UNIT 6. THERMODYNAMICS

1. THERMODYNAMICS

It is the study of flow of energy. It encompasses the study of flow of heat as well as mass.

2. THERMODYNAMICS

2.1 System

The part of the Universe under observation is called system.

Surrounding

The part of the Universe not under observation is called Surrounding.

System + Surrounding = Universe

Types of system

Open System : A system in which both flow of mass and heat is possible.

Closed System : A system in which flow of heat is possible but flow of mass is not possible.

Isolated System : A system in which neither heat nor mass can flow in or out.

3. STATE OF A SYSTEM

The state variables (P, V, T, n) describes the condition of a system. On changing any one or more of these variables the state of the system changes.

4. PROPERTIES OF SYSTEM

All the properties of a system can be categorized into one of the following two types :

Extensive Properties

Such properties of a system which depends on the mass or the total number of particles in the system are categorized as Extensive Properties. eg. Total Energy, volume.

Intensive Properties

Such properties of a system which depends on concentration and does not depend on the mass or the total number of particles in the system are categorized as Intensive properties. eg. Pressure, Density, Reractive Index.

5. STATE AND PATH FUNCTION

Such thermodynamic functions which depend only on the initial and final states of the system and not on the path followed are called state functions eg. Internal energy, Enthalpy and the functions which depend on the path followed while changing from one state to the other are called path functions. eg. work heat.

6. THERMODYNAMIC EQUILIBRIUM

A system is said to be under thermodynamic equilibrium when none of the state variables are changing and it satisfies the three equilibriums.

Mechanical Equilibrium

There is no mechanical motion and the pressure and the volume of the system is not changing.

Thermal Equilibrium

There is no flow of heat and the temperature of the system does not change with time.

Chemical Equilibrium

If any chemical reaction is taking place in the system then the rate of forward reaction is equal to the rate of backward reaction which means that the overall moles of the system is constant.

7. INTERNAL ENERGY

It is the sum total of the components of energy of the system due to the internal factors. It is denoted by U (sometimes by E). Since the system under observation is an ideal gas thus the internal energy of the system is dependent only on the kinetic energy of the gas and therefore is only a function of temperature. U a T. Since internal energy depends only on temperature thus, it is a state function.

8. MODES OF ENERGY

There are two methods to alter the internal energy of a system viz. Heat and work.

Heat

Heat is the energy transferred due to temperature difference between the system and the surrounding. On heating, the kinetic energy of the molecules increases and therefore the internal energy increases.

Work

Work is the energy spent to overcome an external force. When the system does work against an external pressure (expansion) it tends to reduce the internal energy and on the other hand when the system contracts due to the external pressure it tends to increase the internal energy.

9. FIRST LAW OF

The first law of Thermodynamics states that Energy can neither be created nor destroyed.

$\Delta U = q + w$

Conventions: In the above system if work is done by the system then w is negative and if work is done on the system then w is positive. Also, if heat flows into the system then q is positive and if heat flows out of the system then q is negative.

10.

A process whose direction can be changed by an infinitesimal change to the system or surroundings and which can be reversed by retracing the original path and the system is restored to the initial state. The driving force of a reversible process is very-very small and such a process is extremely slow. For a process to be reversible there must not be any dissipative forces and also the system should be in a Quasi Static State.

10.1 Quasi Static State

A quasi static state means that the system seems to be static at all intervals of time but actually is not. The motion is so slow that it is almost impossible to detect the motion and the system seems to be in equilibrium with the surroundings at all instants of time.

11. EXPANSION WORK

It is the work done due to the volume changes of the gas. The mathematical expression for the expansion work is $w = -\int P_{ex}\, dV$.

Always remember, be it expansion or compression we always take the external pressure as the driving force. For a reversible process,

$P_{ex} = P_{GAS}$ and $w = -\int P_{GAS} dV$.

If we draw a process curve between P and V then the work done is represented by the area covered under the P-V graph as shown in Fig.
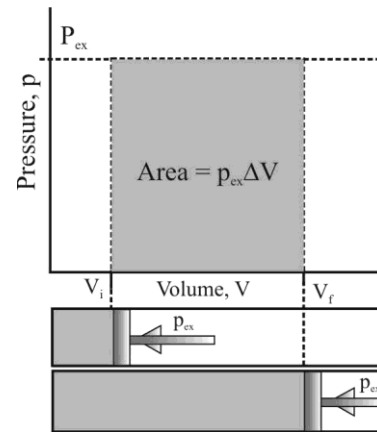
NOTE

Sign of w : If the volume of the system is increasing then the sign of w is −ve and if volume is decreasing w is +ve

Sign of ΔU : If the temperature of the system is decreasing or the product pressure and volume (PV) is reducing then the sign of ΔU is −ve else, the sign of ΔU is +ve.

Sign of q : The sign of q needs to be determined using the first law of thermodynamics.

12. CYCLIC

A cyclic process is one which comes back to its initial state. The graph of a cyclic process is always a closed graph. For a cyclic process, $\Delta U_{net} = 0$ and $q_{net} = - w_{net}$.

13. ENTHALPY

Enthalpy is another thermodynamic function (like internal energy, work and heat) which we study in various thermodynamic processes. It is also a state function like internal energy. It is defined as the sum of the energy stored in the system and the energy used in doing work. Mathematically, $H = U + PV$. At constant pressure $\Delta H = q_p$ and at constant volume $\Delta U = q_v$.

14. HEAT CAPACITY

The heat capacity of the system is the amount of heat needed to raise the temperature of the system by 1°C or 1K.

$C = q/\Delta T$.

14.1 Molar Heat Capacity

The molar heat capacity of a system (C_M) is the amount of heat needed to raise the temperature of one mole gas by 1°C or K.

$$C_M = \frac{q}{n\Delta T}$$

The molar heat capacity of a system at constant pressure (C_p) is the amount of heat needed to raise the temperature of one mole gas the system by 1°C at constant pressure.

$C_p = q_p/n\Delta T$.

The molar heat capacity of a system at constant volume (C_V) is the amount of heat needed to raise the temperature of one mole gas by 1°C at constant volume.

$C_V = q_v/n\Delta T$.

Thus, we can say that : $\Delta H = nC_p\Delta T$ and $\Delta U = nC_V\Delta T$ and $C_P = C_V + R$.

Type of Gas	C_V	C_P	$\gamma = C_P/C_V$
monotomic	3R/2	5R/2	5/3 = 1.67
diatomic	5R/2	7R/2	7/5 = 1.4
Non-linear Polyatomic	3R	4R	4/3 = 1.34

15. TYPES OF THERMODYNAMIC PROCESSES

There are four important types of processes to be studied in this chapter. The basic meanings and difference of these four processes are :

Isothermal Process

These processes are the ones in which the temperature is constant throughout the process.

$\Delta U = 0$; $\Delta H = 0$

$w = -2.303\ nRT\ \log_{10}(V_2/V_1) = -2.303\ nRT\ \log_{10}(P_1/P_2)$

$q = +2.303\ nRT\ \log_{10}(V_2/V_1) = +2.303\ nRT\ \log_{10}(P_1/P_2)$

Adiabatic Process

These processes are the ones in which the heat exchanged with the surroundings is zero. Such processes are defined by the equation $TV^{\gamma-1} = $ constant, $T^{\gamma}P^{1-\gamma} = $ constant, $PV^{\gamma} = $ constant.

$q = 0 \rightarrow w = \Delta U$

$\Delta U = nC_V\Delta T = (P_2V_2 - P_1V_1)/(\gamma-1) = (nR\Delta T)/(\gamma - 1)$

$\Delta H = nC_p\Delta T$

Isochoric Process

These processes are the ones in which the volume remains constant. Since the change in volume is zero therefore we can say that

$w = 0$

$\Delta U = nC_V\Delta T = q$ $\Delta H = nC_p\Delta T$

Isobaric Process

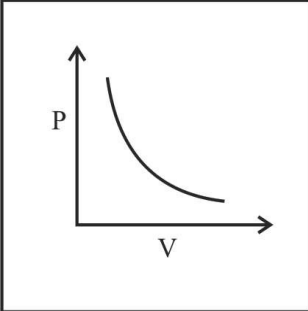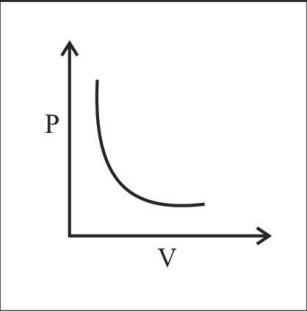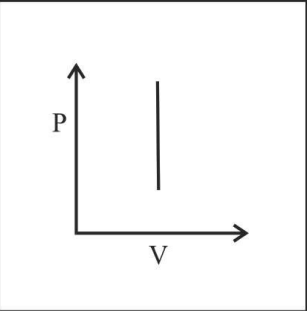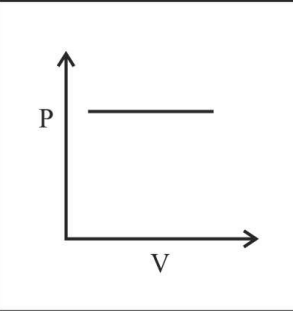These are the processes in which the pressure remains constant.
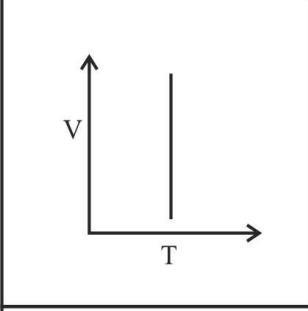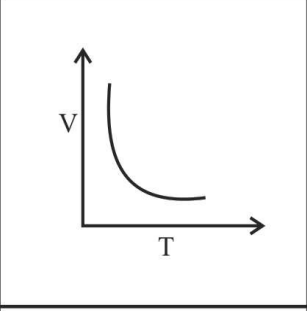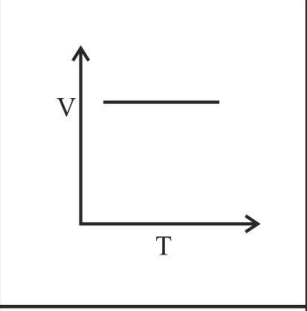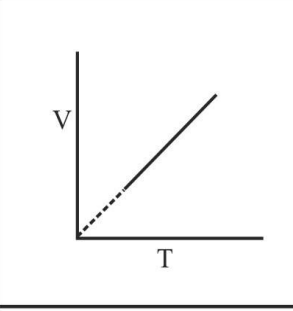
$w = -P\Delta V = -nR\Delta T$

$\Delta U = nC_V\Delta T$
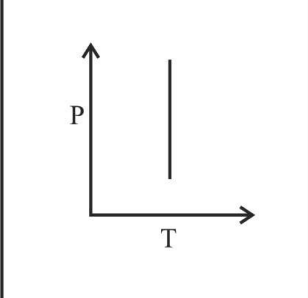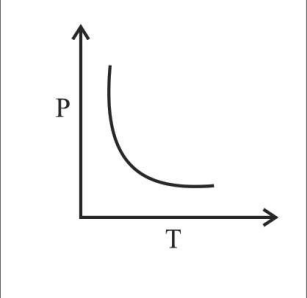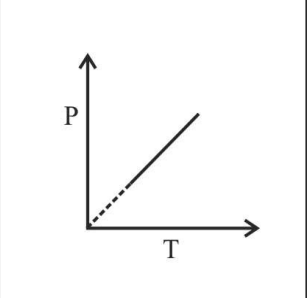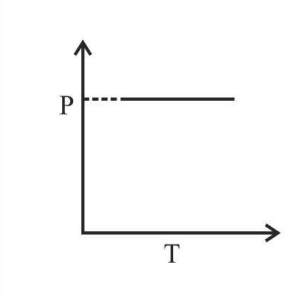
$\Delta H = nC_p\Delta T$

NOTE

All these processes are happening on a system containing an
we find suitable.   PV   RT

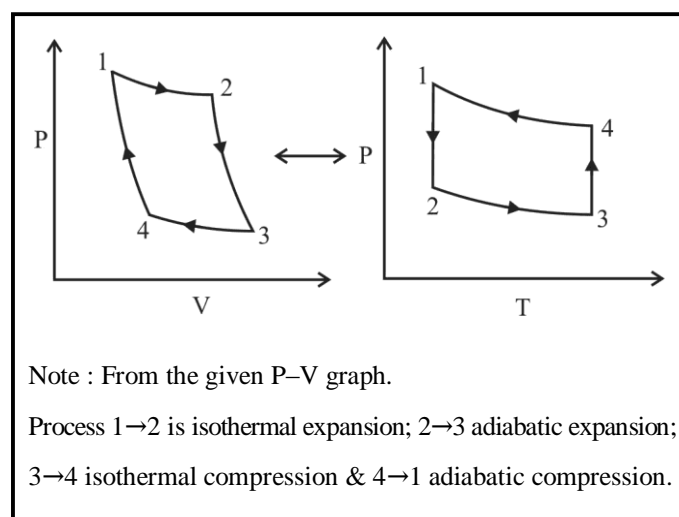| Isothermal	Adiabatic	Isochoric	Isobaric
P vs V	P vs V	P vs V	P vs V
V vs T	V vs T	V vs T	V vs T
P vs T	P vs T	P vs T	P vs T

Although the graph of isothermal and adiabatic processes are similar in nature it should be noted that the P-V graph of an adiabatic process is steeper than that of an isothermal process.

16. GRAPH

When a thermodynamic process is plotted in terms of two state variable it can be transformed into a graph involving the other state variable by doing the following :

1. Identify the type of curve given, whether it is P-V, V-T or P-T graph.

2. Then, Identify every step of the process

3. Then one by one convert every step into the required graph bearing in mind critical points like, an expansion process will remain an expansion process and so on.

4. A cyclic process should remain cyclic whichever graph we make.

Note : From the given P–V graph.

Process 1→2 is isothermal expansion; 2→3 adiabatic expansion;

3→4 isothermal compression & 4→1 adiabatic compression.

17. IRREVERSIBLE

For an irreversible process the work done is given by

$W = -\int P_{EXT}dV$. We cannot take the external pressure to be equal to the pressure of the gas in these processes.

18. FREE

If the external pressure of the gas is zero that is the gas is expanding against vaccum then the work done is always zero, this is called the case of free expansion. In this process the gas does no work as there is no effort put in expansion process. If no heat is supplied to the gas then there is no change in temperature too. That is why such a process is both Isothermal and Adiabatic.

19. POLYTROPIC

It is a generalized form of any thermodynamic process which has a form PV^n = constant where n is a real number. For an isothermal process n = 1 and for an adiabatic process n = y. The heat capacity of a polytropic process can be calculated using the first law of thermodynamics and comes out to be :

$C = C_V - R/(n - 1)$.

20. NEED FOR

The first law talks about the conservation of energy in a process but does not speak of the feasibility of a process. It does not tell whether a process will happen on its own i.e. whether the process is spontaneous or not. A spontaneous process is one which happens on its own. Example, heat always flows spontaneously from higher temperature to lower temperature : Nothing in the first law mentions that the opposite process cannot happen. According to first law any process where energy remains conserved is feasible. But we need some other basis for feasibility of a process. This is where the second law is important.

21. TYPES OF

Spontaneous processes

Spontaneous processes have a natural tendency to take place and no external work is needed to carry out these processes. All natural processes are spontaneous.

Non-Spontaneous processes

They are driven by external work and cannot take place naturally.

22. CONCEPT OF

◆ Matter has a natural tendency to get disordered or randomised

◆ Energy has a tendency to become disordered or dispersed. It was concluded that any such process in which the total randomness of the universe (system + surrounding) increases is a spontaneous process. Entropy is a measure of randomness or disorder. It is a state function represented by S. We can safely say that in a spontaneous process there is a tendency for increase in entropy. Hence the statement of second law :

The entropy of an isolated system/Universe tends to increase OR In a spontaneous process the entropy of the Universe increases.

$\Delta S = q_{rev}/T$.

$$\Delta S_{TOTAL} = \Delta S_{SYSTEM} + \Delta S_{SURROUNDING} > 0$$

(for a sponataneous change)

Thus, In a reversible process the entropy of the Universe remains constant i.e. $\Delta S_{Total} = 0$

Entropy changes in a Thermodynamic Process

The entropy changes in an thermodynamic process can be mathematically calculated by the equation :

→ $\Delta S = nC_V \ln(T_2/T_1) + nR \ln(V_2/V_1)$. This expression can be simplified for the four processes studied earlier as :

Isothermal process : $\Delta S = nR \ln(V_2/V_1)$

Isochoric process : $\Delta S = nC_V \ln(T_2/T_1)$

For isobaric process : $\Delta S = nC_P \ln(T_2/T_1)$

Adiabatic process : $\Delta S = 0$ ($q_{rev} = 0$)

Important points to Remember

1. Entropy of a system remains constant in a reversible adiabatic process. Therefore, it is also known as "isentropic process".

2. Entropy of an ideal gas will always increase in isothermal expansion.

3. In a reversible adiabatic process the entropy of both system and surroundings remains the same and there is no overall change in entropy as well.

$$\Delta S_{SYSTEM} = \Delta S_{SURROUNDINGS} = \Delta S_{TOTAL} = 0$$

4. In a reversible isothermal expansion the entropy of surroundings will always decrease to balance the increase in system's entropy to make the overall entropy constant.

5. In free expansion the entropy of the system always increases and that of surrounding remains constant. Free expansion is both isothermal and adiabatic and is irreversible.

23. GIBB'S FREE

Gibb's Free energy function gives us a very convenient parameter to judge the spontaneity of a process from system's perspective. At a constant temperature and pressure, $\Delta G = -T\Delta S_{TOTAL}$ and for a process to be spontaneous, $\Delta G < 0$. The change in Gibb's free energy can also be represented in terms of the system parameters as :

$\Delta G_{SYS} = \Delta H - T\Delta S_{sys}$ at a constant temperature.

24. THERMOCHEMICAL

A chemical equation which gives us all the information like energy changes associated with a chemical reaction and phases of various reactants and products is called Thermochemical Equation.

All reactions can be categorized into one of the following two categories :

Endothermic Reactions

Are those chemical reactions which absorb energy.

(ΔH = positive)

Exothermic Reactions

Are those chemical reactions which release energy.

(ΔH = negative)

For a chemical reaction, $\Delta H_{REACTION} = H_{PRODUCTS} - H_{REACTANTS}$
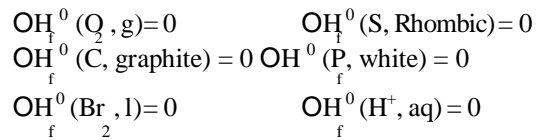The change in enthalpy during a chemical reaction occurs due to breaking and making of bonds.

Also, $\Delta H = \Delta U + \Delta n_g RT$.

25. ENTHALPY OF

Enthalpy change can be calculated for all reactions and is sometimes called the Heat of Reaction. Let's take a look at various types of reactions and enthalpy changes associated with them :

Enthalpy of Formation ΔH_f^0

It is the heat absorbed or released when one mole of a compound is formed from its constituent elements under their standard elemental forms. The enthalpy for formation of the following substances is taken to be zero under 1 bar pressure and 298 K.

$\Delta H_f^0 (O_2, g) = 0$ $\Delta H_f^0 (S, \text{Rhombic}) = 0$
$\Delta H_f^0 (C, \text{graphite}) = 0$ $\Delta H_f^0 (P, \text{white}) = 0$
$\Delta H_f^0 (Br_2, l) = 0$ $\Delta H_f^0 (H^+, aq) = 0$

Enthalpy of Combustion

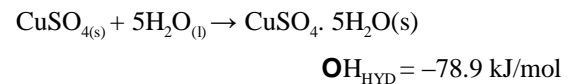It is the heat released or absorbed when one mole of a substance undergoes combustion in presence of oxygen.

$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g)$ $\Delta H = -890$ kJ/mol
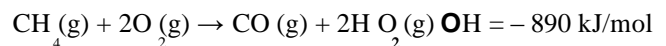
Enthalpy of Solution

It is the heat released or absorbed when 1 mole of a compound is dissolved in excess of a solvent (water).

$MgSO_4 (s) + H_2O (\text{excess}) \rightarrow Mg^{2+} (aq) + SO_4^{2-} (aq)$

$\Delta H_{Sol}^0 = -91.211$ kJ/mol
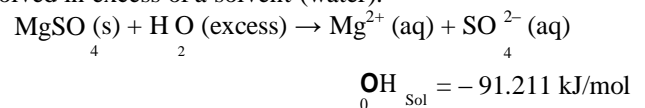
Enthalpy of Hydration

It is the energy released or absorbed when 1 mole of anhydrous or partially hydrated salt undergoes hydration by the addition of water of crystallisation. e.g.

$CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4 \cdot 5H_2O(s)$

$\Delta H_{HYD} = -78.9$ kJ/mol

Enthalpy of Neutralization

It is the heat released or absorbed when one equivalent of an acid undergoes neutralisation with one equivalent of a base. e.g.

$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$
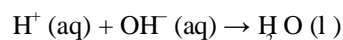
$\Delta H_R = -57.3$ kJ/mol

26. HESS LAW OF CONSTANT HEAT SUMMATION

Since enthalpy is a state function thus for a reaction which takes place in steps the net change in enthalpy can be calculated by adding the enthalpy changes of each step. This is called the Hess Law.

27. BORN HABER

The entire thermodynamics process of formation of an ionic crystal lattice is called Born Haber cycle. An ionic compound is formed from its constituents through a series of steps involving conversion of atoms/molecules into gaseous phase for ion formation, ionisation and electron gain to form ions and then the reaction of gaseous ions to form solid lattice.

28. BOND DISSOCIATION

The energy needed to break the bonds of one mole molecules is called the Bond Dissociation Enthalpy of the substance. It is defined per mol of molecule. eg. Bond dissociation enthalpy of H_2 is 436 kJ/mol

29. HEAT OF

It is defined as the energy required to convert any substance to gaseous atoms. This is defined per mol of the gaseous atoms. For example Heat of atomisation of H will be 218 kJ/mol atoms.
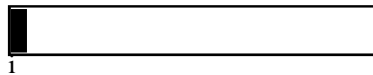
Example : 1

Calculate the internal energy change in each of the following cases :

(i) A system absorbs 15 kJ of heat and does 5 kJ of work.

(ii) 5 kJ of work is done on the system and 15 kJ of heat is given out by the system.

Sol. (i) Here, $q = +15\,kJ$

$w = -5\,kJ$

According to first law of thermodynamics,

$\Delta U = q + w = 15 + (-5) = 10\,kJ$

Thus, internal energy of the system increases by 10 kJ.

(ii) Here, $w = +5\,kJ$

$q = -5\,kJ$

According to first law of thermodynamics,

$\Delta U = q + w = -15 + (+5) = -10\,kJ$

Thus, the internal energy of the system decreases by 10 kJ.

Example : 2

Calculate w, q and ΔU when 0.75 mol of an ideal gas expands isothermally and reversibly at $27^{o}C$ from a volume of 15 L to 25 L.

Sol. For isothermal reversible expansion of an ideal gas,

$w = -2.303\,nRT\log\dfrac{V_2}{V_1}$ Putting $n = 0.75$ mol, $V_1 = 15\,L$, $V_2 = 25\,L$, $T = 27 + 273 = 300\,K$ and $R = 8.314\,J\,K^{-1}\,mol^{-1}$, we get

$w = -2.303 \times 0.75 \times 8.314 \times 300 \log\dfrac{25}{15} = -955.5\,J$

(–ve sign represents work of expansion)

For isothermal expansion of an ideal gas, $\Delta U = 0$

$\Delta U = q + w$ gives $q = -w = +955.5\,J$.

Example : 3

Carbon monoxide is allowed to expand isothermally and reversibly from $10\,m^3$ to $20\,m^3$ at 300 K and work obtained is 4.754 kJ. Calculate the number of moles of carbon monoxide.

Sol. $w = -2.303\,nRT\log\dfrac{V_2}{V_1}$

$-4754 = -2.303 \times n \times 8.314 \times 300 \log\dfrac{20}{10}$.

This given n = 2.75 moles.

Example : 4

A 5-litre cylinder contained 10 moles of oxygen gas at $27^{o}C$. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure is 1.0 atmosphere, calculate the work done by the gas. (1 L atm = 101.3 J)

Sol. $V_{initial} = 5L, T = 27^{o}C = 27 + 273\,K = 300\,K$

$V_{final} = \dfrac{nRT}{P} = \dfrac{10 \times 0.0821 \times 300}{1.0} = 246.3\,L$

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

$w_{exp} = -P\Delta V = -1 \times 241.3\,Latm = -241.3 \times 101.3\,J$

$= -24443.7\,J$.

Example : 5

Two moles of an ideal gas initially at $27^{o}C$ and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas is 10 atm.

Calculate q, w and ΔU for the process.

Sol. Here, $n = 2$ moles $T = 27^{o}C = 300\,K, P_1 = 1\,atm, P_2 = 10\,atm$

$w = -2.303\,nRT\log\dfrac{P_1}{P_2} = -2.303 \times 2 \times 8.314\,JK^{-1}\,mol^{-1} \times$

$300\,K \times \log\dfrac{1}{10} = 11488\,J$

For isothermal compression of ideal gas, $\Delta U = 0$

Further, $\Delta U = q + w$ $q = -w = -11488\,J$.

Example : 6

10g of argon gas is compressed isothermally and reversibly at a temperature of $27°C$ from 10L to 5L. Calculate q, W, ΔU and ΔH for this process.

$R = 2.0\,cal\,K^{-1}\,mol^{-1}$. $\log_{10}2 = 0.30$ Atomic wt. of Ar = 40

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

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

W = 103.991 cal

ΔU = 0 ; ΔH = 0 (Constant temperature)

q = ΔU – W   q = – W = – 103.991 cal

Example : 7

A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.

Sol. Since, work is done against constant pressure and thus, irreversible.

Given, ΔV = (6 – 2) = 4 litre; P = 1 atm

W = – 1 × 4 litre-atm = – 4 × 1.01325 × 10² J

= 405.3 J

Now from first law of thermodynamics

q = ΔU – W

800 = ΔU + 405.3 ΔU = 394.7 Joule

Example : 8

5 moles of an ideal gas at 300 K are expanded isothermally from an initial pressure of 500 Pa to a final pressure of 100 Pa against a constant external pressure of 100 Pa. Calculate w, q, ΔU and ΔH for the process. What will be the difference if the same process is carried out irreversibly? What are the values of w, q, ΔU, ΔH for the irreversible process ?

Sol.   For an isothermal irreversible expansion :

ΔU = ΔH = 0

$w = -P_{EXT}(V_2 - V_1)$

V_2 and V_1 can be calculated from ideal gas equation.

$V_1 = nRT/P_1 = 5 \times 8.314 \times 300/500 = 24.9 \text{ m}^3$

$V_2 = nRT/P_2 = 124.7 \text{ m}^3$

Therefore, w = – 100 × (124.5 – 24.9)

= – 9980 J

q = + 9980 J

If this process is done reversibly then the internal and external pressure should be same throughout.

ΔU = ΔH = 0 (temperature is constant)

$w = - nRT \ln (V_2/V_1)$

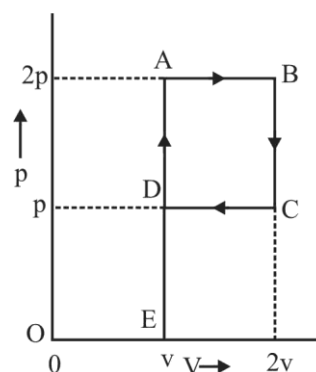= – 5 × 8.314 × 300 × ln 5

= – 20071.3 J

q = + 20071.3 J

Example : 9

The state of a mole of an ideal gas changed from state A (2p, v) through four different processes and finally returns to initial State A reversibly as shown below.

Calculate the total work done by the system and heat absorbed by the system in the cyclic process.

Sol.   State A to State B (Isobaric expansion)

Pressure is held constant at 2p and the gas is heated until the volume v becomes 2v.

$W_1 = -p\Delta V = -2p(2v - v) = -2pv$

State B to State C (Isochoric process)

Volume is held constant at 2v and the gas is coolled until the pressure 2P reaches p.

$W_2 = 0$ (ΔV = 0)

State C to State D (Isobaric compression)

Pressure is held constant at p and the gas is further cooled until the volume 2v becomes v.

$W_3 = -p(v - 2v) = pv$

State D to State A (Isochoric process)

Volume is held constant at v and the gas is heated until the pressure p reaches 2p.

$W_4 = 0$ (ΔV = 0)

Total work done by the gas $= W = W_1 + W_2 + W_3 + W_4$

or $W = -2pv + 0 + pv + 0 = -pv$ (= area ABCD)

As the process is cyclic $\Delta E = 0$

$\quad q = -w \rightarrow q = +pv$

where q is the heat absorbed in the cylic process.

Example : 10

Two mole of a perfect gas undergo the following processes:
(a) a reversible isobaric expansion from

(1.0 atm, 20.0L) to (1.0 atm, 40.0L).

(b) a reversible isochoric change of state from
(1.0 atm, 40.0L) to (0.5 atm, 40.0L)

(c) a reversible isothermal compression from

(0.5 atm, 40.0L) to (1.0 atm, 20.0L).

(i) sketch with labels each of the processes on the same P-V diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the value of ΔU, ΔH and ΔS for the overall process ?

Sol. The overall is cyclic one, i.e., initial state is regained, thus
$\Delta U = 0$; $\Delta H = 0$ and $\Delta S = 0$.

AB – Isobaric expansion
(w = -ve)
BC – Isochoric change
(w = 0)
CA – Isothermal compression
(w = + ve)
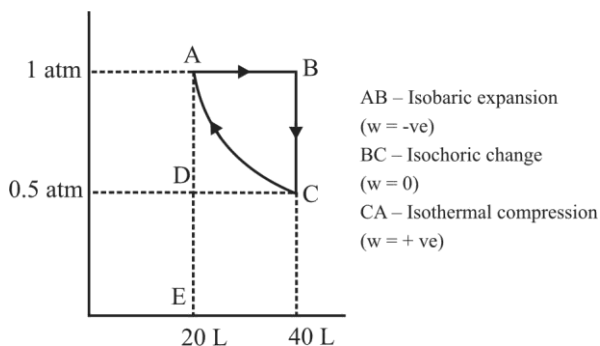
Now, total work $W = W_{A \rightarrow B} + W_{B \rightarrow C} + W_{C \rightarrow A}$

$W_{AB} = -P (V_B - V_A)$

$= -1 (40 - 20) = -20 L$ atm

$= -20 \times 1.01325 \times 10^2$ J

$= -2026.5$ J

$W_{BC} = O$ (Isochoric)

$W_{CA} = -2.303 \, nRT \log_{10} \dfrac{V_A}{V_C}$

$n = 2$ mol.

At point C : P = 0.5 atm, V = 40L

$PV = nRT$

$T = \dfrac{0.5 \times 40}{(0.0821)(2)} = 121.8$K.

$W_{CA} = -2.303(2)(8.314)(121.8) \log_{10} \left(\dfrac{20}{40} \right)$

$= 1404.07$ J

Total work, $W = -2026.5 + 0 + 1404.07$

$= -622.43$ J

For cyclic process : $\Delta U = 0$

$\rightarrow \quad q = -w$

$q = +622.43$ J

Example : 11

Calculate the amount of work done in each of the following cases :

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

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

Calculate the internal energy change (ΔU) in each case if the process were carried out adiabatically.

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

As expansion taks place into the evacuated bulb, i.e., against vacuum, $P_{ext} = 0$. Henc, w = 0.

For adiabatic process, $q = 0$ $\Delta U = q + w = 0 + 0 = 0$.

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

$P = 1$ atm $w = -P\Delta V$

$= -1 \times 4$ litre atm $= -4$ litres atm

$= -4 \times 101.3$ J $= -405.2$ J (1 L – atm = 101.3J)

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

For adiabatic process, $\Delta U = q + w = 0 - 405.2$ J $= -405.2$ J.

Example : 12

5.6 dm^3 of an unknown gas at S.T.P. required 52.25 J of heat to raise its temperature by 10°C at constant volume. Calculate C_v, C_p and **y** of the gas

Sol. The 22.4 dm^3 of a gas at S.T.P. = 1 mol

$$5.6 \text{ dm}^3 \text{ of the gas at S.T.P.} = \frac{1}{22.4} \times 5.6 = 0.25 \text{ mol}$$

Thus, for 10° rise, 0.25 mol of the gas at constant volume require heat = 52.25 J

For 1° rise, 1 mol of the gas at constant volume will require heat = $\dfrac{52.25}{10 \times 0.25}$ = 20.9

C_v = 20.9 J K^{-1} mol^{-1}

Now, $C_p = C_v + R$ = 20.9 J K^{-1} mol^{-1} + 8.314 J K^{-1} mol^{-1} = 29.214 J K^{-1} mol^{-1}

$$y = \frac{C_p}{C_v} = \frac{29.214}{20.9} = 1.4$$

Example : 13

A heated copper block at 130°C loses 340 J of heat to the surroundings which are at room temperature of 32°C. Calculate

(i) the entropy change of the system (copper block)

(ii) the entropy change in the surroundings

(iii) the total entropy change in the universe due to this process

Assume that the temperature of the block and the surroundings remains constant.

**Sol.** T_{system} = 130°C = 130 + 273 K = 403 K, T_{surr} = 32°C = 32 + 273 K = 305 K q_{system} = − 340 J, q_{surr} = + 340 J

(i) $\text{O}S_{system} = \dfrac{q_{system}}{T_{system}} = \dfrac{-340 \text{ J}}{403 \text{K}}$ = -0.84 JK^{-1}

(ii) $\text{O}S_{surr} = \dfrac{q_{surr}}{T_{surr}} = \dfrac{+340 \text{J}}{305 \text{K}}$ = +1.11 JK^{-1}

(iii) $\text{O}S_{total}$ or $\text{O}S_{universe} = \text{O}S_{system} + \text{O}S_{surr}$ = −0.84 + (+1.11) J K^{-1} = 0.27 J K^{-1}

Example : 14

An ideal gas is originally confined to a volume V_1 in an insulated container of volume $V_1 + V_2$. The remainder of the container is evacuated. The portion is then removed and the gas expands to fill the entire container. If the initial temperature of the gas was T, what is the final temperature. Also predict qualitatively, the entropy change of system, surroundings and the universe.

Insulated container
V_1 V_2 vacuum
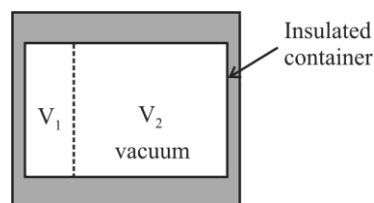
Sol. This is a process of adiabatic free expansion of an ideal gas. The internal energy does not change thus the temperature also stays the same, i.e., the final temperature is still T.
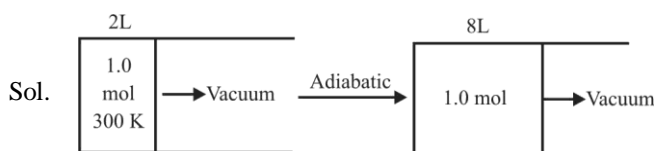
$$\text{O}S_{system} = nR \ln \frac{V_1 + V_2}{V_1} > 0 \quad V_1 + V_2 > V_1$$

$\text{O}S_{surr}$ = 0 $q_{surr.}$ = 0

→ $\text{O}S_{univ} > 0$

Example : 15

1.0 mol of an ideal gas, initially present in a 2.00 L insulated cylinder at 300 K is allowed to expand against vacuum to 8.00 L. Determine W, $\text{O}E$, $\text{O}H$, $\text{O}S_{univ}$ and $\text{O}G$.

Sol.

2L | 1.0 mol 300 K →Vacuum | Adiabatic | 8L | 1.0 mol →Vacuum

$W = -p_{ext}\text{O}V = 0$, q = 0, → $\text{O}E = 0 = \text{O}H$

→ T_f = 300 K

$\text{O}S_{sys} = R \ln \dfrac{V_2}{V_1} = R \ln 4 = 11.52 \text{ JK}^{-1}$

$\text{O}S_{surr}$ = 0 $\quad\quad\quad q_{sys} = q_{surr} = 0$

→$\text{O}S_{univ}$ = 11.52 JK^{-1}

→ $\text{O}G = -T\text{O}S_{univ}$ = − 300 × 11.52 = − 3456 J/mol.

The heat of combustion of benzene in a bomb calorimeter (i.e., constant volume) was found to be 3263.9 kJ mol^{-1} at 25°C. Calculate the heat of combustion of benzene at constant pressure.

Sol. The reaction is:

$$C_6H_6(A) + 7\tfrac{1}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(A)$$
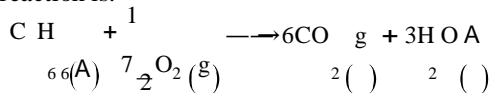
In this reaction, O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$$\Delta n_g = n_p - n_r = 6 - 7\tfrac{1}{2} = -1\tfrac{1}{2} = -\tfrac{3}{2}$$

Also, we are given ΔU (or q_v) $= -3263.9$ kJ mol^{-1}

$$T = 25°C = 298K$$

$$R = 8.314 \text{ J K}^{-1}\text{ mol}^{-} = \frac{8.314}{1000}\text{ kJ K}^{-1}\text{ mol}^{-1}$$

$$\Delta H \text{(or } q_p) = \Delta U + \Delta n_g RT = -3263.9 \text{ kJmol}^{-1} +$$

$$\left\{-\frac{3}{2}\text{ mol}\right\}\left\{\frac{8.314}{1000}\text{ kJ K}^{-1}\text{ mol}^{-1}\right\}(298\text{ K})$$

$$= -3263.9 - 3.7 \text{ kJ mol}^{-1} = -3267.6 \text{ kJ mol}^{-1}.$$

Calculate the amount of heat evolved when

(i) 500 cm^3 of 0.1 M hydrochloric acid is mixed with 200 cm^3 of 0.2 M sodium hydroxide solution

(ii) 200 cm^3 of 0.2 M sulphuric acid is mixed with 400 cm^3 of 0.5 M potassium hydroxide solution.

Assuming that the specific heat of water is 4.18 JK^{-1} g^{-1} and ignoring the heat absorbed by the container, thermometer, stirrer etc., what would be the rise in temperature in each of the above cases ?

Sol. (i) moles of HCl $= \dfrac{0.1}{1000} \times 500 = 0.05 = 0.05$ mole of H$^+$ ions

$$200 \text{ cm}^3 \text{ of } 0.2M \text{ NaOH} = \frac{0.2}{1000} \times 200$$

mole of NaOH $= 0.04$ mole $= 0.04$ mole of OH$^-$ ions

Thus, 0.04 mole of H$^+$ ions will combine with 0.04 mole of OH$^-$ ions to from 0.04 mole of H_2O and 0.01 mole of H$^+$ ions will remain unreacted.

Heat evolved when 1 mole of H$^+$ ions combine with 1 mole of OH$^-$ ions = 57.1 kJ.

Heat evolved when 0.04 mole of H$^+$ ions combine with 0.04 mole of OH$^-$ ions = $57.1 \times 0.04 = 2.284$ kJ

(ii) 200 cm^3 of 0.2 M $H_2SO_4 = \dfrac{0.2}{1000} \times 200$ mole of H_2SO_4

$= 0.04$ mole of $H_2SO_4 = 0.08$ mole of H$^+$ ions

400 cm^3 of 0.5 M KOH $= \dfrac{0.5}{1000} \times 400$ mole of KOH $=$

0.2 mole of KOH = 0.2 mole of OH$^-$ ions

Thus, 0.08 mole of H$^+$ ions will neutralize 0.08 mole of OH$^-$ ions. (out of 0.2 mole of OH$^-$ ions) to form 0.08 mole of H_2O.

Hence, heat evolved $= 57.1 \times 0.08 = 4.568$ kJ

In case (i), heat produced = 2.284 kJ = 2284 J

Total volume of the solution $= 500 + 200 = 700$ mL

Assuming density of solution = 1g/mL

So mass of solution = 700g

Specific heat = 4.18 J K^{-1} g^{-1}

$$Q = m \times C \times \Delta T \qquad \Delta T = \frac{Q}{m \times C} = \frac{2284}{700 \times 4.18} = 0.78°C$$
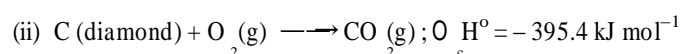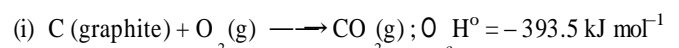
In case (ii), heat produced = 4.568 kJ = 4568 J

Total mass of the solution $= 200 + 400 = 600$ g

$$\Delta T = \frac{Q}{m \times C} = \frac{4568}{600 \times 4.18} = 1.82°C$$

Calculate the enthalpy change accompanying the transformation of C (graphite) to C(diamond). Given that the enthalpies of combustion of graphite and diamond are and 395.4 kJmol^{-1} respectively.

Sol. Remember, enthalpy of combustion is always negative we are given

(i) C (graphite) $+ O_2(g) \longrightarrow CO_2(g)$; $\Delta H^o_c = -393.5$ kJ mol^{-1}

(ii) C (diamond) $+ O_2(g) \longrightarrow CO_2(g)$; $\Delta H^o_c = -395.4$ kJ mol^{-1}

We aim at $\quad$ C(graphite) $\longrightarrow$ C(diamond), $\Delta_{trans}H^\circ = ?$
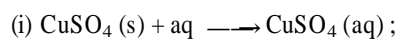
Subtracting eqn. (ii) from eqn. (i), we get
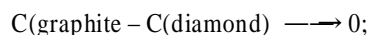
$$C(graphite) - C(diamond) \longrightarrow 0;$$

$$\Delta H_r^\circ = -393.5 - (-395.4) = +1.9 \text{ kJ}$$

or $\quad$ C(graphite) $\longrightarrow$ (diamond) ; $\Delta_{trans}H = +1.9$ kJ
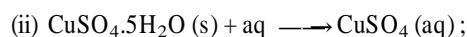
Example : 19

Calculate the enthalpy of hydration of anhydrous copper sulphate ($CuSO_4$) into hydrated copper sulphate ($CuSO_4.5H_2O$). Given that the enthalpies of solutions of anhydrous copper sulphate and hydrated copper sulphate are -66.5 and $+11.7$ kJ mol^{-1} respectively

Sol. $\quad$ We are given

(i) $CuSO_4$ (s) + aq $\longrightarrow CuSO_4$ (aq) ;

$$\Delta_{sol}H_1 = -66.5 \text{ kJ mol}^{-1}$$

(ii) $CuSO_4.5H_2O$ (s) + aq $\longrightarrow CuSO_4$ (aq) ;

$$\Delta_{sol}H_2 = +11.7 \text{ kJ mol}^{-1}$$

We aim at $CuSO_4$ (s) + $5H_2O$ (l) $\longrightarrow CuSO_4.5H_2O(s)$;

$$\Delta_{hyd}H = ?$$

$$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - (+11.7) = -78.2 \text{ kJ/mol}$$

Calculate the enthalpy of formation of methane, given that the enthalpies of combustion of methane, graphite and hydrogen are 890.2 kJ, 393.4 kJ and 285.7 kJ mol^{-1} respectively.
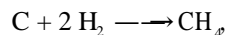
Sol. Remember : Enthalpy of combustion is always negative.

We are given :

(i) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O, \Delta H = -890.2 \text{ kJ mol}^{-1}$

(ii) $C + O_2 \longrightarrow CO_2, \Delta H = -393.4 \text{ kJ mol}^{-1}$

(iii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O, \Delta H = -285.7 \text{ kJ mol}^{-1}$
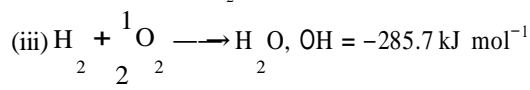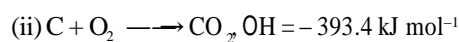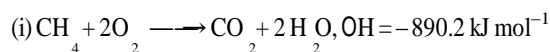
We aim at : $C + 2H_2 \longrightarrow CH_4, \Delta H = ?$

In order to get this thermochemical equation, multiply eqn. (iii) by 2 and add it to eqn. (ii) and then subtract eqn. (i) from their sum. We get :

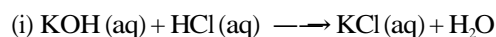$$C + 2H_2 \longrightarrow CH_4,$$
$$\Delta H = -393.4 + 2(-285.7)$$
$$- (-890.2) \text{ kJ mol}^{-1} = -74.6 \text{ kJ mol}^{-1}$$

Hence, the heat of formation of methane is :

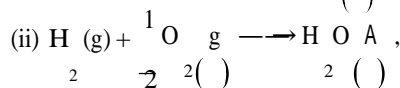$$\Delta_f H = -74.6 \text{ kJ mol}^{-1}$$

Example : 21

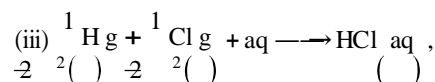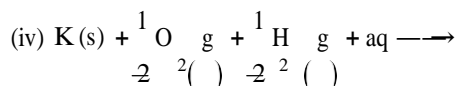Calculate the heat of formation of KCl from the following data:

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

(ii) $H_2 (g) + \frac{1}{2}O_2 (g) \longrightarrow H_2O (l)$,
$$\Delta H = -286.2 \text{ kJ mol}^{-1}$$

(iii) $\frac{1}{2}H_2 (g) + \frac{1}{2}Cl_2 (g) + aq \longrightarrow HCl (aq)$,
$$\Delta H = -164.4 \text{ kJ mol}^{-1}$$

(iv) $K (s) + \frac{1}{2}O_2 (g) + \frac{1}{2}H_2 (g) + aq \longrightarrow$
$$KOH (aq), \Delta H = -487.4 \text{ kJ mol}^-$$

(v) $KCl (s) + aq \longrightarrow KCl (aq), \Delta H = +18.4 \text{ kJ mol}^{-1}$
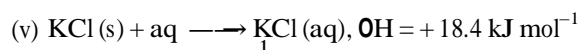
Sol. $\quad$ We aim at : $K(s) + \frac{1}{2}Cl_2 (g) \longrightarrow KCl (s), \Delta_f H = ?$

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

Step 1. Adding Eqns. (iii) and (iv) and subtacting Eq. (v). we have

$$K (s) + \frac{1}{2}Cl_2 (g) + H_2 (g) + \frac{1}{2}O_2 (g) \longrightarrow KCl (s) +$$
$$HCl (aq) + KOH (aq) - KCl (aq)$$
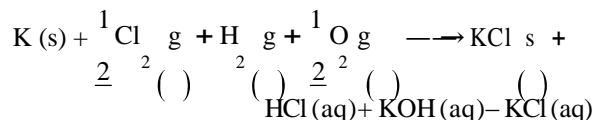
$\Delta H = -487.4 + (-164.4) - (18.4) = -670.2 \text{ kJ mol}^{-1} ...(vii)$

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

$$K (s) + \frac{1}{2}Cl_2 (g) \longrightarrow KCl (s) ;$$
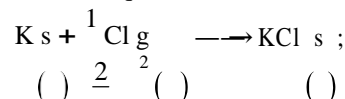
$$\Delta_f H = -670.2 + 57.3 - (-286.2) = -441.3 \text{ kJ}$$

The combustion of 1 mole of benzene takes place at 298 K and 1 atm. After combustion, CO_2(g) and H_2O(l) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^o$ of benzene. Standard enthalpies of formation of CO_2(g) and H_2O(l) are -393.5 kJ mol^{-1} and -285.83 kJ mol^{-1} respectively.
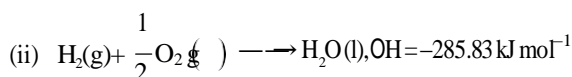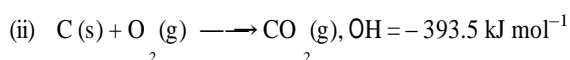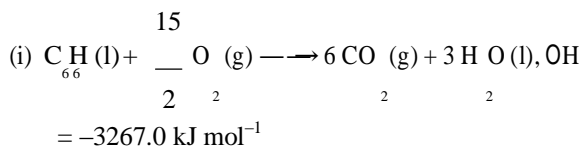
Sol. Aim : $6\,C\,(s) + 3\,H_2(g) \longrightarrow C_6H_6\;(A)$, $\Delta H = ?$

Given :

(i) $C_6H_6\,(l) + \dfrac{15}{2}\,O_2\,(g) \longrightarrow 6\,CO_2\,(g) + 3\,H_2O\,(l)$, $\Delta H = -3267.0$ kJ mol^{-1}

(ii) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$, $\Delta H = -393.5$ kJ mol^{-1}

(iii) $H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$, $\Delta H = -285.83$ kJ mol^{-1}

In order to get the required thermochemical equation, multiply Eq. (ii) by 6 and Eq. (iii) by 3 and subtract Eq. (i) from their sum, i.e. operating $6 \times$ Eqn. (ii) $+ 3 \times$ Eqn. (iii) $-$ Eqn. (i), we get

$$6C\,(s) + 3H_2(g) \longrightarrow C_6H_6\,(l) ;$$
$$\Delta H = 6\,(-393.5) + 3\,(-285.83) - (-3267.0)$$
$$= -2361 - 857.49 + 3267.0 = 48.51 \text{ kJ mol}^{-1}$$

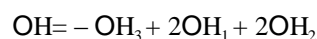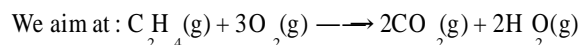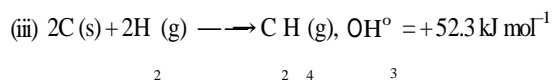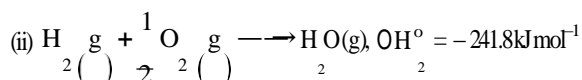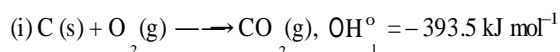Thus, the enthalpy of formation of benzene is

$\Delta_f H = -48.51$ kJ mol^{-1}

Calculate the enthalpy of combustion of ethylene (gas) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of CO_2, H_2O and C_2H_4 are -393.5, -241.8, $+52.3$ kJ per mole respectively.
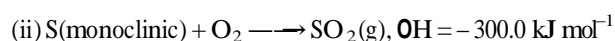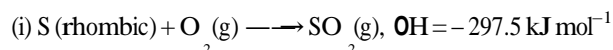
Sol. We are given :

(i) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$, $\Delta H^o_1 = -393.5$ kJ mol^{-1}

(ii) $H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$, $\Delta H^o_2 = -241.8$ kJ mol^{-1}

(iii) $2C\,(s) + 2H_2\,(g) \longrightarrow C_2H_4\,(g)$, $\Delta H^o_3 = +52.3$ kJ mol^{-1}

We aim at : $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O(g)$

$\Delta H = -\Delta H_3 + 2\Delta H_1 + 2\Delta H_2$

$= -1322.9$ kJ mol^{-1}

Given the following thermochemical equations:

(i) $S\,(\text{rhombic}) + O_2\,(g) \longrightarrow SO_2\,(g)$, $\Delta H = -297.5$ kJ mol^{-1}

(ii) $S(\text{monoclinic}) + O_2 \longrightarrow SO_2(g)$, $\Delta H = -300.0$ kJ mol^{-1}

Calculate ΔH for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur.

Sol. We aim at

$S\,(\text{rhombic}) \to S\,(\text{monoclinic})$, $\Delta H = ?$
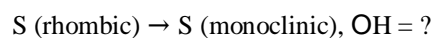
Equation (i) $\to$ Equation (ii) gives

$S(\text{rhombic}) - S(\text{monoclinic}) \longrightarrow 0$,
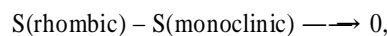
$\Delta H = 297.5 - (-300.0) = 2.5$ kJ mol^{-1}

or $S(\text{rhombic}) \longrightarrow S(\text{monoclinic})$, $\Delta H = +2.5$ kJ mol^{-1}
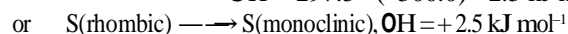
Thus, for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur, 2.5 kJ mol^{-1} of heat is absorbed.

Enthalpy of solution (ΔH) for $BaCl_2.2H_2O$ and $BaCl_2$ are and -20.6 kJ mol^{-1} respectively. Calculate the heat of hydration of $BaCl_2$ to $BaCl_2.2H_2O$.

Sol. We are given
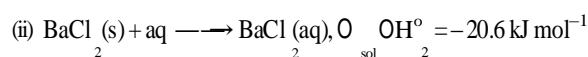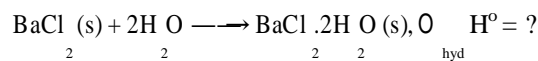
(i) $BaCl_2.2H_2O(s) + aq \longrightarrow BaCl_2(aq)$, $\Delta_{sol} H^o_1 = 8.8$ kJ mol^{-1}

(ii) $BaCl_2(s) + aq \longrightarrow BaCl_2(aq)$, $\Delta_{sol} H^o_2 = -20.6$ kJ mol^{-1}

We aim at

$BaCl_2(s) + 2H_2O \longrightarrow BaCl_2.2H_2O(s)$, $\Delta_{hyd} H^o = ?$

$\Delta H = \Delta H_2 - \Delta H_1 = -29.4$ kJ mol^{-1}

Calculate the enthalpy of hydrogenation of ethylene, given that the enthalpy of combustion of enthylene, hydrogen and ethane are -1410.0, -286.2 and -1560.6 kJ mol^{-1} respectively at 298 K.

Sol. We are given (i) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$, $\Delta H = -1410$ kJ mol^{-1}

(ii) $H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(l), \Delta H = -286.2 \text{ kJ mol}^{-1}$

(iii) $C_2H_6(g) + 3\dfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l), \Delta H = -1560.6 \text{ kJ mol}^{-1}$

We aim at: $C_2H_4 + H_2(g) \longrightarrow C_2H_6(g), \Delta H = ?$
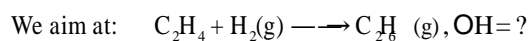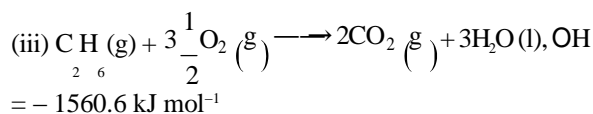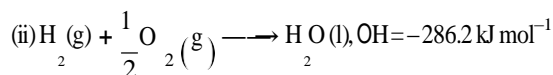
Equation (i) + Equation (ii) − Equation (iii) gives

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g),$

$\Delta H = -1410.0 + (-286.2) - (1560.6) = -135.6 \text{ kJ mol}^{-1}$

Example : 27

The thermite reaction used for welding of metals involves the reaction

$2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$
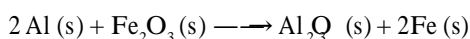
What is ΔH^o at 25°C for this reaction ? Given that the standard heats of formation of Al_2O_3 and Fe_2O_3 are −1675.7 kJ and −828.4 kJ mol^{-1} respectively.

Sol.　We aim at $2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s), \Delta_r H^o = ?$

$\Delta_r H$ = Sum of $\Delta_f H^o$ of products − Sum of $\Delta_f H^o$ of reactants

$= [\Delta_f H^o(Al_2O_3) + 2 \times \Delta_f H^o(Fe)] - [2 \times \Delta_f H^o(Al) + \Delta_f H^o(Fe_2O_3)]$

$= [-1675.7 + 0] - [0 + (-828.4)] = -847.3 \text{ kJ mol}^{-1}$

Example : 28

The heat evolved in the combustion of methane is given by the equation:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l), \Delta H = -890.3 \text{ kJ mol}^{-1}$

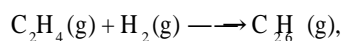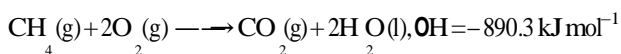(a) How many grams of methane would be required to produce 445.15 kJ of heat of combustion ?

(b) How many grams of carbon dioxide would be formed when 445.15 kJ of heat is evolved ?

(c) What volume of oxygen at STP would be used in the combustion process (a) or (b) ?

Sol.　(a) From the given equation.

890.3 kJ of heat is produced from 1 mole of CH_4, i.e.,
12 + 4 = 16 g of CH_4

445.15 kJ of heat is produced from 8 g of CH_4

(b) From the given equation, when 890.3 kJ of heat is evolved, CO_2 formed = 1 mole = 44 g

When 445.15 kJ of heat is evolved, CO_2 formed = 22 g

(c) From the equation, O_2 used in the production of 890.3 kJ of heat = 2 moles = 2 × 22.4 litres at STP

$= 44.8$ litres at STP

Hence, O_2 used in the production of 445.15 kJ of heat = 22.4 litres at STP.

Example : 29

From the thermochemical equation,
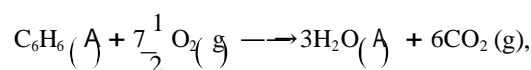
$C_6H_6(l) + 7\dfrac{1}{2}O_2(g) \longrightarrow 3H_2O(l) + 6CO_2(g), \Delta_c H = -3264.64 \text{ kJ mol}^{-1},$

calculate the energy evolved when 39 g of C_6H_6 are burnt in an open container.

Sol.　From the given equation,

When 1 mole of C_6H_6 (78 g of C_6H_6) is burnt, heat evolved = 3264.64 kJ

When 39 g of C_6H_6 is burnt, heat evolved = $\dfrac{3264.64}{78} \times 39 = 1632.32$ kJ

Example : 30

The thermochemical equation for solid and liquid rocket fuel are given below :

$2Al(s) + 1\dfrac{1}{2}O_2(g) \longrightarrow Al_2O_3(s)$;

$\Delta H = -1667.8 \text{ kJ mol}^{-1}$

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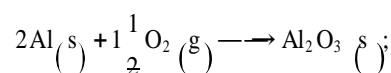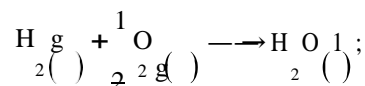
$\Delta H = -285.9 \text{ kJ mol}^{-1}$

(a) If equal masses of aluminium and hydrogen are used, which is a better rocket fuel ?

(b) Determine ΔH for the reaction :

$Al_2O_3(s) \longrightarrow 2Al(s) + 1\dfrac{1}{2}O_2(g)$.
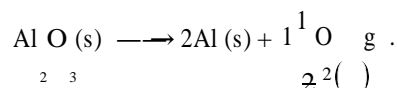
Sol.　(a) From the first given equation,

2 moles of Al (i.e., 2×27 g $= 54$ g) on combustion give heat $= 1667.8$ kJ

$\quad$ 1 g of Al on combustion gives heat $= \dfrac{1667.8}{54} = 30.9$ kJ

From the second given equation, 1 mole of H_2 ($= 2$ g) on combsution gives heat $= 285.9$ kJ

$\quad$ 1 g of H_2 on combustion gives heat $= \dfrac{285.9}{2} = 142.95$ kJ

Thus, H_2 is a better rocket fuel.

(b) Writing the reverse of the first reaction, we have

$Al_2O_3 (s) \longrightarrow 2Al (s) + \dfrac{1}{2} O_2(g)$; $\quad \Delta H = +1667.8$ kJ mol^{-1}
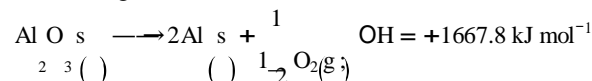
Thus, for the reaction given in part (b) of the problem,

$\Delta H = +1667.8$ kJ mol^{-1}

Example : 31

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

Sol. $\quad$ Molar mass of naphthalene ($C_{10}H_8$) $= 128$ g mol^{-1}

When 1 g of liquid naphthalene solidified, heat evolved $= 149$ joules.

When 1 mole, i.e., 128 g of naphthalene solidifies, heat evolved $= 149$ joules.

When 1 mole, i.e., 128 g of naphthalene solidifies, heat evolved $= 149 \times 128$ joules $= 19072$ joules

Since fusion is reverse of solidification, therefore, heat absorbed for fusion of one mole of naphthalene $= 19072$ joules.

i.e., Enthalpy of fusion ($\Delta_{fus}H$) $= +19072$ joules/mole

---

Example : 32

The heat evolved in the combustion of glucose is shown in the equation:

$C_6H_{12}O_6 + 6O_2 (g) \longrightarrow 6CO_2 (g) + 6 H_2O (g)$, $\Delta_c H = -2840$ kJ mol^{-1}
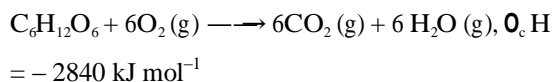
What is the energy requirement for production of 0.36 g of glucose by the reverse reaction ?

Sol. $\quad$ The given equation is :

$C_6H_{12}O_6 + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O (g)$;

$\quad\quad\quad\quad\quad\quad \Delta_r H = -2840$ kJ mol^{-1}
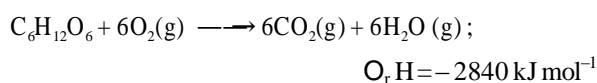
Writing the reverse reaction, we have

$6CO_2 (g) + 6H_2O(g) \longrightarrow C_6H_{12}O_6 (s) + 6O_2(g)$; $\Delta_r H = +2840$ kJ mol^{-1}
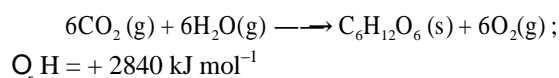
Thus, for production of 1 mole of $C_6H_{12}O_6$ ($= 72 + 12 + 96 = 180$ g), heat required (absorbed) $= 2840$ kJ.

$\quad$ For production of 0.36 g of glucose, heat absorbed $= \dfrac{2840}{180} \times 0.36 = 5.68$ kJ

Example : 33

Calculate the bond energy of C–H bond, given that the heat of formation of CH_4, heat of sublimation of carbon and heat of dissociation of H_2 are -74.8, $+719.6$ and 435.4 kJ mol^{-1} respectively.

Sol. $\quad$ Here, we are given

$C (s) + 2H_2 (g) \longrightarrow CH_4 (g)$, $\Delta_r H^o = -74.8$ kJ
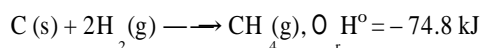
$\Delta H = e_{sub(C)} + 2e_{H-H} - 4e_{C-H}$

$-74.8 = 719.6 + 2 (435.4) - 4e_{C-H}$

$e_{C-H} = 416.3$ kJ/mol

Example : 34

Calculate the enthalpy change for the reaction

$H_2 (g) + Br_2 (g) \quad\quad 2HBr (g)$
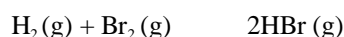
Given that the bond enthalpies of H–H, Br–Br, H–Br are 435, 192 and 364 kJ mol^{-1} respectively.

Sol. $\quad \Delta_r H = \Sigma$ B.E. (Reactants) $- \Sigma$ B.E. (Products)

$= [\text{B.E. } (H_2) + \text{B.E. } (Br_2)] - 2 \text{ B.E. (HBr)} =$

$435 + 192 - 2 \times 364 = -101$ kJ

Example : 35

Propane has the structure $H_3C–CH_2–CH_3$. Calculate the change in enthalpy for the reaction:

$$C_3H_8 (g) + 5\, O_2 (g) \longrightarrow 3\, CO_2 (g) + 4\, H_2O (g)$$

Given that average bond enthalpies are:

C–C	C–H	C = O	O = O	O–H
347	414	741	498	464 kJ mol^{-1}

Sol.

$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H + 5\ O=O \rightarrow 3\ O=C=O + 4\ H-O-H$$

$\Delta H = (2e_{C-C} + 8e_{C-H} + 5e_{O=O}) - (6e_{C=O} + 8e_{O-H})$

$= 2\,(347) + 8\,(414) + 5\,(498) - 6\,(741) - 8\,(464)$

$= -1662$ kJ mol^{-1}

Example 36

Calculate the entropy change involved in conversion of one mole (18 g) of solid ice at 273 K to liquid water at the same temperature (latent heat of fusion = 6025 Jmol^{-1}).

Sol.   Entropy change for ice → water is given by $\Delta_f S = \dfrac{\Delta_f H}{T_f}$

Here, $\Delta_f H = 6025$ J mol$^-$, $T_f = 273$ K

$$\Delta_f S = \frac{6025\ JK^{-1}\,mol^{-1}}{273K} = 22.1\ J\ K^{-1}\,mol^{-1}.$$

Example 37

Calculate the entropy change involved in the conversion of one mole of liquid water at 373 K to vapour at the same temperature (latent heat of vaporization of water $\Delta_{vap} H = 2.257$ kJ/g)

Sol.   For the conversion of water → vapour, the entropy change is given by $\Delta_{vap} S = \dfrac{\Delta_{vap} H}{T_b}$

Here, $\Delta_{vap} H = 2.257$ kJ/g $= 2.257 \times 18$ kJ/mol $= 40.626$ kJ/mol, $T_b = 373$ K

$$\Delta_{vap} S = \frac{40.626\ kJ\ mol^{-1}}{373\ K} = 0.1089\ kJ\ K^{-1}$$

$mol^{-1} = 108.9$ J K^{-1} mol^{-1}.

Example : 38

At 0°C, ice and water are in equilibrium and $\Delta H = 6.00$ kJ mol^{-1} for the process $H_2O\,(s) \rightarrow H_2O\,(l)$. What will be ΔS and ΔG for the conversion of ice to liquid water ?

Sol.   Since the given process is in equilibrium, $\Delta G = 0$ Putting this value in the relationship, $\Delta G = \Delta H - T\Delta S$, we get
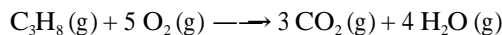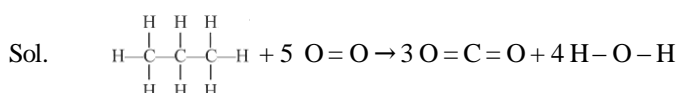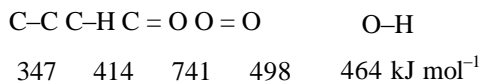
$$0 = \Delta H - T\Delta S \text{ or } T\Delta S = \Delta H \text{ or } \Delta S = \frac{\Delta H}{T}$$

We are given $\Delta H = 6.0$ kj mol$^{-1} = 6000$ J mol^{-1} and $T = 0°C = 273$ K

$$= \frac{6000\ J\,mol^{-1}}{273K} = 21.98\ J\ K^{-1}\ mol^{-1}$$

Example : 39

$$A + B \longrightarrow C + D\ ;\ \Delta H = -10,000\ J\ mol^{-1},$$
$$\Delta S = -33.3\ J\ mol^{-1}\ K^{-1}$$
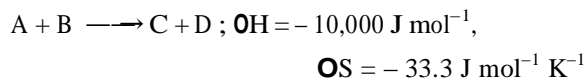
(i) At what temperature the reaction will occur spontaneously from left to right ?

(ii) At what temperature, the reaction will reverse?

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

At equilibriu, $\Delta G = 0$ so that $\Delta H = T\Delta S$ or

$$T = \frac{\Delta H}{\Delta S} = \frac{-10000\ J\ mol^{-1}}{-33.3\ JK^{-1}\ mol^{-1}} = 300.03\ K$$

(i) For spontaneity from left to right. ΔG should be –ve for the given reaction. This will be so if T < 300.3 K

(ii) For reverse reaction to occur, ΔG should be +ve forward reaction. This will be so if T > 300.3 K.

Example 40

Calculate the standard free energy change for the reaction,

$4NH_3 (g) + 5O_2 (g) \longrightarrow 4NO (g) + 6H_2O (l)$
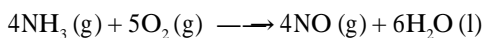
Given that the standard free energies of formation (ΔG_f^o) for NH_3 (g), NO (g) and H_2O (l) are $- 16.8$, $+ 86.7$ and $- 237.2$ kJ mol^{-1} respectively. Predict the feasibility of the above reaction at the standard state.

Sol. Here, we are given

$$\Delta G_f^o (NH_3) = - 16.8 \text{ kJ mol}^{-1}$$

$$\Delta G_f^o (NO) = + 86.7 \text{ kJ mol}^{-1}$$

$$\Delta G_f^o (H_2O) = - 237.2 \text{ kJ mol}^{-1}$$

$\Delta_r G^o = \Sigma \Delta_f G^o (\text{Products}) - \Sigma \Delta_f G^o (\text{Reactants}) =$
$[14 \times$
$\Delta_f G^o (NO) + 6 \times \Delta_f G^o (H_2O)] - [4 \times \Delta_f G^o (NH_3)$
$+ 5 \times \Delta_f G^o (O_2)]$

$= [4 \times (86.7) + 6 \times (-237.2)] - [4 \times (- 16.8) + 5 \times$
$0] = - 1009.2 \text{ kJ}$

Since $\Delta_r G^o$ is negative, the process is feasible.

Example 41

Calculate the entropy change for the rusting of iron according to the reaction :

$4 \text{ Fe (s)} + 3 O_2 (g) \longrightarrow 2 \text{ Fe}_2O_3 (s), \Delta H^o = -1648 \text{ kJ mol}^{-1}$

Given that the standard entropies of Fe, O_2 and Fe_2O_3 are 27.3, 205.0 and 87.4 J K^{-1} mol^{-1} respectively. Will the reaction be spontaneous at room temperature (25^oC) ? Justify your answer with appropriate calculations.

Sol. $\Delta_r S^o = \Sigma S^o (\text{Products}) - \Sigma S^o (\text{Reactants}) =$
$2 S^o(Fe_2O_3) - [4 S^o (Fe) + 3 S^o (O_2)]$

$= 2 \times 87.4 - [4 \times 27.3 + 3 \times 205.0] \text{ J K}^{-1}\text{mol}^{-1} =$
$- 549.4 \text{ J K}^{-1} \text{ mol}^{-1}$

This is the entropy change of the reaction, i.e., system (ΔS_{system})

Now, $\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o$

$= - 1648000 \text{ J mol}^{-1} - 298 \text{ K} \times$
$(-549.4 \text{ J K}^{-1}\text{mol}^{-1})$

As ΔG^o is $-$ve, the reaction is spontaneous.

Example 42

Calculate the standard enthalpy of formation of CH_3OH (l) from the following data :

(i) $CH_3OH (l) + \dfrac{3}{2} O_2 (g) \longrightarrow CO_2 (g) + 2 H_2O (l)$; $\Delta_r H^o = -726 \text{ kJ mol}^{-1}$

(ii) $C (s) + O_2 (g) \longrightarrow CO_2 (g)$; $\Delta_c H^o = - 393 \text{ kJ mol}^{-1}$

(iii) $H_2 (g) + \dfrac{1}{2} O_2 (g) \longrightarrow H_2O (l)$; $\Delta_f H^o = - 286 \text{ kJ mol}^{-1}$.

Sol. Aim : $C (s) + 2 H_2 (g) + \dfrac{1}{2} O_2 (g) \longrightarrow CH_3OH (l)$,

$$\Delta_f H^o = ?$$

Eqn. (ii) + 2 × Eqn. (iii) − Eqn. (i) gives the required eqn. with $\Delta H = - 393 + 2 (-286) - (- 726) \text{ kJ mol}^{-1} =$

$- 239 \text{ kJ mol}^{-1}.$

Example 43

Calculate enthalpy of formation of methane (CH_4) from the following data :

(i) $C (s) + O_2 (g) \longrightarrow CO_2 (g)$, $\Delta_r H^o = - 393.5 \text{ kJ mol}^{-1}$

(ii) $H_2 (g) + \dfrac{1}{2} O_2 (g) \longrightarrow H_2O (l)$,
$\Delta_r H^o = - 285.8 \text{ kJ mol}^{-1}$

(iii) $CH_4 (g) + 2O_2 (g) \longrightarrow CO_2 (g) + 2 H_2O (l)$,
$\Delta H^o = -890.3 \text{ kJ mol}^{-1}$

Sol. We aim at : $C (s) + 2 H_2 (g) \longrightarrow CH_4 (g)$; $\Delta_f H^o = ?$

Multiplying eqn. (ii) with 2, adding to eqn. (i) and then subtracting eqn. (iii) from the sum, i.e., operating eqn.

(i) + 2 × eqn. (ii) − eqn. (iii), we get

$C (s) + 2 H_2 (g) - CH_4 (g) \longrightarrow 0$; $\Delta_r H^o = - 393.5 + 2 (-285.8) - (-890.3) - 74.8 \text{ kJ mol}^{-1}$

or $C(s) + 2H_2(g) \longrightarrow CH_4(g); \Delta H_f^o = -74.8 \, kJ \, mol^{-1}$
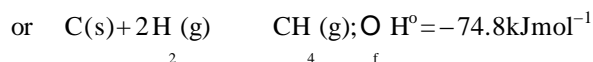
Hence, enthalpy of formation of methane is :

$$\Delta H_f^o = -74.8 \, kJ \, mol^{-1}$$
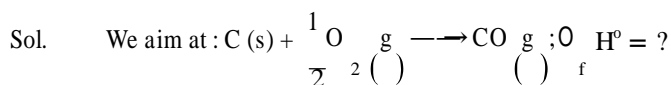
Example 44

Calculate the enthalpy of formation of carbon monoxide (CO) from the following data :

(i) $C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H_r^o = -393.5 \, kJ \, mol^{-1}$

(ii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow (g); \Delta H_r^o = -283.0 \, kJ \, mol^{-1}$

Sol. We aim at : $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \Delta H_f^o = ?$

Subtracting eqn. (ii) from eqn. (i), we get

$$C(s) + \frac{1}{2}O_2(g) - CO(g) \longrightarrow 0;$$

$$\Delta H_r^o = -393.5 - (-283.0) = -110.5 \, kJ \, mol^{-1}$$

or $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \Delta H_r^o = -110.5 \, kJ.$
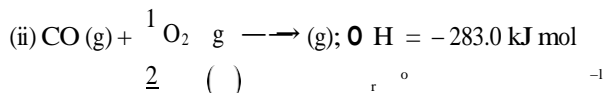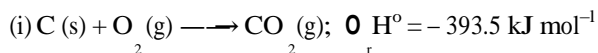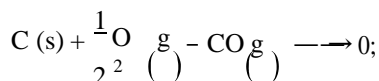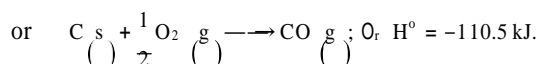
Heat of formation of CO is : $\Delta H_f^o = -110.5 \, kJ \, mol^{-1}$

Example 45

Determine whether or not, it is possible for sodium to reduce aluminium oxide to aluminium at 298 K. Given that G_f^0 of Al_2O_3 at 298 K $= -1582 \, kJ \, mol^{-1}$; G_f^0 of $Na_2O(s)$ at 298 K $= -377 \, kJ \, mol^{-1}$.

Sol. The given reaction is :

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

Hence, $\Delta G^o = 3 \times G_f^0(Na_2O) - G_f^0(Al_2O_3)$
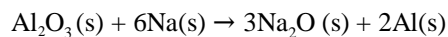
(G° for Na and Al = 0)

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

The reaction cannot occur since ΔG^o (298 K) is positive.

Example 46

The heat liberated on complete combustion of 7.8g benzene is 327 kJ. This heat has been measured at constant volume and at 27ºC. Calculate heat of combustion of benzene at constant pressure at 27ºC.

$$(R = 8.3 \, J \, mol^{-1} \, K^{-1}).$$

Sol. $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$
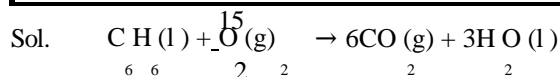
$$\Delta n = 6 - \frac{15}{2} = -\frac{3}{2}$$

Also, ΔU per mol $= -\frac{327 \times 78}{7.8} = -3270 \, kJ$

Now, $\Delta H = \Delta U + \Delta n RT$

$$= -3270 + \left\{-\frac{3}{2}\right\} \times 8.3 \times 300 \times 10^{-3}$$

$$\Delta H = -3273.735 \, kJ$$

Example 47

Calculate standard heat of formation of CS_2. Given that standard heat of combustion of C, S and CS_2 are -393.3, -293.72 and $-1108.76 \, kJ \, mol^{-1}$.

Sol. We have to find ΔH for

$C + 2S \rightarrow CS_2;$ $\Delta H = ?$

Given, $C + O_2 \rightarrow CO_2;$ $\Delta H = -393.3 \, kJ$ .... (1)

$S + O_2 \rightarrow SO_2;$ $\Delta H = -293.72 \, kJ$ .... (2)

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2; \Delta H = -1108.76 \, kJ$ ....(3)
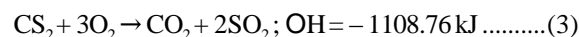
Multiply Eq. (2) by 2 and add in Eq. (1)

$C + 2S + 3O_2 \rightarrow CO_2 + 2SO_2; \Delta H = -980.74 \, kJ$ (4)

Subtract Eq. (3) from Eq. (4)

$C + 2S \rightarrow CS_2;$ $\Delta H = +128.02 \, kJ$
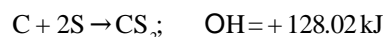
ΔH_f of $CS_2 = +128.02 \, kJ$

Example 48

Estimate the average S–F bond energy in SF_6. The standard heat of formation value of $SF_6(g)$, S(g) and F(g) are: -1100, 275 and 80 kJmol^{-1} respectively.

Sol. $\Delta H = e_{sub(s)} + 6e_F - 6e_{S-F}$
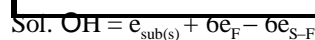
$$-1100 = 275 + 6(80) - 6e_{S-F}$$

$$e_{S-F} = 309.17 \, kJ/mol$$

Example 49

From the following themochemical equations, calculate the enthalpy of formation of cane sugar ($C_{12}H_{22}O_{11}$) :

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

$$\Delta_r H_1 = -5644 \text{ kJ mol}^{-1}$$

(ii) C (s) + O_2 (g) → CO_2 (g) $\Delta_r H_2 = -393 \text{ kJ mol}^{-1}$

(iii) H_2 (g) + 1/2 O_2 (g) → H_2O (l) $\Delta_r H_3 = -286 \text{ kJ mol}^{-1}$
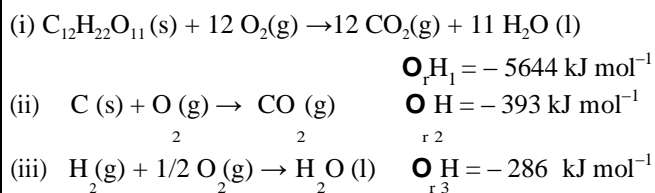
Sol. AIM : 12C (s) + 11 H_2 (g) → $C_{12}H_{22}O_{11}$ (s) $\Delta H = ?$

$\Delta H = 12\Delta H_2 + 11 \Delta H_3 - \Delta H_1$

$= 12 (-393) + 11 (-286) - (-5644)$

$= -2218 \text{ kJ/mol}$

Example 50

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 to estimate the magnitude of the resonance energy of benzene.

Sol. Enthalpy of formation of 3 carbon-carbon double bonds

$$\Delta H_f(\text{cyclohexane}) - \Delta H_f(\text{benzene})$$

$$= -156 - (+49) \text{ kJ}$$

$$= -205 \text{ kJ.}$$

Given, that,

$$\text{cyclohexene} + H_2 \rightarrow \text{cyclohexane} ; \Delta H = -119 \text{ kJ}$$
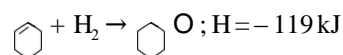
Theoretical enthalpy of formation of 3 double bonds in benzene ring

$= 3 \times (-119) \text{ kJ}$ $= -357 \text{kJ.}$

resonance energy of benzene $= -357 - (-205) \text{ kJ}$

$= -152 \text{ kJ mol}^{-1}.$

EXERCISE– 1 : BASIC OBJECTIVE QUESTIONS

State Functions & Path Functions, Intensive & Extensive Properties

1. Which of the following is not a state function ?
    (a) Heat   (b) Internal energy
    (c) Enthalpy   (d) Entropy

2. Which of the following quantities is not a state function ?
    (a) Temperature   (b) Entropy
    (c) Enthalpy   (d) Work

3. Which of the following is not an intensive property ?
    (a) Entropy   (b) Pressure
    (c) Temperature   (d) Molar volume

4. Which of the following is a state function and also an extensive property?
    (a) Internal energy   (b) Pressure
    (c) Molar heat capacity   (d) Temperature

First Law of Thermodynamics & Cyclic Process

5. A system absorb 10 kJ of heat at constant volume and its temperature rises from 27°C to 37°C. The value of ΔU is
    (a) 100 kJ   (b) 10 kJ
    (c) 0   (d) 1 kJ

6. A sample of liquid in a thermally insulated container (a calorimeter) is stirred by a motor. Taking liquid as a system for this process choose the appropriate option :
    (a) $w < 0$; $q = 0$; $\Delta U = 0$ (b) $w > 0$; $q > 0$; $\Delta U > 0$
    (c) $w < 0$; $q > 0$; $\Delta U = 0$ (d) $w > 0$; $q = 0$; $\Delta U > 0$

7. An ideal gas is taken around the cycle ABCA as shown in P-V diagram
    The net work done by the gas during the cycle is equal to :

    (a) 12 $P_1 V_1$ (b) 6$P_1 V_1$
    (c) 5$P_1 V_1$ (d) $P_1 V_1$
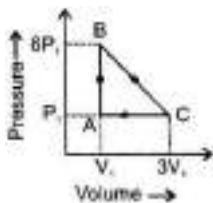
8. An ideal gas receives 10 J of heat in a reversible isothermal expansion. Then the work done by the gas:
    (a) would be more than 10 J

    (b) 10 J
    (c) would be less than 10 J
    (d) cannot be determined

Types of processes

9. Two moles of Helium gas undergo a reversible cyclic process as shown in figure. Assuming gas to be ideal. What is the work for the process C to D ?

    (a) –800 RAn2   (b) zero
    (c) +200 RAn2   (d) –600 RAn2
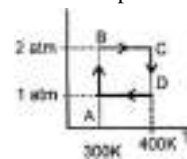
10. In an isothermal expansion of an ideal gas
    (a) q = 0   (b) $\Delta V = 0$
    (c) $\Delta U = 0$ (d) w = 0

11. The maximum work obtained by an isothermal reversible expansion of 1 mole of an ideal gas at 27°C from 2.24 to 22.4 L is (R = 2 cal)
    (a) – 1381.8 cal   (b) – 600 cal
    (c) –138.18 cal   (d) – 690.9 cal

12. 1 mole of NH_3 gas at 27°C is expanded in reversible adiabatic condition to make volume 8 times (γ = 1.33). Final temperature and work done by the gas respectively are :
    (a) 150 K, 900 cal   (b) 150 K, 400 cal
    (c) 250 K, 1000 cal   (d) 200 K, 800 cal

13. One mole of an ideal gas expands reversibly and adiabatically from a temperature of 27°C. If the work done during the process is 3 kJ, then final temperature of the gas is:(C_V = 20 J/K)
    (a) 100 K   (b) 150 K
    (c) 195 K   (d) 255 K

14. Molar heat capacity of water in equilibrium with ice at constant pressure is
    (a) zero   (b) ∞
    (c) 40.45 kJK^{-1} mol^{-1} (d) 75.48 J K^{-1} mol^{-1}

15. The pressure of a gas is 100 kPa. If it is compressed form $1 m^3$ to 10 dm^3, find the work done.
    (a) 990 J   (b) 9990 J
    (c) 9900 J   (d) 99000J

16. An ideal gas expands in volume from 1×10^{-3} to 1×10^{-2} m^3 at 300 K against a constant pressure 1×10^5 Nm^{-2}. The work done is
    (a) – 900 J   (b) – 900 kJ
    (c) 270 kJ   (d) 900 kJ

17. Calculate the work done when 1 mol of an ideal gas is compressed reversibly from 1 bar to 4 bar at a constant temperature of 300 K
    (a) 4.01 kJ (b) – 8.02 kJ
    (c) 18.02 kJ (d) None of these

18. 16g of oxygen gas expands isothermally and reversibly at 300 K from 10 dm^3 to 100 dm^3. The work done is (in J)
    (a) zero (b) – 2875 J
    (c) + 2875 J (d) infinite

19. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is
    (a) – 6J (b) – 608 J
    (c) + 304 J (d) – 304 J

Entropy & Gibb's Free Energy

20. Entropy is a measure of
    (a) disorder (b) internal energy
    (c) efficiency
    (d) useful work done by the system

21. The enthalpy of vaporisation of a substance is 8400 J mol^{-1} and its boiling point is –173ºC. The entropy change for vaporisation is :
    (a) 84 J mol^{-1} K^{-1} (b) 21 J mol^{-1} K^{-1}
    (c) 49 J mol^{-1} K^{-1} (d) 12 J mol^{-1} K^{-1}

22. The enthalpy of vaporisation of a compound AB at its boiling point (127°C) is 6.4 kJ mol^{-1}. Its entropy of vaporisation is :
    (a) 2.56 kJ mol^{-1} (b) 16 J mol^{-1}
    (c) 16×10^{-3} J mol^{-1} (d) 1.6×10^{3} kJ mol^{-1}

23. The entropy change for the conversion of 1 mol of α–tin (at 13°C, 1 atm) to 1 mol of β–tin (13°C, 1 atm), if enthalpy of transition is 2.095 kJ mol^{-1} is :
    (a) 7.32 J mol^{-1} K^{-1} (b) 14.62 J K^{-1} mol^{-1}
    (c) 56.3 J mol^{-1} K^{-1} (d) 0

24. The following data is known about the melting of a compound AB. $\Delta H = 9.2$ kJ mol^{-1}. $\Delta S = 0.008$ kJ K^{-1} mol^{-1}. Its melting point is :
    (a) 736 K (b) 1050 K
    (c) 1150 K (d) 1150°C

25. The entropy change when two moles of ideal monoatomic gas is heated from 200°C to 300°C reversibly and isochorically ?
    (a) $\frac{3}{2} R \ln\left(\frac{300}{200}\right)$ (b) $\frac{5}{2} R \ln\left(\frac{573}{273}\right)$

26. (c) $3 R \ln\left(\frac{573}{473}\right)$ (d) $\frac{3}{2} R \ln\left(\frac{573}{473}\right)$

26. When one mole of an ideal gas is compressed to half of its initial volume and simultaneously heated to twice its initial temperature, the change in entropy of gas (ΔS) is :
    (a) $C_{p,m} \ln 2$ (b) $C_{v,m} \ln 2$
    (c) $R \ln 2$ (d) $(C_{v,m} - R) \ln 2$

27. One mole of an ideal diatomic gas ($C_v = 5$ cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. The entropy change of the process can be expressed as (R = 2 calories/mol/K)
    (a) $3 \ln\frac{298}{373} + 2 \ln 10$ (b) $5 \ln\frac{373}{298} + 2 \ln 10$
    (c) $7 \ln\frac{373}{298} + 2 \ln\frac{1}{10}$ (d) $5 \ln\frac{373}{298} + 2 \ln\frac{1}{10}$

28. Which of the following conditions is not favourable for the feasibility of a process ?
    (a) $\Delta H = -$ve, $T\Delta S = -$ve and $T\Delta S < \Delta H$
    (b) $\Delta H = +$ve, $T\Delta S = +$ve and $T\Delta S > \Delta H$
    (c) $\Delta H = -$ve, $T\Delta S = +$ve and $\Delta H > T\Delta S$
    (d) $\Delta H = +$ve, $T\Delta S = +$ve and $\Delta H > T\Delta S$

29. In which of the following cases, the reaction is spontaneous at all temperatures ?
    (a) $\Delta H > 0, \Delta S > 0$ (b) $\Delta H < 0, \Delta S > 0$
    (c) $\Delta H < 0, \Delta S < 0$ (d) $\Delta H > 0, \Delta S < 0$

30. Which of the following is true for the reaction ?
    $H_2O(\ell) \rightleftharpoons H_2O(g)$ at 100°C and 1 atm pressure
    (a) $\Delta S = 0$ (b) $\Delta H = T\Delta S$
    (c) $\Delta H = \Delta U$ (d) $\Delta H = 0$

31. A reaction has $\Delta H = - 33$ kJ and $\Delta S = +58$ J/K. This reaction would be :
    (a) spontaneous below a certain temperature
    (b) non-spontaneous at all temperature
    (c) spontaneous above a certain temperature
    (d) spontaneous at all temperature

Thermochemistry

32. For the reaction :
    $C(s) + O_2(g) \longrightarrow CO_2(g)$
    (a) $\Delta H < \Delta U$ (b) $\Delta H > \Delta U$
    (c) $\Delta H = \Delta U$ (d) $\Delta H = 0$

33. For which of the following reactions, ΔH is greater than ΔU ?
    (a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
    (b) $CH_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

(c) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

(d) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(aq)$

34. $(\Delta U - \Delta H)$ for the formation of NH_3 from N_2 and H_2 is :
    (a) $-2\,RT$ (b) $2\,RT$
    (c) RT (d) $\dfrac{1}{2}RT$

35. The difference between heats of reaction at constant pressure and constant volume for the reaction.
    $2C_2H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ at $25°C$ is
    (a) -7.43 kJ   (b) $+3.72$ kJ
    (c) -3.72 kJ   (d) 7.43 kJ

36. Consider the reaction at 300 K

    $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g);$ $\Delta H° = -185$ kJ
    If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl. What is $\Delta U°$ for this reaction ?
    (a) 0   (b) -185 kJ
    (c) 370 kJ   (d) -370 kJ

37. The enthalpies of formation of N_2O and NO at 298 K are 82 and 90 kJ mol^{-1}. The enthalpy of the reaction :
    $N_2O(g) + \tfrac{1}{2}O_2(g) \longrightarrow 2NO(g)$
    (a) -8 kJ   (b) 98 kJ
    (c) -74 kJ   (d) 8 kJ

38. The enthalpies of solution of anhydrous $CuSO_4$ and $CuSO_4.5H_2O$ are -15.89 and 2.80 k cal mol^{-1} respectively. The enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$ is :
    (a) -18.69 kcal   (b) 13.09 kcal
    (c) -13.09 kcal   (d) 18.69 kcal

39. If $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O + x$ kJ

    $H^+ + OH^- \longrightarrow H_2O + y$ kJ

    The enthalpy change for the reaction :
    $CH_3COOH \longrightarrow CH_3COO^- + H^+$ is
    (a) $x + y$ (b) $x - y$
    (c) $y - x$ (d) $x - y/2$

40. For the reaction,
    $2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$ $\Delta H = 571.6$ KJ
    ΔH^0_f of water is :
    (a) 285.8 kJ   (b) -285.8 kJ
    (c) 1143.2 kJ   (d) -1143.2 kJ

41. ΔH for the reaction,
    $SO_2(g) + \dfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ $\Delta H = -98.3$ kJ
    If the enthalpy of formation of $SO_3(g)$ is -395.4 kJ then the enthalpy of formation of $SO_2(g)$ is :
    (a) -297.1 kJ   (b) 493.7 kJ

(c) -493.7 kJ   (d) 297.1 kJ

42. When 0.5 g of sulphur is burnt to SO_2 4.6 kJ of heat is liberated. What is the enthalpy of formation of sulphur dioxide ?
    (a) -147.2 kJ   (b) $+147.2$ kJ
    (c) $+294.4$ kJ   (d) -294.4 kJ

43. The heat of formation of $Fe_2O_3(s)$ is -824.2 kJ mol^{-1}. ΔH for the reaction.
    $2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g)$ is :
    (a) -412.1 kJ   (b) -1648.4 kJ
    (c) -3296.8 kJ   (d) 1648.4 kJ

44. The ΔH^0 for the reaction,
    $4S(s) + 6O_2(g) \longrightarrow 4SO_3(g)$
    is -1583.2 kJ. Standard enthalpy of formation of sulphur trioxide is :
    (a) -3166.4 kJ   (b) 3166.4 kJ
    (c) -395.8 kJ   (d) 395.8 kJ

45. Calculate the heat of formation of $PCl_5(s)$ from the following data :
    $2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l)$ $\Delta H = -151.8$ kcal
    $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$ $\Delta H = -32.8$ kcal
    (a) -108.7 kcal   (b) 108.7 kcal
    (c) -184.6 kcal   (d) 184.6 kcal

46. If $S + O_2 \longrightarrow SO_2$ $\Delta H = -298.2$ kJ
    $SO_2 + \dfrac{1}{2}O_2 \longrightarrow SO_3$ $\Delta H = -98.2$ kJ
    $SO_3 + H_2O \longrightarrow H_2SO_4$ $\Delta H = -130.2$ kJ
    $H_2 + \dfrac{1}{2}O_2 \longrightarrow H_2O$ $\Delta H = -287.3$ kJ
    the enthalpy of formation of H_2SO_4 at 298 K will be
    (a) -433.7 kJ   (b) -650.3 kJ
    (c) $+320.5$ kJ   (d) -813.9 kJ

47. The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283.0 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide is :
    (a) -676.5 kJ   (b) 110.5 kJ
    (c) -110.5 kJ   (d) 676.5 kJ

48. Which of the following pairs has heat of neutralisation equal to -57.1 kJ ?
    (a) HNO_3, KOH (b) HCl, NH_4OH
    (c) H_2SO_4, NH_4OH (d) $CH_3COOH, NaOH$

49. Which of the following neutralisation reactions is most exothermic ?
    (a) HCl and NaOH   (b) HCN and NaOH
    (c) HCl and NH_4OH (d) CH_3COOH and NH_4OH

50. The enthalpy of neutralisation of HCl by NaOH is -57.1 kJ and that of HCN by NaOH is -12.1 kJ mol^{-1}. The enthalpy of ionization of HCN is :
    (a) -69.2 kJ   (b) -45.0 kJ

(c) 69.2 kJ (d) 45.0 kJ

51. For the reaction at 300 K

A(g) + B(g) $\longrightarrow$ C(g)

$\Delta U = -3.0$ kcal $\Delta S = -10.0$ cal/K

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

ΔG is :

(a) –600 cal (b) –3600 cal

(c) 2400 cal (d) 3000 cal

52. The standard enthalpies of formation of HCl(g), H(g) and Cl(g) are –92.2, 217.7 and 121.4 kJ mol^{-1} respectively. The bond dissociation energy of HCl is:

(a) +431.3 kJ (b) 236.9 kJ

(c) –431.3 kJ (d) 339.1 kJ

53. The enthalpy changes at 25°C in successive breaking of O–H bonds of water are :

$H_2O(g) \longrightarrow H(g) + OH(g)$ $\Delta H = 498$ kJ mol^{-1}

$OH(g) \longrightarrow H(g) + O(g)$ $\Delta H = 428$ kJ mol^{-1}

the bond enthalpy of the O–H bond is :

(a) 498 kJ mol^{-1} (b) 463 kJ mol^{-1}

(c) 428 kJ mol^{-1} (d) 70 kJ mol^{-1}

54. Calculate the heat of the reaction

$CH_2 = CH_2(g) + H_2(g) \longrightarrow CH_3CH_3(g)$

given that bond energy of C – C, C = C, C – H and H – H is 80, 145, 98 and 103 kcal.

(a) –28 kcal mol^{-1} (b) –5.6 kcal mol^{-1}

(c) –2.8 kcal mol^{-1} (d) –56 kcal mol^{-1}

55. The enthalpy change for the following reaction is 368 kJ. Calculate the average O–F bond energy.

$OF_2(g) \rightarrow O(g) + 2F(g)$

(a) 184 kJ/mol (b) 368 kJ/mol

(c) 536 kJ/mol (d) 736 kJ/mol

56. The enthalpy change for the reaction, $C_2H_6(g) \rightarrow 2C(g) + 6H(g)$ is X kJ. The bond energy of C–H bond is:

(a) $\dfrac{X}{2}$ (b) $\dfrac{X}{3}$

(c) $\dfrac{X}{6}$ (d) data insufficient

57. Based on the values of B.E. given, $\Delta_f H^\circ$ of N_2H_4 (g) is:

Given: N–N = 159 kJ mol^{-1}, H–H = 436 kJ mol^{-1}

N÷N = 941 kJ mol^{-1}, N–H = 398 kJ mol^{-1}

(a) 711 kJ mol^{-1} (b) 62 kJ mol^{-1}

(c) –98 kJ mol^{-1} (d) –711 kJ mol^{-1}

58. The dissociation energy of CH_4 and C_2H_6 are respectively 360 and 620 kcal/mole. The bond energy of C–C is

(a) 260 k cal/mole (b) 180 k cal/mole

(c) 130 k cal/mole (d) 80 k cal/mole

59. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔE and W corresponds to

(a) $\Delta E < 0$, W = 0 (b) $\Delta E = 0$, W < 0

(c) $\Delta E > 0$, W = 0 (d) $\Delta E = 0$, W > 0

60. The bond energies C – C, C = C, H – H and C – H linkages are 350, 600, 400 and 410 kJ/mol respectively. The heat of hydrogenation of ethylene is

(a) – 170 kJ mol^{-1} (b) – 260 kJ mol^{-1}

(c) – 400 kJ mol^{-1} (d) – 450 kJ mol^{-1}

61. The standard heats of formation of CH_4, H_2O and CH_3OH are –76, –242 and –266 kJ/mol respectively. The enthalpy change for the following reaction is

$CH_3OH(l) + H_2(g) \longrightarrow CH_4(g) + H_2O(l)$

(a) –4 kJ/mol (b) –556 kJ/mol

(c) –318 kJ/mol (d) –52 kJ/mol

62. Which of the following reaction defines ΔH°_f ?

(a) C (diamond) $+ O_2(g) \longrightarrow CO_2(g)$

(b) $\dfrac{1}{2}H_2(g) + \dfrac{1}{2}F_2(g) \longrightarrow HF(g)$

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

(d) $CO(g) + \dfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$

63. The heat of combustion of solid benzoic acid at constant volume is –321.30 kJ at 27ºC. The heat of combustion at constant pressure is

(a) –321.30 –300 R (b) –321.30 + 300 R

(c) –321.30 – 150 R (d) –321.30 + 900 R

64. ΔH for the reaction,

$C(graphite) + 2H_2(g) \longrightarrow CH_4(g)$ at 298 K

and 1 atm is – 17900 cal. The ΔE for the above conversion would be

(a) – 17900 cal (b) 17900 cal

(c) 17308 cal (d) – 17308 cal

65. If 150 kJ of energy is needed for muscular work to walk a distance of one km, then how much 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} is)

(a) 75 g (b) 30 g

(c) 180 g (d) 150 g

66. For the reaction,

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$; $\Delta H^\circ = -573.2$ kJ

The heat of decomposition of water per mole is

(a) 286.6 kJ   (b) 573.2 kJ

(c) – 28.66 kJ   (d) zero

EXERCISE– 2 : PREVIOUS YEAR COMPETITION QUESTIONS

First Law & Reversible and Irreversible Processes

1. Which of the following units represents largest amount of energy ?   (CPMT 1980)
   (a) Calorie   (b) Joule
   (c) Erg   (d) Electron volt.

2. During isothermal expansion of an ideal gas, its
                                  (PMT 1991,94)
   (a) internal energy increases
   (b) enthalpy decreases
   (c) enthalpy remains unaffected
   (d) enthalpy reduces to zero.

3. A well stoppered thermos flask contains some ice cubes. This is an example of a   (AIIMS 1992,94)
   (a) closed system
   (b) open system
   (c) isolated system
   (d) non-thermodynamic system.

4. In a closed insulated container a liquid is stirred with a paddle to increase the temperature. Which of the following is true ?   (PMT 2002)
   (a) $\Delta E = W \neq 0, q = 0$ (b) $\Delta E = W = q \neq 0$
   (c) $\Delta E = 0, W = q \neq 0$ (d) $W = 0, \Delta E = q \neq 0$

5. An adiabatic expansion of an ideal gas always has
                                  (PMT 2002)
   (a) increase in temperature   (b) $q = 0$
   (c) $w = 0$ (d) $\Delta H = 0$

6. For an adiabatic process, which of the following is correct ?   (CPMT 1990)
   (a) $\Delta V = 0$ (b) $q = + w$
   (c) $\Delta E = q$ (d) $q = 0$.

7. In a reversible isothermal process, the change in internal energy is   (PMT 1993)
   (a) zero   (b) positive
   (c) negative   (d) none of the above.

8. Heat capacity is   (PMT 1996)
   (a) $\dfrac{dQ}{dT}$ (b) $dQ \times dT$
   (c) $\Sigma Q. \dfrac{1}{dT}$ (d) None of these.

9. The relation between enthalpy (H), pressure (P), volume (V) and internal energy (E) is given by
                                  (PMT 1998)
   (a) $E = H + PV$ (b) $H = E + PV$
   (c) $H = E - PV$ (d) $H = E + P + V$.

10. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is
    $(R = 2\ cal\ mol^{-1}\ K^{-1})$ (PMT 1998)
    (a) 163.7 cal   (b) zero
    (c) 1381.1 cal   (d) 9 lit atom.

11. If 1 mole of an ideal gas expands isothermally at 37°C from 15 L to 25 L, the maximum work obtained is   (AFMC 2010)
    (a) -13 L-atm   (b) -6.43 L-atm
    (c) -8.57 L-atm   (d) -2.92 L-atm

Entropy & Gibb's Free Energy

12. For a spontaneous chemical process, the free energy change is   (BHU 1981)
    (a) positive
    (b) negative
    (c) either positive or negative
    (d) zero.

13. For which reaction from the following, ΔS will be maximum ?   (AIIMS 1982,83)
    (a) $Ca\ (s) + \dfrac{1}{2}O_2(g) \rightarrow CaO\ (s)$
    (b) $CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$
    (c) $C\ (s) + O_2\ (g) \rightarrow CO_2(g)$
    (d) $N_2(g) + O_2(g) \rightarrow 2NO\ (g)$.

14. All the naturally occurring processes proceed spontaneously in a direction which leads to
                                  (PMT 1985)
    (a) decrease of entropy
    (b) increase of enthalpy
    (c) increase of free energy
    (d) decrease of free energy

15. The occurrence of reaction is impossible if
                                  (AIIMS 1994)
    (a) ΔH is +ve ; ΔS is also +ve
    (b) ΔH is –ve ; ΔS is also –ve
    (c) ΔH is –ve ; ΔS is +ve
    (d) ΔH is +ve ; ΔS is –ve

16. In which of the following, the entropy decreases ?
                                  (CPMT 1988)
    (a) Crystallisation of sucrose from solution
    (b) Rusting of iron
    (c) Melting of ice

(d) Vaporization of camphor.

17. Which of the following statements is true ? The entropy of the universe (PMT 1993)

(a) increases and tends towards maximum value

(b) decreases and tends to zero

(c) remains constant

(d) decreases and increases with a periodic rate.

18. The total entropy change for a system and its surroundings increases, if the process is (PMT 1993)

(a) reversible   (b) irreversible

(c) exothermic   (d) endothermic.

19. A chemical reaction will be spontaneous if it is accompanied by a decrease of (PMT 1994)

(a) entropy of the system

(b) enthalpy of the system

(c) internal energy of the system

(d) free energy of the system.

20. Gibb's free energy G, enthalpy H and entropy S are related to one another by (BUU 1994)

(a) $G = H + TS$ (b) $G = H - TS$

(c) $G - TS = H$ (d) $S = H - G$.

21. $\Delta S°$ will be highest for the reaction (AIIMS 1994)

(a) $Ca\ (s) + \dfrac{1}{2}\ O_2\ (g) \rightarrow CaO\ (s)$

(b) $CaCO_3\ (g) \rightarrow CaO\ (s) + CO_2\ (g)$

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

(d) $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$.

22. For a reaction to occur spontaneously (PMT 1995)

(a) ΔS must be negative

(b) $(\Delta H - T\Delta S)$ must be negative

(c) $(\Delta H + T\Delta S)$ must be negative

(d) ΔH must be negative.

23. According to third law of thermodynamics, which one of the following quantities for a perfectly crystalline solid is zero at absolute zero? (PMT 1996)

(a) Entropy   (b) Free energy

(c) Internal energy   (d) Enthalpy.

24. The enthalpy and entropy change for a chemical reaction are $- 2.5 \times 10^3$ cal and 7.4 cal deg^{-1} respectively. The reaction at 298 K will be

(AFMC 1998)

(a) spontaneous   (b) reversible

(c) irreversible   (d) non-spontaneous.

25. Identify the correct statement regarding entropy.

(BHU 1998)

(a) At absolute zero of 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 positive

(c) Absolute entropy of a substance cannot be determined

(d) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero.

26. One mole of an ideal gas is allowed to expand freely and adiabatically into vacuum until its volume has doubled. The expression which is not true concerning statement is (PMT 1998)

(a) $\Delta H = 0$ (b) $\Delta S = 0$

(c) $\Delta E = 0$ (d) $W = 0$

27. For which of the process, ΔS is negative ?

(PMT 1998)

(a) $H_2\ (g) \rightarrow 2\ H\ (g)$

(b) $N_2\ (g\ 1\ atm) \rightarrow N_2\ (g\ 8\ atm)$

(c) $2\ SO_3(g) \rightarrow 2\ SO_2\ (g) + O_2\ (g)$

(d) $C_{(diamond)} \rightarrow C_{(graphite)}$.

28. Heat exchanged in a chemical reaction at constant temperature and pressure is called (PMT 2001)

(a) entropy

(b) enthalpy

(c) internal energy

(d) free energy

29. Which one of the following has $\Delta S°$ greater than zero? (AIIMS 2003)

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

(b) $NaCl\ (aq) \rightleftharpoons NaCl\ (s)$

(c) $NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$

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

30. If the enthalpy of vaporisation of water is 186.5J mol^{-1}, the entropy of its vaporisation will be

(CPMT 1988)

(a) 0.5 JK^{-1} mol^{-1} (b) 1.0 JK^{-1} mol^{-1}

(c) 1.5 JK^{-1} mol^{-1} (d) 2.0 JK^{-1}mol^{-1}.

31. If 900 J/g of heat is exchanged at boiling point of water, then what is increase in entropy? (BHU 1998)

(a) 43.4 J/mole   (b) 87.2 mole

(c) 900 J/mole   (d) zero.

32. 1 mole of ice is converted to liquid at 273 K ; H_2O (s) and H_2O (l) have entropies 38.20 and 60.03 J mol^{-1} deg^{-1}. Enthalpy change in the conversion will be

    (DPMT 1994)

    (a) 59.59 J/mol   (b) 595.95 J/mol
    (c) 5959.5 J/mol   (d) 595959.0 J/mol.

33. 2 mole of an ideal gas at 27ºC temperature is expanded reversibly from 2 lit to 20 lit. Find entropy change (R = 2 cal/mol K)   (PMT 2002)

    (a) 92.1   (b) 0
    (c) 4   (d) 9.2

34. What is the entropy change (in JK^{-1} mol^{-1}) when one mole of ice is converted into water at 0ºC ?

    (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0ºC)

    (CBSE Med. 2003)

    (a) 20.13   (b) 2.013
    (c) 2.198   (d) 21.98

35. What is the free energy change, ΔG, when 1.0 mole of water at 100ºC and 1 atm pressure is converted into steam at 100ºC and 1 atm pressure ?

    (PMT 1998)

    (a) 540 cal   (b) – 9800 cal
    (c) 9800 cal   (d) 0 cal.

36. The densities of graphite and diamond at 298 K are 2.25 and 3.31 g cm^{-3} respectively. If the standard free energy difference (ΔG^0) is equal to 1895 J mol^{-1}, the pressure at which graphite will be transformed into diamond at 298 K is   (CBSE 2003)

    (a) 9.92×10^8 Pa   (b) 9.92×10^7 Pa
    (c) 9.92×10^6 Pa   (d) None of these

Thermochemistry

37. The compound with negative heat of formation is known as   (DPMT 1981)

    (a) endothermic compound
    (b) exothermic compound
    (c) endoergic compound   (d) none of the above.

38. $\Delta H_{combustion}$ of a compound is   (PMT 1985)

    (a) positive   (b) negative
    (c) zero   (d) positive or negative

39. Heat of neutralization of NH_4OH and HCl is

    (PMT 1985)

    (a) 13.7 kcal/mole   (b) < 13.7 kcal/mole
    (c) > 13.7 kcal/mol   (d) zero

40. Heat of neutralisation of a strong acid and a strong base is nearly equal to   (AIIMS 1988)

    (a) 10 kJ/mole   (b) 10 Cal/mole
    (c) – 57 kJ/mole   (d) – 57 Cal/mole.

41. The mutual heat of neutralisation of 40 g NaOH and 60 g CH_3COOH will be   (AIIMS 1988)

    (a) 57.1 kJ   (b) less than 57.1 kJ
    (c) more than 57.1 kJ   (d) 13.7 kJ.

42. For the transition   (PMT 2002)

    C (diamond) → C (graphite); $\Delta H = -1.5$ kJ.

    It follows that

    (a) diamond is exothermic
    (b) graphite is endothermic
    (c) graphite is stabler than diamond
    (d) diamond is stabler than graphite.

43. Which of the following reaction can be used to define the heat of formation of $CO_2(g)$?   (PMT 1989)

    (a) C (graphite) $+ O_2(g) \rightarrow CO_2(g)$
    (b) $CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2 H_2O (l)$
    (c) $CO (g) + \dfrac{1}{2} O_2(g) \rightarrow CO_2 (g)$
    (d) $C_6H_6 (l) + 7\dfrac{1}{2} O_2 (g) \rightarrow 6 CO_2 (g) + 3 H_2O (l)$

44. The molar neutralisation heat for KOH and HNO_3 as compared to molar neutralisation heat of NaOH and HCl is   (PMT 1989)

    (a) less   (b) more
    (c) equal   (d) depends on pressuree

45. If ΔH is the change in enthalpy and ΔE, the change in internal energy accompanying a gaseous reaction, then   (CBSE PMT 1990)

    (a) ΔH is always greater than ΔE
    (b) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of moles of the reactants
    (c) ΔH is always less than ΔE
    (d) $\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants.

46. Heat of neutralisation is least when

    (PMT 1990)

    (a) NaOH is neutralised by CH_3COOH
    (b) NaOH is neutralised by HCl
    (c) NH_4OH is neutralised by CH_3COOH
    (d) NH_4OH is neutralised by HNO_3.

47. $H_2(g) + I_2(g) \rightarrow 2\,HI(g)$; $\Delta H = 12.40$ kcal.

According to this reaction heat of formation of HI will be   (PMT 1990)

(a) 12.4 kcal   (b) – 12.4 kcal

(c) – 6.20 kcal   (d) 6.20 kcal.

48. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true ?

(PMT 1994)

(a) x = y   (b) $x = \frac{1}{2} y$

(c) x = 2 y   (d) None of these.

49. Which of the following values of heat of formation indicates that the product is least stable ?

(PMT 1991)

(a) – 94 kcal   (b) – 231.6 kcal

(c) + 21.4 kcal   (d) + 64.8 kcal.

50. In which of the following neutralization reaction, the heat of neutralisation will be highest? (PMT 1989,91)

(a) NH_4OH and H_2SO_4

(b) HCl and NaOH

(c) CH_3COOH and KOH

(d) CH_3COOH and NH_4OH.

51. For the reaction   (PMT 1991)

$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$, $\Delta H = ?$

(a) $\Delta E + 2\,RT$ (b) $\Delta E - 2\,RT$

(c) $\Delta E + RT$ (d) $\Delta E - RT$.

52. An exothermic reaction is one in which the reacting substances   (CPMT 1974)

(a) Have more energy than the products

(b) Have less energy than the products

(c) Have the same energy as the products

(d) Are at a higher temperature than the products.

53. The enthalpy change (–ΔH) for the neutralisation of 1 M HCl by caustic potash in dilute solution at 298 K is

(BHU 1993)

(a) 68 kJ   (b) 65 kJ

(c) 57.3 kJ   (d) 50 kJ.

54. Evaporation of water is   (PMT 1993)

(a) An exothermic change

(b) An endothermic change

(c) A process where no heat changes occur

(d) A process accompanied by chemical reaction.

55. At constant T and P which one of the following statements is correct for the reaction ?

$S_8(s) + 8\,O_2(g) \rightarrow 8\,SO_2(g)$ (PMT 1993)

(a) $\Delta H < \Delta E$ (b) $\Delta H = \Delta E$

(c) $\Delta H > \Delta E$ (d) ΔH is independent of the physical state of the reactants.

56. Consider the following reaction occurring in an automobile $2\,C_8H_{18}(g) + 25\,O_2(g) \rightarrow 16\,CO_2 + 18\,H_2O(g)$ the sign of ΔH, ΔS and ΔG would be

(PMT 1994)

(a) +, –, +   (b) –, +, –

(c) –, +, +   (d) +, +, –.

57. Heat of neutralisation of strong acid against strong base is constant and is equal to   (PMT 1993)

(a) 13.7 kcal   (b) 57 kJ

(c) 5.7×10^4 J   (d) All of the above.

58. When water is added to quick lime, the reaction is

(PMT 1995)

(a) explosive   (b) endothermic

(c) exothermic   (d) photochemical

59. The heat of formation of the compound in the following reaction is

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g) + 44$ kcal

(PMT 1995)

(a) – 44 kcal mol^{-1} (b) – 22 kcal mol^{-1}

(c) 11 kcal mol^{-1} (d) – 88 kcal mol^{-1}.

60. For the reaction $C + O_2 \rightarrow CO_2$ (BHU 1995)

(a) $\Delta H > \Delta E$ (b) $\Delta H < \Delta E$

(c) $\Delta H = \Delta E$ (d) None of these.

61. Enthalpy of a reaction ΔH is expressed as

(AIIMS 1996)

(a) $\Delta H = \Sigma \Delta H_P - \Sigma \Delta H_R$ (b) $\Delta H = dH_P + dH_R$

(c) $\Delta H = \dfrac{dH_P}{dH_R}$ (d) $\Delta H = \dfrac{\Sigma H_P}{dH_R}$.

62. The enthalpy change of a reaction does not depend on

(AIIMS 1997)

(a) the state of reactants and products

(b) nature of reactants and products

(c) different intermediate reactions

(d) initial and final enthalpy change of a reaction.

63. Given that $C + O_2 \rightarrow CO_2, \Delta H^0 = -x$ kJ

$2CO + O_2 \rightarrow 2CO_2, \Delta H^0 = -y$ kJ

the enthalpy of formation of carbon monoxide will be

(PMT 1997)

(a) $\dfrac{2x - y}{2}$

(b) $\dfrac{y - 2x}{2}$

(c) $2x - y$

(d) $y = 2x$.

64. The neutralisation of a strong acid by a strong base liberates and amount of energy per mole of H^+

(BHU 1998)

(a) depends upon which acid and base are involved

(b) depends upon the temperature at which the reaction takes place

(c) depends upon which catalyst is used

(d) is always the same.

65. Equal volumes of methanoic acid and sodium hydroxide are mixed. If x is the heat of formation of water, then heat evolved on neutralisation is

(BHU 1998)

(a) more than x

(b) equal to x

(c) less than x

(d) twice x.

66. $S + \dfrac{3}{2}O_2 \rightarrow SO_3 + 2x$ kcal

$SO_2 + \dfrac{1}{2}O_2 \rightarrow SO_3 + y$ kcal

Find out the heat of formation of SO_2 (PMT 1999)

(a) $(y - 2x)$

(b) $-(2x + y)$

(c) $-(x + y)$

(d) $-2x/y$.

67. For the reaction

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ at constant temperature, $\Delta H - \Delta E$ is

(CBSE Med. 2003)

(a) $+ RT$

(b) $- 3RT$

(c) $+ 3RT$

(d) $- RT$

68. For which one of the following equations is $\Delta H^\circ_{reaction}$ equal to ΔH°_f for the product ? (CBSE Med. 2003)

(a) $N_2(g) + O_3(g) \rightarrow N_2O_3(g)$

(b) $CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl_2(l) + 2HCl(g)$

(c) $Xe(g) + 2F_2(g) \rightarrow XeF_4(g)$

(d) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

69. In which of the following process of neutralisation magnitude of $\Delta H_{neutralisation}$ is less than that of $\Delta H_{ionization}$ of water ? (BHU 2003)

(a) $HCl + NaOH$

(b) $H_2SO_4 + NaOH$

(c) $CH_3COOH + NaOH$

(d) $HClO_4 + KOH$

70. The enthalpy of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25ºC and 1 atm pressure are 52, – 394 and – 286 kJ mol^{-1} respectively. The enthalpy of combustion of $C_2H_4(g)$ will be (PMT 1995)

(a) $+ 1412$ kJ mol^{-1}

(b) $– 1412$ kJ mol^{-1}

(c) $+ 141.2$ kJ mol^{-1}

(d) $– 141.2$ kJ mol^{-1}.

71. The heat of combustion of benzene at 27ºC found by bomb calorimeter i.e. for the reaction

$C_6H_6(l) + 7\dfrac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ is 780 kcal mol^{-1}. The heat evolved on burning 39 g of benzene in an open vessel will be (PMT 2001)

(a) 390 kcal

(b) 780.9 kcal

(c) 390.45 kcal

(d) 780 kcal.

72. If $S + O_2 \rightarrow SO_2, \Delta H = -298.2$ kJ

$SO_2 + \dfrac{1}{2}O_2 \rightarrow SO_3, \Delta H = -98.7$ kJ

$SO_3 + H_2O \rightarrow H_2SO_4, \Delta H = -130.2$ kJ

$H_2 + \dfrac{1}{2}O_2 \rightarrow H_2O, \Delta H = -287.3$ kJ.

Then the enthalpy of formation of H_2SO_4 at 298K will be (DPMT 1994)

(a) $– 814.4$ kJ

(b) $+ 320.5$ kJ

(c) $– 650.3$ kJ

(d) $– 933.7$ kJ

73. $H_2 + 1/2 O_2 \rightarrow H_2O$; $\Delta H^\circ = -68$ kcal (CPMT 1988)

$K + H_2O + aq \rightarrow KOH(aq) + 1/2 H_2$; $\Delta H^\circ = -48$ kcal

$KOH + aq \rightarrow KOH(aq)$; $\Delta H^\circ = -14$ kcal

From the above data, the standard heat of formation of KOH in kcal is :

(a) $– 68 + 48 – 14$

(b) $– 68 – 48 + 14$

(c) $68 – 48 + 14$

(d) $68 + 48 + 14$.

74. The enthalpies of combustion of carbon and carbon monoxide are – 390 kJ mol^{-1} and – 278 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide is (BHU 1994)

(a) 668 kJ mol^{-1}

(b) 112 kJ mol^{-1}

(c) $– 112$ kJ mol^{-1}

(d) $– 668$ kJ mol^{-1}

75. $C + O_2 \rightarrow CO_2, \Delta H = -x$

$CO + \dfrac{1}{2}O_2 \rightarrow CO_2, \Delta H = -y$

then ΔH_f for CO will be (DPMT 2002)

(a) $2x + y$

(b) $x - y$

(c) $y - 2x$

(d) $y - x$

76. The amount of energy released when 20 ml of 0.5 M NaOH are mixed with 100 mL of 0.1 M HCl is x kJ. The heat of neutralisation (in kJ mol^{-1}) is

(PMT 2002)

(a) $– 100x$

(b) $– 50x$

(c) $+ 100x$

(d) $+ 50x$

77. Heat of neutralisation for the reaction

    $NaOH + HCl \rightarrow NaCl + H_2O$

    is 57.1 kJ mol^{-1}. What will be the heat released when

    0.25 mole of NaOH reacts with 0.25 mole of HCl ?

    (PMT 1990)

    (a) 22.5 kJ mol^{-1} (b) 57.1 kJ mol^{-1}

    (c) 14.3 kJ mol^{-1} (d) 28.6 kJ mol^{-1}.

78. Enthalpy of neutralisation of HCl with NaOH is x.
    The heat evolved when 500 mL of 2 NHCl are mixed
    with 250 ml of 4 N NaOH will be   (AFMC 2002)

    (a) 500x   (b) 100x

    (c) x   (d) 10x

79. The enthalpy of dissolution of $BaCl_2$ (s) and
    $BaCl_2.2H_2O$ (s) are -20.6 and 8.8 kJ mol^{-1}
    respectively. The enthalpy of hydration for
    $BaCl_2$ (s) $+ 2 H_2O \rightarrow BaCl_2.2H_2O$ (s) is (PMT 1994)

    (a) 29.4 kJ   (b) -29.4 kJ

    (c) -11.8 kJ   (d) 38.2 kJ.

80. The heats of combustion of rhombic and monoclinic
    sulphur are respectively 70960 and 71030 calories.
    What will be the heat of conversion of rhombic
    sulphur to monoclinic ?   (PMT 1988)

    (a) 70960 calories   (b) 71030 calories

    (c) -70 calories   (d) $+70$ calories.

81. ΔH_f of graphite is 0.23 kJ/mole and ΔH_f of diamond
    is 1.896 kJ/mol. $\Delta H_{\text{transition}}$ from graphite to diamond
    is   (BHU 2003)

    (a) 1.66 kJ/mol   (b) 2.1 kJ/mole

    (c) 2.33 kJ/mole   (d) 1.5 kJ/mole

82. The enthalpies of formation of N_2O and NO are 82
    and 90 kJ/mole respectively. The enthalpy of the
    reaction

    $2 N_2O (g) + O_2 (g) \rightarrow 4 NO (g)$ is equal to

    (PMT 1991)

    (a) 8 kJ   (b) 88 kJ

    (c) -16 kJ   (d) 196 kJ.

83. Based on the following thermochemical equations

    $H_2O (g) + C (s) \rightarrow CO (g) + H_2 (g); \Delta H = 131 kJ$

    $CO (g) + \dfrac{1}{2} O_2 (g) \rightarrow CO_2 (g); \Delta H = -282 kJ$

    $H_2 (g) + \dfrac{1}{2} O_2 (g) \rightarrow H_2O (g); \Delta H = -242 kJ$

    $C (s) + O_2 (g) \rightarrow CO_2 (g); \Delta H = X kJ$,

    the value of X will be   (PMT 1992)

    (a) -393 kJ   (b) -655 kJ

    (c) $+393$ kJ   (d) $+655$ kJ.

84. If ΔH_f^0 for H_2O_2 and H_2O are -188 kJ/mole and
    -286 kJ/mole, what will be the enthalpy change of
    the reaction $2 H_2O_2 (l) \rightarrow 2 H_2O (l) + O_2 (g)$?

    (PMT 1992)

    (a) -196 kJ/mole   (b) 146 kJ/mole

    (c) -494 kJ/mole   (d) -98 kJ/mole.

85. Considering the following reactions,

    $C + \dfrac{1}{2} O_2 \rightarrow CO$ $\Delta H = -26.4 K.$

    $H_2 + \dfrac{1}{2} O_2 \rightarrow H_2O (l)$ $\Delta H = -57.8$ kcal,

    ΔH for the reaction

    $H_2O + C \rightarrow H_2 + CO$ is   (PMT 1994)

    (a) 62.8 kcal   (b) 31.4 kcal

    (c) -31.4 kcal   (d) -84.2 kcal.

86. Given :

    $C (graphite) + \dfrac{1}{2} O_2 (g) \rightarrow CO (g); \Delta H = -110.5 kJ$

    $CO (g) + \dfrac{1}{2} O_2 (g) \rightarrow CO_2 (g); \Delta H = -283.2 kJ$

    The heat of reaction for

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

    (PMT 1989)

    (a) -393.7 kJ   (b) $+393.7$ kJ

    (c) -172.2 kJ   (d) $+172.2$ kJ

87. Heat of combustion ΔH for C (s), H_2(g) and

    CH_4 (g) are -94, -68 and -213 kcal/mol. Then ΔH

    for $C(s) + 2H_2(g) \rightarrow CH_4(g)$ is   (PMT 2002)

    (a) -17 kcal   (b) -111 kcal

    (c) -170 kcal   (d) -85 kcal

88. The enthalpy changes at 298 K in successive breaking
    of O–H bonds of HOH are

    $H_2O (g) \rightarrow H (g) + OH (g), \Delta H = 498$ kJ mol^{-1}

    $OH (g) \rightarrow H (g) + O (g), \Delta H = 428$ kJ mol^{-1}

    The bond enthalpy of the O–H bond is (PMT 1994)

    (a) 498 kJ mol^{-1} (b) 463 kJ mol^{-1}

    (c) 428 kJ mol^{-1} (d) 70 kJ mol^{-1}

89. The bond energy of an O–H bond is 109 kcal mol^{-1}.
    When a mole of water is formed   (PMT 1994)

    (a) 218 kcal is released   (b) 109 kcal is released

    (c) 218 kcal is absorbed (d) 109 kcal is absorbed.

90. Energy required to dissociate 4 g of gaseous
    hydrogen into free gaseous atoms is 208 kcal at 25ºC.
    The bond energy of H–H bond will be (CPMT 1989)

    (a) 104 kcal   (b) 10.4 kcal

    (c) 1040 kcal   (d) 104 kcal.

91. Given the reaction at 1240 K and 1 atm. $CaCO_3(s) \rightarrow$ $CaO(s) + CO_2(g)$

    $\Delta H = 176$ kJ/mol, the ΔE equals   (BHU 1993)

    (a) 160.0 kJ   (b) 165.6 kJ

    (c) 186.4 kJ   (d) 180.0 kJ.

92. The latent heat of vaporisation of a liquid at 500 K and 1 atm. pressure is 10.0 kcal/mol. What will be the change in internal energy of 3 moles of the liquid at the same temperature and pressure ? (PMT 1994)

    (a) 27.0 kcal   (b) 13.0 kcal

    (c) – 27.0 kcal   (d) – 13.0 kcal.

93. Given the following entropy values (in JK^{-1} mol^{-1}) at 298 K and 1 atm : $H_2(g)$: 130.6, $Cl_2(g)$: 223.0 and HCl (g) : 186.7. The entropy change (in JK mol^{-1}) for the reaction

    $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is   (PMT 1996)

    (a) + 540.3   (b) + 727.0

    (c) – 166.9   (d) 19.8.

94. One gram sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6.12 K. The heat capacity of the system is 1.23 kJ/g/deg. What is the molar heat of decomposition for NH_4NO_3 ?   (AIIMS 2003)

    (a) – 7.53 kJ/mol   (b) – 398.1 kJ/mol

    (c) – 16.1 kJ/mol   (d) – 602 kJ/mol

95. How much energy is released when 6 moles of octane is burnt in air? Given ΔH_f^o for $CO_2(g)$, $H_2O(g)$ and C_8H_{18} (A) respectively are –490, –240 and +160 J/mol   (AIIMS 2004)

    (a) –6.2 kJ   (b) –37.4 kJ

    (c) –35.5 kJ   (d) –20.0 kJ

96. ΔH_f^o (298 K) of methanol is given by the chemical equation,   (AIIMS 2005)

    (a) $CH_4(g) + \dfrac{1}{2}O_2(g) \rightarrow CH_3OH(g)$

    (b) $C(graphite) + \dfrac{1}{2}O_2(g) + 2H_2(g) \rightarrow CH_3OH(A)$

    (c) $C(diamond) + \dfrac{1}{2}O_2(g) + 2H_2(g) \rightarrow CH_3OH(A)$

    (d) $CO(g) + 2H_2(g) \rightarrow CH_3OH(A)$

97. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?

    (CBSE AIPMT 2006)

    (a) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

    (b) $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$

    (c) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

    (d) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

98. 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   (AIIMS 2007)

    (a) –92.38 kJ   (b) –87.42 kJ

    (c) –97.34 kJ   (d) –89.9 kJ

99. 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   (AIIMS 2007)

    (a) –208.1 kJ mol^{-1} (b) –269.9 kJ mol^{-1}

    (c) –358.5 kJ mol^{-1} (d) –508.9 kJ mol^{-1}

100. One mole of methanol when burnt in O_2, gives out 723 kJ mol^{-1} heat. If one mole of O_2 is used, what will be the amount of heat evolved? (AIIMS 2007)

    (a) 723 kJ   (b) 924 kJ

    (c) 482 kJ   (d) 241 kJ

101. What will be the heat of formation of methane, if the heat of combustion of carbon is '-x' kJ, heat of formation of water is '–y' kJ and heat of combustion of methane is '-z' kJ? (AIIMS 2008)

    (a) (–x–y+z) kJ   (b) (–z–x+y) kJ

    (c) (–x–2y–z) kJ   (d) (–x–2y+z) kJ

102. Enthalpy of combustion of methane and ethane are –210 kcal/mol and –368 kcal/mol respectively. The enthalpy of combustion of decane is (AIIMS 2009)

    (a) –158 kcal   (b) –1632 kcal

    (c) –1700 kcal   (d) Data is incomplete

103. The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at 25°C increases the temperature of 18.94 kg of water by 0.632°C. If the specific heat of water at 25°C is 0.998 cal/g-deg, the value of the heat of combustion of benzoic acid is   (AFMC 2010)

    (a) 881.1 kcal   (b) 771.4 kcal

    (c) 981.1 kcal   (d) 871.2 kcal

104. Enthalpy change for the reaction, $4H(g) \rightarrow 2H_2(g)$ is –869.5 kJ. The dissociation energy of H—H bond is   (CBSE AIPMT 2011)

    (a) +217.4 kJ   (b) – 434.8 kJ

    (c) –869.6 kJ   (d) +434.8 kJ

ANSWER KEY

EXERCISE– 1 : BASIC OBJECTIVE QUESTIONS

1. (a)	2. (d)	3. (a)	4. (a)	5. (b)	6. (d)	7. (c)	8. (b)	9. (a)	10. (c)
11. (a)	12. (a)	13. (b)	14. (b)	15. (d)	16. (a)	17. (d)	18. (b)	19. (b)	20. (a)
21. (a)	22. (b)	23. (a)	24. (c)	25. (c)	26. (d)	27. (b)	28. (d)	29. (b)	30. (b)
31. (d)	32. (c)	33. (c)	34. (c)	35. (a)	36. (d)	37. (b)	38. (a)	39. (c)	40. (b)
41. (a)	42. (d)	43. (d)	44. (c)	45. (a)	46. (d)	47. (c)	48. (a)	49. (a)	50. (d)
51. (a)	52. (a)	53. (b)	54. (a)	55. (a)	56. (d)	57. (b)	58. (d)	59. (a)	60. (a)
61. (d)	62. (b)	63. (c)	64. (d)	65. (d)	66. (a)				

EXERCISE– 2 : PREVIOUS YEARS COMPETITION QUESTIONS

1. (a)	2. (c)	3. (c)	4. (a)	5. (b)	6. (d)	7. (a)	8. (a)	9. (b)	10. (b)
11. (a)	12. (b)	13. (b)	14. (d)	15. (d)	16. (a)	17. (a)	18. (b)	19. (d)	20. (b)
21. (b)	22. (b)	23. (a)	24. (a)	25. (a)	26. (b)	27. (b)	28. (b)	29. (c)	30. (a)
31. (a)	32. (c)	33. (d)	34. (d)	35. (d)	36. (d)	37. (b)	38. (b)	39. (b)	40. (c)
41. (b)	42. (c)	43. (a)	44. (c)	45. (d)	46. (c)	47. (d)	48. (b)	49. (d)	50. (b)
51. (b)	52. (a)	53. (c)	54. (b)	55. (b)	56. (b)	57. (d)	58. (c)	59. (b)	60. (c)
61. (a)	62. (c)	63. (b)	64. (d)	65. (c)	66. (a)	67. (b)	68. (c)	69. (c)	70. (b)
71. (c)	72. (a)	73. (b)	74. (c)	75. (d)	76. (a)	77. (c)	78. (c)	79. (b)	80. (c)
81. (a)	82. (d)	83. (a)	84. (a)	85. (b)	86. (a)	87. (a)	88. (b)	89. (a)	90. (a)
91. (b)	92. (a)	93. (d)	94. (d)	95. (b)	96. (b)	97. (a)	98. (b)	99. (a)	100. (c)
101. (d)	102. (b)	103. (b)	104. (d)						

Dream on !!

OOOOOOO