms(T_2 - T_1)$

Hence, $\Delta H = \frac{Q}{100} \text{x}1000 \times \frac{1}{N}$



Neu.

Here, Q = Heat change during the process

S = Specific heat of solution

M = Mass of solution

N = Normality of acid/base.

Illustrations

24. The heat of neutralization is due to the following reaction:

$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l) + 57.1$ kJ

Calculate the amount of heat evolved when

(i) 0.25 mole of H_2SO_4 is neutralized by 0.5 mole of NaOH and

(ii) 0.25 mole of CH_3COOH is mixed with 0.25 mole of NaOH, assuming 0.25 J of heat is utilized in the ionization of CH_3COOH.

Solution

(i) As 1 mole of H_2SO_4 = 2 mole H^+

So 0.25 mole of $H_2SO_4 = 0.25 \times 2$ mole H^+

= 0.50 mole H^+

As 1 mole of H^+ + 1 mole OH^- = 57.1 kJ

So 0.50 mole H^+ + 0.50 mole OH^-

$= 57.1 \times 0.5$ kJ = 28.55 kJ

(ii) 1 mole CH_3COOH = 1 mole H^+

0.25 mole CH_3COOH = 0.25 mole H^+

(If it is completely ionized)

Assuming the complete ionization of CH_3COOH, we get

0.25 mole of CH_3COOH + 0.25 mole NaOH gives 0.25×57.1 kJ

Heat expected = 16.27

But the actual heat obtained

= 16.27 – heat used in the ionization

= 16.27 – 0.25

= 16.02 kJ

25. Calculate the heat of neutralization from the following data, 200 ml of 1 M HCl is mixed with 400 ml of 0.5 M NaOH. The temperature rise in calorimeter was found to be 4.4°C. Water equivalent of calorimeter is 12 g and specific heat is cal/ml/degree for solution.

Solution The heat produced (ΔH_1) during neutralization of 200 Meq. of NaOH and HCl each (Meq. = N × V) is taken up by calorimeter and solution in it.

ΔH_1 = Heat taken up calorimeter and solution in it.

$\Delta H_1 = m_1 S_1 \Delta T + m_2 S_2 \Delta T = 12$

Total solution = (200 + 400) ml = 2692.8 cal

As neutralization of 200 Meq. gives heat

= –2692.8 cal

So neutralization of 1000 Meq. gives heat

$= -2692 \times 5 = -13464$ cal

= –13.464 kcal

Heat of Hydration

The enthalpy change during hydration of one gm mole substance is called heat of hydration.

$CuSO_4 + 5H_2O \rightarrow CuSO_4.5H_2O$

+ 78.21 kJ/mole

or 18.7 Kcal/mole

$\Delta H = -18.7$ K.cal/mole

- It is exothermic mostly

  $H_{sol} = \Delta H_{hy}$.: Lattice energy

- If ΔH_H > L.E.: solute dissolve in H_2O

- ΔH_H < L.E.: solute does not dissolve in H_2O
- $\Delta H \simeq$ L.E.: solute is in equilibrium with solvent in H_2O

Bond Energy

It may be defined as, "The quantity of heat evolved when a bond is formed between two free atoms in a gaseous state to form a molecular product in a gaseous state". It is also known as enthalpy of formation of the bond.

Or

It may also be define as, "The average quantity of heat required to break (dissociate) bonds of that type present in one mole of the compound".

Example,

$$C\ (g) + 4H\ (g) \rightarrow CH_4\ (g) \quad \Delta H = -398 \text{ Kcal}$$

The average bond energy per mole of C – H bond =

$$\frac{-398}{4} = -99.5 \text{ Kcal}$$

$$H - OH \rightarrow H + O - H$$

$$\Delta H = 497.8 \text{ Kj/m}$$

$$(B.E.)_{AV} = \frac{497.8 + 428.5}{2} = 463.15 \text{ Kj/m}$$

When a reaction is carried out in the gas phase at constant pressure, then enthalpy of the reaction can be given as

$$\Delta H = \sum B.E_R - \sum B.E_P$$

ΔH = (Energy needed to break the bonds in the molecules of the reactants) – (Energy released when bonds in the molecules of the products are formed).

Example, In the case of formation of HCl (g) from H_2 (g) and Cl_2 (g), ΔH = –185 kJ/mol

$$E_{H-H} = 437 \text{ kJ}$$

$$E_{C-Cl} = 244 \text{ kJ}$$

$$E_{H-Cl} = 433 \text{ kJ}$$

$$\text{So} \quad \Delta H = E_{H-H} + E_{C-Cl} - (2E_{H-Cl})$$

$$= 437 + 244 - (2 \times 433)$$

$$= -185 \text{ kJ}$$

Illustrations

26. Calculate the enthalpy of combustion (enthalpy change) of the given reaction:

$$CH_4\ (g) + 2O = O\ (g) \rightarrow O = C = O\ (g) + 2H - O - H\ (g)$$

From the following B.E. data.

BE of C – H = 414 kJ/mol

BE of C = O = 741 kJ/mol

BE of O = O = 395 kJ/mol

BE of O – H = 464 kJ/mol

Solution ∑(B.E.) reactants

$$= 4 \times \text{B.E. of } C - H + 2 \times \text{B.E. of } O = O$$

$$= 4 \times 414 + 2 \times 395$$

$$= 1656 + 790 = 2446 \text{ kJ}$$

(B.E.) products

$$= 2 \times \text{B.E. of } C = O + 2 \times (2 \times \text{B.E. of } O - H)$$

$$= 2 \times 741 + 4 \times 1856$$

$$= 3338 \text{ kJ}$$

$$\Delta H = (\sum B.R.)_R - (\sum B.E\ )_P$$

$$= 2446 - 3338$$

$$= -892 \text{ kJ}$$

27. Calculate the resonance energy of N_2O from the following data:

ΔH^o_f of N_2O = 82 kJ mol^{-1}

Bond energy of N ≡ N, N = N, O = O and N = O bonds is 946, 418, 498 and 607 kJ mol^{-1} respectively.

Solution $N \equiv N\ (g) + ½\ (O = O) \rightarrow N = N = O\ (g)$

$$\Delta H_f\ (N_2O) = [\Delta H\ (N \equiv N) + ½\ \Delta H(O = O)]$$

$$- [\Delta H(N = O) + \Delta H(N = N)]$$

$$= (946 + ½ \times 498) - (607 + 418)$$

$$= 946 + 249 - 607 - 418$$

$$= 1195 - 1025$$

$$= 170 \text{ kJ mol}^{-1}$$

Resonance energy = Observed heat of formation

~ Calculated heat of formation

= 82 ~ 170

= 88 kJ mol^{-1}

Heat of Dilution

It is change in enthalpy when solution containing one mol of solute is diluted from one concentration to another concentration. Its value depends upon the concentration of solution and on the amount of the solvent added.

$KCl \rightarrow KCl$

$(x\ H_2O)\quad (Y\ H_2O)$

$HCl + 10\ H_2O \rightarrow HCl.10\ H_2O$

$\Delta H = -69$ KJ /M.

Heat of Solution

It is change in enthalpy when one mole of a solute is dissolved in excess of solvent.

- ΔH = +ve for (hydrated salts)
- ΔH = –ve for (anhydrous salts)

Example,

$KCl + H_2O \rightarrow KCl\ (aq)$

$\Delta H = -18.6$ KJ/Mole

$H_2SO_4 + H_2O \rightarrow H_2SO_4$

$\Delta H = -20.2$ K.Cal.

Heat of Fusion

It is change in enthalpy in converting one mole of solid into the liquid state at its melting point. It is equal to latent heat of fusion per gram multiplied by the molar mass. It is always positive as heat is needed to overcome the intermolecular forces between constituents particles of solid.

Example, Heat of fusion of H_2O

$H_2O \rightarrow H_2O$; $\Delta H = +0.6$ kJ/mole

(s) (l) = 1.44 K.Cal.

Heat of Vaporization

It is the change in enthalpy in converting 1 mole of liquid into the gaseous state at its boiling point

Example,

$H_2O \rightarrow H_2O$; $\Delta H = 42$ kJ/mole

(l) (g) = 10.5 K.cal.

Heat of Sublimation

It is the change in enthalpy in converting one mole of a solid directly into vapour at a temperature below its melting point.

$I_2 \rightarrow I_2$; $\Delta H = 62.4$ kJ/mole

(s) (g) = 14.9 K.cal /mole

- $\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus}$

Heat of Atomization

It is the enthalpy change (heat required) when bonds of one mole of a substance are broken down completely to obtain atoms in the gaseous phase (isolated) or it is the enthalpy change when one mole of atoms in the gas phase is formed from the corresponding element in its standard state.

In case of diatomic molecules it is also called bond dissociation enthalpy.

It is denoted by ΔH_a or $\Delta H^{\bullet}$.

Example,

$H_2\ (g) \rightarrow 2H\ (g) - 435$ kJ

$\Delta H = +435$ kJ/mol

$CH_4\ (g) \rightarrow C\ (g) + 4H\ (g) + 1665$ kJ

$\Delta H = +1665$ kJ/mol

Enthalpy of Dissociation or Ionization

It is defined as, "The quantity of heat absorbed when one mole of a substance is completely dissociated into its ions". Example,

$H_2O\ (l) \rightarrow H^+ + OH^- \quad \Delta H = 13.7$ Kcal

Phase Transition and Transition Energy

- The change of matter from one state (solid, liquid or gas) to another state is called Phase Transition.
- Such changes occur at definite temperatures such as melting point (solid to liquid), boiling point (liquid to vapours) etc., and are accompanied by absorption or evolution of heat. The enthalpy change during such phase transitions is called heat of transition or transition energy.

Example,

C (diamond) → C (amorphous)

$\Delta H = 3.3$Kcal

Illustrations

28. Calculate the amount of heat needed to convert 20 g of ice at 0°C to steam at 100°C. If specific heat of water is 1 cal/g, heat of fusion is 80 cal /g and heat of vapourisation is 540 cal/g.

Solution

$$\Delta H_{total} = \Delta H_{fus} + \Delta H_{heat} + \Delta H_{vap}$$
$$= (20 \times 80) + (20 \times 1 \times 100) + (20 \times 540)$$
$$= 1600 + 2000 + 10800$$
$$= 14400 \text{ cal.} = 14.4 \text{ kcal}$$

Law's of Thermochemistry

Lavosier and Laplace Law

The heat which is required to break a compound into its element is equal to the heat evolved during its formation.

$$\Delta H_D = -\Delta H_f$$

Example,

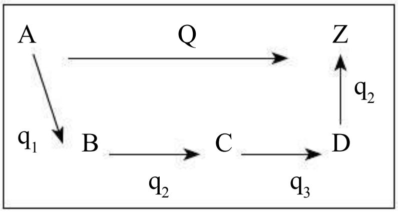
$C (s) + O_2 (g) \rightarrow CO_2 (g); \Delta H = -94.3$ kcal

$CO_2 (g) \rightarrow C (g) + O_2 (g); \Delta H = +94.3$ kcal

Hess's Law

This rule is a consequence of first Law of Thermodynamics and according to it,

"The enthalpy change for a process is independent of path or way of a process. The enthalpy change (ΔH or ΔE). for any physical or chemical process remains same whether process is carried out in one step or in many steps."



$$Q = q_1 + q_2 + q_3 + q_4 \ldots\ldots$$

Example,

$C + O_2 \rightarrow CO_2 ; \Delta H = -94.3$ K.cal

$C + ½ O_2 \rightarrow CO ; \Delta H = -68.3$ K.cal

$CO + ½ O_2 \rightarrow CO_2 ; \Delta H = -26$ K.cal

that is, $Q = Q_1 + Q_2 = -194.3$

Hence it proves that

- ΔH or ΔE is not proportional to path or way of reaction
- ΔH or ΔE is a state function which depends only on initial and final state (first law of thermodynamics)

Applications Hess Law

It has the following applications:

1. It helps in finding enthalpy changes for those reactions also which are experimentally not possible.

   Example, C_2H_6, C_2H_4
2. It also helps in finding $\Delta H_{formation}$, $\Delta H_{combustion}$ etc.
3. For the determination of resonance energy and lattice energy.
4. For the determination of enthalpies of reactions occurring very slowly.

Second Law of Thermodynamics

It is not possible to convert heat into work without compensation.

- Work can always be converted into heat but the conversion of heat into work does not take place under all conditions.
- It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency (Clausius statement).
- The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work (Thomson statement).
- It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects (Kelvin-Planck statement).
- Nature tends to pass from a less probable to more probable state (Ludwig Boltzmann statement).

- Whenever a spontaneous process takes place it is accompanied by an increase in the total entropy of the universe.

Spontaneous Process

It is defined as one that proceeds on it's own without any outside influence. It's reverse is always non spontaneous which occurs in presence of some continues external influence. Or

The chemical or physical process which occurs in a particular set of conditions either of its own or after proper initiation is known as spontaneous process.

Example,

(i) All natural processes

(ii) $\underset{g}{2H_2} + \underset{g}{O_2} \rightarrow \underset{l}{2H_2O}$

Formation of water is spontaneous however it's decomposition is not spontaneous as it's possible by applying electrical energy for electrolysis.

- Spontaneous Process always occur with the decrease in energy and, increase in disorder (Entropy) and decrease of free energy.

Spontaneous changes which take place by themselves	**Spontaneous changes which take place in intiation**
Dissolution of KNO_3 in water	Lighting of a candle
Evaporation of water	Decomposition of calcium corbonate .
Flow of heat energy from higher temperature to lower temperature.	Combination of H_2 and O_2 to form water.
Flow of water from higher level to lower level.	Combustion of methane gas.

ENTROPY

It is a thermodynamic state quantity which is used to measure disorder or randomness of the molecules in a system The disorder or randomness in a system is measured in terms of entropy (S). The absolute value of 'S' is not determined so mostly change in entropy ΔS is measured.

Randomness α Entropy

It is a state function which depends only on the initial and final state of the system that is, it is independent of the path used in going from the initial to final state.

$$\Delta S = S_{Final} - S_{Initial}$$

For a general chemical reaction at 298K and 1 atm:

$$m_1P + m_2Q \rightarrow n_1 R + n_2S$$

$$\Delta S^o = [(n_1S^o_R + n_2S^o_S) - (m_1S^o_P + m_2 S^o_Q)]$$

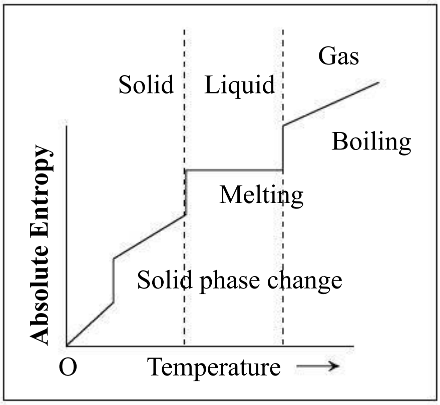
$$\mathbf{\Delta S^o = \sum S^o_P - \sum S^o_R}$$

- It is an extensive property and a state function which depends on state variables like T, P, V and n which govern the state of a system.

Entrophy and Temprature

Entropy increases with the increase of temperature as it is associated with the molecular motion which increases with the increase of temperature due to increase in the average kinetic energy of the molecules.

The entropy of a perfectly ordered Crystalline substance is taken as zero at Zero Kelvin (0K) . It is third law of Thermodynamics. However in case of N_2O, NO, LO, Solid Cl_2 etc. the value of entropy is not found to be zero at O Kelvin also.



Mathematical Definition of Entropy

For a reversible isothermal process, Clausius defined it as the integral of all the terms involving heat exchange (q) divided by the absolute temperature T.

$$ds = \int \frac{q_{rev}}{T}$$

OR

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

Unit: J K^{-1} mol^{-1}

Here mol^{-1} is also used as entropy being an extensive property depends upon the mass of substance.

Entropy Changes in Processes

1. During isothermal reversible expansion of an ideal gas

   As for a reversible path $\Delta E = 0$

   $$\text{So } q_{rev} = -\text{ W rev.} = -\,2.303\,\frac{nR}{T}\log_{10}\frac{V_2}{V_1}$$

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

   $$\Delta S = 2.303\text{ nR }\log_{10}\frac{(P_1)}{(P_2)}$$

2. During adiabatic reversible expansion

   As $q = 0$, so $\Delta S = 0$

3. **Isobaric process:**

   $$\Delta S = 2.303\text{ n }C_P\log_{10}\frac{(T_2)}{(T_1)}\text{ or }\frac{(V_2)}{(V_1)}$$

4. **Isochoric process:**

   $$\Delta S = 2.303\text{ n }C_V\log_{10}\frac{(T_2)}{(T_1)}\text{ or }\frac{(P_2)}{(P_1)}$$

5. **Entropy change in irreversible processes:**

   Suppose in a system at higher temperature T_1 and its surroundings at lower temperature T_2. 'q' amount of heat goes irreversibly from the system to the surroundings.

   $$\Delta S_{system} = -\frac{q}{T_1}.$$

   $$\Delta S_{surroundings} = +\frac{q}{T_2}.$$

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

   $$= -\frac{q}{T_1} + \frac{q}{T_2} = q\,\frac{[T_1 - T_2]}{T_1 T_2}$$

   But $T_1 > T_2$

   So $T_1 - T_2 = +\text{ ve}$

   $\Delta S_{process} > 0$

   So entropy increases in an irreversible process like conduction radiation etc.

6. **Entropy changes during phase transition:**

   $$\Delta S = S_2 - S_1 = \frac{q_{rev.}}{T} = \frac{\Delta H}{T}$$

   For fusion

   Solid $\rightleftharpoons$ Liquid

   ΔH = Heat of fusion [Heat required to convert one mole of a solid at constant temperature (melting point) and constant pressure into liquid keeping solid and liquid]

   $$\Delta S_{fusion} = S_{liquid} - S_{solid}$$

   $$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{\text{fusion or M.P}}}$$

   ΔH_{fusion} = Latent heat of fusion

   For Vapourization

   Liquid $\rightleftharpoons$ Vapour

   $$\Delta S_{vap.} = S_{vapour} - S_{liquid}$$

   $$\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T_{\text{vap or B.P.}}}$$

   $\Delta H_{vap.}$ = Latent heat of vapourization

   For Sublimation

   Solid $\rightleftharpoons$ Vapour

   $$\Delta S_{sub} = S_{vapour} - S_{solid}$$

   $$\Delta S_{sub} = \frac{\Delta H_{sub}}{T}$$

   ΔH_{sub} = Heat of sublimation

7. **Entropy change when liquid is heated:**

   When a definite amount of liquid of mass 'm' and specific heat 's' is heated

   $$\partial q = m\,s\,T$$

   $$\partial S = \frac{m\,s\,dT}{T}$$

   $$\text{or}\quad \Delta S = m\,s\log_e\frac{T_2}{T_1}$$

8. **Entropy Change in Mixing of Ideal Gases**:

   Suppose n_1 mole of gas 'P' and n_2 mole of gas 'Q' are mixed; then total entropy change can be calculate as:

   $$\Delta S = -2.303\,R\,[n_1\log_{10}X_1 + n_2\log_{10}X_2]$$

Here X_1 and X_2 are mole fractions of gases P and Q respectively.

$$X_1 = \frac{n_1}{n_1 + n_2}.$$

$$X_2 = \frac{n_2}{n_1 + n_1}.$$

$$\Delta S/\text{mol} = -2.303R \frac{[n_1 \log_{10} X_1}{n_1 + n_2} + \frac{n_2 \log_{10} X_2]}{n_1 + n_2}$$

$$\Delta S/\text{mol} = -2.303\ R\ [X_1 \log_{10} X_1 + X_2 \log_{10} X_2]$$

Some Facts About Entropy

- In nature all process are irreversible followed by an increase in entropy. Entropy of universe tends towards a maximum.

  $S_{\text{Universe}} > 0$

- $\Delta S_{\text{sys}} + \Delta S_{\text{surr.}} = 0$ for reversible process

  $S_{\text{sys}} + \Delta S_{\text{surr.}} > 0$ for irreversible process

- ΔS for a cyclic process and at the equilibrium state is zero.

- For a reversible process

  S_{Total} or $\Delta S_{\text{Universe}} = 0$

  So $\Delta S_{\text{system}} = \Delta S_{\text{surrounding}}$

- For adiabatic reversible process entropy change is zero.

  $\Delta S_{\text{Total}} = 0$ so

  Hence $\Delta S_{\text{system}} = \Delta S_{\text{surrounding}}$

- Entropy change associated which change in temperature from T_2 to T_1 at constant pressure P is given as

  $$\Delta S = 2.303 \times C_P \log \frac{T_2}{T_1}$$

- C_P = Molar heat capacity at constant pressure.

Some Examples of Entropy Change

- When a rubber band is stretched, entropy decreases because the macromolecules get uncoiled and hence arranged in a more ordered manner that is randomness decreases.

- When an egg is boiled, the entropy increases because denaturation occurs resulting into a change of proteins from helical form into random coiled form.

- Molecule kept in large volume container will have high entropy.

- Cases of increase in entropy—(1) dissolution of solute in water (2) decomposition of compound (3) vaporization and fusion (4) expansion of ideal gas from one container to an evacuated chamber.

- Decrease of entropy cases are crystallization, combination.

- Entropy is directly proportional to atomic weight for example—$I_2 > Br_2 > Cl_2$

- Entropy is directly proportional to number of bonds example—Ethane > ethylene > ethylene

Physical Significance of Entropy

1. Randomness in a system ∝ Entropy.

2. As according to the 2nd law of thermodynamics, the lost energy is directly proportional to absolute temperature during the process. Hence Entropy is unavailable energy of a system that is,

   Unavailable energy ∝ Temperature

   Unavailable energy = Entropy × temperature

   $$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{T in Kelvin}}$$

3. Entropy and Probability: It may be defined as a function of probability of a thermodynamic state as both entropy and thermodynamic probability increase simultaneously in a process so the state of equilibrium is the state of maximum probability.

   Boltzman told that the entropy of a particular state is related to the number of ways that the state can be achieved as follows

   S = K In W

   Here W is the natural logarithm of the number of ways that the state can be achieved.

   K is the Boltzman constant

   $$K = \frac{R}{N_A} = 1.38 \times 10^{-23}\ \text{J/K}.$$

Illustrations

29. Calculate the entropy change involved in the conversion of one mole of water at 373 K to vapour at the same temperature. (Latent heat of vapourization of water = 2.257 kJ g^{-1}).

Solution $\Delta S_V = \dfrac{\Delta H_V}{T_b}$

$\Delta H_V = 2.257 \times 18 \times 10^3 \text{ J mol}^{-1}$

$T_b = 373 \text{ K}$

$$\Delta S_V = \frac{2.257 \times 18 \times 10^3}{373} = 108.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

30. Calculate the standard entropy change associated with the following reaction at 298K.

$P_4 \text{ (s)} + SO_2 \text{ (g)} \rightarrow P_4O_{10} \text{ (s)}$

At 298 K S° for $P_4 = 41.1 \text{ JK}^{-1} \text{ mol}^{-1}$

$O_2 = 205.0 \text{ JK}^{-1} \text{ mol}^{-1}$ and

$P_4O_{10} = 231.0 \text{ JK}^{-1} \text{ mol}^{-1}$

Solution $\Delta S^o = \sum \Delta S^o{}_P - \sum \Delta S^o{}_R$

$\Delta S^o = [\Delta S^o\ P_4O_{10} - (\Delta S^o\ P_4 + 5\Delta S^o\ O_2)\ ]$

$= 231 - (41.1 + 5 \times 205.0)$

$= 231 - 1066.1 = -835.1 \text{ JK}^{-1} \text{ mol}^{-1}$.

31. 5 moles of an ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27°C. Calculate the change in entropy.

Solution $\Delta S = 2.303 \text{ nR} \log_{10} \dfrac{V_2}{V_1}$

$\Delta S = 2.303 \times 5 \times 8.314 \times \log_{10} \dfrac{80}{8}$

$= 95.736 \times 1$

$= 95.736 \text{ JK}^{-1}$

32. Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{total} at 25°C for the reaction

$N_2 \text{ (g)} + 2O_2 \text{ (g)} \rightarrow N_2O_4 \text{ (g)}$

Is this reaction spontaneous under standard state conditions at 25°C?

Here $\Delta H^o{}_f (N_2O_4) = 9.16 \text{ kJ}$,

$S^o (N_2) = 191.5 \text{ J K}^{-1} \text{ mol}^{-1}$,

$S^o (O_2) = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}$,

$S^o (N_2O_4) = 304.2 \text{ J K}^{-1} \text{ mol}^{-1}$

Solution $N_2 \text{ (g)} + 2O_2 \text{ (g)} \rightarrow N_2O_4 \text{ (g)}$

$\Delta H^o = \Delta H^o{}_f (N_2O_4) = 9.16 \text{ kJ}$

$\Delta S_{sys} = \Delta S^o = S^o(N_2O_4) - [S^o(N_2) + 2S^o(O_2)]$

$\Delta S_{sys} = (1)\ (304.2) - [(1)\ (191.5) - (2)\ (205.0)]$

$= -297.3 \text{ J/K}$

$$\Delta S_{surr} = \frac{-\Delta H^o}{T} = -\frac{9.16 \text{ kJ}}{298} = -0.0307 \text{ kJ/K}$$

$= -30.7 \text{ J/K}$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

$= -297.3 \text{ J/K} + (-30.7 \text{ J/K})$

$= -328.0 \text{ J/K}$

Because $\Delta S_{total} < 0$, the reaction is non-spontaneous.

33. Consider a two fold expansion of an ideal gas at 25°C in the isolated system.

(a) What are the values of ΔH, ΔS and ΔG for the process?

(b) How does this process illustrate the second law of thermodynamics?

Solution (a) $\Delta H = 0$

$\Delta S = R \text{ In } \dfrac{V_{final}}{V_{initial}}$.

$= (8.314 \text{ J/K}) \text{ In } 2 = 5.76 \text{ J/K}$

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

As $\Delta H = 0, \Delta G = -T\Delta S$

$= -(298 \text{ K})\ (5.76 \text{ J/K})$

$= -1717 \text{ J} = -1.72 \text{ kJ}$

(b) For a process in an isolated system, $\Delta S_{surr} = 0$. Therefore, $\Delta S_{total} = \Delta S_{sys} > 0$, and the process is spontaneous.

Gibbs's Free Energy

It was introduced in order to relate H, S and to explain spontaneity. According to J. Willard Gibb's Free energy of a system is defined as the maximum amount of energy available to a system during a process that can be converted into useful work.

or

It is the thermodynamic quantity specially characterizing the system, the decrease in whose value during a process is equal to the useful work done by the system.

It is denoted by G and it is given mathematically as follows:

As enthalpy (H) is a function of S and P which is given as follows:

$$H = f(S, P)$$

$$dH = \left(\frac{\partial H}{\partial S}\right) ds_{P} + \left(\frac{\partial H}{\partial P}\right) dP_{s} \quad ---------(i)$$

As $dH = TdS + VdP$ --------(ii)

On comparing these two equation

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

On integrating equation (ii) wet get,

$$\int dH = \int TdS + \text{Intiegration Constant}$$

$$= \int TdS + G$$

$$H = TS + G$$

$$G = H - TS$$

H = Enthalpy

T = Absolute temperature

S = Entropy

As $H = E + PV$

So $G = E + PV - TS$

Free energy change at constant temperature and pressure is given as:

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

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

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

At standard conditions that is, 298 K and 1 atm pressure

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

It is called Gibbs Helmholtz's equation and it is used to explain criterion of spontaneity, driving force etc.

- It is a state function and an extensive property. So it is determined as ΔG or $\Delta G^{o.}$

For a general reaction, it can be given as follows:

$$pA + q\,bB \rightarrow rC + sD$$

$$\Delta G^o = \sum \Delta G^o_P - \sum \Delta G^o_R$$

$$= [(r \sum \Delta G^o_C + s \sum \Delta G^o_P) - (p. \sum \Delta G^o_A + q \sum \Delta G^o_S)]$$

ΔG and Criteria of Spontaneity

Suppose we consider a system which is not isolated from its surroundings then for such a system ΔS is given as:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \quad \ldots\ldots (i)$$

If we consider that q_p amount of heat is given by the system to the surroundings at constant temperature and constant pressure then

$$(q_p)_{surroundings} = -(q_p)_{system} = -\Delta H_{system}$$

$$\Delta S_{surroundings} = \frac{(q_p)_{surroundings}}{T} = \frac{-\Delta H_{system}}{T} \quad \ldots. (ii)$$

So from equation (i) and (ii)

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

or $T\,\Delta S_{total} = T\Delta S_{system} - \Delta H_{system}$

$$-T\Delta S_{total} = \Delta H_{system} - T\Delta S_{system} \quad \ldots\ldots (iii)$$

As according to Gibb-Helmholtz equation,

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

So $\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$

$$\Delta G_{system} = -T\Delta S_{total}$$

As for spontaneous process

$$\Delta S_{total} > 0$$

Hence $\Delta G = -ve$

Thus for a spontaneous process $T\Delta S_{total}$ must be positive or ΔG must be negative.

Case I: Suppose both energy and entropy factors oppose a process that is,

$\Delta H = +ve$ and $T\Delta S = -\Delta e$

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

$$= (+ve) - (-ve) = +ve$$

Thus, ΔG is positive for a non-spontaneous process.

Case II: Suppose both tendencies be equal in magnitude but opposite, that is,

$\Delta H = +ve$ and $T\Delta S = +ve$

$\Delta H = T\Delta S$

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

$= 0$

Thus, the process is said to be at equilibrium.

Case III: Suppose entropy and energy, both factors are favourable for a process, that is,

$\Delta H = -ve$ and $T\Delta S = +ve$

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

$= (-ve) - (+ve) = -ve$

Thus, ΔG is negative for a spontaneous process.

ΔH	ΔS	$\Delta G = \Delta H - T\,\Delta S$	Remark
–	+	Always –ve	Spontaneous
+	–	Always +ve	Non-spon.
+	+	+ve at low temp –ve at high temp	Non spon. Spontaneous.
–	–	–ve at low temp +ve at high temp	Spontaneous Non-spon.

- $\Delta G = -ve$ (spontaneous process)
- $\Delta G = +ve$ (non spontaneous process)
- $\Delta G = 0$ (process in equilibrium)
- In exoergonic reaction $\Delta G = -ve$
- In endoergonic reaction $\Delta G = +ve$
- Temperature also plays an important role to decide the spontaneity of a process. A process which is not spontaneous at low temperature can become spontaneous at high temperature and vice-versa.

Relationship between ΔG or ΔG^o with E or E^o:–

Free energy change (ΔG) in an electrochemical cell can be related to electrical work done (E) in cell as follows

$\Delta G = -nFE$

when we use standard conditions than

$\Delta G^o = -\, nFE^o$

Here E^o = standard E.M.F of the cell

n = No. of moles of e^- transferred

F = Faraday's constant

Relationship between ΔG^o and Equlibrium constant (K_{eq}.)

for a reversible reaction

$P + Q \rightleftharpoons R + S$

ΔG , ΔG^o and Reaction Quotient (Q) are related as follows

$\Delta G = \Delta G^o + RT \log_e Q$

as at equilibrium $\Delta G = 0$

$Q = Keq$

$0 = \Delta G^o + RT \log_e Keq$

$\Delta G^o = -RT \log_e Keq$

$\Delta G^o = -2.303\ RT \log_{10} Keq$

Illustrations

34. $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

$\Delta H = -270.6\ kJ\ mol^{-1}\ K^{-1}$

$\Delta S = -139\ J$

(i) Is the reaction favoured by entropy, enthalpy both or none?

(ii) Find ΔG it T = 300 K

Solution

(i) As ΔH = negative, exothermic process and is favoured, so it will be spontaneous.

(ii) $\Delta G = \Delta H - T\Delta S$

$= -270.6 \times 1000 - 300 \times (-139)$

$= -228900\ J$

$= -228.9\ kJ$

35. Urea (NH_2CONH_2), an important nitrogen fertilizers is produced industrially by the reaction

$$2NH_3\,(g) + CO_2\,(g) \rightarrow NH_2CONH_2\,(aq) + H_2O\,(l)$$

Given that $\Delta G^o = -13.6$ kJ, Calculate ΔG at 25^oC for the following set of conditions

(a) 10 atm NH_3, 10 atm CO_2, 1.0 M NH_2CONH_2

(b) 0.10 atm NH_3, 0.10 atm CO_2, 1.0 M NH_2CONH_2

Is the reaction spontaneous for the conditions in part (a) or part (b)?

Solution $\Delta G = \Delta G^o + RT \text{ In } \dfrac{[NH_2CONH_2]}{(PNH_3)^2 (PCO_2)}$

(a) $\Delta G = -13.6 + [8.314 \times 10^{-3}] (298 \text{ K}) \text{ In } [1.0/(10)^2 (10)]$

$= -30.7$ kJ/mol

As ΔG is negative, the reaction is spontaneous.

(b) $\Delta G = -13.6 + [8.314 \times 10^{-3}] (298 \text{ K}) \text{ In } [1.0/(0.10)^2 (0.10)]$

$= +3.5$ kJ/mol

As ΔG is positive, the reaction is non-spontaneous.

36. Calculate K_p at 25°C for this reaction

$CO (g) + 2H_2 (g) \rightleftharpoons CH_3OH (g)$

What is ΔG for this reaction at 25°C when each reactant and product is present at a partial pressure of 20 atm?

Here $\Delta G^o_f (CH_3OH) = -161.9$ kJ/mol

$\Delta G^o_f (CO) = -137.2$ kJ/mol

Solution $CO (g) + 2H_2 (g) \rightleftharpoons CH_3OH (g)$

$\Delta G^o = \Delta G^o_f (CH_3OH) - \Delta G^o_f (CO)$

$\Delta G^o = 1 \times (-161.9) - (1) (-137.2) = -24.7$ kJ

$\Delta G^o = -RT \text{ In } K_P$

$$\text{In } K_P = \frac{-\Delta G^o}{RT} = \frac{-(-24.7)}{(8.314 \times 10^{-3}) (298)} = 9.97$$

$K_P = e^{9.97} = 2.1 \times 10^4$

$\Delta G = \Delta G^o + RT \text{ In } Q$

$= (-24.7) + (8.314 \times 10^{-3}) + (298 \text{ K})$

$$\text{In } \frac{[20]}{(20)(20)^2}$$

$= -39.5$ kJ/mol

37. For a reaction $M_2O (s) \rightarrow 2M (s) + ½ O_2 (g)$; $\Delta H = 30 \text{ kJ mol}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at atm. Calculate upto which temperature, the reaction would not be spontaneous.

Solution

$\Delta H = 30 \times 10^3 \quad \text{J mol}^{-1}$

$\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$

For a spontaneous reaction

$\Delta G = +ve$

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

So $\Delta H - T\Delta S$ should be positive

$\Delta H > T\Delta S$

$$T < \frac{\Delta H}{\Delta S}$$

$$T < \frac{30 \times 10^3}{70}$$

$T < 428.57$ K

Enhance Your Knowledge

Calorimeter

It is used to find enthalpy of reaction

$$\Delta H = \frac{Z \times \Delta T \times M}{W}$$

- It fails when (i) reaction is slow (ii) ΔH is low (iii) reaction does not complete
- ΔH does not change with temperature appreciably

Resonance Energy

Resonance energy = Expected heat of hydrogenation – calculate heat of hydrogenation

Example,

Resonance energy of CO_2 is 32 calorie per mole.

- For adults, 2500–3000 Kcal energy per day is needed.

Trauton's Law

$$\frac{\Delta H_{vap}}{T_b} = 88 \text{ Joule/K mol}$$

Solved Problems from the IITs

1. A gas mixture of 3.67 litre of ethylene and methane on complete combustion at 25°C produces 6.11 litre of CO_2. Calculate the heat evolved on burning 1 litre of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol^{-1} at 25°C.

[IIT 1991]

Solution $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

a litre 2a litre

$C_2H_4 \quad + \quad 3O_2 \quad \rightarrow \quad 2CO_2 \quad + \quad 2H_2O$

(3.67 – a) lit (3.67 – a) lit

2a + 3.67 – a = 6.11

a =2.44 litre

Volume of ethylene in mixture = 2.44 litre

Volume of methane in mixture = 1.23 litre

Volume of ethylene in 1 lit mixture = $\frac{2.44}{3.67}$.

= 0.6649 lit

Volume of methane 1 lit mixture = $\frac{1.23}{3.67}$.

= 0.3351 lit

24.45 litre of a gas at 25°C correspond to 1 mole.

So heat evolved by burning 0.6649 litre of ethylene

$= -\frac{1423}{24.5} \times 0.6649 = -38.69$ kJ

Heat evolved by burning 0.3351 litre of methane

$= -\frac{891}{24.45} \times 0.3351 = -12.21$ kJ

So total heat evolved by burning 1 litre of mixture

= –38.69 – 12.21

= –50.90 kJ

2. The polymerization of ethylene to linear polyethylene is represented by the reaction

$nCH_2 = CH_2 \rightarrow [—CH_2 – CH_2 —]n$

Where n has a large integral value. Given that the average enthalpies of bond dissociation for C = C and C – C at 298 K are +590 and +331 kJ mol^{-1} respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K.

[IIT 1995]

Solution During the polymerization of ethylene, one mole of ethylene breaks that is, one double bond breaks and the two CH_2– groups are linked with single bonds so forming three single bonds. But in the whole unit of polymer, number of single bonds formed/mole of ethylene is 2.

Energy released = Energy due to formation of 2 single bonds

= 2 × 331 = 662 kJ mol^{-1} of ethylene

Energy absorbed = Energy due to dissociation of 1 double bond

= 590 kJ mol^{-1} of ethylene

Enthalpy of polymerization/mol of ethylene or ΔH (Polymerization) = 590 – 662 kJ mol^{-1}

= –72 kJ mol^{-1}

3. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are –156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is –119 kJ mol^{-1}. Use these data of estimate to magnitude of the resonance energy of benzene.

[IIT 1996]

Solution Cyclohexene (l) + H_2 (g) → Cyclohexane (l)

ΔH = –119 kJ

Enthalpy of formation of cyclohexane (l)

= –156 kJ mol^{-1}

So enthalpy of formation of cyclohexane

= –156 – (–119) kJ

= –37 kJ mol^{-1}

As $\Delta H_{Cyclohexane}$ is –156 kJ mol^{-1}, for every double bond the energy decreases by an amount +119 kJ mol^{-1} and therefore for the introduction of three double bonds (present in benzene ring) the energy required.

$= 3 \times 119$ kJ mol^{-1} = 357 kJ mol^{-1}

So, theoretical ΔH_f for benzene

= (357 – 156) kJ mol^{-1}

= 201 kJ mol^{-1}

Resonance energy

= Theoretical ΔH_f – Observed ΔH_f

= (201 – 49) kJ mol^{-1}

= 152 kJ mol^{-1}

4. Compute the heat of formation of liquid methyl alcohol in kJ per mole using the following data. Heat of vapourization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states are H = 218 kJ mol^{-1}, C = 715 kJ mol^{-1} and O = 249 kJ mol^{-1}.

Average bond energies are:

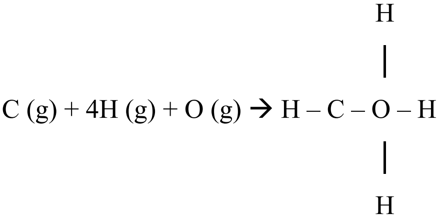
C – H = 415 kJ mol^{-1}

C – O = 356 kJ mol^{-1}

O – H = 463 kJ mol^{-1}

[IIT 1997]

Solution The thermochemical reaction is as follows:



$$C(g) + 4H(g) + O(g) \rightarrow H-\overset{H}{\underset{H}{C}}-O-H$$

$\Delta H_f = ?$

$\Delta H_f = [\Delta H_{C(S)\rightarrow C(g)} + 2\Delta H_{H-H} + ½\,\Delta H_O = 0]$

$-[3\Delta H_{C-H} + \Delta H_{C-O} + \Delta H_{O-H} + \Delta H_{vap.\ CH3\ OH\ (l)}]$

$= [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38]$

= 1836 – 2102 kJ mol^{-1}

= –266 kJ mol^{-1}

5. The enthalpy change involved in the oxidation of glucose is –2880 kJ mol^{-1}. 25% of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after 120 g of glucose?

[IIT 1997]

Solution As energy available for muscular work by 1 mole of glucose

$$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$$

So 180 g glucose (mol. wt. of glucose) supplies 720 kJ.

120 g of glucose will supply = $\frac{720}{180} \times 120$

= 480 kJ

100 kJ is needed to walk 1 km.

480 kJ is needed to walk $\frac{1}{100} \times 480 = 4.8$ km.

6. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_2 (g), H_2O (l) and propene (g) are –393.5, –285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomeriyation of cyclopropane to propene is –33.0 kJ mol^{-1}.

[IIT 1998]

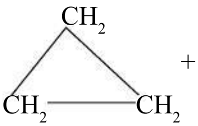
Solution $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kJ ….. (i)

$H_2(g) + ½\,O_2(l) \rightarrow H_2O(l)$; $\Delta H = -285.8$ kJ ……. (ii)

$3C(s) + 3H_2(g) \rightarrow C_3H_6(g)$; $\Delta H = 20.42$ ….. (iii)

Cyclopropane → Propene(C_3H_6); $\Delta H = -33.0$ kJ …… (iv)

The required thermochemical reaction is



$+ 9/2\ O_2 \rightarrow 3CO_2 + 3H_2O$

$\Delta H = ?$ …. (v)

This equation (v) can be obtained by multiplying equation (i) and (ii) by 3, reversing equation (iii), keeping equation (iv) as such and adding, so formed new equation as follows:

ΔH =[(i) × 3]+[(ii) × 3]+[Reverse of (iii) + (iv)]

$= [-393.5 \times 3] + [-285.8 \times 3] + [-20.42] + [-33.0]$

$= -1180.5 - 857.4 - 20.42 - 33.0$

$= -2091.32$ kJ.

7. Estimate the average S – F bond energy in SF_6. The standard heat of formation values of SF_6 (g), S (g) and F (g) are –1100, 275 and 80 kJ mol^{-1} respectively.

[IIT 1999]

Solution Given

S (s) → S (g); $\Delta H = 275$ kJ mol^{-1} … (i)

[½ F_2 (g) → F (g); $\Delta H = 80$ kJ mol^{-1}] × 6 …… (ii)

S (s) + $3F_2$ (g) → SF_6 (g); $\Delta H = -1100$ kJ mol^{-1} …… (iii)

The required reaction

S (g) + 6F (g) → SF_6 (g); ΔH = ?

is obtained by adding the reverse of equations (i) and (ii) with the direct reaction (iii)

S (g) + $3F_2$ (g) + S (s) + 6F (g) →

SF_6 (g) + S (s) + $3F_2$ (g);

$\Delta H = -1100 - 275 - 80 \times 6$

S (g) + 6F (g) → SF_6 (g);

$\Delta H = -1855$ kJ mol^{-1}

Total bond energy in SF_6 = 1855 kJ

Average S – F bond energy is SF_6

$= \frac{1855}{6} = 309.16$ kJ mol^{-1}

8. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{v.m.}$ for argon is 12.48 J K^{-1} mol^{-1}.

[IIT 2000]

Solution Number of moles of argon present in the sample

$$= \frac{PV}{RT} = \frac{1.25 \times 1}{0.0821 \times 300} = 0.05075$$

For adiabatic expansion,

$T_1/T_2 = (V_2/V_1)^{\gamma - 1}$

$300/T_2 = (2.50/1.25)^{1.66 - 1}$

$T_2 = 188.55$ K

$C_P = C_V + R$

$= 12.48 + 8.314$

$= 20.794$ J K^{-1} mol^{-1}

$\Delta H = n \times C_P \times \Delta T$

$= 0.05075 \times 20.794 \times (300 - 188.55)$

$= 117.6$ J

9. Show that the reaction,

CO (g) + ½ O_2 (g) → CO_2 (g)

at 300 K is spontaneous and exothermic, when the standard entropy change is –0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1} respectively.

[IIT 2000]

Solution CO (g) + ½ O_2 (g) → CO (g)

$\Delta G^o = G^o(CO_2) - G^o(CO) - \frac{1}{2} G^o(O_2)$

$= -394.4 - (-137.2) - 0$

$= -257.2$ kJ mol^{-1}

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

$-257.2 = \Delta H^o - 298 \times (0.094)$

$\Delta H^o = -288.2$ kJ

As ΔG^o is negative so the process is spontaneous and ΔH^o is also negative so the process is also exothermic.

10. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

B_2H_6 (g) + $3O_2$ (g) → B_2O_3(s) + $3H_2O$ (g)

From the following data, calculate the enthalpy change for the combustion of diborane:

2B (s) + 3/2 O_2 (g) → B_2O_3(s);

$\Delta H = -1273$ kJ

H_2(g) + ½ O_2(g) → H_2O(l); $\Delta H = -286$ kJ

H_2O (l) → H_2O (g); $\Delta H = 44$ kJ

2B(s) + $3H_2$(g) → B_2H_6(g); $\Delta H = 36$ kJ

[IIT 2000]

Solution $B_2H_6\,(g) + 3O_2\,(g) \rightarrow B_2O_3\,(s) + 3H_2O\,(g)$

This reaction can be obtained as follows:

Eq, (i) + 3 × Eq (ii) + 3 × Eq. (iii) – Eq. (iv)

$= -1273 - 858 + 132 - 36$

$= -2035$ kJ mol^{-1}

11. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is slowly converted into an equilibrium mixture of 1.3 % of 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria:

$B \rightleftharpoons A \qquad \Delta G^o_1 = ?$

$B \rightleftharpoons C \qquad \Delta G^o_2 = ?$

From the calculated value of ΔG^o_1 and ΔG^o_2 indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

[IIT 2001]

Solution Pentyne-1 ⇌ Pentyne-2 + 1,2-pentadiene

	(A)	(B)	(C)
t_{eq}	1.3	95.2	3.5

$$K_{eq} = \frac{[B]\,[C]}{[A]} = \frac{95.2 \times 3.5}{1.3} = 256.31$$

$B \rightleftharpoons A$

$$K_1 = \frac{[A]}{[B]} = \frac{[C]}{K_{eq}} = \frac{3.5}{256.31} = 0.013$$

$\Delta G^o_1 = -2.303\,RT \log_{10} K_1$

$= -2.303 \times 8.314 \times 448 \log_{10} 0.013$

= 16178 J

= 16.178 kJ

$B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_{eq}\,[A]}{[B]^2} = \frac{256.31 \times 1.3}{(95.2)^2} = 0.037$$

$\Delta G^o_2 = -2.303\,RT \log_{10} K_2$

$= -2.303 \times 8.314 \times 448 \log_{10} 0.037$

= 12282 J = 12.282 kJ

The stability order is as follows:

B > C > A.

12. An insulated container contains 1 mole of a liquid, molar volume 100 ml at 1 bar. When liquid is steeply passed to 100 bar, volume decreases to 99 ml. Find the ΔH and ΔU for the process.

[IIT 2004]

Solution According to first law of thermodynamics

$\Delta U = q + W$

$\Delta U = q + P\Delta U$

$= 0 + [-100\,(99 - 100)]$

= 100 bar ml

$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$

$= 100 + (100 \times 99 - 1 \times 100)$

= 9900 bar ml

13. For the reaction, $2CO + O_2 \rightarrow 2CO_2$, ΔH = –560 kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K.

(1 L atm = 0.1 kJ)

[IIT 2006]

$\Delta H = \Delta U + \Delta(PV)$

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

$\Delta U = \Delta H - V\Delta P = -560 + 1 \times 30 \times 0.1$

$= -557$

Absolute value = 557 kJ

Calorimetry

Heat exchange

= Heat capacity × temp change

(heat exchange – when no chemical change or state change occurs)

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. Under the same conditions how many ml of 1 M KOH and 0.5 MH_2SO_4 solutions, respectively, when mixed to form total volume of 100 ml, produces the highest rise in temperature?

   a. 67, 33 **b.** 33, 67
   c. 40, 60 **d.** 50, 50

2. Identify the state function among the following:

   a. q **b.** q – w
   c. q/w **d.** q + w

3. For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be

   a. less than ΔH
   b. zero
   c. more than ΔH
   d. equal to ΔH.

4. Which of the following equations represent standard heat of formation of C_2H_4?

   a. $2C\ (diamond) + 2H_2\ (g) \rightarrow C_2H_4\ (g)$
   b. $2C\ (graphite) + 2H_2\ (g) \rightarrow C_2H_4\ (g)$
   c. $2C\ (diamond) + 4H\ (g) \rightarrow C_2H_4\ (g)$
   d. $2C\ (graphite) + 4H\ (g) \rightarrow C_2H_4\ (g)$

5. A glucose solution in 100 gm of water boils at 100.26°C. If this solution is heated to 101°C. What will be the mass of water left at equilibrium?

   a. 76 gm **b.** 120 gm
   c. 100 gm **d.** 26 gm

6. The enthalpy of hydrogenation of cyclohexene is -119.5 kJ mol^{-1}. If resonance energy of benzene is -150.4 kJ mol^{-1}, its enthalpy of hydrogenation would be

   a. -269.9 kJ mol^{-1}
   b. -358.5 kJ mol^{-1}
   c. -508.9 kJ mol^{-1}
   d. -208.1 kJ mol^{-1}

7. A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water then

	Δ	Δ
a.	+ve	+ve
b.	–ve	–ve
c.	–ve	+ve
d.	+ve	–ve

8. The enthalpy change (ΔH) for the reaction,

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

   is –92.38 kJ at 298 K. The internal energy change ΔU at 298 K is

   a. –92.38 kJ **b.** –87.42 kJ
   c. –97.34 kJ **d.** –89.9 kJ

9. For a phase change

   $$H_2O\ (l) \xleftrightarrow{0^\circ C,\ 1\ bar} H_2O\ (s)$$

   a. ΔG = 0 **b.** ΔS = 0
   c. ΔH = 0 **d.** ΔU = 0

10. The enthalpy and entropy change for the reaction

    $Br_2\ (l) + Cl_2\ (g) \rightarrow 2BrCl\ (g)$

    are 30 kJ mol^{-1} and 105 J K^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is

    a. 450 K **b.** 300 K
    c. 285.7 K **d.** 273 K

11. For a spontaneous process, the correct statement is

    a. entropy of the system always increases
    b. free energy of the system always increases
    c. total entropy change is always negative
    d. total entropy change is always positive

12. A heat engine absorbs heat q_1 from a source at temperature T_1 and heat q_2 from a source at temperature T_2. Work done is found to be J $(q_1 + q_2)$. This is in accordance with:

    a. first law of thermodynamics
    b. second law of thermodynamics
    c. joules equivalent law
    d. none of these

13. Identify the correct statement for change of Gibb's energy for a system (ΔG_{system}) at constant temperature and pressure:

    a. if $\Delta G_{system} = 0$, the system is still moving in a particular direction

b. if ΔG_{system} = –ve, the process is not spontaneous

c. if ΔG_{system} = +ve, the process is spontaneous

d. if $\Delta G_{system} = 0$, the system has attained equilibrium

14. For the reaction of one mole of Zn –dust with one mole of H_2SO_4 in a bomb calorimeter, ΔU an W corresponds to:

a. $\Delta U < 0, W = 0$

b. $\Delta U < 0, W < 0$

c. $\Delta U > 0, W = 0$

d. $\Delta U > 0, W > 0$

15. ΔH^o_f (298) of methanol is given by chemical equation

a. $CH_4 (g) + \frac{1}{2} O_2 (g) \rightarrow CH_3OH (g)$

b. $CO (g) + 2H_2 (g) \rightarrow CH_3OH (l)$

c. $C \text{ (graphite)} + \frac{1}{2} O_2 (g) + 2H_2 (g) \rightarrow CH_3OH (l)$

d. $C \text{ (diamond)} + \frac{1}{2} O_2 (g) + 2H_2 (g) \rightarrow CH_3OH (l)$

16. Assume each reaction is carried out in an open container. For which reaction will ΔH = ΔU?

a. $PCl_5 (g) \rightarrow PCl_3 (g) + Cl_2 (g)$

b. $2CO (g) + O_2 (g) \rightarrow 2CO_2 (g)$

c. $H_2 (g) + Br_2 (g) \rightarrow 2HBr (g)$

d. $C (s) + 2H_2O (g) \rightarrow 2H_2 (g) + CO_2 (g)$

17. The absolute enthalpy of neutralization of the reaction

$MgO (s) + 2HCl (aq) \rightarrow MgCl_2 (aq) + H_2O(l)$

will be

a. –57.33 kJ/mole

b. > – 57.33 kJ/ mole

c. < – 57.33 kJ/mole

d. 57.33 kJ /mole.

18. A reaction occurs spontaneously if

a. $T\Delta S < \Delta H$ and both ΔH, ΔS are +ve

b. $T\Delta S > \Delta H$ and ΔH = +ve, ΔS = –ve

c. $T\Delta S > \Delta H$ and both ΔH, ΔS are +ve

d. $T\Delta S = \Delta H$ and both ΔH, ΔS are +ve

19. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction

$H_2C = CH_2 (g) + H_2 (g) \rightarrow H_3C - CH_3 (g)$

at 298 K will be

a. +250 kJ	**b.** –250 kJ
c. +125 kJ	**d.** –125 kJ

20. A gas expands into a vacuum (external pressure = 0) while in thermal isolation from the surroundings. For this expansion

a. ΔE does not change

b. ΔE increases

c. $\Delta E = T^1S$

d. ΔE decreases

21. For a process at constant volume,

a. w = 0 and ΔE = ΔH

b. w = 0 and ΔH = q

c. q = 0, w = 0 and ΔE = 0

d. w = 0 and ΔE = q

22. In an irreversible process taking place at constant T and P and in which only pressure –volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria:

a. $(dS)_{V, E} < 0, (dG)_{T, P} < 0$

b. $(dS)_{V, E} > 0, (dG)_{T, P} < 0$

c. $(dS)_{V, E} = 0, (dG)_{T, P} = 0$

d. $(dS)_{V, E} = 0, (dG)_{T, P} > 0$

23. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?

a. exothermic and increasing disorder

b. exothermic and decreasing disorder

c. endothermic and increasing disorder

d. endothermic and decreasing disorder

24. The internal energy change when a system goes from state A to B is 40 kJ/mol. if the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy?

a. 40 kJ	**b.** > 40 kJ
c. < 40 kJ	**d.** zero

25. Standard state Gibbs free energy change for isomerization reaction,

Cis-2-pentene ↔ trans-2-pentene

is –3.67 kJ/mol at 400 K. if more trans-2-pentene is added to the reaction vessel, then:

a. more cis-2-pentene is formed

b. additional trans-2-pentene is formed

c. equilibrium remains unaffected

d. equilibrium is shifted in the forward direction

26. An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is

a. –900 kJ **b.** –900 J
c. 270 kJ **d.** 940 kJ

27. For a reaction to occur spontaneously

a. $(\Delta H - T\Delta S)$ must be negative
b. $(\Delta H + T\Delta S)$ must be negative
c. ΔH must be negative
d. ΔS must be negative

28. Which one of the following has ΔS^o greater than zero?

a. $CaO\ (s) + CO_2\ (g) \leftrightarrow CaCO_3\ (g)$
b. $NaCl\ (aq) \leftrightarrow NaCl\ (s)$
c. $NaNO_3\ (s) \leftrightarrow Na^+\ (aq) + NO_3^-\ (aq)$
d. $N_2\ (g) + 3H_2\ (g) \leftrightarrow 2NH_3\ (g)$

29. For an explosion in an open vessel, one would expect

a. ΔH to be negative and ΔE to be greater than ΔH
b. ΔH to be negative and ΔE to be less than ΔH
c. ΔH to be positive and ΔE to be less than ΔH
d. ΔH to be positive and ΔE to be greater than ΔH

30. Which of the following is correct equation?

a. $\Delta U = \Delta Q - W$
b. $\Delta W = \Delta U + \Delta Q$
c. $\Delta U = \Delta W + \Delta Q$
d. none of these

31. Consider the reaction $N_2 + 3H_2 \leftrightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction. Which of the following expressions is true?

a. $\Delta H = 0$ **b.** $\Delta H = \Delta U$
c. $\Delta H < \Delta U$ **d.** $\Delta H > \Delta U$

32. 1 mol of an ideal gas at 300 K is expanded isothermally and reversible from an initial volume of 1 litre to 10 litre. The work in this process is (R = 2 cal mol^{-1} K^{-1})

a. 163.7 cal **b.** zero
c. –1381.8 cal **d.** 9 litre atm

33. Identify the correct statement regarding entropy.

a. At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero
b. At absolute zero of temperature the entropy of a perfectly crystalline substance is +ve
c. At absolute zero of temperature the entropy of all crystalline substance is to be zero
d. At 0°C, the entropy of a perfectly crystalline substance is taken to be zero

34. A gas expands against a non-zero external pressure while in thermal isolation from the surroundings. For this expansion

a. $\Delta E = q$
b. ΔE increases
c. ΔE does not change
d. ΔE decreases

35. The standard enthalpy of formation $(\Delta_f H^o)$ at 298 K for methane, $CH_4(g)$ is –74.8 kJ mol^{-1}. the additional information required to determine the average energy for C – H bond formation would be

a. the dissociation energy of H_2 and enthalpy of sublimation of carbon
b. latent heat of vapourization of methane
c. the first four ionization energies of carbon and electron gain enthalpy of hydrogen
d. the dissociation energy of hydrogen molecule, H_2

36. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as

$S_2\ (s) + 2O_2\ (g) \rightarrow 2SO_2\ (g)\ ;\ \Delta G = -544$ kJ

$2Zn\ (s) + S_2\ (s) \rightarrow 2ZnS\ (s)\ ;\ \Delta G = -293$ kJ

$2\ Zn\ (s) + O_2\ (g) \rightarrow 2\ ZnO\ (s)\ ;\ \Delta G = -480$ kJ

the ΔG for the reaction,

$2ZnS\ (s) + 3O_2\ (g) \rightarrow 2\ ZnO\ (s) + 2SO_2\ (g)$
will be

a. –357 kJ **b.** –731 kJ
c. –773 kJ **d.** –229 kJ

37. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If Ti is the initial temperature and T_f is the final temperature, which of the following statements is correct?

a. $(T_f)_{irrev} > (T_F)_{rev}$
b. $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
c. (T_f)irrev = (T_F)rev
d. $T_f = T_i$ for both reversible and irreversible processes

38. The entropy change in the fusion of 1 mol of a solid melting at 27°C (Latent heat of fusion, 2930 J mol^{-1}) is

a. 9.77 JK^{-1} mol^{-1}
b. 10.73 JK^{-1} mol^{-1}

c. 2930 JK^{-1} mol^{-1}

d. 108.5 JK^{-1} mol^{-1}

39. As a given temperature and pressure, which of the following would be expected to have the greatest molar entropy?

a. Br_2 (g)

b. Br_2 (s)

c. Br_2 (l)

d. All of these would be expected to have the same molar entropy.

40. The standard enthalpy of formation ($\Delta_f H^o$) at 298 K for methane, CH_4(g) is –74.8 kJ mol^{-1}. the additional information required to determine the average energy for C – H bond formation would be

a. the dissociation energy of H_2 and enthalpy of sublimation of carbon

b. latent heat of vapourization of methane

c. the first four ionization energies of carbon and electron gain enthalpy of hydrogen

d. the dissociation energy of hydrogen molecule, H_2

41. When 1 mol gas is heated at constant volume temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct?

a. $q = W = 500$ J, $\Delta U = 0$

b. $q = \Delta U = 500$ J, $W = 0$

c. $q = W = 500$ J, $\Delta U = 0$

d. $\Delta U = 0$, $q =$

42. For the reaction:

$S_8 (s) + 8O_2 (g) \rightarrow 8SO_2 (g)$

a. $\Delta H < \Delta E$

b. $\Delta H = \Delta E$

c. $\Delta H > \Delta E$

d. ΔH is independent of the physical state of reactants.

43. 2 mol of an ideal gas at 27°C temperature is expanded reversibly from 2 L to 20 L. Find entropy change in cal. (R = 2 cal/mol K)

a. 92.1 **b.** 0

c. 4 **d.** 9.2

44. (ΔH – ΔU) for the formation of carbon monoxide (CO) from its elements at 298 K is

a. –1238.78 J mol^{-1}

b. 1238.78 J mol^{-1}

c. –2477.57 J mol^{-1}

d. 2477.57 J mol^{-1}

45. For the reaction,

$C_3H_8 (g) + 5O_2 (g) \rightarrow 3CO_2 (g) + 4H_2O (l)$

at constant temperature, ΔH – ΔE is

a. + 3RT **b.** –RT

c. +RT **d.** –3RT

46. What is the entropy change (in JK^{-1} mol^{-1}) when 1 mol of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C)

a. 2.198 **b.** 21.98

c. 20.13 **d.** 2.013

47. An ideal gas expand against a constant external pressure of 5.0 atmosphere from 40 to 60 litre and absorb 40 kJ of energy from surrounding. The change in internal energy of the system will be

a. 20.52 kJ **b.** 52.75 kJ

c. 32.75 kJ **d.** 35.95 kJ

48. The molar heat capacity of water at constant pressure, C, is 75 JK^{-1} mol^{-1}. When 1.0 kJ of heat is supplied to 100 g of water which is free to expand, the increase in temperature of water is

a. 4.8 K **b.** 6.6 K

c. 1.2 K **d.** 2.4 K

49. The incorrect statement amongst the following is

a. at equilibrium $\Delta H_{S, P} = 0$

b. the condition of equilibrium at constant P and T is that G must be minimum

c. at equilibrium $\Delta G_{P, T} = 0$

d. ΔG^o calculated using the equation; $\Delta G^o = -RT$ In Kp, is the free energy change of the reaction when each of the species (reactants and products) is in the standard state of unit activity that is, roughly unit concentration.

50. The heat liberated on complete combustion of 7.8 gm of benzene is 327 kJ. This heat was measured at constant volume and at 27°C. Calculate the heat of combustion of benzene at constant pressure (R = 8.3 J/mole/K)

a. –1637 kJ/mole **b.** –3274 kJ/mole

c. –3270 kJ/mole **d.** none of these

51. AB, A_2 and B_2 are diatomic molecule if the bond enthalpies of A_2, AB and B_2 are in the ratio 1:1 : 0.5 and the enthalpy of formation of AB from A and B_2 is 100 kJ/mole. What is the bond enthalpy of A_2?

a. 400 kJ/mole **b.** 300 kJ/mole
c. 200 kJ/mole **d.** 100 kJ/mole

52. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

a. $\Delta S_{system} + \Delta S_{surroundings} > 0$
b. $\Delta S_{system} - \Delta S_{surroundings} > 0$
c. $\Delta S_{system} > 0$ only
d. $\Delta S_{surroundings} > 0$ only

53. The gas in a refrigerator causes cooling on expansion because

a. work done by the gas is converted into heat
b. heat of the gas is lost as work is done by the gas
c. the heat is spread over a larger space
d. None

54. The standard heats of formation of NO_2 (g) and N_2O_4 (g) are 8.0 and 2.0 kcal mol^{-1} respectively. The heat of dimerization of NO_2 in kcal is

a. 10.0 **b.** –6.0
c. –12.0 **d.** –14.0

55. Calculate the work done during isothermal expansion of one mole of an ideal gas from 10 atm to 1 atm at 300K.

a. –1382 cal **b.** –1382 joule
c. –13.82 cal **d.** –1.382 cal

56. The heats of neutralization of four acids a, b, c and d when neutralized against a common base and 13.7, 9.4, 11.2 and 12.4 kcal respectively. the weakest among these acids is

a. a **b.** b
c. c **d.** d

57. Which of the following salts shall cause maximum cooling when one mole of the salt is dissolved in the same amount of water? (integral heat of solution at 298 K is given for each solute)

a. KNO_3, $\Delta H = 35.4$ kJ mol^{-}
b. NaCl, $\Delta H = -5.35$ kJ mol^{-}
c. KOH, $\Delta H = -55.6$ kJ mol^{-}
d. KBr, $\Delta H = -83.3$ kJ mol^{-}

58. The melting point of a solid is 27°C and it's latent heat of fusion is 600 calories per mole. The entropy change for the fusion of one mole of the solid (in cal K^{-1}) is

a. 180 **b.** 22.2
c. 2 **d.** 0.5

59. Devitrification of glass is a process for which change in entropy (ΔS)

a. –ve
b. +ve
c. 0
d. ΔS value depend on the nature of glass

60. In a flask, colourless N_2O_4 is in equilibrium with brown coloured NO_2. At equilibrium, the brown colour deepens on heating the flask to 100°C and on cooling it become less coloured. ΔH for the system is

a. positive **b.** negative
c. zero **d.** undefined

61. Which of the following modes of energy constitute both kinetic and potential energy?

a. nuclear energy
b. transitional energy
c. rotational energy
d. vibrational energy

62. Which of the following is not expected to be correct?

a. $\Delta H^{o}_{f}(CO_2)$ = negative
b. ΔH_{comb} (NO) = positive
c. ΔH_{hyd} ($BaCl_2$) = negative
d. ΔH_{neut} = negative

63. The standard heat of formation of diamond is

a. same as that of graphite
b. greater than that of graphite
c. less than that of graphite
d. taken as zero

64. How many calories are required to heat 40 gram of argon from 40 to 100°C at constant volume? (R = 2 cal/mol.K)

a. 120 **b.** 180
c. 1800 **d.** 2400

65. Which of the following does not express criterion of spontaneity?

a. $(dS)_{P.T.} > 0$ **b.** $(dA)_{V.T.} \geq 0$
c. $(dG)_{P.T.} < 0$ **d.** All of these

66. Which one of the following set of units represents the smallest and the largest amount of energy respectively?

a. eV and lit atm
b. Cal and eV
c. J and erg
d. erg and cal

67. If $K < 1.0$, what will be the value of ΔG^o of the following?

a. Zero **b.** Negative
c. Positive **d.** 1.0

68. Which of the following are not state functions?

(I) q + w (II) q
(III) w (IV) H – TS

a. (I), (II) and (III)
b. (II) and (III)
c. (I) and (IV)
d. (II), (III) and (IV)

69. Oxidizing power of chlorine in aqueous solution can be determined by the parameters indicated below:

$$\tfrac{1}{2}\,Cl_2\,(g) \xrightarrow{\tfrac{1}{2}\,\Delta_{diss}\,H^-} Cl\,(g) \xrightarrow{\Delta_{eg}\,H^-}$$

$$Cl^-\,(g) \xrightarrow{\Delta_{hyd.}\,H^-} Cl^-\,(aq)$$

The energy involved in the conversion of $\tfrac{1}{2}\,Cl_2$ (g) to Cl^- (g)

(Using the data, $\Delta_{diss}\,H^-Cl_2 = 240$ kJ mol^{-1}, $\Delta_{eg}\,H^-Cl = -349$ kJ mol^{-1}, $\Delta_{hyd}\,H^-Cl = -381$ kJ mol^{-1})
will be

a. +152 kJ mol^{-1} **b.** –610 kJ mol^{-1}
c. –850 kJ mol^{-1} **d.** +120 kJ mol^{-1}

70. For the gas phase reaction,

$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

Which of the following conditions are correct?

a. $\Delta H < 0$ and $\Delta S < 0$
b. $\Delta H > 0$ and $\Delta S < 0$
c. $\Delta H = 0$ and $\Delta S < 0$
d. $\Delta H > 0$ and $\Delta S > 0$

71. Using the following thermochemical equations

(i) $S_{(rh)} + 3/2\,O_{2(g)} \rightarrow SO_{3(g)}$; $\Delta H = -2x$ kJ mol^{-1}

(ii) $SO_{2(g)} + \tfrac{1}{2}\,O_{2(g)} \rightarrow SO_{3(g)}$; $\Delta H = -y$ kj mol^{-1}

Find out the heat of formation of $SO_{2(g)}$ in kJ mol^{-1}.

a. (× + y) **b.** (2x + y)
c. (2x/y) **d.** (y – 2x)
e. (2x – y)

72. When compared to ΔG^o for the formation of Al_2O_3, the ΔG^o for the formation of Cr_2O_3 is

a. Lower **b.** Unpredicted
c. Higher **d.** Same

73. For one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then

a. $\Delta H = \Delta U$

b. $\Delta H < \Delta U$

c. There is no relationship

d. $\Delta H > \Delta U$An s = (A)

74. At a given pressure and volume, in the P – V plot, of an ideal gas,

$$\frac{\text{Slope of an adiabatic curve}}{\text{Slope of an isothermal curve}} \text{ is}$$

a. C_P/R **b.** C_V/C_P
c. $C_{P/}C_V$ **d.** R

75. Enthalpy is equal to

a. $-T^2\,[\partial(G/T)/\partial T]_V$

b. $T^2\,[\partial(G/T)/\partial T]_V$

c. $-T^2\,[\partial(G/T)/\partial T]_P$

d. $T^2\,[\partial(G/T)/\partial T]_P$

Brainteasers Objective Type Questions (Single choice only)

76. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are—156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of Cyclohexene (l) at 25°C is –119 kJ/mol. Find resonance energy of benzene.

a. –152 kJ mol^{-1} **b.** –159 kJ mol^{-1}
c. + 152 kJ mol^{-1} **d.** + 159 kJ mol^{-1}

77. 0.50mol of ammonium nitrate is added to 50.0 mL or water in a thermally insulated reaction vessel. Both are initially at 20.0°C. After stirring the temperature of the solution is found to be less than 10°C. Which statement best explains the temperature change?

a. Heat is evolved from the system to the surroundings.

b. Heat is absorbed from the surroundings by the system.

c. Heat is absorbed by ammonium nitrate when it dissolves and becomes hydrated.

d. Heat is evolved by ammonium nitrate when it dissolves and becomes hydrated.

e. The heat energy of the hydrated ions is less than the ions in solid ammonium nitrate.

78. Determine the sign of ΔS^o for each of the following processes:

(I) $C_6H_6\ (s) \rightarrow C_6H_6\ (l)$

(II) $2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$

a. ΔS^o should be positive for I and positive for II.

b. ΔS^o should be positive for I and negative for II

c. ΔS^o should be negative for I and negative for II.

d. ΔS^o should be negative for I and positive for II.

79. The difference between heats of reaction at constant pressure and constant volume for the reaction

$2\ C_6H_6(l) + 15\ O_2\ (g) \rightarrow 12\ CO_2\ (g) + 6H_2O(l)$

at 25°C in kJ is

a. –7.43 **b.** +3.72
c. –3.72 **d.** + 7.43

80. 100 ml of 0.3 M HCl solution is mixed with 100 ml of 0.33 M KOH solution. The amount of heat liberated is

a. 1.713 kJ **b.** 17.42 kJ
c. 1.31 kJ **d.** 17.13 kJ

81. An athlete is given 100 g of glucose of energy equivalent to 1560 kJ. He utilizes 50 % of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. Enthalpy of H_2O for evaporation is 44 kJ mol^{-1}.

a. 346 g **b.** 316 g
c. 323 g **d.** 319 g

82. The enthalpies of formation of CO_2 (g) and CO (g) at 298 K are in the ratio 2.56: 1. For the reaction,

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

$CO\ (g)$, $\Delta H = 177.5$ kJ, ΔH_f of CO (g) is

a. –113.78 kJ mol^{-1}

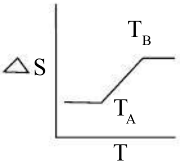
b. 113.78 kJ mol^{-1}

c. –141.6 kJ mol^{-1}

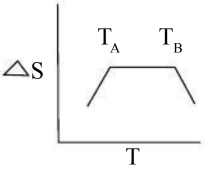
d. –180.6 kJ mol^{-1}

83. If for a given substance, T_B is the m.p. and T_A is the freezing point, then correct variation of entropy by graph between entropy change (ΔS) and temperature is

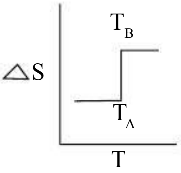
a.



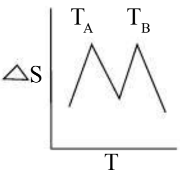
b.



c.



d.



84. The standard enthalpy of combustion at 25°C of H_2, C_6H_{10} and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ mol^{-1} respectively. Calculate heat of hydrogenation of cyclohexane (C_6H_{10})

a. –161 kJ mol^{-1} **b.** –131 kJ mol^{-1}
c. –121 kJ mol^{-1} **d.** None

85. Classify each of the following processes as spontaneous or non spontaneous.

I. $H_2O\ (l) \rightarrow H_2O\ (g)$ T = 25°C vessel open to atmosphere with 50 % relative humidity.

II. $H_2O\ (s) \rightarrow H_2O\ (l)$ T = 25°C, P = 1 atm

a. I and II are both non spontaneous
b. I and II are both spontaneous
c. I is non spontaneous and II is spontaneous
d. I is spontaneous and II is non spontaneous.

86. The standard heats of formation of CH_4 (g), CO_2 (g) and H_2O (g) are –76.2, –394.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1m^3 methane measured under normal conditions.

a. 162897.3 kJ **b.** 64078.2 kJ
c. 35182 kJ **d.** none

87. For an explosion in an open vessel, one would expect

a. ΔH to be negative and ΔE to be greater than ΔH

b. ΔH to be negative and ΔE to be less than ΔH

c. ΔH to be positive and ΔE to be less than ΔH

d. ΔH to be positive and ΔE to be greater than ΔH

88. Calculate the resonance energy of N_2O from the following data: ΔH_f of N_2O = 82 kJ mol^{-1}. Bond energies of $N \equiv N$, $N = N$, $O = O$ and $N = O$ bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively.

a. –88 kJ mol^{-1} **b.** –170 kJ mol^{-1}
c. –82 kJ mol^{-1} **d.** –258 kJ mol^{-1}

89. The enthalpy changes for the following processes are listed below

Cl_2 (g) = 2Cl (g) ; 242.3 kJ mol^{-1}

I_2 (g) = 2I (g) ; 151.0 kJ mol^{-1}

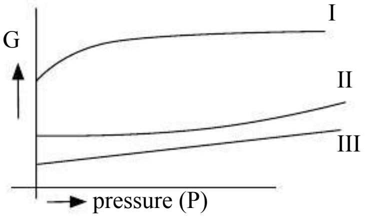
ICl (g) = I (g) + Cl(g) ; 211.3 kJ mol^{-1}

I_2 (s) = I_2 (g) ; 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are I_2 (s) and Cl_2 (g), the standard enthalpy of formation for ICl (g) is

a. –14.6 kJ mol^{-1} **b.** –16.8 kJ mol^{-1}
c. +16.8 kJ mol^{-1} **d.** +244.8 kJ mol^{-1}

90. The following curve represents the variation of Gibbs function 'G' with pressure at constant temperature.



Correct match of given plots with the physical state of a substance is

a. I – solid, III– gas, II – liquid
b. I – gas, II – liquid, III – solid
c. I – liquid, II – solid, III – gas
d. III – gas, II – solid, I - liquid

91. Which of the following is in accord with the three laws of thermodynamics?

(I) The entropy of the universe never decreases.

(II) A non-spontaneous process can occur if it is coupled to a process that is sufficiently spontaneous.

a. I is true and II is false.

b. I is false and II is true.

c. Both I and II are true.

d. Both I and II are false.

92. Which of CH_4 (g), C_2H_2 (g) and CH_3OH (l) provides the most energy per gram upon combustion and which provides the least?

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

$\Delta H^o = -890$ kJ

$2C_2H_2 (g) + 5O_2 (g) \rightarrow 4CO_2 (g) + 2H_2O (l)$

$\Delta H^o = -2599$ kJ

$2CH_3OH (l) + 3O_2 (g) \rightarrow 2CO_2 (g) + 4H_2O(l)$

$\Delta H^o = -1453$ kJ

a. C_2H_2 provides the most energy per gram and CH_3OH the least.
b. C_2H_2 provides the most energy per gram and CH_4 the least.
c. CH_4 provides the most energy per gram and C_2H_2 the least.
d. CH_4 provides the most energy per gram and CH_3OH the least.

93. Calculate ΔH^o_f for chloride ion from the following data:

$\frac{1}{2} H_2 (g) + \frac{1}{2} Cl_2 (g) \rightarrow HCl (g)$

$\Delta H^o_f = -92.4$ kJ

$HCl (g) + nH_2O (l) \rightarrow H^+ (aq) + Cl^- (aq)$

$\Delta H_{298} = -74.8$ kJ

$\Delta H^o_f[H^+] = 0.0$ kJ

a. –189 kJ **b.** –167 kJ
c. + 167 kJ **d.** –191 kJ

94. The signs of ΔG, ΔH and ΔS at 25°C are shown below for three reactions.

Reaction	ΔG	ΔH	ΔS
I.	–	+	+
II.	–	–	+
III.	–	–	–

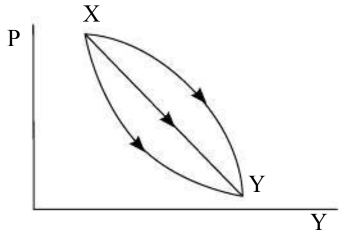
Which reaction could go in the reverse direction at high temperature?

a. II only **b.** III only
c. I and II **d.** II and III

95. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat was measured at constant volume and at 27°C. Calculate the heat of combustion of benzene at constant pressure (R = 8.3 J mol^{-1} K^{-1})

a. –3274 kJ mol^{-1} **b.** –1637 kJ mol^{-1}
c. –3270 kJ mol^{-1} **d.** –3637 kJ mol^{-1}

96. A given masss of gas expands from the state × to the staste Y by three paths 1, 2 and 3 as shown I in the figure. If w1 and w_2 and w_3 respectively be the work done by the gas along three paths then:



a. $w_1 > w_2 > w_3$

b. $w_2 < w_1 < w_2$

c. $w_1 = w_2 = w_3$

d. $w_1 < w_2 < w_3$

97. Calculate ΔG° for the reaction below and tell whether it is spontaneous or non-spontaneous under standard conditions at 25°C.

$2S\ (s) + 3O_2\ (g) + 2H_2O\ (l) \rightarrow 2H_2SO_4\ (l)$

$\Delta H^\circ = -1056$ kJ/mol

$\Delta S^\circ = -505$ J/mol

a. ΔG° = –906 kJ and the process is spontaneous

b. ΔG° = –1206 and the process is spontaneous

c. ΔG° = –906 kJ and the process is non-spontaneous

d. ΔG° = –1206 kJ and the process is non-spontaneous

98. Generally, alkali metals form their oxides by an average increment of 6 kJ $mol^{-1}\ K^{-1}$ in their entropies. If at 25°C, ΔG°_f of Al_2O_3 (s) = –1582 kJ mol^{-1} ; ΔH°_f of Li_2O (s) = 1244 kJ and ΔH°_f of Na_2O (s) = 1411 kJ. The aluminium oxide can be reduced to Al metal by

a. Lithium **b.** Sodium

c. Both (a) and (b) **d.** None of these

99. For the reaction,

$A\ (g) + 2B\ (g) \rightarrow 2C\ (g) + 3D\ (g)$

The value of ΔH at 27°C is 19.0 kcal. The value of ΔE for the reaction would be

(given R = 2.0 cal $K^{-1}\ mol^{-1}$)

a. 20.8 kcal **b.** 19.8 kcal

c. 18.8 kcal **d.** 17.8 kcal

100. Determine ΔH and ΔE for reversible isothermal evaporation of 90 g of water at 100°C. Assume that water vapour behaves as an ideal gas and heat of evaporation of water is 540 cal g^{-1} (R = 2.0 cal $mol^{-1}\ K^{-1}$)

a. 48600 cal, 44870 cal

b. 43670 cal, 47700 cal

c. 47700 cal, 43670 cal

d. 44870 cal, 48670 cal

101. If work done by a gas is 144.5 J when heat given to the gas in isobaric process is 506 J. then the gas is

a. SO_2 **b.** NH_3

c. He **d.** O_2

102. A process is carried out at constant pressure. Given that ΔH is negative and ΔE is less than ΔH,

a. The system loses heat and contracts during the process

b. The system loses heat and expands during the process

c. The system absorbs heat and expands during the process

d. The system absorbs heat and contracts during the process

103. ΔG° for the reaction, x + y ↔ z is –4.606 kcal. The value of equilibrium constant of the reaction at 227°C is.

a. 0.01 **b.** 100

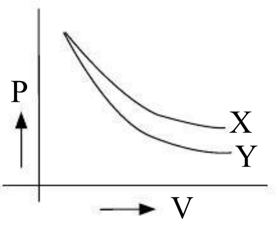
c. 2 **d.** 10

104. Assume a heteronuclear diatomic molecule, AB, forms a one dimensional crystal by lining up along the X-axis. Also assume that each molecule can only have one of six possible orientations, corresponding to atom A facing in either the positive or negative direction along the X-, Y-, or Z-axis. If the molecules are arranged randomly in the six directions, the molar entropy at absolute zero should be

a. zero **b.** R In 60

c. R In 6 **d.** R In 6^6

105. P–V plot for two gases (assuming ideal) during adiabatic process are given in the fig. Plot X and plot Y should correspond respectively to:



a. He and H_2 **b.** H_2 and He

c. Cl_2 and H_2 **d.** H_2 and Cl_2

106. The solubility of manganese (II) fluoride in water is 6.6 g/ml at 40°C and 4.8 g/litre at 100°C. Based on this data, what is the sign of ΔH^o and ΔS^o for the following process?

$MnF_2\ (s) \rightleftharpoons Mn^{2+}\ (aq) + 2F^-\ (aq)$

a. ΔH^o is negative and ΔS^o is positive

b. ΔH^o is negative and ΔS^o is negative

c. ΔH^o is positive and ΔS^o is positive

d. ΔH^o is positive and ΔS^o is negative

107. For the system represented by the equation

$CaCO_3\ (s) + 42.5\ \text{Kcal} \rightarrow CaO\ (s) + CO_2\ (g)$

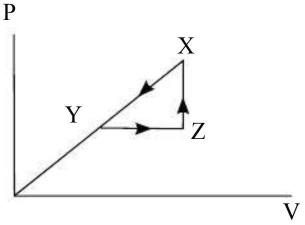
a. the reaction is exoenergic

b. the size of Δ E is negative

c. the net energy flow is from the system to the environment

d. the internal chemical energy of one mole $CaCO_3$ (s) is less than that of [one mole CaO (s) + one mole CO_2 (g)]

108.



(I) $Q_X \rightarrow Y = (-)$ ve

(II) $\Delta U_Y \rightarrow Z = (+)$ ve

(III) $\Delta U_Z \rightarrow \times = (-)$ ve

(IV) $W_{ZXY} = (-)$ ve.

a. I, II, III **b.** I, II, IV

c. I, III, IV **d.** II, III, IV

109. Consider these two statements.

(i) The reversible work done by 2 moles of an ideal gas, isothermally at 300 k, as it expands from 10 atm to 1 atm. pressure is roughly 2.764 k. cal.

(ii) 2 moles of a gas expand against a constant pressure of 1 atm, the change in the volume being 82.12 ml. The work done by the gas is roughly 3 cal.

a. (i) and (ii) are correct

b. (i) and (ii) are incorrect

c. (i) is incorrect, (ii) is correct

d. (i) is correct, (ii) is incorrect

110. The reversible adiabatic expansion of an ideal monatomic gas, the final volume is 10 times to the initial volume. The ratio

$\dfrac{\text{Final temperature}}{\text{Initial temperature}}$ is

a. $(1/10)^{0.666}$ **b.** $10^{1.666}$

c. $10^{0.666}$ **d.** $(1/10)^{1.666}$

111. 4.8 g of C (diamond) on complete combustion evolves 1584 kJ of heat. The standard heat of formation of gaseous carbon is 725 kJ/mol. The energy required for the process

(i) C (graphite) → C (gas)

(ii) C (diamond) → C (gas) are

a. 725, 723 **b.** 725, 727

c. 727, 725 **d.** None of these

112. Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is

a. –93 kJ mol^{-1}

b. 245 kJ mol^{-1}

c. 93 kJ mol^{-1}

d. –245 kJ mol^{-1}

113. Consider the reaction:

$N_2\ (g) + 3F_2\ (g) \rightarrow 2NF_3\ (g)$

$\Delta H^o = -249$ kJ and $\Delta S^o = -278\ JK^{-1}$ at 25°C

Calculate ΔG^o and state whether the equilibrium composition should favour reactants or products at standard conditions.

a. $\Delta G^o = -166$ kJ; the equilibrium composition should favour reactants.

b. $\Delta G^o = -166$ kJ; the equilibrium composition should favour products.

c. $\Delta G^o = -322$ kJ; the equilibrium composition should favour products.

d. $\Delta G^o = -166$ kJ; the equilibrium composition should favour reactants.

114. Which provides the greatest increase in entropy?

a. H_2O (l, 0°C) → H_2O (l, 25°C)

b. H_2O (s, 0°C) → H_2O (l, 0°C)

c. H_2O (l, 100°C) → H_2O (g, 100°C)

d. H_2O (g, 0.1°C) → H_2O (s, 0.1°C)

115. Consider these two statements.

(I) The reversible work done by 2 moles of an ideal gas, isothermally at 300 k, as it expands from 10 atm to 1 atm. pressure is roughly 2.764 k. cal.

(II) 2 moles of a gas expand against a constant pressure of 1 atm, the change in the volume being 82.12 ml. The work done by the gas is roughly 3 cal.

a. (i) and (ii) are correct

b. (i) and (ii) are incorrect

c. (i) is incorrect, (ii) is correct

d. (i) is correct, (ii) is incorrect

116. (Standard free energies of formation (in kJ /mol) at 298 K are –237.2, –394.4 and –8.2 for H_2O (l), CO_2 (g) are pentane (g) respectively. The value of E^o_{cell} for the pentane-oxygen fuel cell is:

a. 1.0968 V **b.** 0.0698 V

c. 1.968 V **d.** 2.0968 V

Given that

$3C\ (s) + 2Fe_2O_3\ (s) \rightarrow 4Fe\ (s) + 3CO_2\ (g)$

$\Delta H^o = -93657$ kcal at 25°C

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

$\Delta H^o = -94050$ kcal at 25°C

The value of ΔH^o (Fe_2O_3) is

a. –19.650 kcal **b.** –196.5 kcal

c. 93.657 kcal **d.** –286.4 kcal

117. The enthalpy of solution of $BaCl_2$ (s) and $BaCl_2.2H_2O$ (s) are –20.6 and 8.8 kJ mol^{-1} respectively. The enthalpy change for the hydration of $BaCl_2$ (s) is

a. 29.8 kJ **b.** –11.8 kJ

c. –20.6 kJ **d.** –29.4 kJ.

118. The heat of formation of CO_2 is –409 kJ/mol. The energy required for the process

$3CO_2\ (g) \rightarrow 3C\ (g) + 2O_3\ (g)$ is

a. Is equal to 1227 kJ

b. Less than 1227 kJ

c. More than 1227 kJ

d. Cannot be predicted

119. Calculate Q and W for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.

a. 5.22 kJ, –5.22 kJ

b. –27.3 kJ, 27.3 kJ

c. 27.3 kJ, –27.3 kJ

d. –5.22 kJ, 5.22 kJ

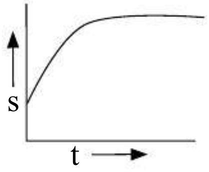
120. Calculate the heat of combustion of methane at constant volume. The thermal capacity of the calorimeter system is 177 kJ K^{-1} (R = 8.314 J K^{-1} mol^{-1})

a. –695 kJ mol^{-1} **b.** –1703 kJ mol^{-1}

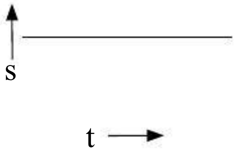
c. –890 kJ mol^{-1} **d.** –885 kJ mol^{-1}

121. If a copper block of mass m at temperature ‘T1’ is kept in the open atmosphere at temperature ‘T2’ and T2 > T1. The variation of entropy of the copper block with time can be best illustrated by which of these graph.

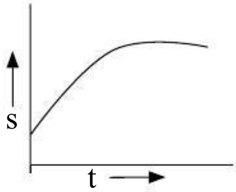
a.



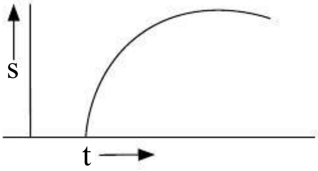
b.



c.



d.



122. The lattice energy of NaCl is 780 kJ mol^{-1} The enthalpies of hydration of Na^+ (g) and Cl^- (g) ions are –406 kJ mol^{-1} and –364 kJ mol^{-1}. The enthalpy of solution of NaCl (s) is

a. 10 kJ mol^{-1} **b.** –10 kJ mol^{-1}

c. 736 kJ mol^{-1} **d.** 100 kJ mol^{-1}

124. The enthalpy (heat) of formation of water is 286 kJ $mole^{-1}$. From this it can be concluded that

a. the enthalpy change when 1 g of hydrogen is burnt in oxygen is –286 kJ

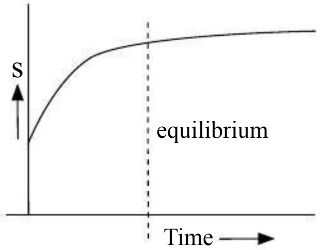
b. there is a decrease in the enthalpy of the system when water is formed

c. the mean bond dissociation energy of O–H is 143 kJ mol^{-1}.

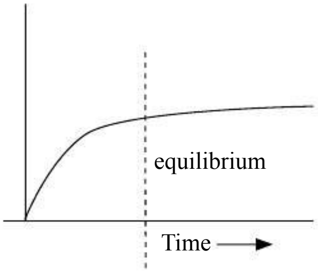
d. the enthalpy change for the reaction $H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$ is –286 kJ mol^{-1}

125. Which of these correctly represents the entropy (s) of an isolated system during a process?

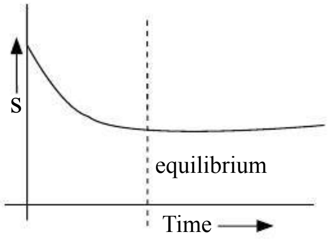
a.



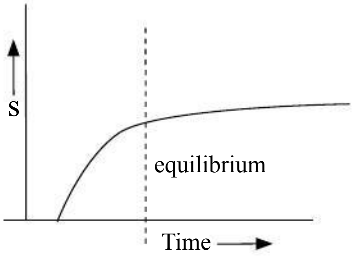
b.



c.



d.



Multiple Correct Answer Type Questions

126. Which of the following statement is/are correct?

a. From the following reaction

$CO (g) + O_2 (g) \rightarrow CO_2 (g), \Delta H = q_1$

Heat of formation of CO_2 (g) is q_1

b. From the following reaction

$C (graphite) + ½ O_2(g) \rightarrow CO (g), \Delta H = q_2$

Heat of combustion of carbon is q_2.

c. From the above reaction, heat of combustion of CO (g) is q_1 and that of carbon is $q_1 + q_2$.

d. From the above reaction, heat of formation of CO_2 is $q_1 + q_2$.

127. Which of the following statements is/are true?

a. A highly spontaneous process need not occur rapidly

b. A non spontaneous process cannot be caused to occur.

c. The reverse of a spontaneous reaction is always non spontaneous.

d. A spontaneous process always moves towards equilibrium.

128. $C_P – C_V = R$. This R is not equal to:

a. Change in rotational energy

b. Change in KE

c. Change in PE

d. Work done which system can do on expanding the gas per mol per degree increase in temperature.

129. For which of the following reaction is the standard entropy of reaction ΔS° positive?

a. $C_2H_5OH (l) + 3O_2 (g) \rightarrow 2CO_2 (g) + 3H_2O (l)$

b. $2H_2O (g) \rightarrow 2H_2 (g) + O_2 (g)$

c. $CO (g) + 2H_2 (g) \rightarrow CH_3OH (g)$

d. $C_2H_5OH (g) + 3O_2 (g) \rightarrow 2CO_2 (g) + 3H_2O (g)$

130. The enthalpy change for a reaction depend upon the

a. physical state of reactants and products

b. use of different reactants for the same product

c. nature of intermediate reaction steps

d. difference in initial or final temperatures of involved substances

131. Which of the following always increase with increase in temperature?

a. pressure of the gas at constant volume

b. solubility of gas

c. entropy

d. rate of reaction

132. Which of the following is/are spontaneous process?

a. $2NH_3$ (g) → N_2 (g) + $3H_2$ (g) if $p_{NH_3} = 1$ atm, $p_{H_2} = P_{N_2} = 0$ and $Kp = 2 \times 10^{-6}$

b. N_2 (g) + $3H_2$ (g) → $2NH_3$ (g) if $pH_2 = PN_2 = 1$ atm, $pNH_3 = 0$ and $Kp = 4 \times 10^5$

c. the expansion of gas into a vacuum

d. dissolving more solute in a saturated solution

133. Internal energy and entropy are state functions

a. internal energy (U) is a state function and ΔU is independent of path.

b. In a cyclic process: $\Delta S = 0$ but $\Delta U \neq 0$

c. Cv values of H_2 and He are equal at all temperatures

d. q and w are path dependent

134. For which of the following processes will the entropy decrease?

a. Reaction of magnesium with oxygen to form magnesium oxide.

b. Reaction of nitrogen and hydrogen to form ammonia.

c. Sublimation of dry ice.

d. Condensation of steam.

135. Which of the following statements must be true for the entropy of a pure solid to be zero?

a. Temperature must be 0 K.

b. The solid must be perfectly ordered

c. The solid must be an element.

d. The solid must be crystalline, not amorphous

136. For an ideal gas undergoing isothermal and reversible process

a. ΔU and ΔH both are zero

b. $\Delta U = 0$ but $\Delta H \neq 0$

c. ΔS is +ve during expansion and –ve during compression

d. $\Delta S = 0$ and $\Delta U = 0$

137. In certain chemical process both ΔH and ΔS have values greater than zero. Under what conditions, the reaction would not be spontaneous?

a. $\Delta H > T\Delta S$ **b.** $\Delta H < T\Delta S$

c. $\Delta G > 0$ **d.** $\Delta G < 0$

138. Which statement is/are not true about the standard states of F_2 (g) and $C_6H_{12}O_6$ (aq)?

a. The standard state for F_2 (g) is the pure gas at 1 atm and for $C_6H_{12}O_6$ (aq) is the solution at a concentration of 1 mol/L.

b. The standard state for F_2 (g) is the pure gas at 1 mol/L and for $C_6H_{12}O_6$ (aq) is the solution at a concentration of 1 mol/L.

c. The standard state for F_2 (g) is the pure gas at 1 atm and for $C_6H_{12}O_6$ (aq) is the pure solid at 1 atm.

d. The standard state for F_2 (g) is the pure gas at 1 mol/L and for $C_6H_{12}O_6$ (aq) is the pure solid at atm.

139. The heat evolved during the combustion of 46 gm of ethanol in a bomb calorimeter wad determined to be 670.5 kcal/mol at 25°C. The value of ΔU of the reaction at the same temperature is

a. –335.25 Kcal **b.** –660.3 Kcal

c. –670.5 Kcal **d.** –2802.6 kJ

140. Which of the following process/es proceed towards more disordered state?

a. sublimation of dry ice

b. crystallization of salt from solution

c. dissolution of sugar in water

d. stretching of the rubber

141. Identify the incorrect statement/s regarding entropy.

a. at absolute zero temperature , entropy of perfectly crystalline substance is taken to zero

b. at absolute zero temperature , the entropy of perfectly crystalline substance is positive

c. at 0°C the entropy of perfectly crystalline substance is positive

d. at absolute zero temperature, the entropy of all crystalline substances is taken to be zero

142. xy, x_2 and y_2 are diatomic molecules if ΔH_{x-x}, ΔH_{y-y} and ΔHxy are in the ratio of 2 : 1 : 2 and enthalpy of formation of x – y form x_2 and y_2 is –100 kJ/mol. The value of $\Delta Hx - x$ is

a. 47.85 Kcal/mol

b. 23.92 Kcal/mol

c. 100 kJ/mol

d. 200 Kcal/mol

143. Which of the following statement is/are true?

a. work is a state function

b. temperature is a state function

c. change in the state is completely defined when the initial and final state are specified

d. all of them

144. Which of the following is/are true?

a. A spontaneous process is one that can proceed on its own.
b. The reverse of a non-spontaneous process is always spontaneous.
c. A spontaneous process need not occur immediately.
d. A spontaneous process must be exothermic and must have an increase in entropy.

145. Which of the following expression is correct for an adiabatic process?

a. $(T_2/T_1) = (V_1/V_2)^{\gamma - 1}$
b. $P_2/P_1 = (T_1/T_2)^{\gamma - 1/r}$
c. $P_2V_2^{\gamma} = P_1V_1^{\gamma}$
d. $P_1V_1^{\gamma - 1} = P_2 V_2^{\gamma - 1}$

146. For which change $\Delta H = \Delta E$

a. $H_2 + I_2 \leftrightarrow 2HI$
b. $HCl + NaOH \rightarrow NaCl + H_2O$
c. $C(s) + O_2 (g) \leftrightarrow CO_2 (g)$
d. $N_2 + 3H_2 \rightarrow 2NH_3$

147. Which statement is/ are not true about the formation of $CaCO_3$ (s) from CaO (s) and CO_2 (g) at 1.00 atm?

$CaO (s) + CO_2 (g) \rightarrow CaCO_3 (s)$
$\Delta H^o = -178.7$ kJ and $\Delta S^o = -150.4$ JK^{-1}

a. The reaction is spontaneous at low temperature.
b. The reaction is spontaneous at all temperatures.
c. The reaction is not spontaneous at any temperature
d. The reaction is spontaneous at high temperatures.

148. The correct statement/s among the following is/are

a. mass plus energy of the universe remains always constant while entropy of the universe remains increasing continuously
b. an exothermic reaction with ΔS being positive, will be spontaneous only at high temperature
c. in a reversible process, the system always in equilibrium with surroundings
d. in any cyclic process ΔX = 0 where X is a state fuction.

149. Which of the following reaction is exothermic?

a. C (diamond) → C (graphite)
b. $C_2H_6 \rightarrow C_2H_4 + H_2$
c. $C_2H_6 + 7/2\ O_2 \rightarrow 2CO_2 + 3H_2O$ (l)
d. $2NaOH (aq) + H_2SO_4 (aq) \rightarrow Na_2SO_4 (aq) + 2H_2O$ (l)

150. For which reaction change of entropy will be negative?

a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
b. $MgO_{(s)} + H_{2(g)} \rightleftharpoons Mg_{(g)} + H_2O_{(l)}$
c. $NH_4NO_{3(s)} \rightleftharpoons N_2O_{(g)} + 2H_2O_{(g)}$
d. $HCl_{(g)} + NH_{3(g)} \rightleftharpoons NH_4Cl_{(s)}$

151. The correct statement amongst the following is/are

a. at equilibrium $\Delta H_{S, P} = 0$
b. the condition of equilibrium at constant P and T is that G must be minimum
c. at equilibrium $\Delta G_{P, T} = 0$
d. ΔG^o calculated using the equation; $\Delta G^o = -RT$ In Kp, is the free energy change of the reaction when each of the species (reactants and products) is in the standard state of unit activity that is, roughly unit concentration.

152. Correct statement among the following is/are

a. mass plus energy of the universe remains always constant while entropy of the universe remains increasing continuously
b. an exothermic reaction with ΔS being positive, will be spontaneous only at high temperature
c. in a reversible process the system always in equilibrium with surroundings
d. in any cyclic process ΔX = 0 where Xs a state fuction.

153. The enthalpy change for a reaction depends upon:

a. The differences in initial or final temperatures of involved substances
b. The nature of intermediate reaction steps
c. Use of different reactants for the same product
d. The physical states of reactants and products

154. Which of the following is/are correct?

a. Numerical value of ΔH is less than that of ΔE for the reaction $C (s) + ½\ O_2 (g) \rightleftharpoons CO (g)$
b. In an exothermic reaction, the enthalpy of products is less than that of the reactants
c. ΔH (fusion) = ΔH (sub) – ΔH (vap)
d. A reaction for which $\Delta H^o < 0$ and $\Delta S^o > 0$ is possible at all temperatures.

155. Among the following, the state function(s) is/are

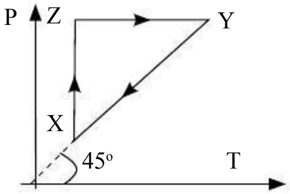
a. Internal energy
b. Irreversible expansion work
c. Reversible expansion work
d. Molar enthalpy

[IIT 2009]

Linked-Comprehension Type Questions

Comprehension 1

A cyclic process XYZX is shown in figure. The process is for 2 mole of monatomic gas. As the gas behaves ideally. So one can apply $PV = nRT$ for the gas. The work done by the gas in a process is given as $W = \int PdV$ P

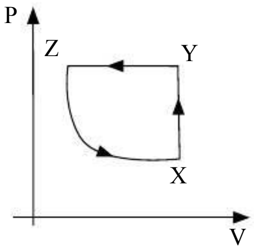


156. The process X→Y is isochoric. The volume of the gas numerically in this process is

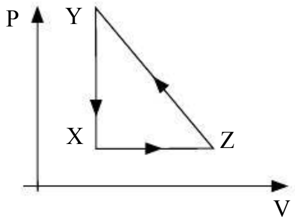
a. 3R **b.** 3R
c. 5/2 R **d.** 2R

157. The same cyclic process in the PV – diagram is

a.



b.



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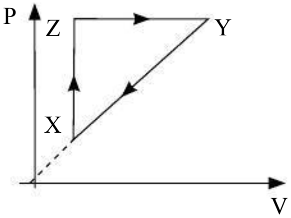
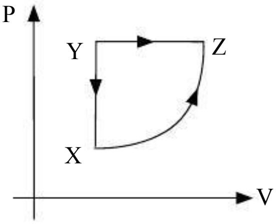


d.



158. During the process X→ Y, The internal energy of the gas

a. Depends on volume
b. Decreases
c. Increases
d. Does not change

Comprehension 2

The values of ΔH and ΔS generally do not vary much with temperature. As a consequence, the dependence of ΔG with temperature is governed mainly by the value of T in then expression $\Delta G = \Delta H - T\Delta S$. The entropy term $- T\Delta S$ has the greater effect on the spontaneity of the process.

Under non-standard conditions, ΔG is related to ΔG° and the value of the reaction quotient, Q : $\Delta = \Delta G^o - RT \ln Q$. At equilibrium ($\Delta G = 0$, $Q = K$), $\Delta G^o = -RT \ln$

159. If the value of equilibrium constant for the reaction given below is 4.4×10^{-4} at 298 K.

$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

Find ΔG° for this reaction.

a. –38.28 kJ **b.** –19.14 kJ
c. –9.57 kJ **d.** Zero

160. Find the value of ΔG when $[H^+] = 3.0 \times 10^{-10}$ M, $[CH_3NH_3^+] = 8.0 \times 10^{-3}$ M, and $[CH_3NH_2]$ =0.070M.

a. +11.8 **b.** –5.9
c. –10.8 **d.** – 11.8

161. A particular reaction given below can be spontaneous if

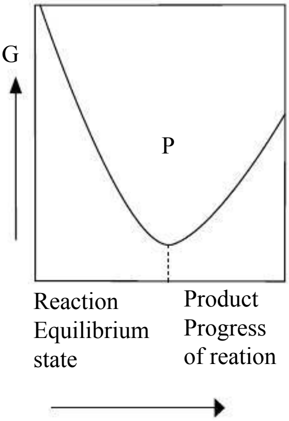
$2POCl_3(g) \rightarrow 2PCL_3(g) + O_2(g)$

$\Delta H^o = 572$ kJ; $\Delta S^o = 179$ J/K

a. T > 1200 K **b.** T > 1600 K
c. T > 2400 K **d.** T >3200 K

Comprehension 3

For a reversible reaction at constant temperature and at constant pressure the equilibrium composition of reaction mixture corresponds to the lowest point on Gibbs energy Vs progress of reaction diagrams as shown. At equilibrium, Gibbs energy of reaction (ΔG) is equal to zero.



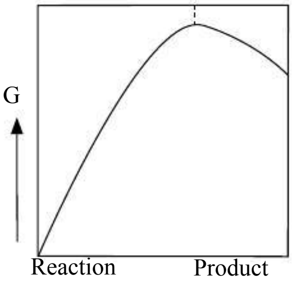
162. The value of $\log_{10} k_{eq}$ (equilibrium constant) can be given as

a. $\frac{\Delta G^o}{RT}$ **b.** $\frac{T\Delta S^o - \Delta H^o}{2.303RT}$

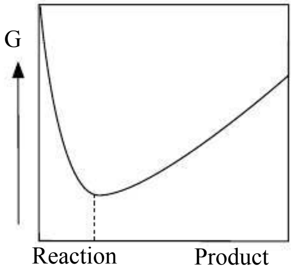
c. $\frac{\Delta H^o - T\Delta S^o}{2.303\ RT}$ **d.** $\frac{2.303\ RT}{T\Delta\ S^o - \Delta\ H^o}$

163. Which diagram represents the large value of equilibrium constant for the reversible reaction?

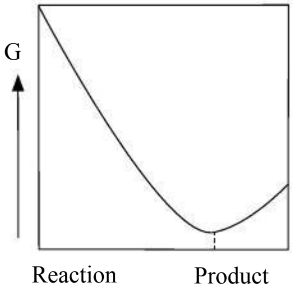
a.



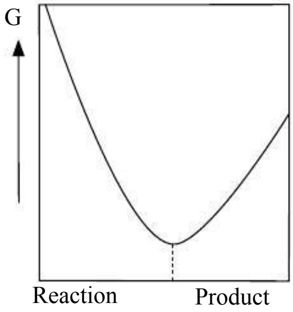
b.



c.



d.



164. The temperature dependence of the equilibrium constant can be given by the equation

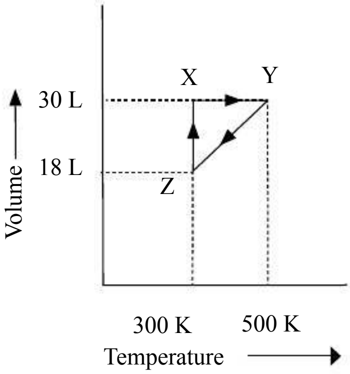
a. $\ln K = \frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$

b. $\ln K = -\frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$

c. $\ln K = \frac{\Delta G^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$

d. $\ln K = -\frac{\Delta G^o}{R}(T) + \frac{\Delta S^o}{R}$

Comprehension 4



Answer the following questions based on the given diagram:

165. Process , X → Y represents

a. Isobaric **b.** isochoric

c. isothermal **d.** adiabatic

166. The pressure at Z is

a. 3.518 atm **b.** 1.368 atm

c. 0.0821 atm **d.** 0.821 atm

167. The process which occurs in going from, Y → Z is

a. isothermal **b.** adiabatic

c. isochoric **d.** isobaric

Comprehension 5

Entropy is a measurement of randomness or disorder of any system. When a liquid is converted to the vapour state entropy of the system increases. Entropy in any of the phase transformation can be calculated by using this relation $\Delta S = \Delta H/T$.

In a reversible adiabatic process ΔS is zero. The rise in temperature in isobaric or isochoric process increases the randomness of system and it can be given by

$$\Delta S = 2.303 n\, C \log_{10} \frac{T_2}{T_1}$$

Here $C = C_P$ or C_V

168. The element gallium, Ga, freezes at 2.8°C, and its enthalpy of fusion is $\Delta H_{fus} = 5.59$ kJ /mol. Calculate the value of ΔS for the freezing of 90.0 g of Ga(*l*) at 29.8°C.

a. 47.6 J/K **b.** 23.8 J/K

c. 4.76 J/K **d.** 32.86 J/ K

169. Write the correct sequence of entropy change when a solid melt, a gas liquefies, liquid vapourizes and a solid dissolves in water.

a. Increases, increases, increases, increases respectively

b. Increases , decreases, increases, decreases respectively

c. Increases , decreases, increases, increases respectively

d. Decreases, increases, decreases, increases respectively

170. Find the entropy change when 0.5 M of an ideal gas expands at a constant temperature from an initial volume of 10 L to a final volume of 75 L.

a. 8.376 J /K **b.** 4.188 J/K

c. 16.752 J /K **d.** 7.367 J/ K

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

a. if A and R both are correct and R is the correct explanation of A;

b. if A and R both are correct but R is not the correct explanation of A;

c. A is true but R is false;

d. A is false but R is true,

e. both A and R are false.

171. **(A):** The enthalpy of formation of H_2O (*l*) is greater than that of H_2O (g).

(R): Enthalpy change is –ve for the condensation reaction,

$$H_2O\,(g) \rightarrow H_2O\,(l)$$

172. **(A):** Cp – Cv = R for ideal gas

(R): $(dU/dV)_T = 0$ for ideal gas

173. **(A):** All combustion reactions are exothermic.

(R): Products are more stable than reactants in exothermic process.

174. **(A):** Chlorine when tried to be solidified does not have zero entropy when at absolute zero.

(R): Chlorine contains a mixture of isotopes and is difficult to solidify.

175. **(A):** Heat of neutralization of HF is more than that of HCl by NaOH.

(R): HCl is stronger acid than HF.

176. **(A):** The thermodynamic function which determines the spontaneity of a process is the free energy, for a process to be spontaneous, the change in free energy must be negative.

(R): The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must be always positive if it is spontaneous.

177. **(A):** All exothermic reactions are spontaneous at room temperature.

(R): In ($\Delta G = \Delta H - T\Delta S$), ΔG becomes negative and negative sign of ΔG indicates spontaneous reaction.

178. **(A):** Endothermic reaction is spontaneous at all temperatures.

(R): ΔG is negative when $T\Delta S > \Delta H$

179. **(A):** As temperature increases, heat of reaction also increases for exothermic as well for endothermic reactions.

(R): ΔH varies with temperatures as given by

$$\Delta H_2 \text{ (at } T_2) = \Delta H_1 \text{ (at } T_1) + \Delta C_P (T_2 - T_1)$$

180. **(A):** Efficiency of a reversible engine is maximum (100%) when temperature of the sink is $-273^\circ C$ (T_1)

(R): η (efficiency) $= \dfrac{T_2 - T_1}{T_2}$

181. **(A):** As solid changes to liquid and then to vapour state, entropy increases.

(R): As going from solid to liquid and then to vapour state, disorder increases.

182. **(A):** In the case of an ideal gas, the changes in Gibbs and Helmholtz free energies are equal to each other ($\Delta G = \Delta A$) for isothermal reversible processes.

(R): There is no change in internal energies and enthalpies for ideal gases at constant temperature.

183. **(A):** When H_2O is added to CaO, heat is liberated.

(R): Reaction between CaO and H_2O is exothermic.

184. **(A):** In the following reaction

$$C(s) + O_2 (g) \rightarrow CO (g),$$

$$\Delta H = \Delta E - RT$$

(R): ΔH is related to ΔE by equation

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

185. **(A):** In the following reaction

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2, \Delta H = -68 \text{ kcal}$$

and thus

$$\Delta H_f(CO_2) = -68 \text{ kcal mol}^{-1}$$

(R): 1 mol of CO_2 is formed and enthalpy change is the heat of formation of CO_2.

186. **(A):** Heat of neutralization of HF (aq), a weak acid, with NaOH (aq) is less than 13.7 kcal, in an exothermic reaction.

(R): Some heat is lost in the ionization of a weak acid.

187. **(A):** The standard enthalpy of formation of graphic is taken as zero but of diamond is not zero but it is equal to 1.816 kJ/mol.

(R): Among carbon allotropes, diamond is taken as standard state.

188. **(A):** In case of some glassy solids having mixture of isotopes, crystals of CO, N_2O, NO etc. entropy is not zero even at absolute zero temperature

(R): These kind of solids do not have perfect order even at absolute zero temperature.

189. **(A):** Enthalpy changes are positive when $Na_2SO_4.10H_2O$, $CuSO_4.5H_2O$ and salts like NaCl, KCl etc. which do not form hydrates are dissolved in water. But enthalpy changes are negative when anhydrous salts capable of forming hydrates are dissolved in water.

(R): The difference in the behaviour is due to large differences in the molecular weights of hydrated and anhydrous salts. The substances with larger molecular weights usually show positive enthalpy change on dissolution.

190. **(A):** ΔE is state function of the system.

(R): As it depends upon the final and initial state of the system.

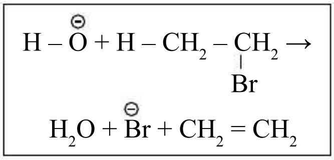
191. **(A):** In any reversible cycle process, the net increase in entropy of the system is zero.

(R): As $\Delta S_{universe} = \Delta S_{system} + \Delta Ssurr$ as in case of reversible cyclic process ΔSsystem is positive, but of surrounding is negative in same amount. That is why $\Delta S_{universe} = 0$

192. **(A):** The enthalpy of neutralization of equivalent of HF and 1 equivalent NaOH is 14 kcal/mol. which is higher than HCl and NaOH?

(R): It is because the enthalpy of hydration of F^- is higher that of is heat enthalpy of dissociation.

193. **(A):** The entropy change in the reaction.



$$H - \overset{\ominus}{O} + H - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH_2}} \rightarrow H_2O + \overset{\ominus}{Br} + CH_2 = CH_2$$

is positive

(R): Entropy increase when no. of particles or (i.e. molecules or ions) of the product or, in the product directions increases.

(194) (A) The amount of work done in the isothermal expansion is greater than work done in the adiabatic system for same final volume.

(R) In the adiabatic expansion of a gas temperature and pressure both decrease due to decrease in internal energy of the system.

195. **(A):** There is a natural asymmetry between converting work to heat and converting heat to work.

(R): No process is possible in which the sole result in the absorption of heat from a reservation and its complete conversion into work

Matrix-Match Type Questions

196. Match the following:

List I	List II
A. Cyclic process	(p) ΔH is positive
B. Spontaneous	(q) $\Delta E = 0, \Delta H = 0$
C. Endothermic	(r) ΔG is negative
D. A process in equilibrium	(s) $\Delta G = 0$

197. Match the following:

List I	List II
A. Reversible adiabatic compression	(p) $\Delta_{\text{Surrounding}} < 0$
B. Reversible vaporization of liquid	(q) $\Delta_{\text{Surrounding}} = 0$
C. $2N(g) \rightarrow N_2(g)$	(r) $\Delta S_{\text{system}} > 0$
D. $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$	(s) $\Delta S_{\text{system}} < 0$

198. Match the following:

List I	List II
A. Reversible isothermal expansion	(p) $w = -RPext\dfrac{[T_2P_1 - T_1P_2]}{P_1 P_2}$
B. Irreversible isothermal expansion	(q) $w = \dfrac{R}{\gamma - 1}[T_2 - T_1]$
C. Reversible adiabatic expansion	(r) $w = -Pext(V_2 - V_1)$
D. Irreversible adiabatic expansion	(s) $w = -2.303\ RT \log_{10} V_2/V_1$

199. Match the following.

List I	List II
A. Ice $\rightleftharpoons$ H_2O (*l*) at room temperature 25°C	(p) ΔH = –ve, ΔS = +ve
B. $NH_2COONH_4(s) \rightarrow 2NH_3(g) + CO_2(g)$	(q) ΔG = +ve
C. $2O_3(g) \rightarrow 3O_2(g)$	(r) ΔH = +ve, ΔS = –ve
D. $3O_2(g) \rightarrow 2O_3(g)$	(s) ΔG = –ve

200. Match the following:

List I	List II
A. Internal energy of O_2 gas at 0 K (–273°C)	(i) exothermic reaction
B. heat of combustion of N_2	(ii) < 13.7 Kcal
C. heat of neutralization of HCl and CH_3COOH	(iii) 0
D. $2CO + O_2 \rightarrow CO_2$	(iv) +ve

201. Match the following:

List I	List II
A. Formation of ammonia	(p) Endothermic
B. Formation of nitric oxide	(q) Exothermic
C. Heat of neutralization of HF	(r) > 13.7 kcal
D. Heat of combustion	(s) may be exothermic or endothermic

202. Match the following:

List I	List II
A. ΔS gas for isothermal of an ideal gas	(p) $nR \ln\left(\dfrac{P_1}{P_2}\right)$
B. Work done in reversible isothermal ideal gas expansion	(q) –nFE
C. ΔG for reversible isothermal expansion of an ideal gas	(r) $nRT \ln\left(\dfrac{P_2}{P_1}\right)$
D. $(\Delta G_{\text{system}})T, P$	(s) $nR \ln\left(\dfrac{V_2}{V_1}\right)$

203. Match the following:

List I	List II (Heat of neutralization)
A. $H_2SO_4 + NaOH$	(p) 13.7 Kcal
B. $H_2SO_4 + NH_4OH$	(q) > 13.7 kcal
C. $CH_3COOH + NH_4OH$	(r) < 13.7 kcal
D. NaOH + HF	(s) cannot be said

204. Match the following:

List I	**List II**
1. Exothermic substance	(i) Less stable
2. Endothermic substance	(ii) More stable
3. Heat of formation	(iii) Exothermic
4. Heat of combustion	(iv) May be exothermic or endothermic
	(v) Endothermic

The IIT-JEE Corner

205. Molar heat capacity of water in equilibrium with ice at constant pressure is

a. zero
b. infinity
c. 40.45 J K^{-1} mol^{-1}
d. 75.48 J K^{-1} mol^{-1}

[IIT 1997]

206. Standard molar enthalpy of formation of CO_2 is equal to

a. zero
b. the standard molar enthalpy of combustion of gaseous carbon.
c. the sum of standard molar enthalpies of formation of CO and CO_2
d. the standard molar enthalpy of combustion of carbon (graphite)

[IIT 1997]

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

a. 7.9 km **b.** 9.7 km
c. 4.8 km **d.** 8.4 km

[IIT 1997]

208. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (ionization energy of Al = 5137 kJ mol^{-1}, $\Delta H_{\text{hydration}}$ for Al^{+3} = – 4665 kJ mol^{-1}, $\Delta H_{\text{hydration}}$ for Cl^- = –381 kJ mol^{-1})

a. ionic **b.** covalent
c. both **d.** none

[IIT 1997]

209. Calculate the enthalpy change for the combustion of cyclopropane at 298 K, if the enthalpy of formation CO_2 (g), $H_2O(l)$ and propene (g) are –393.5, –385.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerization of cyclopropane to propene is –33.0 kJ mol^{-1}.

a. 1802 kJ mol^{-1} **b.** 2091 kJ mol^{-1}
c. 2196 kJ mol^{-1} **d.** none

[IIT 1998]

210. Which of the following is not an endothermic reactions?

a. combustion of methane
b. decomposition of water
c. dehydrogenation of ethane or ethylene
d. conversion of graphite to diamond

[IIT 1999]

211. The ΔH^o_f for $CO_2(g)$, CO(g) and $H_2O(g)$ are –393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$CO_2\ (g) + H_2\ (g) \rightarrow CO(g) + H_2O(g)$ is

a. 524.1 **b.** 41.2
c. –262.5 **d.** –41.2

[IIT 2000]

212. Which of the following statement is false?

a. work is a state function
b. temperature is a state function
c. change of state is completely defined when initial and final states are specified.
d. work appears at the boundary of the solution.

[IIT 2001]

213. In thermodynamics, a process is called reversible when

a. surroundings and system change into each other
b. there is no boundary between system and surroundings
c. the surroundings are always in equilibrium with the system
d. the system changes into the surroundings spontaneously

[IIT 2001]

214. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU = 30.0 L atm. The change in enthalpy (ΔH) of the process in L atm is

a. 40.0
b. 42.3
c. 44.0
d. not defined, because pressure is not constant

[IIT 2002]

215. Which of the following reaction defines ΔH^o_f?

a. C (diamond) + O_2 (g) → CO_2 (g)

b. ½ H_2 (g) + ½ F_2 (g) → HF (g)

c. N_2 (g) + $3H_2$ (g) → $2NH_3$ (g)

d. CO (g) + ½ O_2 (g) → CO_2 (g)

[IIT 2003]

216. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre of 10 litre at 300 K. The enthalpy change (in kJ) for the process is

a. 11.4 kJ **b.** –11.4 kJ

c. 0 kJ **d.** 4.8 kJ.

[IIT 2004]

217. The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is 5 J mol^{-1} K. The boiling point of the liquid at 1 atm is

a. 250 K **b.** 400 K

c. 450 K **d.** 600 K

[IIT 2004]

218. One mole of monatomic ideal gas at T (K) is expanded from 1_l to 2_l adiabatically under a constant external pressure of 1 atm the final temperature of the gas in Kelvin is

a. T

b. $T/2^{5/3-1}$

c. $T - \dfrac{2}{3 \times 0.0821}$

d. $T + \dfrac{3}{2 \times 0.0821}$

[IIT 2005]

219. For the reaction, $2CO + O_2 \rightarrow 2CO_2$, $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K.

(1 L atm = 0.1 kJ)

a. 557 KJ **b.** 55.7 KJ

c. 278 KJ **d.** 27.8 KJ

[IIT 2006]

220. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given

$$\Delta S_{(A \rightarrow C)} = 50 \text{ e.u.}$$
$$\Delta S_{(C \rightarrow D)} = 30 \text{ e.u.}$$
$$\Delta S_{(B \rightarrow D)} = 20 \text{ e.u.}$$

where e.u. is entropy unit then ΔS (A →B) is

a. +100 e.u. **b.** +60 e.u.

c. –100 e.u. **d.** –60 e.u.

221. For the process

H_2O (l) (1 bar, 373 K) → H_2O (g) (1 bar, 373 K), the correct set of thermodynamic parameters is

a. ΔG = 0, ΔS = +ve

b. ΔG = 0, ΔS = –ve

c. ΔG = +ve, ΔS = 0

d. ΔG = –ve, ΔS = +ve

[IIT 2007]

222. The value of $\log_{10}$ K for a reaction A ⇌ B is (Given: $\Delta_r H^o_{298\,K} = -54.07$ kJ mol^{-1}, $\Delta_r S^o_{298\,K} = 10$ JK^{-1} mol^{-1} and R = 8.314 JK^{-1} mol^{-1}; 2.303 × 8.314 × 298 = 5705)

a. 10 **b.** 100

c. 5 **d.** 95

[IIT 2007]

223. In a constant volume calorimeter, 3.5 of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

a. 10 **b.** 100

c. 5 **d.** 95

[IIT 2009]

ANSWERS

Straight Objective Type Questions

1. d	**2.** d	**3.** d	**4.** b	**5.** d	**6.** d	**7.** a	**8.** b	**9.** a
10. c	**11.** d	**12.** c	**13.** d	**14.** a	**15.** c	**16.** c	**17.** c	**18.** c
19. d	**20.** a	**21.** d	**22.** d	**23.** a	**24.** d	**25.** a	**26.** b	**27.** a
28. c	**29.** b	**30.** a	**31.** c	**32.** c	**33.** a	**34.** d	**35.** a	**36.** b

37. a **38.** a **39.** a **40.** a **41.** b **42.** b **43.** d **44.** b **45.** d

46. b **47.** d **48.** d **49.** c **50.** b **51.** a **52.** a **53.** b **54.** d

55. a **56.** b **57.** a **58.** c **59.** a **60.** a **61.** d **62.** b **63.** b

64. b **65.** d **66.** a **67.** c **68.** b **69.** b **70.** d **71.** d **72.** c

73. a **74.** c **75.** c

Brainteasers Objective Type Questions

76. a **77.** c **78.** b **79.** a **80.** a **81.** d **82.** a **83.** a

84. c **85.** b **86.** c **87.** b **88.** a **89.** c **90.** b **91.** c

92. d **93.** b **94.** b **95.** a **96.** d **97.** a **98.** a **99.** d

100. a **101.** d **102.** b **103.** b **104.** c **105.** b **106.** b **107.** d

108. b **109.** d **110.** a **111.** a **112.** a **113.** b **114.** c **115.** d

116. a **117.** b **118.** d **119.** c **120.** a **121.** d **122.** a **123.** a

124. b **125.** a

Multiple Correct Answer Type Questions

126. c, d **127.** a, c, d **128.** a, b, c **129.** a, d **130.** a, b, d **131.** a, c, d

132. a, b, c **133.** a, d **134.** b, c, d **135.** a, b, d **136.** a, c **137.** a, c

138. b,c,d **139.** c, d **140.** c, d **141.** b, c, d **142.** a, d **143.** b, c

144. a, b, c **145.** a, c **146.** a,b,d **147.** b,c,d **148.** a,c.d **149.** a,c,d

150. a, b, d **151.** a, b, d **152.** a, c, d **153.** a, c, d **154.** b, c, d **155.** a, c, d

Linked-Comprehension Type Questions

Comprehension 1

156. d **157.** a **158.** c

Comprehension 2

159. b **160.** d **161.** d

Comprehension 3

162. b **163.** c **164.** b

Comprehension 4

165. b **166.** b **167.** d

Comprehension 5

168. b **169.** c **170.** a

Assertion-Reason Type Questions

171. a **172.** b **173.** a **174.** a

175. b **176.** a **177.** a **178.** a

179. d **180.** a **181.** a **182.** a

183. b **184.** d **185.** e **186.** e

187. c **188.** a **189.** a **190.** a

191. c **192.** a **193.** a **194.** a

195. a

Matrix-Match Type Questions

196. A-(q), B-(r), C-(p), D-(s)

197. A – (q), B – (p, r), C – (s), D – (p, r)

198. A-(s), B-(r), C-(q), D-(p)

199. A - (s), B – (q), C- (p, s), D – (q, r)

200. A – (r), B- (s), C – (q), D - (p)

201. A -(q), B – (p), C – (r), D – (q)

202. A – (q), B – (r), C – (r), D – (p, s)

203. A – (p), B – (r), C – (r), D – (q)

204. A – (q), B – (p), C- (s), D – (r)

The IIT-JEE Corner

205. b **206.** d **207.** c **208.** a **209.** b **210.** a **211.** b **212.** a

213. c **214.** c **215.** b **216.** c **217.** b **218.** c **219.** a **220.** b

221. a **222.** a **223.** c

Hints and Explanations

1. It gives the neutralization of 1 mole H^+ and 1 mole of OH^- ions.

2. $q = \Delta E - w$ (first law of thermodynamics)

$q + w = \Delta E$

Now q + w is a state function as it is equal to ΔE (state function).

3. Equal to ΔH.

4. Standard heat of formation of C_2H_4 is the heat change when 1 mole of C_2H_4 is formed from its elements in the standard state [carbon as graphite and hydrogen as H_2]

6. ΔHobs = ΔH + Energy needed to disturb resonance

$= 3 \times -119.5 + 150.4 = -208.1$ kJ mol^{-1}

8. $\Delta H = \Delta U + \Delta nRT$

(here Δn = number of molecules of products – no. of molecules of reactants)

$-92.38 \times 1000 = \Delta U - 2 \times 8.314 \times 298$

$\Delta U = -87424$ J $= -87.424$ kJ.

9. $\Delta G^{o} = -RT\ \text{In}K$

[ΔG^{o} = standard free energy change,

K = equilibrium constant

If a substance is in equilibrium between two phases at constant temperature and pressure , its chemical potential must have the same value in both the phases.

So $\Delta G^{o} = 0$

10. At equilibrium ΔG = 0. So ΔH = TΔS

So $T = \Delta H/\Delta S = 30 \times 10^{-3}/105$

$= 285.7$ K

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

For a spontaneous process ΔS_{total} must be positive that is, $\Delta S_{\text{total}} > 0$

13. At equilibrium ΔG = 0

14. Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so $w = 0$ and $\Delta U = q$.

$\Delta U < 0$, $w = 0$.

15. Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst.

$$\text{C (graphite)} + \tfrac{1}{2}O_2 \rightarrow \text{CO (g)} \ \ldots\text{(i)}$$

$$\underline{\text{CO (g)} + 2H_2\text{ (g)} \rightarrow CH_3OH\ (l) \ \ldots\text{(ii)}}$$

$$\text{C(graphite)} + \tfrac{1}{2}O_2\text{(g)} + 2H_2\text{(g)} \rightarrow CH_3OH(l)$$

16. As $\Delta n = 0$ so $\Delta H = \Delta U$

17. MgO is the oxide of weak base and we know that heat of neutralization of 1 eq. of strong acid with strong base is –57.33 kJ/mol.

⇒ With weak base some heat is absorbed in dissociation of weak base.

⇒ Heat of neutralization of weak base with strong acid will be –57.33 kJ/mol.

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

ΔG = –ve for spontaneous reaction

when ΔS = +ve, ΔH = +ve

and $T\Delta S > \Delta H \Rightarrow \Delta G$ = –ve

When randomness favours and energy factor do nor favour then spontaneity depends upon the temperature dependent means at high temperature.

$T\Delta S > \Delta H$, ΔG = –ve and reaction is feasible.

19. $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

ΔH = (BE)reactants – (BE)products

$= 4\,(BE)_{C-H} + (BE)_{C=C}^{+} + (BE)_{H-H}$

$- [6(BE)_{C-H} + (BE)_{C-C}]$

$= -125$ kJ

23. For a spontaneous reaction ΔH = –ve,

ΔS = +ve spontaneity depends upon both critical minimum energy and maximum randomness/disorder.

24. $\Delta E = 0$, in a cyclic process.

26. Work done due to change in volume against constant pressure is

$W = -P(V_2 - V_1) = -1 \times 10^5\ \text{Nm}^{-2}$

$(1 \times 10^{-2} - 1 \times 10^{-3})\ \text{m}^3$

$= -900$ Nm $= -900$ J.

28. From solid state to liquid state entropy increases.

31. $N_2 + 3H_2 \rightarrow 2NH_3$

$\Delta n = 2 - 4 = -2$

$\Delta H = \Delta U + \Delta nRT = \Delta U - 2RT$

$\Delta H < \Delta U$.

32. $W = -2.303\ nRT \log \dfrac{V_2}{V_1}$

$= -2.303 \times 1 \times 2 \times 300 \times \log \dfrac{10}{1}$

$= -1381.8$ cal.

37. Work done is reversible process is maximum. Thus $T_2 << T_1$ in reversible process or $T_{2rev} << T_2$ irr.

42. $\Delta H = \Delta E + \Delta ng\ RT$

as $\Delta ng = np - nr = 8 - 8 = 0$,

thus $\Delta H = \Delta E$.

44. $C(s) + \tfrac{1}{2}O_2\ (g) \rightarrow CO\ (g)$; $(\Delta n = 1 - \tfrac{1}{2}) = \tfrac{1}{2}$

$\Delta H - \Delta U = \Delta nRT = +\tfrac{1}{2} \times 8.314 \times 298$

$= +1238.78\ \text{J mol}^{-1}$

45. For the reaction

$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 3CO_2\ (g) + 4H_2O\ (l)$

$\Delta n = n_P - n_R$

$= 3 - 6 = -3$

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

$\Delta H - \Delta E = \Delta nRT = -3RT$

46. $\Delta S = \dfrac{\Delta H_f}{T} = \dfrac{6.0}{273} = 0.02198\ \text{kJ K}^{-1}\ \text{mol}^{-1}$

$= 0.02198 \times 1000\ \text{JK}^{-1}\ \text{mol}^{-1}$

$= 21.98\ \text{JK}^{-1}\ \text{mol}^{-1}$

48. $C = \dfrac{q}{m(T_2 - T_1)}.$

$75 = \dfrac{1000}{5.55(\Delta T)}$ (m = 100/8 = 5.55)

$\Delta T = \dfrac{1000}{5.55 \times 75} = 2.4$ K

50. In irreversible process

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

so in the spontaneous process ΔS is positive

54. (i) $\frac{1}{2} N_2 + O_2 \rightarrow NO_2$; $\Delta H = 8.0$ kcal

(ii) $N_2 + 2O_2 \rightarrow N_2O_4$; $\Delta H = 2.0$ kcal

$2NO_2 \rightarrow N_2O_4$; $\Delta H = ?$

multiply (i) by 2 subtract from (ii), we get

$2NO_2 \rightarrow N_2O_4$; $\Delta H = -14$ kcal

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

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

$= -1381.8 \approx -.1382$ cal

56. Weakest acid has the lowest heat of neutralization because more heat is absorbed in the ionization of weak acid

57. A salt which absorbs more heat for dissolution in water give maximum cooling.

58. T (m.p) = 27 + 273 = 300 K

$\Delta H_{fus.} = 600$ cal/mole

$\Delta S = \frac{\Delta H}{T} = \frac{600}{300} = 2$

59. On set of crystallization in a super cooled liquid is called Devitrification. The process of crystallization leads to decrease in entropy.

60. $N_2O_4 \leftrightarrow 2NO_2$

On heating, since the colour depends that is more of NO_2 is formed and the forward reaction is favoured. Thus, the forward reaction is endothermic that is, $\Delta H = +ve$

62. Heat of combustion is always negative.

63. ΔH^o_f of graphite is taken as zero. For diamond, its value is 1.9 kJ mol^{-1} that is, greater than graphite.

64. The molar heat capacity is the heat required to raise the temperature of one mole of the gas by 1°C.

$C_V = \frac{3}{2} R$

40 gram of argon means 1 mole.

Here $C_V = 3$ cal

Thus the heat required to raise the temperature by 60°C is 60 × 3 = 180 cal.

66. Smallest = eV and largest = lit atm

1 eV = 1.6×10^{-19} J,

1 cal = 4.186 J,

1 erg = 10^{-7} J

1 lit atm = 101.3 J

67. As $\Delta G^o = -RT \ln K$.

When K < 1.0, $\Delta G^o = +ve$

68. State functions or state variables depend only on the state of the system. Here 'w' represents work done and 'q' represents amount of heat so both of these are not state functions.

69. For this process $\frac{1}{2} Cl_2\ (g) \rightarrow Cl^-\ (aq)$

$\Delta H = \frac{1}{2} \Delta H_{diss}$ of $Cl_2 + \Delta_{eq} Cl + \Delta_{hyd} Cl^-$

$= +\frac{240}{2} - 349 - 381$

70. $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

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

Here, Δn = Change in number of moles of product and reactant

As Δn + ve, so ΔH = +ve

$\Delta S = S_{Product} - S_{Reactant}$

ΔS = +ve

71. $S(rh) + 3/2O_{2(g)} \rightarrow SO_{3(g)}$, $\Delta H_1 = 2x$kJ mol^{-1} (i)

$SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow SO_{3(g),}$ $\Delta H_2 = -$ yJ mol^{-1} (ii)

From equation (i) – (ii) we have

$S_{(rh)} + O_{2(g)} \rightarrow SO_{2(g)}$; $\Delta H_f = \Delta H_1 = \Delta H_2 = -2x + y$

Here of formation of SO_2 $(\Delta H_f) = y - 2x$

72. Al acts as a good reducing agent and reduces oxides of metals like Cr, Fe, Mn, etc.

$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$ + heat

Therefore ΔG° for the formation of Al_2O_3 is lower in comparison to ΔG° for the formation of Cr_2O_3.

73. $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(g)}$

Δn = no. of moles of product – no. of moles of reactant

= 1 – 2

Δn = – 1

Now, $\Delta H = \Delta E + \Delta nRT$

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

As, ΔE > ΔH (ΔE – ΔU) = change in internal energy.

75. It can be derived as

$[\partial(\Delta G/T)/\partial T]_P = -\Delta H/T^2$

$\Delta H = -T^2 [\partial(G/T)/\partial T]_P$

It is a form of Gibbs-Helmholtz equation.

Brainteasers Objective Type Questions

76. Given

(i) $C_6H_{10} + H_2 \rightarrow C_6H_{12}$; $\Delta H = -119$ kJ mol^{-1}

This reaction involves breaking up of one double bond and addition of one H_2 molecule.

$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$;

$\Delta H = 3 \times -119 = -357$ kJ

(because, this reaction involves breaking up of one double bond and addition of three H_2 molecules).

Also given

$6C + 6H_2 \rightarrow C_6H_{12}$; $\Delta H = -156$ kJ

$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$; $\Delta H = -357$ kJ

$6C + 3H_2 \rightarrow C_6H_6$; $\Delta H = +201$ kJ

Thus, resonance energy = difference between ΔH_f (obs) – ΔH_f (calc) = 49 – 201 = – 152 kJ

77. (c) For the temperature of the solution decrease the solvent water must lose energy. The process of ammonium and nitrate ions in solid ammonium nitrate dissolving and becoming hydrated must therefore absorb energy from water.

79. $\Delta H - \Delta E = \Delta ng\ RT$

$$= (12 - 15) \times \frac{8.314}{1000} \times 298$$

$= -7.433$ kJ mol^{-1}

80. Amount of HCl added $= \dfrac{100 \times 0.3}{1000}$

= 0.03 mol

Amount of NaOH added $= \dfrac{100 \times 0.33}{1000}$

= 0.033 mol

limiting reagent = 0.03 mol of HCl

So amount of heat evolved = 57.1 × 0.03

= 1.713 kJ

81. Amount of energy left unused

$$= \frac{1560}{2} = 780 \text{ kJ}$$

Amount of water perspired

$$= \frac{\text{Energy left unused}}{\text{Enthalpy of evaporation of water}}$$

$$= \frac{780 \text{ kJ}}{44 \text{ kJ mol}^{-1}} = \frac{780}{44} \text{ mole}$$

$$= \frac{780 \times 18}{44} = 319.14 \text{ g}$$

82. $\Delta H_{CO_2}/\Delta H_{CO} = 2.56$

$\Delta H_{CO2} = 2.56\ \Delta H_{CO}$

$177.5 = \Delta H_{CO} - \Delta H_{CO2}$

$= \Delta H_{CO} - 2.56\ \Delta H_{CO}$

$$\Delta H_{CO} = -\frac{177.5}{1.56} = -113.78 \text{ kJ mol}^{-1}$$

83. For dissolution of gases in water, ΔS = –ve (non-favorable factor). Since this process is spontaneous (ΔG = –ve) so ΔH has to be –ve (favorable factor) and the process is exothermic.

84. Given that

(i) $H_2\ (g) + ½\ O_2\ (g) \rightarrow H_2O\ (l)$;

$\Delta H = -241$ kJ

(ii) $C_6H_{10} + 17/2\ O_2 \rightarrow 6CO_2\ (g) + 5H_2O$;

$\Delta H = -3800$ kJ

(iii) $C_6H_{12} + 9O_2 \rightarrow 6CO_2\ (g) + 6H_2O\ (l)$;

$\Delta H = -3920$ kJ

Our aim is to get

$C_6H_{10} + H_2 \rightarrow C_6H_{12}$; $\Delta H = ?$

So Add (i) and (ii) and then subtract (iii), to get

$\Delta H = -121$ kJ mol^{-1}

86. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$= [\Delta H_f(CO_2) + 2\ \Delta H_f(H_2O)] - [\Delta H_f(CH_4) + 2\ \Delta H_f(CO_2)]$

$= [-394.8 + 2 \times -241.6] - [-76.2 + 0]$

$= -878.0 + 76.2 = 802.2\ \text{kJ mol}^{-1}$

now 22.4 L (or $22.4 \times 10^{-3}\ \text{m}^3$) of CH_4 on combustion give heat = $802.2\ \text{kJ mol}^{-1}$

$$1\ \text{m}^3 = \frac{802.2}{22.4 \times 10^{-3}}.$$

$= 35812\ \text{kJ mol}^{-1}$

88. $N \equiv N + \frac{1}{2} O = O \rightarrow N = N = O$

$\Delta H^\circ_f = \sum BE$ of reactants – $\sum BE$ of products

$= [BE\ (N{\equiv}N) + \frac{1}{2}\ BE(O{=}O)] - [BE(N{=}N) + BE(N{=}O)]$

$= (946 + \frac{1}{2} \times 498) - (418 + 607) = 170\ \text{kJ}$

resonance energy

$= \Delta H^\circ_f$ (observed) – ΔH°_f (calculated)

$= 82 - 170 = -88\ \text{kJ mol}^{-1}$

89. $I_2\ (s) + Cl_2\ (g) \rightarrow 2ICl\ (g); \Delta H$

$\Delta H = [\varepsilon Cl_2 + \varepsilon 2(s) \rightarrow (g) + \varepsilon I_2(g)] - 2 \times [\varepsilon ICl]$

$= [242.3 + 62.76 + 151.0] - 2 \times [211.3]$

$= 33.46$

$$\Delta H_f = \frac{33.46}{2} = 16.83\ \text{kJ mol}^{-1}$$

93. Our aim is $\frac{1}{2} Cl_2\ (g) + (aq) \rightarrow Cl^-\ (aq)$;

$\Delta H = ?$

Given is

(i) $\frac{1}{2} H_2 (g) + \frac{1}{2} Cl_2\ (g) \rightarrow HCl\ (g)$

$\Delta H = -92.4\ \text{kJ}$

(ii) $HCl\ (g) + (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$

$\Delta H = -74.8\ \text{kJ}$

(iii) $\frac{1}{2} H_2\ (g) + (aq) \rightarrow H^+\ (aq);$

$\Delta H = 0.0\ \text{kJ}$

Operate (i) + (ii) – (iii), we obtain

ΔH°_f of Cl^- (aq) = –167.2 kJ

0.16 g of methane is subjected to combustion at 27°C in a bomb calorimeter system. The temperature of the calorimeter system (including water) was found to rise by 0.5°C.

95. $$\Delta E \text{ per mole} = \frac{327}{7.8} \times 78 = -3270\ \text{kJ}$$

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

$R = 8.3/1000\ \text{kJ mol}^{-1}\ K^{-1}$

$C_6H_6\ (l) + 15/2\ O_2\ (g) \rightarrow 6CO_2\ (g) + 3H_2O(l)$

$\Delta n_g = n_p - n_r = 6 - 15/2 = -3/2$

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

$\Delta H = -3270 + [(-3/2) \times (8.3/1000) \times 300]$

$\Delta H = -3274$ kJ]

98. For Li_2O,

$2Li\ (s) + \frac{1}{2} O_2\ (g) \rightarrow Li_2O\ (s)$

$\Delta G^\circ_f\ (Li_2O) = \Delta H^\circ_f - T\Delta S^\circ$

$= 1244 - (298 \times 6) = -544\ \text{kJ mol}^{-1}$

For Na_2O,

$2Na\ (s) + \frac{1}{2} O_2\ (g) \rightarrow Na_2O\ (s)$

$\Delta G^\circ_f\ (Na_2O) = \Delta H^\circ_f - T\Delta S^\circ$

$= 1411 - (298 \times 6) = -377\ \text{kJ mol}^{-1}$

For reaction,

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

$\Delta G^\circ = 3 \times \Delta G^\circ_f\ (Na_2O) - \Delta G^\circ_f\ (Al_2O_3)$

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

Similarly when Li is used, then

$\Delta G^\circ = 3 \times \Delta G^\circ_f\ (Li_2O) - \Delta G^\circ_f\ (Al_2O_3)$

$= 3 \times (-544) - (-1582)$

$= -1632 + 1582 = -50\ \text{kJ mol}^{-1}$

As ΔG° is negative when Li is used for the reduction, so the reaction is feasible.

99. $\Delta n_g = n_p - n_r = 5 - 3 = 2$

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

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

$= 19 - (2 \times 2 \times 10^{-3} \times 300)$

$= 19 - 1.2 = 17.8$ kcal

100. $\Delta H = m \times T_b$

$= 90 \times 540 = 48600$ cal

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

$\Delta H = \Delta E + P(V_g - V_t)$

since the volume of liquid is negligible as compared to volume of its vapour, so

$V_g > > > V_l$

$\Delta H = \Delta E + P.V_g$

$\Delta H = \Delta E + nRT \qquad (PV = nRT)$

$\Delta E = \Delta H - nRT$

$= 48600 - (90/18 \times 2 \times 373)$

$= 44870$ cal.

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

$= nRT_2 - nRT_1$

$T_2 - T_1 = \frac{W}{nR}.$

$Q = n\,C_P\,(T_2 - T_1)$

$506 = n\,C_P \frac{W}{nR}.$

$506 = \frac{C_P W}{R}$

$C_P = \frac{506\ R}{144.5} = 7/2\ R$

So gas is diatomic O_2.

103. $\Delta G^o = -2.303\ RT \log K$

$-4.606 = -2.303 \times \frac{2}{100} \times 500 \log K$

$\log K = \frac{-4.606}{-2.303 \times 2/100 \times 500} = 2$

K = antilog (2) = 100

107. $CaCO_3\,(s) + 42.5\ \text{Kcal} \rightarrow CaO\,(s) + CO_2\,(g)$

Energy is supply to the system for complete the reaction that is, energy of the reactant side is less than the product side.

108. Here, option c is not correct as

$Z \rightarrow x$ is isochoric process

$V \rightarrow$ constant

i.e., $P \alpha T$

$P_X > P_Z$

$T_X > T_Z$ or $\Delta UZ. \times$ is positive and not negative.

109. (i)

W_{rev}, isothermal $= n \times 2.303\ RT \log \frac{P_1}{P_2}$

$= 2\ \text{mol} \times 2.303 \times 2\ \text{cal}\ K^{-1}\ \text{mol}^{-1} \times 300\ \text{K}x1$

$= 2764$ cal

(ii) Work of expansion = P. ΔV

$= 1$ atm $\times 0.08212$ lit

$= 0.08212$ lit-atm $= 2$ cal

110. For reversible adiabatic change,

$T.V^{\gamma - 1} = \text{constant}$

$\frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} = (1/10)^{\gamma - 1} = (1/10)^{0.666}$

Since γ for a monobasic gas $= 5/3 = 1.666$.

111. As C (graphite) → C (gas)

$\Delta H = 725$ kJ/mol

As graphite is thermodynamically more stable than diamond therefore the heat required to convert graphite to gaseous carbon should be more.

112. $H_2 + Cl_2 \rightarrow 2HCl$

ΔHreaction = Σ(B.E)reactant – Σ(B.E) product

= [(B.E)H – H + (B.E)Cl – Cl] – [2(B.E)H – Cl]

$= 434 + 242 - (431) \times 2$

$= -186$ kJ

As $\Delta_{\text{Hreaction}} = -186$ kJ

So, enthalpy of formation of HCl

$= \frac{-186}{2}\ \text{kJ} = -93\ \text{kJ mol}^{-1}$

115. (i)

W_{rev}, isothermal $= n \times 2.303\ RT \log \frac{P_1}{P_2}$

= 2 mol × 2.303 × 2 cal K^{-1} mol^{-1} × 300 Kx1

= 2764 cal

(ii) Work of expansion = P. ΔV

= 1 atm × 0.08212 lit

= 0.08212 lit-atm = 2 cal

116. C_5H_{12} (g) + $8O_2$ (g) → $5CO_2$ (g) + $6H_2O$ (*l*)

ΔG° = [(–394.4 × 5) + (–237.2 × 6)] – [(–8.2) + (8 × 0)]

= –3387.5 kJ.

The standard free energy change of elementary substances is taken as zero.

For the fuel cell, the complete cell reaction is:

C_5H_{12} (g) + $8O_2$ (g) → $5CO_2$ (g) + $6H_2O$ (*l*)

This reaction is the combination of the following two half reactions:

C_5H_{12}(g) + $10H_2O$(*l*)→$5CO_2$(g)+ $32H^+$ + 32e

$8O_2$ (g) + 32 H^+ + 32e → $16H_2O$ (*l*)

As the number of electrons exchanged is 32 here, so n = 32

ΔG° = –nFE°

–3387.5 × 10^3 J = –32 × 96500 J/Volt × E°

On solving, we get

E° = 1.09698 V.

117. 2Fe (s) + 3/2 O_2 (g) → Fe_2O_3 (s)

ΔH° = ?

Given

3C (s) + $2Fe_2O_3$ (s) → 4Fe (s) + $3CO_2$ (g)

ΔH° = –93657 kcal …(1)

C (s) + O_2 (g) → CO_2 (g)

ΔH° = –94050 kcal ….(2)

On subtracting equation (1) from (2), we get

4Fe + $3O_2$ → $2Fe_2O_3$ (s),

ΔH° = –393 kcal

So

2Fe + 3/2 O_2 → Fe_2O_3 (s)

ΔH° = –196.5 kcal at 25°C

118. Given

(i) $BaCl_2$ (s) → $BaCl_2$ (aq) ; ΔH_1 = –20.6 kJ

(ii) $BaCl_2.2H_2O$ (s) → $BaCl_2$ (aq);

ΔH_2 = 8.8 kJ

now subtract (ii) from (i), we obtain

$BaCl_2$ (s) → $BaCl_2.2H_2O$ (s);

ΔH = ΔH_1 – ΔH_2 = –29.4 kJ

119. $3CO_2$ (g) → 3C (g) + $2O_3$ (g)

ΔH = $3\Delta H_{\text{atomisation}}$ [C(s) → C(g)] + $2\Delta H^\circ_f$ [O_3 (g)] – $3\Delta H^\circ_f$ [CO_2 (g)]

ΔH = $3\Delta_{\text{Hatomisation}}$ [C(s) → C(g)] + $2\Delta H^\circ_f$ [O_3 (g)] – 3 × 409

As energy will be required for the processes

C (s) → C (g) and

$3O_2$ (g) → $2O_3$ (g)

So ΔH will be more than 1227 kJ.

120. n = 1, P_1 = 1 bar,

P_2 = 0.1 bar, T = 273 K

W = –2.303 nRT log P_1/P_2

= –2.303 × 1 × 8.314 × 273 log 1/0.1

= –2.303 × 1 × 8.314 × 273 × 1

= –5227 J

= –5.227 kJ

now, q = ΔE – w

since temperature is constant, ΔE = 0

q = –w = + 5.227 kJ

121. Heat produced by the combustion of 0.16 g of CH_4 = 17.7 × 0.5 = 8.85 kJ

Heat produced by the combustino of 1.0 mole of

$$CH_4\ (16\ g) = \frac{8.85 \times 16}{0.16} = 885\ kJ$$

As combustion has been carried in bomb, calorimeter (closed vessel), the heat produced is qv that is,

qv = –885 kJ

123. NaCl (s) → Na^+ (g) + Cl^- (g)ΔH = +780 kJ

Na^+ (g) + aq → Na^+ (aq) ΔH = –406 kJ

Cl^- (g) + aq → Cl^- (aq) ΔH = –364 kJ

The net reaction is dissolution of NaCl (s). $\Delta H_{solution}$ = 780 – (406 + 364) = 10 kJ mol^{-1}

Multiple Correct Answer Type Questions

150. Entropy of gas is greater than that of liquid and solid. In option (c) solid is converted in to gaseous phase.

Entropy of gas > liquid > solid.

Linked-Comprehension Type Questions

161. To be spontaneous, ΔG must be negative (ΔG < 0)

Thus, $\Delta H^o - T\Delta S^o < 0$;

$\Delta H < T\Delta S^o$;

$T > \Delta H^o / \Delta S^o$

$$T > \frac{572 \text{ kJ}}{0.179 \text{kJ} / \text{K}}$$

= 3200 K

The IIT-JEE Corner

206. C (graphite) + O_2 (g) → CO_2 (g)

The standard molar enthalpy of formation of CO_2 is equal to the standard molar enthalpy of combustion of carbon (graphite).

207. As energy available for muscular work

$$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$$

so energy available for muscular work for 120 g of

$$\text{glucose} = 720 \times \frac{120}{180} = 480 \text{ kJ}$$

as 100 kJ is used for walking = 1 km

so 480 kJ is used for walking

$$= 1 \times \frac{480}{100} = 4.8 \text{ km}$$

208. If $AlCl_3$ is present in ionic state in aqueous solution (Al^{+3} and three Cl^- ions), then standard heat of hydration of Al^{3+} and three Cl^- ions.

ΔH^o (hydration) = – 4665 + (3 × –381)

= – 5808 kJ mol^{-1}.

As hydration energy is greater than ionization energy of Al, so $AlCl_3$ would be ionic in solution.

210. Combustion is always exothermic.

ΔH = –ve

211. $\Delta H = \sum\Delta H^o_f \text{(products)} - \sum\Delta H^o_f \text{(reactants)}$

$= [\Delta H^o_f (CO) + \Delta H^o_f (H_2O)] - [\Delta H^o_f (CO_2)$

$+ \Delta H^o_f (H_2)]$

= [–110.5 – 241.8] – [–393.5 + 0]

= – 352.3 + 393.5 = + 41.2 kJ

212. Statement A is false, as work is a path function213 The driving force and the opposing force differ by infinitesimal small amount. So, the system and surroundings always remain in equilibrium state with one another

214. ΔH = ΔU + Δ(PV)

$= \Delta U + (P_2V_2 - P_1V_1)$

= 30 + (4 × 5 – 2 × 3)

= 30 + 14 = 44 atm

216. As $\Delta H = nC_p \Delta T$

As for isothermal process, ΔT = 0,

hence ΔH = 0

217. $$\text{As } \Delta S = \frac{\Delta Q \text{ rev}}{T}$$

$$\text{So } T = \frac{\Delta Q}{\Delta S} = 30 \times \frac{1000}{75} = 400 \text{ K}$$

218. During adiabatic irreversible process, W surr. = ΔE = –PΔV, nCvΔT = –PΔV

$$1 \times \frac{R}{\gamma - 1} \times (T_f - T\ ) = -\ P(V_2 - V_1\ )$$

$$T_f = T - \frac{(\gamma - 1\ )}{R} P(V_2 - V_1)$$

$$T_f = \frac{T\ (5/3 - 1) \times 1 \times (2 - 1)}{0.0821}$$

$$T_f = T - \frac{2}{3 \times 0.0821}.$$

219. $\Delta H = \Delta U + \Delta(PV)$

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

$\Delta U = \Delta H - V\Delta P = -560 + 1 \times 30 \times 0.1$

$= -557$

absolute value = 557 kJ

220. $\Delta S(A \rightarrow B) = \Delta S(A \rightarrow C) + \Delta S(C \rightarrow D) - \Delta S(B \rightarrow D)$

$= 50 + 30 - 20 = 60$ e.u.

221. $$\underset{(1\text{ bar}, 373\text{ K})}{H_2O(l)} \rightleftharpoons \underset{(1\text{ bar}, 373\text{ K})}{H_2O(g)}$$

At 100°C, H_2O (*l*) has equilibrium with H_2O (g) therefore $\Delta G = 0$.

As liquid molecules are converting into gases molecules therefore ΔS = positive.

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

$= -54.07 \times 1000 - 298 \times 10$

$= -57050 \text{ J mol}^{-1}$

$-57050 = -5705 \log_{10} K$

$\log_{10} K = 10$

Numericals For Practice

1. Calculate the heat evolved when 0.500 g of $Cl_2(g)$ reacts with an excess of HBr(g) to form HCl(g) and Br_2 (*l*), given the following standard enthalpies of formation (kJ/ mol): HCl(g), – 92.30; HBr (, –36.20)

a. 0.791 **b.** 7.91

b. 79.1 **d.** 791.0

2. For the reaction,

$2N_2 (g) + O_2 (g) \rightarrow 2N_2O (g)$, at 298 K, ΔH is 164 kJ mol^{-1}. The ΔE of the reaction is

a. 269 kJ mol^{-1}

b. 166.5 kJ mol^{-1}

c. 144.05 kJ mol^{-1}

d. 151.8 kJ mol^{-1}

3. The temperature above which a reaction would become spontaneous, if ΔH and ΔS of the reaction, at this temperature, are respectively 90 kJ and 90 J K^{-1} is

a. 0°C **b.** 1000°C

c. 2000 K **d.** 1000 K

4. The enthalpies of combustion of carbon and carbon monoxide are –393.5 and –283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole is

a. –676.5 kJ **b.** –110.5 kJ

c. 110.5 kJ **d.** 676.5 kJ

5. Given that $\Delta H^\circ = -311$ kJ for the hydrogenation of acetylene, C_2H_2

$H-C \equiv C-H(g) + 2H_2(g) \rightarrow CH_3-CH_3(g)$

and the following bond dissociation energies, estimate a value for the C – to –C triple bond dissociation energy.

Bond	D, kJ/mol
C – C	350
C – H	410
H – H	436

a. 1807 kJ/mol

b. 807 kJ/mol

c. 8017 kJ/mol

d. 708 kJ/mol

6. The enthalpy of combustion of methane is –880 kJ. The volume of the methane at STP to be burnt to produce 2640 kJ of heat is

a. 67.2 L **b.** 89.8 L

c. 22.4 L **d.** 11.2 L

7. Calculate the standard free energy change at 25°C for the reaction

$2NO (g) + O_2 (g) \rightarrow 2NO_2 (g)$

Species	ΔH_f kJ/mol	S°, J K^{-1} mol^{-1}
NO (g)	90.25	210.8
O_2 (g)	0.00	205.1
NO_2 (g)	33.18	240.1

a. –140.46 kJ **b.** –40.86 kJ

c. –70.46 kJ **d.** –270.56 kJ

8. The molar entropy of vapourization of acetic acid is 14.5 cal K^{-1} mol^{-1} at its boiling point 117^{0}C. The latent heat of vapourization of acetic acid is

a. 84 cal g^{-1} **b.** 94.25 cal g^{-1}
c. 64 cal g^{-1} **d.** 47.25 cal g^{-1}

9. A gas absorbs 120 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 L to 1 L. The change in internal energy is

a. 54.02 J **b.** 4.42 J
c. 44.02 J **d.** –44.02 J

10. Find ΔH for:

$C_3H_8\ (g) + 6H_2O\ (g) \rightarrow 3CO_2\ (g) + 10H_2$

Given:

$C_3H_8\ (g) + 3H_2O\ (g) \rightarrow 3CO\ (g) + 7H_2\ (g)$

$\Delta H = 499$ kJ

$CO\ (g) + H_2O\ (g) \rightarrow CO_2\ (g) + H_2\ (g)$

$\Delta H = –41$ kJ

a. 316 kJ **b.** 476 kJ
c. 296 kJ **d.** 376 kJ

11. Given the following data:

$2SO_2\ (g) + O_2(g) \rightarrow 2SO_3\ (g)$

$\Delta H = –196.7$ k/mol

$SO_3(g) + H_2O\ (l) \rightarrow H_2SO_4\ (l)$

$\Delta H = –130.1$ kJ/mol

What is the enthalpy of reaction for

$\underset{g}{2SO_2} + \underset{g}{O_2} + \underset{l}{2H_2O} \rightarrow \underset{l}{2H2_{S}O_4}$

a. –456.9 kJ **b.** 326.7 kJ
c. 456.9 kJ **d.** –326.7 kJ

12. Given the following:

$\underset{l}{C_2H_5OH} + \underset{g}{3O_2} \rightarrow \underset{g}{2CO_2} + \underset{l}{3H_2O}$

$\Delta H = –1366.9$kJ

$CH_3CO_2H + 2O_2 \rightarrow 2CO_2 + 2H_2O$

$\Delta H = –869.9$kJ

What is the enthalpy of reaction for

$\underset{l}{C_2H_5OH} + \underset{g}{2O_2} \rightarrow \underset{l}{CH_3CO_2H} + \underset{l}{H_2O}$

a. 497.0kJ **b.** 2237kJ
c. –497.0 kJ **d.** –2237kJ

13. The $\Delta_f H^o$ for CO_2 (g), CO (g) and H_2O (g) are—393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$CO_2\ (g) + H_2\ (g) \rightarrow CO\ (g) + H_2O\ (g)$ is:

a. –41.4 **b.** –14.2
c. –241.4 **d.** + 41.2

14. At 300 K, the standard enthalpies of formation of C_6H_5COOH (s), CO_2 (g) and H_2O (s) are –408, –393 and –286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at constant volume.

a. –3296 kJ mol^{-1} **b.** –3200 kJ mol^{-1}
c. –3201 kJ mol^{-1} **d.** –3603 kJ mol^{-1}

15. Calculate the standard free energy for the reaction given

$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

Species	ΔG^o_f kJ mol^{-1}
CH_3OH (l)	–166.3
O_2 (g)	0.00
CO_2 (g)	–394.4
H_2O (l)	–237.1

a. –1404.6 kJ **b.** –404.6 kJ
c. –2404.6 kJ **d.** 1804.8 kJ

16. Heats of solution of $BaCl_2$ (s) and $BaCl_2.2H_2O$ (s) are –22.8 kJ mol^{-1} and 10.8 kJ mol^{-1} respectively. ΔH hydration of $BaCl_2$ to $BaCl_2.2H_2O$ is

a. 33.6 kJ **b.** –33.6 kJ
c. 12.0 kJ **d.** –12.0 kJ

17. The molal freezing point constant of naphthalene is 6.9 K mol^{-1}. The enthalpy of fusion of solid naphthalene is 4.635 k cal mol^{-1}. The melting point of solid naphthalene is

a. 40.6°C **b.** 75.7°C
c. 80.45°C **d.** 82.0°C

18. The bond energies of C = C and C – C at 298 K are 592 and 333 kJ mol^{-1} respectively. The enthalpy of polymerization per mole of ethylene is

a. –66 kJ **b.** 76 kJ
c. –76 kJ **d.** –75 kJ

19. If the bond dissociation energies of XY, X_2 and Y_2 are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is –200 kJ/mole. The bond dissociation energy of X_2 will be ?

a. 100 kJ/mole
b. 400 kJ/mole
c. 600 kJ/mole
d. 800 kJ/mole

20. The maximum work done in expanding 16 g oxygen at 300 K and occupying a volume of 7 dm^3 isothermally until the volume becomes 35 dm^3 is:

a. $+2.02 \times 10^3$ J
b. -1.30×10^3 J
c. -2.01×10^3 J
d. -12.11×10^3 J

21. Use the given standard enthalpies of formation to calculate ΔH^o for the following reaction:

$3Fe_2O_3$ (s) + CO (g) → $2Fe_3O_4$ (s) + CO_2 (g)

Species	ΔH^o_f, kJ/mol
Fe_2O_3 (s)	–824.2
Fe_3O_4 (s)	–1118.4
CO (g)	–110.5
CO_2 (g)	–393.5

a. +47.2 kJ
b. –477.2 kJ
c. –417.2 kJ
d. –47.2 kJ

22. Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are –382.64 kJ mol^{-1} and –145.6 JK^{-1} mol^{-1}, respectively. Standard Gibbs energy change for the same reaction at 268 K is

a. –221.1 kJ mol^{-1}
b. –339.3 kJ mol^{-1}
c. –439.3 kJ mol^{-1}
d. –523.2 kJ mol^{-1}

23. The enthalpies of formation of N_2O and NO are 30 and 90 kJ mol^{-1} respectively. The enthalpy of the reaction,

$2N_2O$ (g) + O_2 (g) → 4NO (g) is equal to

a. 300 kJ
b. –360 kJ
c. 360 kJ
d. –300 kJ

24. Calculate the work done when 50 g of iron reacts with HCl in an open beaker at 25°C.

a. –221.32 J
b. –2212.2 J
c. –22.122 J
d. none

25. Using bond energy data, calculate heat of formation of isoprene. Given B.E. of C – H = 98.8 kcal, H – H = 104 kcal, C – C = 83 kcal, C = C = 147 kcal and C(s) → C(g) = 171 kcal.

a. 28.3 kcal
b. 20.3 kcal
c. 283 kcal
d. 206 kcal.

26. For the reaction N_2 (g) + $3H_2$ (g) → $2NH_3$ (g), ΔH = –85.4 kJ and ΔS = –188.3 JK^{-1}. The temperature at which ΔG will be zero is

a. 0 K
b. 548 K
c. 253 K
d. 453.53 K

27. Calculate ΔS^o_f at 25°C for PCl_5 (g). Given $\Delta H^o_f = -374.9$ kJ/mole and $\Delta G^o_f = -305$ kJ/mol

a. –235 J/mole K

b. –23.5 J/mole K

c. –2.35 J/mole K

d. None

28. Given enthalpy of combustion of glucose is 2870 kJ/mol. What will be the amount of glucose a man has to eat in order to climb a height of 100 m assuming 100% efficiency of the body system (weight of man = 60 kg)

a. 37 g
b. 3.7 g
c. 370 g
d. 180 g

29. The enthalpy change accompanying the formation of 1 mole NH_3 (g) from its elements at 298 K is –56.1 kJ. The internal energy is

a. 44.6 kJ
b. –53.6 kJ
c. –34.6 kJ
d. 53.6 kJ

30. ΔG^o for a reaction is 46.06 Kcal/mole. K_p for the reaction at 300 K is

a. $10^{-33.33}$
b. 10^{-8}
c. $10^{-22.22}$
d. None of these

31. Heat of combustion of carbon monoxide at constant volume and at 17°C is –67, 710 calories. The heat of combustion at constant pressure is

a. +68,900 calories

b. –68,000 calories

c. –67,800 calories

d. –67,060 calories

32. Standard heat of formation for CCl_4, H_2O, CO_2 and HCl at 298 K are –25.5, –57.8, –94.1 and –22.1 kJ/mole respectively. For the reaction

$CCl_4 + 2H_2O \rightarrow CO_2 + 4HCl$

What will be ΔH?

a. – 41.4 kJ
b. 45.5 kJ
c. –31.4 kJ
d. 21.7 kJ

33. The bond dissociation energies for Cl_2, I_2 and ICl are 242.3, 151.0 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mole. What is the standard enthalpy of formation for ICl (g) nearly equal to?

a. 11.6 kJ/mole **b.** –15.8 kJ/mole
c. 19.8 kJ/mole **d.** 16.8 kJ/mole

34. Consider the following reactions:

(1) $H^+ (aq) + OH^- (aq) = H_2O (l)$

$\Delta H = -X_1$ kJ mol^{-1}

(2) $H_2 (g) + ½ O_2 (g) = H_2O (l)$

$\Delta H = -X_2$ kJ mol^{-1}

(3) $CO_2 (g) + H_2 (g) = CO (g) + H_2O (l)$

$\Delta H = -X_3$ kJ mol^{-1}

(4) $C_2H_2 (g) + 5/2\, O_2 (g) = 2CO_2(g)+H_2O(l)$

$\Delta H = +X_4$ kJ mol^{-1}

Enthalpy of formation of $H_2O(l)$ is

a. $-X_2$ kJ mol^{-1} **b.** $+X_3$ kJ mol^{-1}
c. $-X_4$ kJ mol^{-1} **d.** $+ X_1$ kJ mol^{-1}

35. Given that bond energies of H–H and Cl–Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is –90 kJ mol^{-1}, bond enthalpy of HCl is

a. 290 kJ mol^{-1} **b.** 380 kJ mol^{-1}
c. 425 kJ mol^{-1} **d.** 245 kJ mol^{-1}

36. If 150 kJ of energy is needed for muscular work to walk a distance of one km. Then how much amount of glucose one has to consume to walk a distance of 5 km, provided only 30% of energy is available for muscular work. The enthalpy of combustion of glucose is 3000 kJ mol^{-1}.

a. 35 g **b.** 45 g
c. 150 g **d.** 175 g

37. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction,

$1/2\, X_2 + 3/2\, Y_2 \rightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be

a. 1250 K **b.** 500 K
c. 750 K **d.** 1000 K

38. A reversible isothermal evaporation of 90 g of water is carried out at 100°C. Heat of evaporation of water is 9.73 kcal mol^{-1}. Assuming water vapour to behave like an ideal gas, what is the change in internal energy of the system?

a. 22.41kcal **b.** 44.82 kcal
c. 54.18 kcal **d.** –44.48 kcal

39. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per cm^3 of the mixture. Heats of formation and densities are as follow:

$Hf_{(Al2O3)} = -\,399$ kcal mol^{-1};

$Hf_{(Fe2O3)} = -199$ kcal mol^{-1}

Density of Fe_2O_3 = 5.2 g/cm^3;

Density of Al = 2.7 g/ cm^3

a. 39.4 kcal **b.** 3.94 kcal
c. 2.42 kcal **d.** 0.394

40. Calculate the enthalpy change for the process: $CCl_4(g) \rightarrow C(g) + 4Cl(g)$

Calculate bond enthalpy by C – Cl in CCl_4 (g)

C Given:

ΔH^o vap CCl_4 = 305 kjmol^{-1}

$\Delta_f H^o$ CCl_4 = –135.5 kj mol^{-1}

$\Delta_a H^o$ (C) = 715 kj mol^{-1} (Enthalpy of atomization)

$\Delta_a H^o$ (Cl_2) = 242 kj mol^{-1} (Enthalpy of atomization)

a. 326 kjmol^{-1} **b.** 163 kjmol^{-1}
c. –326 kj mol^{-1} **d.** –163 kj mol^{-1}

ANSWER KEYS

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	a	**2.**	b	**3.**	b	**4.**	b	**5.**	b
6.	a	**7.**		**8.**	b	**9.**	c	**10.**	d
11.	a	**12.**	c	**13.**	d	**14.**	b	**15.**	a
16.	b	**17.**	c	**18.**	c	**19.**	d	**20.**	c
21.	d	**22.**	b	**23.**	b	**24.**	a	**25.**	b
26.	b	**27.**	d	**28.**	a	**29**	b	**30.**	b
31.	a	**32.**	b	**33.**	a	**34.**	d	**35.**	a
36.	c	**37.**	c	**38.**	c	**39.**	b	**40.**	a

Hints and Explanations

1. As $\Delta H = \Delta E + \Delta n\, RT$

$\Delta n = -1$

$164 \times 10^3 = \Delta E - 1 \times 8.314 \times 298$

$= \Delta E - 2.478 \times 10^3$

$\Delta E = 164 \times 10^3 + 2.478 \times 10^3$

$= 166.5\ \text{kJ mol}^{-1}$

2. At equilibrium, $\Delta G_{T.P.} = 0 = \Delta H - T\Delta S$

$= (90000 - T \times 90)\ \text{J}.$

$$T = \frac{90000}{90} = 1000\ \text{K}$$

If T is > 1000 K, ΔG will be negative and the reaction is spontaneous

4. (i) $C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$

$\Delta H = -393.5\ \text{kJ}$

(ii) $CO\ (g) + ½\ O_2\ (g) \rightarrow CO_2\ (g)$

$\Delta H = -283.0\ \text{kJ}$

eq. (i) and (ii) gives

(iii) $C\ (s) + ½\ O_2\ (g) \rightarrow CO\ (g),$

$\Delta H = -110.5\ \text{kJ}$

This equation (iii) also represents formation of one mole of CO and thus enthalpy change is the heat of formation of CO (g).

5. $$\Delta S = \frac{\Delta H}{T(K)}.$$

$$14.4 = \frac{\Delta H}{390}.$$

$\Delta H = 390 \times 14.5 = 5655\text{cal.mol}^{-1}$

$$= \frac{5655}{60} = 94.25\ \text{cal g}^{-1}$$

6. ΔH combustion for 1 mole of methane

= 880 kJ

2640 kJ of heat will be evolved by 3 moles of methane

3 moles can occupy at STP = 3 × 22.4

= 67.2 L

9. $W = -P\Delta V = -1.5(1 - 0.5)$

$= -0.75\ \text{L atm}$

$= -0.75 \times 101.3\ \text{J} = -75.98\ \text{J}$

(as 1 L atm = 101.3 J)

$\Delta E = q + W$

$= 120 + (-75.98) = 44.02$ J

11. $2SO_2\,(g) + O_2(g) \rightarrow 2SO_3\,(g)$

$\Delta H = -196.7$ k/ mol

$SO_3(g) + H_2O\,(l) \rightarrow H_2SO_4\,(l)$

$\Delta H = -130.1$ kJ /mol

$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$

$\Delta H = -456.9$kJ

12. $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

$\Delta H = -1366.9$ kJ

$2CO_2 + 2H_2O \rightarrow CH_3CO_2H + 2O_2$

$\Delta H = 869.9$kJ

$C_2H_5OH + O_2 \rightarrow CH_3CO_2H + H_2O$

$\Delta H = -497.0$ kJ

13. $C + O_2 \rightarrow CO_2$, $\Delta H^o = -393.5$ kJ ……(i)

$C + \frac{1}{2} O_2 \rightarrow CO$, $\Delta H^o = -110.5$ kJ …..(ii)

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, $\Delta H^o = -241.8$ kJ …(iii)

By equations (ii) + (iii) – (i), we get

$CO_2 + H_2 \rightarrow CO + H_2O$, $\Delta H^o = +41.2$ kJ

14. The reaction is

$C_6H_5COOH\,(s) + 15/2\; O_2\,(g) \rightarrow$

$7\,CO_2\,(g) + 3H_2O\,(l)$

$\Delta H = \sum\Delta H^o_f$ (products) – $\sum\Delta H^o_f$ (reactants)

$= [7 \times \Delta H_f\,(CO_2) + 3 \times \Delta H_f\,(H_2O)]$

$- [\Delta H_f\,(C_6H_5COOH) + 15/2\; \Delta H_f\,(CO_2)]$

$= [7 \times (-393) + 3 \times (-286)] - [-408 + 0]$ kJ

$= -3201$ kJ

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

$\Delta n_g = 7 - 15/2 = -1/2$;

$R = 8.314/1000$ kJ mol^{-1}

Putting the values, we get

$\Delta E = -3199.9$ kJ $= -3200$ kJ

16. $BaCl_2\,(s) + aq \rightarrow BaCl_2\,(aq)$

$\Delta H_1 = -22.8$ kJ

$BaCl_2.2H_2O\,(s) + aq \rightarrow BaCl_2\,(aq)$

$\Delta H_2 = +10.8$ kJ

$\Delta H_3 = \Delta H_1 - \Delta H_2 = -22.8 - 10.8 = -33.6$ kJ

$BaCl_2\,(s) + 2H_2O \rightarrow BaCl_2\,.2H_2O$

17. $$K_f = \frac{0.002\;T^2 \times 128}{1}$$

$$6.9 = \frac{0.002\;T^2 \times 128}{4635}$$

$$T^2 = \frac{6.9 \times 4635}{0.002 \times 128}$$

$T = 353.45$ K $= 80.45^oC$

18. Polymerization reaction

$n\;CH_2 = CH_2 \rightarrow (-CH_2 - CH_2 -)_n$

One mole of C = C bond is broken and two moles of C – C bonds are formed per mole of ethylene.

$\Delta H = 592 - 2 \times 333$

$= 590 - 666 = -76$ kJ per mole of ethylene

19. Let the bond dissociation energy of XY, $X_2$and Y_2 be as x kJ mol^{-1}, x kJ mol^{-1} and 0.5 × kJ mol^{-1} respectively.

$\frac{1}{2} X_2 + \frac{1}{2} Y_2 \rightarrow XY$; $\Delta H_f = -200$ kJ mol^{-1}

ΔH reaction = [(sum of bond dissociation energy of all reactants) – (sum of bond dissociation energy of product)]

$= [\;\frac{1}{2}\,\Delta H_{X_2} + \frac{1}{2}\,\Delta H_{Y_2} - \Delta H\,X_Y\;]$

$$= \frac{x}{2} + \frac{0.5x}{2} - x = -200$$

$$x = \frac{200}{0.25} = 800 \text{ kJ mol}^{-1}$$

22. $$w = -2.303 \times \frac{1}{2} \times 8.314 \times 300 \log_{10} \frac{35}{7}$$

$= -2.01 \times 10^3$ Joule.

23. Given that

$\Delta H = -382.64$ kJ mol^{-1}

$\Delta S = -145.6$ J K^{-1} mol^{-1} $= -145.6 \times 10^{-3}$ kJ K^{-1}

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

so $\Delta G = -382.64 - (298 \times -145.6 \times 10^{-3})$

$= -339.3$ kJ mol^{-1}

23. $N_2 + \frac{1}{2} O_2 \rightarrow N_2O$, $\Delta H = 30$ kJ ….(i)

$\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightarrow NO$, $\Delta H = 90$ kJ ….(ii)

By equation [4 × eq. (ii)] – [2 × eq. (i)], we get

$2N_2O + O_2 \rightarrow 4NO$, $\Delta H = 300$ kJ

24. $W = -P_{ext.}\, \Delta V$

$$\Delta V = V_{final} - V_{initial} = V_{final} = \frac{nRT}{P_{ext}}$$

$$W = -P_{ext}.\, \frac{nRT}{P_{ext}} = -nRT.$$

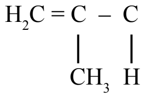
Fe(s) + 2HCl (aq) → $FeCl_2$ (aq) + H_2 (g)
1 mole 1 mole

No. of moles of Fe = No. of moles of H_2

$$= \frac{50}{56}$$

$$W = -\frac{50}{56} \times 8.314 \times 296$$

$= -2212.11$ J.

25. 5C (s) + $4H_2$ (g) →  ; ΔH = ?

$$5C\,(s) + 4H_2\,(g) \rightarrow \underset{CH_3}{\underset{|}{H_2C = C}} - \underset{H}{\underset{|}{C}}\ ;\ \Delta H = ?$$

$\Delta H = \sum$B.E.(reactants) – $\sum$B.E. (products)

$= [5Cs \rightarrow g + 4BE_{H-H}] - [2BE_{C-C} + 2BE_{C-C} + 8BE_{C-H}]$

$= [5 \times 171 + 4 \times 104] - [2 \times 83 + 2 \times 147 + 8 \times 98.8]$

= 20.6 kcal.

26. $\Delta G = \Delta H - T\Delta S = 0$

$\Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-85.4 \times 1000}{-188.3} = 453.53 \text{ K.}$$

27. $\Delta G^o = \Delta H^o - T\Delta S^o$

$T\Delta S^o = \Delta H^o + \Delta S^o$

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

$$= \frac{-374.9 - (-305)}{298}$$

$$= \frac{-374.9 + 305}{298} = \frac{-69.9}{298}$$

$= -0.2346$ kJ/mole K

$= -234.56$ J/mole K

28. W = mgh

= 60 kg × 9.8 ms^{-1} × 100 m

= 58800 J = 58.8 kJ

2870 kJ of heat or work is obtained = 180 g glucose

58.8 kJ of heat or work is obtained from

$$= \frac{180 \times 58.8}{2870} = 3.7 \text{ g glucose}$$

29. $3/2\ H_2$ (g) + $\frac{1}{2} N_2$ (g) → NH_3 (g)

Δn = 1 mole – 1.5 mole – 0.5 mole

= –1.00 mole

$$RT = \frac{8.314 \times 298}{1000} = 2.48 \text{ kJ}$$

$\Delta E = \Delta H - nRT$

$= -56.1 - (-1) \times 2.48$

$= -56.1 + 2.48 = -53.6$ kJ.

30. $\Delta G^o = -RT \text{ In } K_P$

1 cal = 4.182 joule

R = 8.314 J/mol

46.06 × 1000 × 4.182

$= -2.303 \times 8.314 \times 300 \log K_P$

$192622.92 = -5744.142 \log K_P$

$\log K_P = -33.53$

i. $K_P = 10^{-33.33}$

31. ΔE = –67710 cal.

2CO (g) + O_2 (g) → $2CO_2$ (g)

Δn = 2 – 3 = –1

t = (273 + 17) = 290 K

Heat of combustion at constant pressure,

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

$= –67710 + (–1) \times 2 \times 290$

$= –67710 – 580$

$= –68290$ cal.

32. $C\ (s) + 2Cl_2\ (g) \rightarrow CCl_4\ (l)$

$\Delta H_1 = –25.5$ kJ/mol

$H_2\ (g) + ½\ O_2\ (g) \rightarrow H_2O\ (l)$

$\Delta H_2 = –57.8$ kJ/mol

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

$\Delta H_3 = –94.1$ kJ/mol

$½\ H_2\ (g) + ½\ Cl_2\ (g) \rightarrow HCl\ (g)$

$\Delta H_4 = –22.1$ kJ/mol

$CCl_4\ (l) + 2H_2O\ (l) \rightarrow CO_2\ (g) + 4HCl\ (g)$

$\Delta H = (25.5 + 2 \times 57.8 – 94.1 – 4 \times 22.1)$

$= – 41.4$ kJ

33. $Cl – Cl\ (g) \rightarrow 2Cl\ (g)\ \Delta H_1 = 242.3$ kJ/mol

$I – I\ (g) \rightarrow 2I\ (g)\ \Delta H_2 = 151.0$ kJ/mol

$I – Cl\ (g) \rightarrow I\ (g) + Cl\ (g)$

$\Delta H_3 = 211.3$ kJ/mol

$I_2\ (s) \rightarrow I_2\ (g)\ \Delta H_4 = 62.8$ kJ/mol

$½\ I_2\ (s) + ½\ Cl_2\ (g) \rightarrow ICl\ (g)\ \Delta H = ?$

$$\Delta H = [\frac{62.8 + 151.0 + 242.3}{2} – \frac{211.3}{1}]$$

$= 228.05 – 211.3 = 16.75$ kJ/mol

34. $H_2\ (g) + ½\ O_2\ (g) = H_2O\ (l)$

$\Delta H = –X_2$ kJ mol$^{–1}$

This reaction represents the enthalpy of formation of $H_2O\ (l)$.

35. $½\ H_2\ (g) + ½\ Cl_2\ (g) \rightarrow HCl\ (g)$,

$\Delta_f H = –90$ kJ mol$^{–1}$

$\Delta_r H = ½$ BE (H_2) + ½ BE (Cl_2) – BE (HCl)

–90 = ½ (430) + ½ (240) – BE (HCl)

BE (HCl) = 215 + 120 + 90 = 425 kJ mol$^{–1}$

36. Energy consumed for walking a distance of 5 km = 150 × 5 = 750 kJ

1 mole of glucose, $C_6H_{12}O_6$ (180 g) gives theoretically energy = 3000 kJ

Actual energy available $= \frac{30}{100} \times 3000$

= 900 kJ

As, For 900 kJ of energy, glucose required = 180 g

So, for 750 kJ of energy, glucose required

$= \frac{180}{900} \times 750$ g = 150 g

37. $1/2\ X_2 + 3/2\ Y_2 \rightarrow XY_3$

$\Delta S_{reaction} = 50 – (3/2 \times 40 + ½ \times 60)$

$= –40$ J mol$^{–1}$

$\Delta G = \Delta H – T\Delta S$

As at equilibrium $\Delta G = 0$.

So $\Delta H = T\Delta S$

$30 \times 10^3 = T \times 40$

On solving, we get

T = 750 K.

38. Change in enthalpy (ΔH)

= Heat of evaporation × Number of moles

= 9.73 × 5 = 48.65kcal

As $\Delta H = \Delta E + \Delta nRT$

So $\Delta E = 48.65 – (5 \times 2 \times 10^{–3} \times 373)$

= 44.82 kcal.

39. The required equation is:

$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$, $\Delta H = ?$

$\Delta H = \Delta H_{f(products)} – \Delta H_{f\ (reactants)}$

$= [\Delta Hf_{(Al_2O_3)} + 2\Delta H_{f(Fe)}] –[2\Delta H_{f(Al)} + H_{f(Fe_2O_3)]}$

= [–399 + 2 × 0] – [2 × 0 + (–199)]

= – 399 + 199= –200 kcal

At. mass of aluminium = 27,

Mol. mass of Fe_2O_3 = 160

Volume of reactants $= \frac{160}{5.2} + \frac{2 \times 27}{2.7}$

= 50.77 cm

Fuel value per cm^3 = $\frac{200}{5077}$

= 3.94 kcal

40. (i) $CCl_4 \rightarrow CCl_4(g)$ $\Delta H^o = +30.5$ kj mol^{-1}

(ii) $C(s) + 2Cl_2(g) \rightarrow CCl_4(g)$

$\Delta H^o = -135.5$ kj mol^{-1}

(iii) $C(s) \rightarrow C(g)$ $\Delta H^o = +715$ kj mol^{-1}

(iv) $Cl_2(g) \rightarrow 2Cl(g)$ $\Delta H^o = +242$ kj mol^{-1}

Required equation

$CCl_4(g) \rightarrow C(g) + 4Cl(g)$ $\Delta H = ?$

Equation (iii) + 2 × Equation (iv) – Equation (ii) – Equation (i) gives the required equation

$\Delta H = 715 + 2(242) - 30.5 - (-135.5)$

= 1304 kj mol^{-1}

Bond enthalpy of (C-Cl) bond = $\frac{1304}{4}$

= 326 kj mol^{-1}