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THERMODYNAMICS

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THERMODYNAMICS

INTRODUCTION

Chemical reactions involve the change in energy. Some reactions like oxidation, hydration etc. produce energy. Other like hydrolysis, ionisation, splitting of water into hydrogen and oxygen etc. use energy. These energy changes occur due to breaking of bonds in reactant molecules (consume energy) and formation of bonds in product molecule (release energy) during a chemical reaction.

CHEMICAL ENERGETICS

The branch of science which deal with the energy changes associated with chemical reactions is called chemical energetics. While the study of heat energy and its transformation is known as thermodynamics.
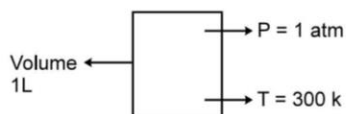
Thermodynamics : The branch of science which deals with different forms of energy & their interconversion.

THERMODYNAMICS

First law of Thermodynamics — Thermochemistry (application of I law in chemical reactions) — Second law of Thermodynamics
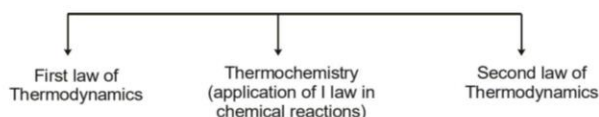
Basic terms

- **System :** Part of the universe which is under study for energy changes.

Volume 1L → P = 1 atm, T = 300 k

Ex. Air in a room, water in a bottle, any living body.

- **Surrounding :** Rest of the universe.
- **Universe :** Universe = System + Surroundings

System / Surroundings / Universe
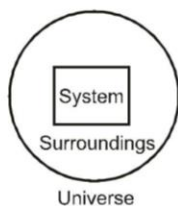
- **Boundary :** Anything which separates system & surroundings is called boundary.
- Boundary can be real or imaginary.
- Boundary can be flexible or rigid
  e.g. - air in a flexible balloon (flexible boundary) while air in a room (fixed boundary).
- Boundary can be adiabatic(non-conducting) or diathermic(conducting).

Classification of system on the basis of nature

(i) Homogenous systems : A system having uniform nature throughout, made up of one phase only

(ii) Heterogeneous system : A system not uniform throughout, consists of more than one phase.

Classification of system on the basis of boundary

- **Open system :** System which can exchange energy & matter with the surroundings.
  e.g. : Living systems(any living organism) are open systems, air in an open room
- **Closed system :** System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.
  e.g. : any matter in a closed container.
- **Isolated system :** System which cannot exchange energy and matter both with the surroundings.
  e.g. : Water in thermos flask.(Though not a perfectly isolated system but can be taken as, for small interval of time as the energy exchanges are negligible).
- Whole of universe is a perfect isolated system.
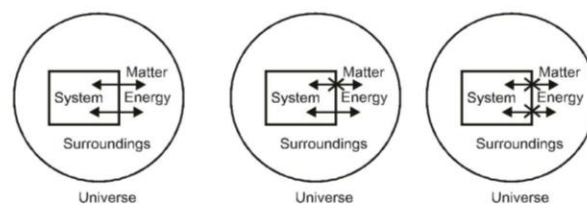
Open System **Close System** **Isolated system**

STATE OF A SYSTEM :

- It means the condition in which the system is present.
- It can be specified/defined by measuring/ specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.

  e.g. For an ideal gaseous system state of the system can be defined by specifying volume, temperature and pressure.

- We may have to specify more properties of the system depending on the complexity of the system.
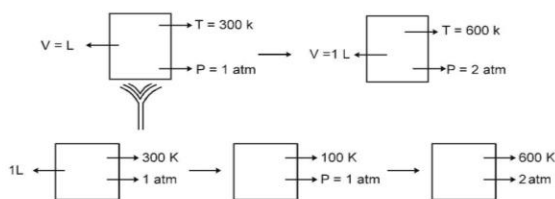
State function :

- Property of a system which is dependent only on the state of the system i.e. it is a point function

- It is independent of the path adopted to attain a particular state.

  e.g. In Mechanics, Displacement of any object will a state function but distance travelled by the object will be a path function.

  For any thermodynamic system,

  Temperature, Pressure, Volume, Total internal energy (E or U), Enthapy(H), Gibbs free energy (G), Entropy (S) are all state functions.

  e.g.

  In the above example the final temperature, pressure, and the volume will be same in both the above ways but the work involved and the heat exchanged during the processes will be different.

- **Note:** ΔH, ΔU, ΔG, ΔP, ΔT etc. are not state function

- **Path function :**

- Quantities which are dependent on the path/way the system has achieved a particular state.

  e.g. Heat, work, Heat capacities(Molar heat capacities, specific heat capacities etc.).

- These quantities are define when there is a process going on.

- These can not have any definite (particular) value in

any particular state of the system.

Types of properties

Extensive properties :

- Functions or properties of the system which are dependent on mass or size of the system are called Extensive Properties .

- Extensive functions are additive in nature [**e.g.** The addition of the volumes of the two parts equals the volume of the whole of the room.

  e.g. Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S).]

Intensive properties :

- Functions or properties which are not mass dependent or size dependent, are called intensive function.

- Intensive properties are not additive in nature.

  eg. Temperature, pressure, molar heat capacity, specific heat capacity, density,concentration, vapour pressure.

How to identify extensive or intensive properties ?

*If a system in a particular state is divided into two equal or unequal parts, the properties which have value equal to the original value of that property for the whole of the system is called an **Intensive property**. While the properties which have values different from the values for whole of the system are called **Extensive Properties**.*

Room is divided into   Room is divided into
two equal halves   two equal halves
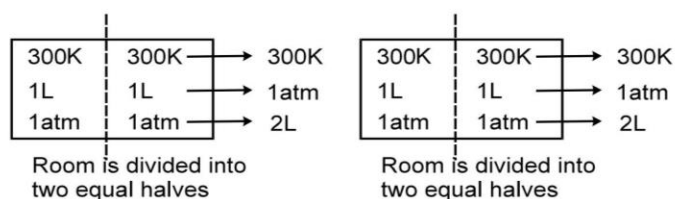
- For example consider air in a room at temp of 300K, 1 atm pressure. Now, if the room is divided by some boundary(imaginary or real) into two parts(equal or unequal) then in these two parts :

- The temperature, pressure, density of the gas, concentration of gaseous molecules etc. will have the same value as that of for whole of the system. (intensive)

- While the volume of two parts, mass of gas in two parts, total energy of the gaseous molecules in the two parts, entropy the two parts etc. will be different from the values of these properties as for the whole of the

system initially. (extensive)

THERMODYNAMIC PROCESS

Isothermal Process

(i) A process in which temperature of the system does not change throughout the studies.

(ii) Means $dT = 0$ and thus $dE = 0$ and $dH = 0$ (for ideal gas only)

(iii) It can be achieved by using thermostatic vessel.

Adiabatic Process

(i) A process in which exchange of heat between system and surrounding does not take place.

(ii) Means $q = 0$

(iii) It can be achieved by insulating the system boundaries .

Cyclic Process

(i) In which initial state of system is attained after a series of physical process

(ii) For a cyclic process $\Delta E = 0$ and $\Delta H = 0$

Isochoric Process

(i) A process in which volume of the system remains constant throughout the porcess.

(ii) For an Isochoric process $\Delta V = 0$, $W = 0$, $dq = De$

Isobaric process

(i) A process in which pressure of the system remains constant throughout process

(ii) Means $\Delta P = 0$

Types of thermodynamic processes on basis of the way the processes are carried out :

- ● **Reversible process :**

  The process that can be reversed by a very small change is known as reversible process.

- Reversivle process is carried out in such a manner so that the system is always in thermodynamic equilibrium at every stage of the process.

- Reversivle the process is carried out such that the difference in driving force and opposing force is infinitesimally small so that process takes place at infinitesimally slow rate.

  $$F_{driving} - F_{opposing} = dF \text{ and } dF \to 0$$

- An ideal reversible process will take infinite time to get completed.

- It is carried out infinitesimally slowly.

- Strictly speaking there is no ideal reversible process in universe.

  To get an idea of a reversible process we can consider the following system.

  An ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will slowing decrease the mass of the sand, lets say, by removing the particles one by one, so the expansion of the gas will take place at infinitesimally small rate and we can always assume the system to in thermodynamic equilibrium. So, the expansion will be of reversible type.

- ● **Irreversible process :** The process, which can not be reversed by a small change is known as irreversible process.

- If a process is carried out in such a manner so that the system is in thermodynamic equilibrium (I) Only at initial & final state of the process but not at the intermediate stages.

  (II) System may be in thermodynamic equilibrium state at some finite number of intermediate stages only. for example - n step irreversible expansion of a gas

- If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate.

- Irreversible processes will get completed in finite time.

- At intermediate stages of the irreversible process, different state function such as Pressure, temperature etc. are not defined.

- All real process are irreversible.

  Consider the below system. If the stopper placed over the piston is removed, then the piston will move with almost infinite acceleration and will keep moving to a position where the pressure of the gas becomes equal to the external pressure. Since the process will get completed in finite time and there was a finite difference between the driving force and the opposing force so, process is irreversible.During the process, the pressure of the gas can not be defined as it will be having different values at different locations.
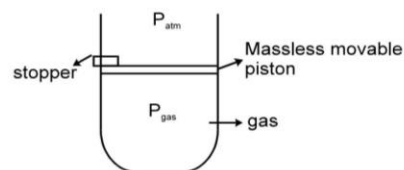
MODES OF ENERGY EXCHANGE :

These are two ways by which a system can interact or can exchange energy with its surroundings.

(i) Heat   (ii) Work

Heat and Work both are forms of energy.

Heat : When the energy transfer takes place because of temperature difference between system & surroundings. It is known as heat.

Work : Energy transfer which is not heat or which is not because of temperature difference is called work.

Work : Product of force and displacement is known as work.

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

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

work done by the gas (in expansion) = W = F.ℓ
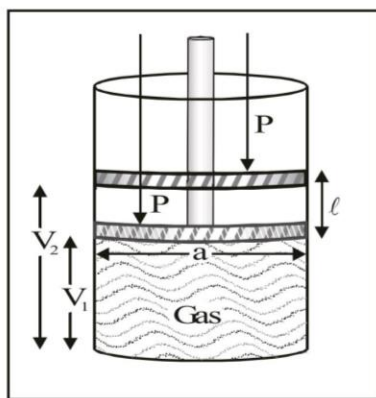
$\because P = \dfrac{F}{a}$ $\therefore F = P \times a$

W = P × a × ℓ (change in volume = a × $\ell = V_2 - V_1$)

W = P × ($V_2 - V_1$)

W = PΔV (According to Physics)

In general $\boxed{W = - P_{external} \Delta V}$ (According to Chemistry)

If system works then $V_2 > V_1$ $\Rightarrow$ work is –ve

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

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

Heat always flows from high T to low T.

Heat flowing into the systum q = +ve

Heat flowing out of the systum q = – ve

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

1 Nm = 1J = 10^7 erg = 0.239 cal

1 cal = 4.184 J = 4.2 J

1 L-atm = 101.3 J = 24.206 cal = 101.3 × 10^7 erg

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

Internal energy [E] : Total of all possible kinds of energy of a system is called its internal energy.

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

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

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

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

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

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

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

Charcteristics of I.E. :–

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

(2) Internal energy is a state property.

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

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

SOLVED EXAMPLE

Example-1

Classify the following into open, closed or isolated systems :

(i) Animals and plants

(ii) A referigerator or a fridge

(iii) A solar cooker

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

(iii) Closed system

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Example-2

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

(i) Human beings
(ii) The Earth
(iii) Can of tomato soup
(iv) Ice-cube tray filled with water
(v) A satellite in a orbit
(vi) Coffee in a thermos flask and
(vii) Helium filled balloon.

Ans.   Open : Human beings, Earth, Ice cube tray
Close : Can of Tomato soup, A satellite in an orbit, Helium filled balloon.
Isolated : Coffee in thermos flask.

Example-3

Separate out the following into extensive and intensive. Volume, Temperature, Pressure, Boiling point, Free energy.

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

Example-4

Which of the following are state functions :

(i) Height of hill
(ii) Distance travelled in climbing the hill
(iii) Energy change in climbing the hill.

Ans.   (i) and (iii)

- **ZEROTH LAW OF THERMODYNAMICS :** When a body A is in thermal equilibrium with a body B, and also separately with a body C, then B and C will be in thermal equilibrium with each other.

- **FIRST LAW OF THERMODYNAMICS :** This law was given by Helmholtz and this law can be expressed as follows-

  (i) Energy can neither be created nor be destroyed

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

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

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

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

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

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

CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS

During isochoric process

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

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

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

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

During an isothermal process

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

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

During an adiabatic process

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

Therefore $\Delta E = W$

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

During Cyclic Process

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

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

During Isobarric process

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

Here, q_p = energy given to system at constant pressure

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

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

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

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

$q_p = \Delta H$

In isobaric process heat behaves as state function,

ENTHALPY (H)

Mathematically it is heat contained in the system measured at constant pressure.

The sum of internal energy and pressure volume (PV) energy is known as enthalpy.

$$\boxed{H = E + PV}$$

It is impossible to determine absolute value of enthalpy so we determine change in enthalpy (ΔH).

$\Delta H = H_{final} - H_{initial}$

Enthalpy is an extensive property because E and V are extensive properties.

It is a state function because E, P and V are state functions .

$\because H = E + PV$

$\therefore \Delta H = \Delta E + \Delta(PV)$ ....(i)

(when P, V and T are variables)

At constant pressure : $\Delta H = \Delta E + P.\Delta V$ ..(ii)

At constant volume : $\Delta H = \Delta E + V.\Delta P$ ....(iii)

For chemical reaction at constant temperature and pressure

$\because P.\Delta V = \Delta n_g RT$

So from equation (i) $\Delta H = \Delta E + \Delta n_g RT$ ... (iv)

where $\Delta H = q_p$; at constant P; $\Delta E = q_v$; at constant V

So equation (iv) can be also written as $q_p = q_v + \Delta n_g RT$ (..v)

- If, $\Delta ng = 0 \rightarrow$ $\boxed{\Delta H = \Delta E}$ eg. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

- If, $\Delta n_g > 0 \rightarrow$ $\boxed{\Delta H > \Delta E}$ eg. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

- If, $\Delta n_g < 0 \leftarrow$ $\boxed{\Delta H < \Delta E}$ eg. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
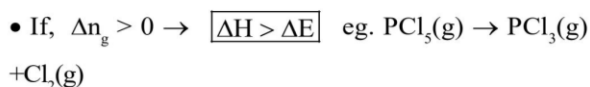
Example-5

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

Ans. $\Delta E = 500$ J

Example-6

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

Ans. q + w = ΔE and ΔE is a state function.

Example-7

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

Ans. $\Delta U = \Delta H - \Delta n_g RT = -92.38 - (-2) \times \dfrac{8.314}{1000} \times 298 = -87.42$ kJ

Example-8

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

Ans. Work

Example-9

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

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

Example-10

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

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

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

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

$\therefore$ According to first law of thermodynamics,

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

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

$\therefore$ According to first law of thermodynamics

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

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

Example-11

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

Sol. The combustion reaction of napthalene.

$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l),$
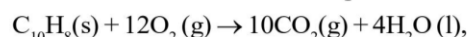
$\Delta E = -5133$ KJ

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

Now applying the relation. ΔH

$= \Delta E + \Delta n_g RT = -5133 \times 10^3 + (-2)(8.314)(298)$

$= -5133000 J - 4955.14 J = -5137955.14$ joule

Heat capacity/molar heat capacity / specific heat capacity

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

$$\text{Heat capcity} = \frac{\text{Heat required}}{\text{rise in temperature}}$$

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

Units : - JK^{-1}, cal K^{-1}, J °C^{-1}, cal °C^{-1}

- Heat capcity is extensive property.

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

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

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{mole of substance}} \Rightarrow \boxed{C_m = \frac{C}{n}}$$

Units:- $J\,mol^{-1}\,K^{-1}$, $cal\,mol^{-1}\,K^{-1}$, $mol^{-1}\,°C^{-1}$, $cal\,mol^{-1}\,°C^{-1}$

• Molar heat capacity is an intensive property .

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

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

$$\boxed{c = \frac{C_m}{\text{molecular weight}}}$$

Units :- $J\,g^{-1}\,K^{-1}$, $cal\,g^{-1}\,K^{-1}$, $J\,g^{-1}\,°C^{-1}$, $cal\,g^{-1}\,°C^{-1}$

• Specific heat capacity is an intensive property.

(iv) Calorie : Amount of heat required to raise temperature of 1g of water by 1°C (14.5°C to 15.5 °C) is called as calorie.

• If heat is supplied at constant pressure, then

$$C_p = \left(\frac{dq}{dT}\right)_p = \frac{dH}{dT} \qquad ....(i)$$

• If heat is supplied at constant volume, then

$$C_v = \left(\frac{dq}{dT}\right)_v = \frac{dE}{dT} \qquad ....(ii)$$

From equation (i) and (ii).

From equation (i)	Unit	From equation (ii)
$\Delta H = C_p dT$ [Heat C_p is heat capacity at constant P]	JK^{-1}	$\Delta E = C_v dT$ [Here C_v is heat capacity at constant V]
For n moles $\Delta H = nC_p dT$ [Here C_p is molar heat capacity at constant P]	$J\,mol^{-1}K^{-1}$	$\Delta E = nC_v dT$ [Here C_v is molar heat capacity at constant V]
For m gram $\Delta H = mC_p dT$ [Heat C_p is gram specific heat (specific heat capacity at constant P]	$J\,g^{-1}\,K^{-1}$	$\Delta E = mC_v dT$

Relation between C_p and C_v for 1 mole of an ideal gas : -

∵ $H = E + PV$

for ideal gas,

$PV = nRT$

$PV = RT$ for 1 mole

Note: C_p is always $> C_v$

∴ $H = E + RT$ differentiate w.r.t. temperature

$$\left(\frac{dH}{dT}\right) = \left(\frac{dE}{dT}\right) + R$$

$C_p = C_v + R$

(i) $\boxed{C_P - C_V = R}$ Mayer's formula

(ii) $\boxed{\dfrac{C_P}{C_V} = \gamma}$, γ Poisson's ratio

• **WORK DONE DURING IN DIFFERENT PROCESS**

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

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

(i) During reversible isothermal process :

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

∵ $PV = nRT$ ∴ $P = \dfrac{nRT}{V} \Rightarrow W = -\int_{V_1}^{V_2}\dfrac{nRT}{V}dV$

∵ In isothermal process $nRT = \text{const}$

∴ $W = -nRT\int_{V_1}^{V_2}\dfrac{1}{V}dV = -nRT\left[\log_e V\right]_{V_1}^{V_2}$

$= -nRT\left[\log_e V_2 - \log_e V_1\right] = -nRT\log_e\dfrac{V_2}{V_1}$

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

∵ State equation of isothermal process is $P_1V_1 = P_2V_2$

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

(ii) During reversible adiabatic process :

Work of expansion in adiabatic reversible process

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

For adiabatic process $PV^\gamma = P_1V_1^\gamma = P_2V_2^\gamma$

$= \text{constant (K)}$ or $P = \dfrac{K}{V^\gamma}$

∴ $W = -\int_{V_1}^{V_2}\dfrac{KdV}{V^\gamma} = -K\int_{V_1}^{V_2}\dfrac{dV}{V^\gamma}$

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

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

∴ $W = \dfrac{-1}{1-\gamma}\left(P_2V_2^\gamma \cdot V_2^{1-\gamma} - P_1V_1^\gamma \cdot V_1^{1-\gamma}\right)$

$= \dfrac{-1}{1-\gamma}\left(P_2V_2 - P_1V_1\right) = \dfrac{-1}{1-\gamma}\left(nRT_2 - nRT_1\right)$

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

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

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

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

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

$\therefore C_V \times \gamma - C_V = R \qquad \text{or} \qquad C_V(\gamma - 1) = R$

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

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

for adiabatic process :- $\boxed{PV^\gamma = \text{cons}\tan t}$

$\boxed{TV^{\gamma-1} = \text{cons}\tan t} \quad \boxed{T^\gamma P^{1-\gamma} = \text{cons}\tan t}$

Example-12
A gas occupies 2 litre at S.T.P. It is provided 300 joule heat so that its volume becomes 2.5 litre at 1 atm. Calculate change in its internal energy.

Ans. Given $V_1 = 2$ litre, $V_2 = 2.5$ litre,
$q = +300 J$, $P_{external} = 1$ atm.
$\therefore \Delta E = q + W$
$W = -P_{external}\Delta V = -P_{external}(V_2 - V_1) = -1 \text{ atm} \times$
$(2.5 - 2) \text{ litre} = -0.5 \text{ litre atm.}$
$W = -0.5 \times 101.3 \text{ J} = -50.65 J$
$\therefore \Delta E = q + W = 300 + (-50.65) = 249.35 \text{ J}$

Example-13
Calculate the work done during the process when one mole of gas is allowed to expand freely into vacuum.

Ans. Given - Gas expands in vaccum i.e., $P_{ext} = 0$
$\Rightarrow W = -P_{ext}\Delta V \qquad \therefore W = 0$

Example-14
Two litre of N_2 at 0°C and 5 atm are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming the gas to be ideal calculate work of expansion ?

Ans. Given $\quad P_1 = 5$ atm, $V_1 = 2$ litre, $P_2 = 1$ atm, $V_2 = ?$
We know that - if T is constant then $\quad P_1V_1 = P_2V_2$

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

$W = -P_{ext}\Delta V = -1(V_2 - V_1) = -1(10 - 2) = -8$ litre atm
$= -8 \times 101.3 = -810.4$ joule

SECOND LAW OF THERMODYNAMICS :

Requirement : Ist law insufficient to Explain

Neutralization, Melting of ice > 0°

Combustion, Freezing of water < 0°

Fall of water , Boiling of water > 100° C

Cooling of a hot body, Free expansion of a gas, mixing of gases.

Spontaneous /Natural /Irreversible Processes :

If a system moves along in a direaction on its own and system, surrounding interactions without the help of any external agency, then that direction is known as spontaneous direction and the process is knwon as a spontaneous process.

Limitation :

First law cannot predict the direction of any process. But in nature a process is found to have a specific direction at certain conditions.

- Energy can be the factor : To achieve stability

  * All exothermic processes are spontaneous.

  * All endothermic processes are non spontaneous.

Exceptions

* melting of ice (above 0°C) although $\Delta H > 0$, $\Delta E > 0$

* Vaporization of water (above 100°C) $\Delta H > 0$, $\Delta E > 0$

* Spreading of ink in water $\Delta H = 0$, $\Delta E = 0$

* Mixing of two gases

* Endothermic solution of salt $\Delta H > 0$, $\Delta E > 0$

- It is observed that nature tries to distribute energy and matter uniformaly (randomization)

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

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

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

ENTROPY

To decide whether a chemical reaction can take place or not, the first factor that has to be considered is whether there is enough energy available. If the reaction is exothermic, there is no reason why it should not take place spontaneously but if the reaction is endothermic then it would not. But in nature, we ...

examples of endothermic reactions, which are spontaneous (for example, evaporation of water). From this, we conclude that energy alone is not the deciding factor. This is where the concept of *entropy* becomes important.

DEFINITION OF ENTROPY

If any process is carried out reversibly, so that dq_{rev} is the heat absorbed by the system in the process at constant temperature(T), then the entropy change (dS) is given by

$$dS = \frac{dq_{rev}}{T}$$

For finite changes, $\Delta S = \dfrac{dq_{rev}}{T}$

MEANING OF ENTROPY

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

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

Entropy is a measure of disorderness of a system.

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

Increase in degree of randomness

(1) Solid   (2) Liquid   (a) High pressure   (b) Low pressure   (3) Gas
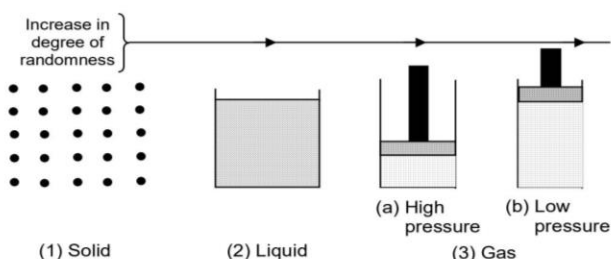
In the gaseous state and at low pressures, the molecules are free to move about unrestricted. If the pressure is increased, the same number of molecules now occupy a smaller volume. The chances of finding a molecule within a given volume are greater under these conditions than when it was at lower pressure.

Hence, the molecules are more ordered (or less randomly distributed) at higher pressure. Added to this, the force of intermolecular attraction increases as the pressure increases and this too has a restricting effect on the molecules.

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

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

freedom.

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

ENTROPY AS THE CAPACITY FOR SPONTANEOUS CHANGE

Let us consider the following examples of spontaneous change.

(i) Expansion of a gas from a region of high pressure to a region of low pressure

Suppose, there are two bulbs filled with a gas at different pressures. If the two bulbs are connected, the gas from the bulb at high pressure will flow into the bulb at low pressure till the pressures in the two bulbs become equal. The greater the pressure difference, the greater the flow of gas, the greater is the capacity of the system for spontaneous change and the greater is the entropy change.

(ii) Solute spreading from a region of high concentration to a region of low concentration.

If the concentration difference between two solutions is considerable, there is obviously a much greater flow of solute from the high concentration to the lower concentration region.

DEGREE OF RANDOMNESS AND SPONTANEOUS CHANGE

The two approaches are two ways of looking at the same problem and we inevitably come to the conclusion that **a system undergoing a spontaneous change is moving to a state of greater randomness.**

This is understood well by considering the two spontaneous processes cited above.

● As a gas expands from a region of high pressure to a region of low pressure, the molecules move farther apart, so that the intermolecular attraction becomes less and the molecules are given a larger volume to move about in. Both these effects give the molecules more freedom and the system has moved to a **state of greater randomness during spontaneous expansion.**

● When a solute spreads from a region of high concentration to a region of low concentration, the molecules move farther apart. Each molecule has more space to move about in and is therefore less restricted in position. Hence, the solute molecules are more randomly distributed throughout the solvent.

(iii) Entropy change for a process : $\Delta S = \dfrac{q_{rev}}{T}$

$\Delta S = nC_V \ell n \dfrac{T_2}{T_1} + nR \ln \dfrac{V_2}{V_1}$	$\Delta S = nC_P \ell n \dfrac{T_2}{T_1} + nR \ln \dfrac{P_1}{P_2}$

● **Calculation of $\Delta S_{surrounding}$:** As the surrounding is an infinite heat reservoir hence, any amount of heat given to the surrounding can cause turbulance in it, hence all heat exhanges with surroundings are considered

to be reversible.

$$\Delta S_{surrounding} = \int \frac{dq_{surrounding}}{T}$$

For surrounding T is constant

$$\therefore \Delta S_{surr} = \frac{1}{T} \int dq_{surr} = \frac{q_{surrounding}}{T}$$

But according to the law of conservation of energy

$$q_{surr} = -q_{system}$$

$$\therefore \Delta S_{surr} = \frac{-q_{system}}{T}$$

Calculation of entropy in different process.

- **Isothermal process :**

(a) Reversible

State A $\xrightarrow{Rev}$ State B

P_1, V_1, T P_2, V_2, T

$$\Delta S_{system} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Since $T_1 = T_2$

$$\Delta S_{system} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{surrounding} = -\frac{q_{system}}{T}$$

$du = dq + dw$ (since $T_1 = T_2$. So, $du = 0$)

$$\therefore dq = -dw$$

$$\therefore q = -w \quad \text{as } w = -nRT \ln \frac{V_2}{V_1}$$

$$q = nRT \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S_{Surr.} = \frac{-nRT \ln \frac{V_2}{V_1}}{T} = -nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

$$= nR \ln \frac{V_2}{V_1} - nR \ln \frac{V_2}{V_1} = 0$$

(b) Irreversible

State A $\xrightarrow{irrev}$ State B

P_1, V_1, T P_2, V_2, T

$$\Delta S_{system} = nR \ln \frac{V_2}{V_1} \qquad \Delta S_{Surrounding} = \frac{-q_{system}}{T}$$

q_{system} is calculated using FLOT

$$q_{system} = P_{ext}(V_2 - V_1)$$

$$\therefore \Delta S_{surrounding} = \frac{-P_{ext}(V_2 - V_1)}{T}$$

$$\Delta S_{universe} = nR \ln \frac{V_2}{V_1} - \frac{-P_{ext}(V_2 - V_1)}{T}$$

$$= \frac{1}{T} \left[(nRT \ln \frac{V_2}{V_1}) - P_{ext}(V_2 - V_1) \right]$$

$$= \frac{1}{T} [W_{rev} - W_{irrev}] > 0$$

As irreversible work of gas is more than reversible work.

- **Adiabatic Process (Isoentropic process)**

(a) Reversible Adiabatic

State A $\xrightarrow{rev}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

$$\Delta S_{system} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$TV^{\gamma-1} = $ constant

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$(\Delta S)_{system} = nC_V \ln \left(\frac{V_1}{V_2}\right)^{\gamma-1} + nR \ln \frac{V_2}{V_1} = 0$$

$$\Delta S_{surr} = -\frac{q_{sys}}{T} = 0 \quad (q_{sys} = 0)$$

$$\therefore \Delta S_{universe} = 0 + 0 = 0$$

(b) Irreversible Adiabatic

State A $\xrightarrow{irre}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

Using irreversible adiabatic process it is not possible to reach same state B which was reached by reversible adiabatic.

$$\Delta S_{system} = nC_V \ln \frac{T_2}{T_1} + nr \ln \frac{V_2}{V_1} > 0$$

$$\Delta S_{surr} = -\frac{q_{sys}}{T} = 0 \qquad \text{as } q = 0$$

For irreversible expansion the decrease in temprature will be lesser as work done is lesser hence, decrease in entropy due to fall in temprature will be lesser in case of irrversible expansion. Hence, net entropy would increase.

- **Isobaric process :**

(a) Reversible Isobaric

State A $\xrightarrow{rev}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = \int \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{-dq_{sys}}{T} = -nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} = 0$$

(b) Irreversible Isobaric

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T} = nC_p \ell n \frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \frac{-nC_p (T_2 - T_1)}{T_2}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} > 0$$

● **Isochoric Process**

(a) Reversible Isochoric

State A $\xrightarrow{rev}$ State B
$P_1, V_1, T_1 \qquad P_2, V_2, T_2$

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = nC_v \ell n \frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{-dq_{sys}}{T} = -nC_v \ell n \frac{T_2}{T_1}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} = 0$$

(b) Irreversible Isochoric

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = nC_p \ell n \frac{T_2}{T_1}$$

$$\Delta S_{surrounding} = \frac{-nC_v (T_2 - T_1)}{T_2}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surrounding} > 0$$

● **Entropy Calculation for phase transformations**

$$\Delta S_{fusion} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{Q}{T}$$

for constant pressure $\Delta S_{fus.} = \dfrac{\Delta H_{fus}}{T}$

for constant volume $\Delta S_{fus.} = \dfrac{\Delta U_{fusion}}{T}$

$$\Delta S_{vap} = \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{Q}{T}$$

for constant Pressure, $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T}$
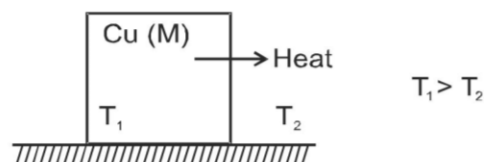
for constant Volume, $\Delta S_{vap} = \dfrac{\Delta U_{vap}}{T}$

● **Entropy Calculation for solid or liquid systems:**

(a) 'Cu' block kept in open atmosphere

$$\Delta S_{system} = \int_{T_1}^{T_2} \frac{msdT}{T} = ms \ln \frac{T_2}{T_1}$$

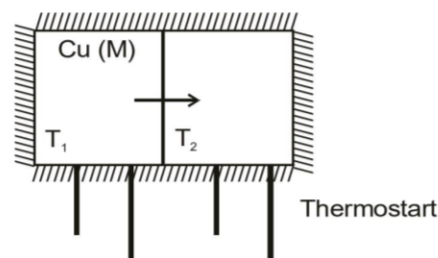$$\therefore \Delta S_{surr} = \int \frac{dq_{surr}}{T} = \frac{q_{surr}}{T_2}$$

but $q_{surr} = -q_{system} = -ms(T_2 - T_1) = ms(T_1 - T_2)$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

$$\therefore \Delta S_{universe} = ms \, \ell n \frac{T_2}{T_1} + \frac{ms(T_1 - T_2)}{T_2} > 0$$

(b) Two copper block kept in contact in thermostat
Two blocks are of same mass

$\Delta S_{surr} = 0$ (since no heat is lost to surrounding)
$\Delta S_{system} = \Delta S_A + \Delta S_B$
System will reach a common temperature (T_f) and
$T_1 > T_f > T_2$

$$\Delta S_{system} = \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T}$$

$$= \int_{T_1}^{T_f} \frac{msdT}{T} + \int_{T_2}^{T_f} \frac{msdT}{T} = ms\left[\ell n \frac{T_f}{T_1} + \ell n \frac{T_f}{T_2} \right]$$

$$\Delta S_{system} = ms\ell n \frac{T_f^2}{T_1 T_2}$$

Since $T_f = \dfrac{T_1 + T_2}{2}$

$$\therefore \Delta S_{system} = ms\ell n \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

Spontaneity of a process in terms of total entropy change:
If, $\Delta S_{total} = +ve \Rightarrow$ spontaneous process
If, $\Delta S_{total} = -ve \Rightarrow$ non spontaneous process
If, $\Delta S_{total} = 0 \Rightarrow$ process is at equilibrium

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THIRD LAW OF THERMODYNAMICS :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

SOLVED EXAMPLE

Example-15

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

Sol. Total pressure of mixture = 1 atm

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

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

For N_2, entropy change

$$\Delta S_{N_2} = -nR\ \ln\frac{P_2}{P_1} = -2.303 \times 3 \times 8.314 \times \log\left(\frac{0.325}{1}\right)$$

$= 28.03$ J/K

For H_2, entropy change

$$\Delta S_{H_2} = -nR\ \ln\frac{P_2}{P_1} = -5 \times 8.314 \times 2.303 \log\frac{0.675}{1}$$

$= 16.34$ J/K.

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

$= \mathbf{44.37\ J/K.}$

Standard Molar Entropies of Elements and compounds

Entropy can be defined very precisely and measured accurately. These are entropies per mole, at 1 atm in the units of Joules per Kelvin (J/K).

(i) Standard molar entropies of substances are always positive quantities $(S° > 0)$.

(ii) Elements as well as compounds are assigned standard entropies. This is in contrast to the heats of formation, when $H_f = 0$ for elements.

(iii) Solids in general have lower entropies than liquids and in turn liquids have lower entropies than gases. For example,

	S°(J/K)
C(s)	5.7
$H_2O(l)$	69.9
$CO_2(g)$	213.6

Example-16

Calculate the standard entropy change for the reaction,

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

The standard entropy change $\Delta S°$

$= \Sigma S°_{products} - \Sigma S°_{reactants}$

The entropies are CaO(s) = 39.7 J/K, $CO_2(g)$ = 213.6 J/K and $CaCO_3(s)$ = 92.9 J/K.

Sol. $\Delta S° = S°_{Cao(s)} + S°_{CO_2(g)} - S°_{CaCO_3(s)}$

$= (39.7 + 213.6 - 92.9)$ J/K $= \mathbf{+160.4\ J/K}$

Note that S° for the decomposition of calcium carbonate is a positive quantity. This is to be expected as the gas formed CO_2, has a much higher molar entropy than either of the solids, CaO or $CaCO_3$.

Free energy change (ΔG)

The two thermodynamic quantities, which affect the spontaneity of a reaction, are **enthalpy (H)** and **entropy (S)**. The next problem is how to arrange two quantities in such a way as to arrive at a single function, which can be used to determine whether a reaction is spontaneous, or not. J. Willard Gibbs introduced a new quantity called the Gibbs free energy and gave it the symbol G. The free energy of a substance, like its enthalpy or entropy is a characteristic property of the substance. In any reaction, the change in free energy, ΔG is the difference in free energies of products and reactants.

$\Delta G = G_{products} - G_{reactants}$

Gibbs showed that the sign of ΔG can be used to determine whether a reaction is spontaneous or not. For a reaction carried out at constant temperature and pressure,

(1) If ΔG is negative, the forward reaction is spontaneous.

(2) If ΔG is positive, the forward reaction is non–spontaneous. Instead, the reverse reaction will be spontaneous.

(3) If ΔG is zero, the system is at equilibrium. There is no tendency for the net reaction to take place in either direction.

It can be inferred that ΔG is a measure of the driving force of a reaction. Reactions (at constant temperature and pressure) go in the direction in which there is a decrease of free energy.

This implies that the direction in which a reaction takes place is determined by the relative free energies of products and reactants. If the products have a lower free energy than the reactants ($G_{products} < G_{reactants}$), the forward reaction will take place. If the reactants have a lower free energy than the products ($G_{reactants} < G_{products}$), the reverse reaction will take place. If $G_{products} = G_{reactants}$, the system is at equilibrium and there is no driving force to make the reaction go in either direction.

RELATIONSHIP BETWEEN ΔG, ΔH AND ΔS

ΔG is made up of two terms; an energy term and an entropy term. $\quad \Delta G = \underset{\text{energy term}}{\Delta H} - \underset{\text{entropy term}}{T\,\Delta S}$

where T is the temperature in Kelvin. This equation tells us that the driving force for a reaction, ΔG, represents two quantities. One of these is the enthalpy change due to the making and breaking of bonds, ΔH. The other is the product of the change in randomness, ΔS times the absolute temperature T.

Why does a reaction take place? The answer is that the reactants are unstable in the presence of each other and can exchange energy, so as to acquire a more stable

state as products. In fact, all systems react so as to acquire a minimum energy irrespective of the fact that whether it is a mechanical, chemical or any other type of system.

The two factors which tend to make ΔG negative and hence gives rise to a spontaneous reaction are

(1) A negative value of ΔH

Exothermic reactions ($\Delta H < 0$) tend to be spontaneous because they contribute to a negative value of ΔG. **Chemically, it means that there will be a tendency to form "strong" bonds at the expense of "weak" bonds.**

(2) A positive value of ΔS

If the entropy change is positive, ($\Delta S > 0$) the term $-T\Delta S$ will make a negative contribution to ΔG. Hence, there will be a tendency for the reaction to be spontaneous provided the products are less ordered than the reactants.

In many physical processes, the increase in entropy is the major driving force. An example is the formation of a solution. When oxygen diffuses into nitrogen, or benzene is dissolved in toluene, the enthalpy change is practically zero, but ΔS is a positive quantity as the solution becomes less ordered than the pure substance. Another example is the spontaneous evaporation of water, although it is an endothermic reaction but liquid water, which is a more ordered arrangement, passes into water vapour, which is less ordered (ΔS increases).

In certain reactions, ΔS is nearly zero and ΔH is the chief and only component of the driving force of spontaneity. An example is the synthesis of hydrogen fluoride from its constituent elements,

$\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \longrightarrow HF(g);\ \Delta H = -268.6$ kJ
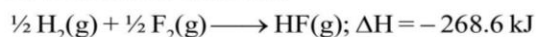
In this reaction, ΔH has a large negative value. This is due to the fact that the bonds in HF are stronger than the bonds in H_2 and F_2 molecules.

In most cases, both ΔH and ΔS make significant contributions to ΔG. To determine the sign of ΔG, the values of ΔH and ΔS must be taken into consideration as well as the temperature.

Gibb's energy change and non expansion work or useful work:-

FLOT : $\Delta E = q + W$

If, work is done by the system, then, $\Delta E = q - W$ ...(i)
According to Gibb's, system does both expansion and non expansion work.

$\therefore\ W = W_{exapnsion} + W_{non\ expansion}$

$W = P\Delta V + W_{non\ expansion}$

Put W in equation (i)

$\Rightarrow \Delta E = q - (P\Delta V + W_{non\ expansion})$

$q = \Delta E + P\Delta V\ \ W_{non\ expansion}$

$q = \Delta H + W_{non\ expansion}\quad (\because \Delta H = \Delta E + P\Delta V)$

$T\Delta S = \Delta H + W_{non\ expansion}\quad (\because \Delta S = q/T)$

$W_{non\ expansion} = T.\Delta S - \Delta H\ (\because \Delta G = \Delta H - T\Delta S)$

$\Rightarrow\ \boxed{W_{non\ expansion} = -\Delta G}$ or $\boxed{W_{useful} = -\Delta G}$

The decrease in Gibb's energy of system is equal to the non expansion work or useful or useful work.

Relation in between ΔG of system and ΔS_{total} or Gibb's energy change and spontaneity :

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

Let system releases heat at constant temperature T and pressure P.

$\therefore\ q = q_p = \Delta H$

$q_{system} = -q_{surroundings}$

$\Rightarrow \Delta H_{system} = -\Delta H_{surroundings}$

$\Delta S_{surr.} = \dfrac{-\Delta Hsurr.}{T}$

$\Delta S_{surr.} = = \dfrac{-\Delta Hsys.}{T}$

$\because \Delta S_{total} = \Delta S_{sys.} + \left(\dfrac{-\Delta H_{sys.}}{T}\right)$

$T\Delta S_{total} = T\Delta S_{sys.} - \Delta H_{sys.}$

$T\Delta S_{total} = -(\Delta H_{sys.} - T\Delta S_{sys.})$

$\boxed{T\Delta S_{total} = -T\Delta S_{total}}$

(i) If, $\Delta S_{total} = +ve \Rightarrow \Delta G_{system} = -ve \Rightarrow$ spontaneous process
(ii) If, $\Delta S_{total} = -ve \Rightarrow \Delta G_{system} = +ve \Rightarrow$ non spontaneous process
(iii) If, $\Delta S_{total} = 0 \Rightarrow \Delta G_{system} = 0 \Rightarrow$ process is at equilibrium

EFFECT OF TEMPERATURE ON SPONTANEITY OF A REACTION

When the temperature of a system is increased, the direction in which the reaction proceeds spontaneously may or may not change. Whether it changes or not depends upon the relative signs of ΔH and $\Delta S°$. The four possibilities are given in table.

Table: Effect of temperature on the spontaneity of a reaction at a given pressure

Case	ΔH	ΔS^O	$\Delta G^O = \Delta H - T\Delta S^O$	Remarks
I	–	+	Always negative.	Spontaneous at all Temperatures Reverse reaction always non-spontaneous, For example $C(s) + O_2 \rightarrow CO_2(g)$
II	+	–	Always positive.	Non-spontaneous at all temperature For example $N_2(g) + 2O_2(g) \rightarrow NO_2(g)$
III	+	+	+at low temperatures, – at high Temperatures.	Non-spontaneous at low temperatures Spontaneous at higher temperature For example, $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$
IV	–	–	–at low temperatures, +at high temperatures.	Spontaneous at low temperatures nonspontaneous at higher temperatures For example $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$

Note: (i) If ΔH and $\Delta S°$ have opposite sign (Case I and II), it is impossible to reverse the direction of spontaneity by temperature change alone. The two terms ΔH and $-T\Delta S$ strengthen one another. Therefore, $\Delta G°$ has the same sign at all temperatures. For the reaction,

$$Cu(s) + H_2O(g) \longrightarrow CuO(s) + H_2(g)$$

$\Delta G°$ is positive at all temperatures. Hence the reaction cannot take place spontaneously at 1 atm whatever be the temperature.

(ii) When ΔH and $\Delta S°$ have the same sign (Case III and IV,) the enthalpy and entropy factors oppose each other. $\Delta G°$ changes sign as temperature increases and the direction of spontaneity reverses. At low temperatures, ΔH predominates and the exothermic reaction is favoured. With increasing temperature, the factor $T\Delta S°$ increases in magnitude and at a certain stage exceeds ΔH. At high temperatures, the reaction leading to an increase in entropy occurs. This explains why exothermic reactions are spontaneous at room temperature.

In the decomposition of calcium carbonate, it is found that ΔH and $\Delta S°$ have the same sign.

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

On calculation,

$\Delta G = 178.0\ kJ - T\ (0.1604\ kJ/K)$

(a) Below 1100 K, ΔH predominates, i.e., $\Delta G°$ is positive and the reaction is not spontaneous at 1 atmosphere pressure.

(b) Above 1100 K, $T\Delta S$ predominates and the reaction becomes spontaneous at 1 atmosphere pressure.

(c) At about 1100 K, $\Delta H = T\Delta S°$. Hence, $\Delta G° = 0$ i.e. the system is at equilibrium at 1 atmosphere, which means if we put some solid $CaCO_3$ in a vessel and heat it to 1100 K, the pressure developed by CO_2 will be 1 atmosphere.

SOLVED EXAMPLE

Example-17

Using $G_f° (HI) = 1.3$ kJ/mole, calculate the standard free energy change for the following reaction,

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

Sol.

$\Delta G° = \Sigma G_f° \text{ (products)} - \Sigma G_f° \text{ (reactants)}$

$= 2 \times (1.3) - (0 + 0)$

$= 2.6 - 0 = \textbf{2.6 kJ/mol}$

Example-18

Calculate free energy change for the esterification reaction,

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

The equilibrium constant for the reaction at 25°C is 4.

Sol. $\Delta G° = -2.303\ RT \log K = -2.303 \times 8.314 \times 298 \log 4$

$= -(2.303 \times 8.314 \times 298 \times 0.6021) = \textbf{-3435.49 J/mol}$

Example-19

Calculate the value of K_p at 25°C for an equilibrium reaction, if $\Delta G° = -20$ kJ/mole.

Sol. $\Delta G_P° = -2.303\ RT \log K_p$

$-20 \times 1000 = -2.303 \times 8.314 \times 298 \log K_p$

$\log K_p = \dfrac{20 \times 1000}{2.303 \times 8.314 \times 298} = 3.464$

$K_p = \text{antilog}\ (3.505) = \textbf{2.91} \times \textbf{10}^3$

Example-20

Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.1 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is 4.2 J g^{-1} K^{-1}, what is the final temperature of water ?

Sol. $W = -2.1\ [6 - 4]$

$= -2.1 \times 2 = -4.2\ \text{atm} \times \text{lit.} = -4.2 \times 101.325\ J$

This work is used to heat up the water

Specific heat of $H_2O = 4.2\ \dfrac{J}{gram \cdot K}$

Heat required for increasing temperature by 1°C of 1 mole

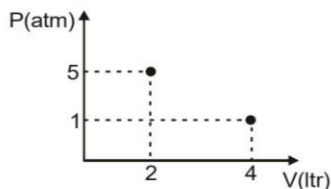$= 4.2 \times 18 = 75.6\,J$

$4.2 \times 101.325 = 75.6\,[T - 293]$

$5.63 = T - 293$

$T = 298.63\,K$

Ans. $298.63\,K$

Example-21

Following graph shows a single stange expansion process, then workdone by the system is
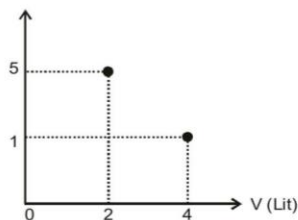

(A) $-9104\,J$ (B) $-202.6\,J$

(C) $-506\,J$ (D) $-101.3\,J$

Ans. **(B)**

$W = -P_{ext}(V_2 - V_1) = -1 \times 2 \times 101.325\,J = -202.6\,J$

Sol.

Example-22

One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is :

$[R = 0.082\ L\ atm\ mol^{-1}\ K^{-1} = 8.3\ J\ mol^{-1}K^{-1}].$

(A) 0   (B) $R\ell n\,(24.6)$

(C) $R\ \ell n\,(2490)$ (D) $3/2\ R\ell n\,(24.6)$

Ans. **(B)**

Sol. $\Delta S = nR\ \ell n\left(\dfrac{V_f}{V_i}\right) = R\ell n\left(\dfrac{P_i}{P_f}\right)$

$= R\ \ell n\left(\dfrac{300R}{1\,L\ \times\ 1\,atm}\right) = R\ell n\,(24.6)$

Example-23

Given the following data :

Substance	$\Delta H°$ (kJ/mol)	$S°$(J/mol K)	$\Delta G°$(kJ/mol)
FeO(s)	-266.3	57.49	-245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	-110.5	197.6	-137.15

Determine at what temperature the following reaction is

spontaneous ?

$FeO(s) + C\ (Graphite) \longrightarrow Fe(s) + CO(g)$
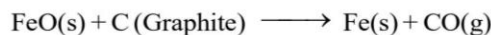
(A) 298 K   (B) 668 K   (C) 966 K

(D) $\Delta G°$ is +ve, hence the reaction will never be spontaneous

Ans. **(C)**

Sol. $FeO\,(s) + C\,(graphite) \longrightarrow Fe\,(s) + CO\,(g)$

$\Delta H = 0 + [-110.5] - (-266.3)$

$= -110.5 + 266.3 \qquad = +155.8\ kJ/mole$

$\Delta S = 27.28 + 197.6 - 57.49 - 5.74 = 161.65\ J/mole$

$\Delta G = \Delta H - T\Delta S = 0 = 155.8 - T \times 161.65 \times 10^{-3}$

$T \times 161.65 \times 10^{-3} = 155.8 \qquad\qquad \Rightarrow T = 963.8\ K$

Example-24

What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm ? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process ?

(A) 1294.0 cal, 11247 cal   (B) 921.4 cal, 11074 cal

(C) 1024.8 cal, 12470.6 cal   (D) 1129.3 cal, 10207 cal

Ans. **(C)**

Sol. Mole of $H_2O = 1.39$

$Pv = nRT$

$1 \times v = 1.39 \times 0.082 \times 373$

$v = 42.80.$

$w = P_{ext}.\,dv = 1 \times [42.80]\ atm \times lit.$

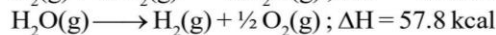$= -42.80 \times 101.325\ J = -\dfrac{42.80 \times 101.325}{4.2}$

$= 1024.8\ cal.$

$\Delta H = \Delta E + [P\Delta v]. = 12470.6\ cal.$

THERMOCHEMISTRY

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

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

For example,

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

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

For exothermic reactions $(q < 0)$

At constant pressure, $\Delta H = (H_P - H_R) = -ve\quad (\because H_P < H_R)$

At constant volume, $\Delta E = (E_P - E_R) = -ve\ (\because E_P < E_R)$

For endothermic reaction, $(q > 0)$

At constant pressure, $\Delta H = (H_P - H_R) = +ve\quad (\because H_P > H_R)$

At constant volume, $\Delta E = (E_P - E_R) = +ve\quad (\because E_P > E_R)$

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

Condition I:

If the volume of the system is kept constant, no work is

done on the system and the first law of thermodynamics reduces to

$$\Delta E = q_V$$

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

Condition II:

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

$$\Delta H = q_P$$

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

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

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

If all the reactants and products are liquids or solids, the PV values change only slightly so dU = dH. For reactions in which gases are involved, the values of $\Delta(PV)$ depends on the change in the number of moles of gas as a result of reaction.

$$\therefore \Delta(PV) = \Delta n_g(RT)$$
$$\therefore \mathbf{\Delta H = \Delta E + \Delta n_g RT}$$

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

Enthalpy of a substance :

- Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value.
- The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol
- H_m(substance) : For example molar enthalpy of water vapours at 398 K and 1 atm pressure may be represented as H_m (H_2O, g, 398 K, 1 atm). In very simple works, enthalpy can be considered as heat constant (amount) of substance, and during reaction this heat is being released or absorbed.
- Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance.

**Standard state of any substance means**

- For a **GAS** standard state means ideal gas at 1 bar partial pressure at any give temperature.
- For a **LIQUID** – pure liquid at 1 bar pressure at any given temperature.
- For a **PURE CRYSTALLINE SOLID** – pure crystalline solid at 1 bar pressure and at any given temperature
- For any **SUBSTANCE or ION IN SOLUTION** – the species should be in unit molality, at one bar pressure and at any given temperature.
- Molar standard enthalpy of water vapours at 398 K will be represented as $H°(H_2O, g, 398 K)$ and molar

standard enthalpy of liquid water at 398 K will be represented as $H_m°$ (H_2O, ℓ, 398 K)

(It is hypothetical but can be calculated).

- We cannot exactly calculate enthalpy content of a substance, only the change in enthalpy can be calculated when substance is taken from one state to other.

For example :
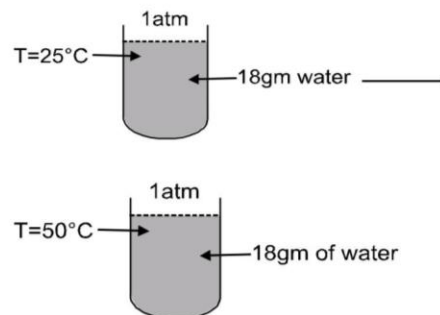
Let enthalpy content initially be $H_{m,1}^0$ & finally enthalpy content be $H_{m,2}^0$

Then, $\Delta H° = H_{m,2}^0 - H_{m,1}^0$

= heat added at constant pressure to change temperature from 25°C to 50°C.

ENTHALPY OR HEAT OF REACTION

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

Enthalpy or heat of reaction is given by

$$\Delta H = \sum H_P - \sum H_R.$$

FACTORS AFFECTING HEAT OF REACTION
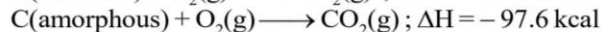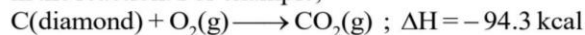
(I)   PHYSICAL STATE OF REACTANTS AND PRODUCTS

Physical state always affects the heat of reaction as heat energy is involved in changing the physical state of a substance. For example,

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

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) ; \Delta H = -68.32 \text{ kcal}$

Difference in the value of ΔH is observed because heat is evolved when steam condenses.

ALLOTROPIC FORMS OF THE ELEMENT

The value of ΔH also depends on the allotropic form used in the reaction. For example,

$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) ; \Delta H = -94.3 \text{ kcal}$

$C(\text{amorphous}) + O_2(g) \longrightarrow CO_2(g) ; \Delta H = -97.6 \text{ kcal}$
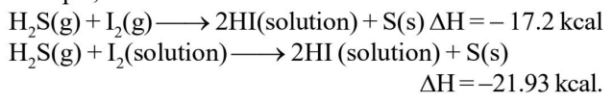
The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is called heat of transition.

$C(\text{diamond}) \longrightarrow C(\text{amorphous}); \Delta H = 3.3 \text{ kcal}.$
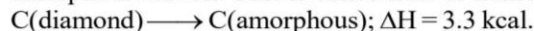
(II)   ENTHALPIES OF SOLUTION

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

$H_2S(g) + I_2(g) \longrightarrow 2HI(solution) + S(s)$ $\Delta H = -17.2$ kcal.

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

(IV)   TEMPERATURE

Enthalpy of reaction also depends on temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature. Relation between ΔH or ΔE and temperature are given by Kirchoff's equation.

$(\Delta H_2 - \Delta H_1) = \Delta C_P (T_2 - T_1)$ $(\Delta E_2 - \Delta E_1) = \Delta C_V (T_2 - T_1)$

The above relations may be derived as follows:

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

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

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

$$= (C_P)_P - (C_P)_R = \Delta C_P \quad \text{or} \quad d(\Delta H) = \Delta C_P dT$$

Integrating this equation within appropriate limits, we get

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

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

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{(T_2 - T_1)} = \Delta C_P \quad \quad ......(xvii)$$

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

Similarly, $\dfrac{\Delta E_{T_2} - \Delta E_{T_1}}{(T_2 - T_1)} = \Delta C_V \quad \quad ......(xviii)$

In the limit as $(T_2 - T_1) \longrightarrow 0$, equation (xvii) yields the

differential form $\dfrac{d(\Delta H)}{dT} = \Delta C_P$

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

ENTHALPY OR HEAT OF FORMATION

The amount of heat evolved or absorbed when one mole of a substance is formed from its constituent elements is called heat of formation.

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$; $\Delta H = -44$ kcal

Thus, enthalpy of formation of HCl is −22 kcal.

The formation reaction of a compound has only one mole of the compound and nothing else on the product side. Only elements in their stable states of aggregation appear on the reactant side.

$$H_T^\circ = H_{298}^\circ + \int_{298}^{T} C_P^\circ dT$$

This expression holds good for both elements as well as compounds. For elements, the first term on the right hand side is zero.

Why do we assign zero value of enthalpy to an element in free state under standard conditions?

Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

$\Delta H_r^\circ = \Sigma \, \nu_B \, \Delta H_f^\circ{}_{,products} - \Sigma \, \nu_B \, \Delta H_f^\circ{}_{,reactants}$

where ν_B is the stoichiometric coefficient above equation holds good for any reaction as the same reference state is used for reactants and products (shown in figure).

$H_2(g) + I_2(g) \longrightarrow 2HI(g) \quad \Delta H_r = -52.5 \text{ kJ mol}^{-1}$
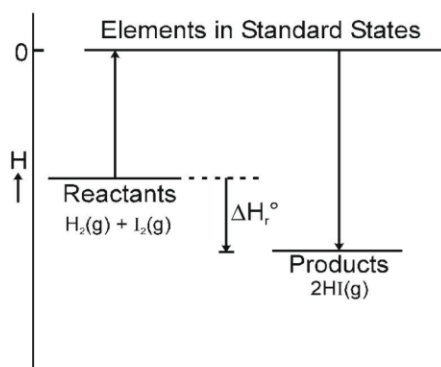
Enthalpy of Reaction

Hess's Law of constant heat summation :

- The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps.

- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpies of reactions are also manipulated in the same way so as to give the enthalpy of reaction for the desired chemical equation.

- Since $\Delta_r H$ stands for the change of enthalpy when reactants (substances on the left hand side of the arrow) are converted into products (substances on the right hand side of the arrow) at the same temperature and pressure, if the reaction is reversed (i.e., products

are written on the left hand side and reactants on the right hand side), then the numerical value of $\Delta_r H$ remains the same, but **its sign changes.**
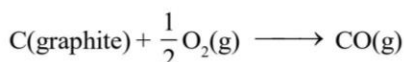
- The utility of Hess's law is considerable. In almost all the thermochemical numericals, Hess's law is used.
- One of the important applications of Hess's law is to determine enthalpy of reaction which is difficult to determine experimentally. For example, the value $\Delta_r H$ for the reaction

$$C(graphite) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$
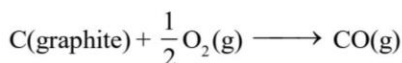
which is difficult to determine experimentally, can be estimated from the following two reactions for which $\Delta_r H$ can be determined experimentally.

$$C(graphite) + O_2(g) \longrightarrow CO_2(g)\Delta_r H_1$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta_r H_2$$
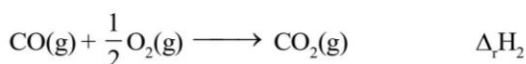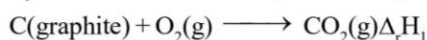
Substracting the latter from the former, we get

$$C(graphite) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

Consequently, $\Delta_r H = \Delta_r H_1 - \Delta_r H_2$

SOLVED EXAMPLE

Example-25

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° is –119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene.

Ans. –152 kJ mole^{-1}

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

$$= \Delta H_F (\bigcirc) - \Delta H_f(\hexagon)$$

$$= -156 - (+49)\,kJ = -205\,kJ.$$

Given that, $\bigcirc + H_2 \longrightarrow \hexagon \; \Delta H = 119\,kJ$
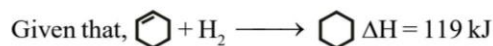
Theoretical enthalpy of formation of 3 double bonds in benzene ring

$$= 3 \times (-119)\,kJ = -357\,kJ.$$

∴ resonance energy of benzene

$$= -357 - (-205)\,kJ = -152\,kJ\,mole^{-1}$$

Example-26

If ΔH_f° for Ag$^+$ (infinitely diluted), NO$_3^-$ (infinitely diluted), Cl$^-$ (infinitely diluted) and AgCl(s) are 105.579, –207.36, –167.159 and –127.068 respectively. Calculate the enthalpy change for the reaction

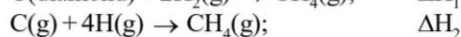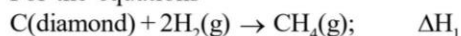$$AgNO_3(aq.) + HCl(aq.) \longrightarrow AgCl(s) + HNO_3(aq.)$$

(A) 21.471 KJ/mol (B) 145.688 KJ/mol
(C) –65.488 KJ/mol (D) None

Ans. **(C)**

Sol. $\Delta H^\circ_{reaction} = [\Delta H_f(AgCl) + \Delta H_f(H^+) + \Delta H_f(NO_3^-)]$
$- [\Delta H^\circ_f(Ag^+)] + \Delta H^\circ_f(NO_3^-) + \Delta H^\circ_f(Cl^-) + \Delta H^\circ_f(H^+)]$
$= -127.068 - [105.579 - 167.159] = -65.488\,KJ/mol.$

Example-27

For the equations
$C(diamond) + 2H_2(g) \to CH_4(g); \qquad \Delta H_1$
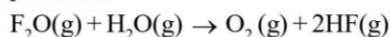$C(g) + 4H(g) \to CH_4(g); \qquad \Delta H_2$
Predict whether
(A) $\Delta H_1 = \Delta H_2$
(B) $\Delta H_1 > \Delta H_2$
(C) $\Delta H_1 < \Delta H_2$
(D) $\Delta H_1 = \Delta H_2 + \Delta_{vap}H(C) + \Delta_{diss}H(H_2)$

Ans. **(B)**

Example-28

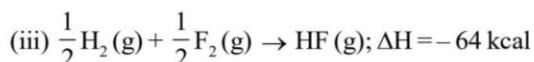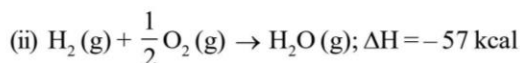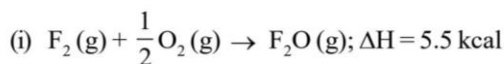Calculate heat of the following reaction at constant pressure,
$F_2O(g) + H_2O(g) \to O_2(g) + 2HF(g)$
The heats of formation of F_2O (g), H_2O(g) and HF (g) are 5.5 kcal, –57kcal and –64 kcal respectively.

Sol. Given that

(i) $F_2(g) + \frac{1}{2}O_2(g) \to F_2O(g); \Delta H = 5.5\,kcal$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \to H_2O(g); \Delta H = -57\,kcal$

(iii) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \to HF(g); \Delta H = -64\,kcal$
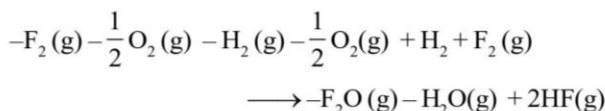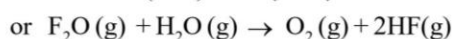
F_2O and H_2O in eqns. (i) and (ii) given in the problem are on the opposite sides, while HF in eqn. (iii) given in the problem is on the same sides.

Thus applying,

$[-Eqn.\,(i) - Eqn.\,(ii) + 2 \times Eqn.\,(iii)]$, we get

$-F_2(g) - \frac{1}{2}O_2(g) - H_2(g) - \frac{1}{2}O_2(g) + H_2 + F_2(g)$

$\longrightarrow -F_2O(g) - H_2O(g) + 2HF(g)$

$\Delta H = -5.5 - (-57) + 2 \times (-64) = -76.5\,kCal$

or $F_2O(g) + H_2O(g) \to O_2(g) + 2HF(g)$
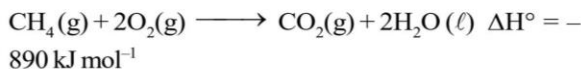
$$\Delta H = -76.5\,kCal.$$

ENTHALPY OR HEAT OF COMBUSTION

- It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.

For example, the standard enthalpy of combustion of methane at 298 K is – 890 kJ mol^{-1}. This implies the

following reaction :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) \quad \Delta H° = -890 \text{ kJ mol}^{-1}$$

The standard enthalpy of combustion of methane at 298 K may be written as

$$\Delta H_c°(CH_4, g, 298 \text{ K}) = -890 \text{ kJ mol}^{-1}$$

The data on the enthalpy of combustion can be determined experimentally.

- With the help of such data, we can determine the enthalpy of formation of a compound, which otherwise is difficult or impossible to determine experimentally. Consider for example, the enthalpy of formation of $CH_4(g)$:

$$C(graphite) + 2H_2(g) \longrightarrow CH_4(g)$$
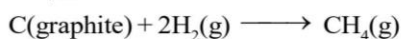
First of all, the combination of carbon and hydrogen does not occur readily. Secondly, if the reaction is even completed, the end product would not be pure methane.

Therefore, the enthalpy of formation of methane can be determined indirectly through the enthalpy of combustion of methane :
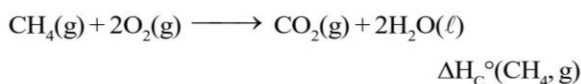
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$
$$\Delta H_c°(CH_4, g)$$
$$= \Delta H_f°(CO_2, g) + 2\Delta H_f°(H_2O, \ell) - \Delta H_f°(CH_4, g)$$

therefore

$$\Delta H_f°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\Delta H_f°(H_2O, \ell)$$
$$- \Delta H_c°(CH_4, g)$$

- The enthalpies of formation of CO_2 and H_2O can be determined experimentally by the combustion of carbon (graphite) and hydrogen. Thus, knowing the mesured value of $\Delta H_c°(CH_4, g)$, the enthalpy of formation of CH_4 can be calculated. The value is

$$\Delta H_f°(CH_4, g) = \Delta H_f°(CO_2, g) + 2\Delta H_f°(H_2O, \ell)$$
$$- \Delta H_c°(CH_4, g)$$
$$= [-393 + 2(-285) - (-890)] \text{ kJ mol}^{-1} = -73 \text{ kJ mol}^{-1}$$

or, equivalently, we may add the following three chemical equations.

$$C(graphite) + O_2(g) \longrightarrow CO_2(g)$$
$$\Delta_c H° = -393 \text{ kJ mol}^{-1}$$

$$2[H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)]$$
$$\Delta_r H° = 2(-285) \text{ kJ mol}^{-1}$$

$$-[CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)]$$
$$\Delta_r H° = -(-890) \text{ kJ mol}^{-1}$$

$$C(graphite) + 2H_2(g) \longrightarrow CH_4(g)$$
$$\Delta_r H° = -73 \text{ kJ mol}^{-1}$$
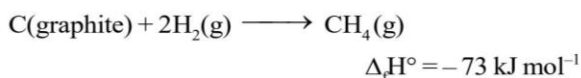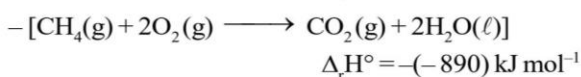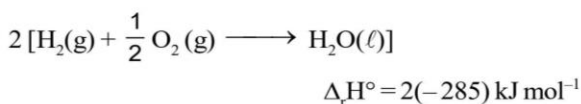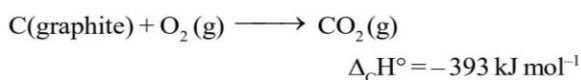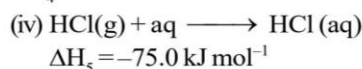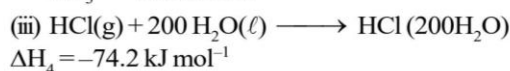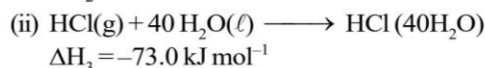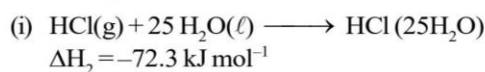
Enthalpy of solution

The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration.

While recording integral enthalpies of solution it is a general practice to state the amount of the solvent in which 1 mole of solute is dissolved ; Thus
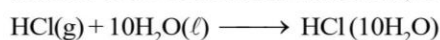
$$HCl(g) + 10H_2O(\ell) \longrightarrow HCl(10H_2O)$$
$$\Delta H_1 = -69.5 \text{ kJ mol}^{-1}$$

indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are

(i) $HCl(g) + 25 H_2O(\ell) \longrightarrow HCl(25H_2O)$
$$\Delta H_2 = -72.3 \text{ kJ mol}^{-1}$$

(ii) $HCl(g) + 40 H_2O(\ell) \longrightarrow HCl(40H_2O)$
$$\Delta H_3 = -73.0 \text{ kJ mol}^{-1}$$

(iii) $HCl(g) + 200 H_2O(\ell) \longrightarrow HCl(200H_2O)$
$$\Delta H_4 = -74.2 \text{ kJ mol}^{-1}$$

(iv) $HCl(g) + aq \longrightarrow HCl(aq)$
$$\Delta H_5 = -75.0 \text{ kJ mol}^{-1}$$

Note: Whenever amount of solvent is not specified then take its amount to be very large just like in equation no. (iv).
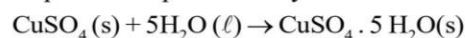
ENTHALPY OF HYDRATION :

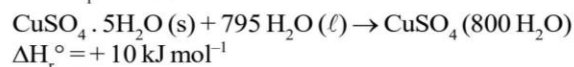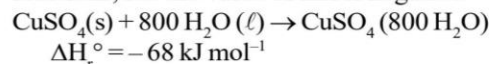Enthalpy of hydration is used in following to ways.

- Enthalpy of hydration of anhydrous or partially hydrated salts :

Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt.

For example, the hydration of anhydrous cupric sulphate is represented by

$$CuSO_4(s) + 5H_2O(\ell) \rightarrow CuSO_4 \cdot 5H_2O(s)$$

There is a almost invariably a liberation of heat in such reactions, i.e. the value of ΔH is negative.

$$CuSO_4(s) + 800 H_2O(\ell) \rightarrow CuSO_4(800 H_2O)$$
$$\Delta H_r° = -68 \text{ kJ mol}^{-1}$$

$$CuSO_4 \cdot 5H_2O(s) + 795 H_2O(\ell) \rightarrow CuSO_4(800 H_2O)$$
$$\Delta H_r° = +10 \text{ kJ mol}^{-1}$$

by subtraction, we get $CuSO_4(s) + 5H_2O(\ell) \rightarrow CuSO_4 \cdot 5H_2O(s) \Delta H_r° = -78 \text{ kJ mol}^{-1}$

- Enthalpy of hydration of gaseous ions.

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqeous ion.

By convention, the standard enthalpy of formation of $H^+(aq)$ is taken to be zero.

Enthalpy of hydration of Cl^- gaseous ions will be represented by :

$$Cl^-(g) + aq. \longrightarrow Cl^-(aq) \quad \Delta H_r° = \Delta H_f°(Cl^-, aq)$$
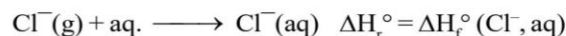
ENTHALPY OF NEUTRALIZATION :

- The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

or

- Enthalpy of neutralization is defined as the enthalpy change when one mole of H^+ in dilute solution combines with one mole of OH^- to give rise to undissociated water, i.e.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$$
$$\Delta H = -57.1 \text{ kJ/mole} = -13.7 \text{ kcal/mol}$$
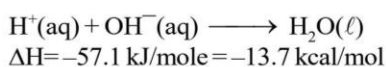
Remember :

- For **Strong Acid + Strong Base**, heat of neutralisation is always equal to –13.7 kcal/mole or –57.1 kJ/mole.

- For any other combination of **acid and base** this heat is less than –13.7 kcal/mole or –57.1 kJ/mole.

Heat of Dilution

The amount of heat evolved or absorbed when solution containing one mole of solute is diluted from one concentration to another. For example,

$$HCl(g) + 10H_2O \longrightarrow HCl.10H_2O ;$$
$$\Delta H_1 = -69.01 \text{ kJ/mol}$$

$$HCl(g) + 25H_2O \longrightarrow HCl.25H_2O ;$$
$$\Delta H_2 = -72.03 \text{ kJ/mol}$$

$$HCl(g) + 40H_2O \longrightarrow HCl.40H_2O ;$$
$$\Delta H_3 = -72.79 \text{ kJ/mol}$$

$$HCl(g) + \infty H_2O \longrightarrow HCl.\infty H_2O ;$$
$$\Delta H_\infty = -74.85 \text{ kJ/mol.}$$

If we subtract first equation from the second in the above set, we get

$$HCl.10H_2O + 15H_2O \longrightarrow HCl.25H_2O ;$$
$$\Delta H = (\Delta H_2 - \Delta H_1) = -3.02 \text{ kJ/mol}$$
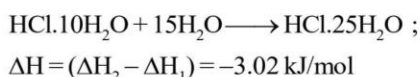
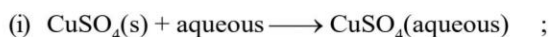This value of ΔH is the heat of dilution. The heat of dilution of a solution is dependent on the original concentration of the solution and on the amount of the solvent added.
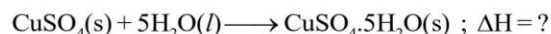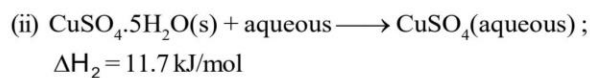
Example-29

The enthalpies of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4.5H_2O$ are –66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$.

Sol. Given that

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

$$\Delta H_1 = -66.5 \text{ kJ/mol}$$

(ii) $CuSO_4.5H_2O(s) + aqueous \longrightarrow CuSO_4(aqueous)$;
$$\Delta H_2 = 11.7 \text{ kJ/mol}$$

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s) ; \Delta H = ?$$
$$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - 11.7 = \mathbf{-78.2 \text{ kJ}}$$

Example-30

150 ml of 0.5 N nitric acid solution at 25.35°C was mixed with 150 ml of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77°C. Calculate the heat of neutralisation of nitric acid with sodium hydroxide.

Sol. Total mass of solution = 150 + 150 = 300 gm

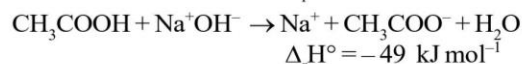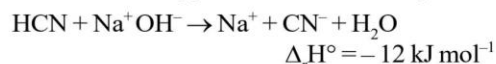$$Q = 300 \times (28.77 - 25.35) = 300 \times 3.42 = 1026 \text{ cal}$$

$$\therefore \text{ Heat of neutralisation} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5}$$

$$= \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ kcal.}$$
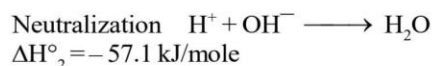
Since, the enthalpy of neutralisation is always –ve, so, heat of neutralisation = **– 13.68 kcal**.
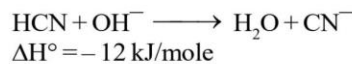
ENTHALPY OF IONIZATION :

- Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than 57.1 kJ mol^{-1}.

- It is because of the fact that these acids or bases are not completely ionized in solution. Some of the heat is consumed in ionizing there acids and bases this heat is known as enthalpy of ionization. Examples are :

$$HCN + Na^+OH^- \rightarrow Na^+ + CN^- + H_2O$$
$$\Delta_r H° = -12 \text{ kJ mol}^{-1}$$

$$CH_3COOH + Na^+OH^- \rightarrow Na^+ + CH_3COO^- + H_2O$$
$$\Delta_r H° = -49 \text{ kJ mol}^{-1}$$

The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,

Ionization $HCN \longrightarrow H^+ + CN^- \quad \Delta H°_1 = x$

Neutralization $H^+ + OH^- \longrightarrow H_2O$
$$\Delta H°_2 = -57.1 \text{ kJ/mole}$$

The complete reaction is obtained by adding the above two steps. Thus

$$HCN + OH^- \longrightarrow H_2O + CN^-$$
$$\Delta H° = -12 \text{ kJ/mole}$$

Obviously, $\Delta H° = \Delta H°_1 + \Delta H°_2$

$$\Delta H°_1 = \Delta H° - \Delta H°_2 = [-12 - (-57.1)] = 45.1 \text{ kJ/mole}$$
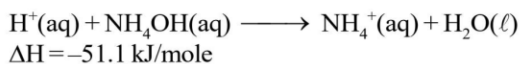
- **Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.**
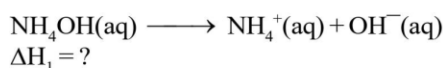
SOLVED EXAMPLE

Example-31

Enthalpy of neutralization of HCl by NaOH is –57.1 kJ/mol and by NH_4OH is –51.1 kJ/mol. Calculate the enthalpy of dissociation of NH_4OH.
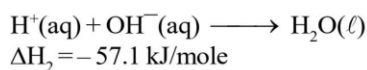
Sol. Given that

$$H^+(aq) + NH_4OH(aq) \longrightarrow NH_4^+(aq) + H_2O(\ell)$$
$$\Delta H = -51.1 \text{ kJ/mole}$$

We may consider neutralization in two steps.

(i) Ionization

$$NH_4OH(aq) \longrightarrow NH_4^+(aq) + OH^-(aq)$$
$$\Delta H_1 = ?$$

(ii) Neutralization

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$$
$$\Delta H_2 = -57.1 \text{ kJ/mole}$$
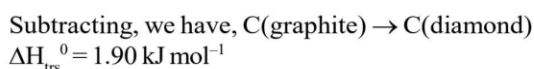
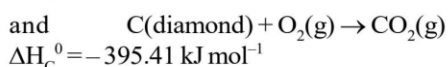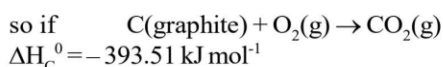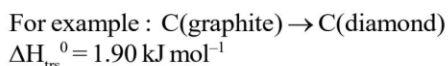Thus, $\Delta H = \Delta H_1 + \Delta H_2$

Therefore,

$$\Delta H_1 = \Delta H - \Delta H_2 = -51.1 \text{ kJ/mol} + 57.1 \text{ kJ mol}^{-1}$$
$$= 6.0 \text{ kJ/mol}$$


ENTHALPY OF TRANSITION :

Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.

For example : $C(graphite) \rightarrow C(diamond)$
$\Delta H_{trs}^0 = 1.90 \text{ kJ mol}^{-1}$

so if $\quad C(graphite) + O_2(g) \rightarrow CO_2(g)$
$\Delta H_C^0 = -393.51 \text{ kJ mol}^{-1}$

and $\quad C(diamond) + O_2(g) \rightarrow CO_2(g)$
$\Delta H_C^0 = -395.41 \text{ kJ mol}^{-1}$

Subtracting, we have, $C(graphite) \rightarrow C(diamond)$
$\Delta H_{trs}^0 = 1.90 \text{ kJ mol}^{-1}$

ENTHALPY OF PRECIPITATION :

Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.

For example :
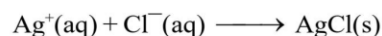$BaCl_2(aq.) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
$\Delta_r H^0 = -24.27 \text{ kJ mol}^{-1}$
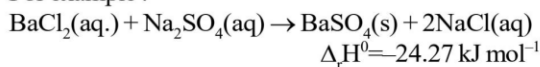
SOLVED EXAMPLE

Example-32

Calculate $\Delta H°$ for the reaction,

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

at 25°C. Given $\Delta_f H°$ (Ag^+, aq) = 105 kJ mol^{-1}, $\Delta_f H°$ (Cl^-, aq) = –167 kJ mol^{-1} and $\Delta_f H°$(AgCl, s) = – 127 kJ mol^{-1}

Sol. For the reaction $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
we have

$$\Delta H° = \Delta_f H° (AgCl, s) - \Delta_f H°(Ag^+, aq) - \Delta_f H°(Cl^-, aq)$$
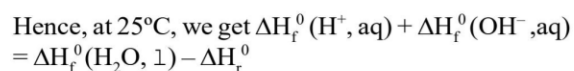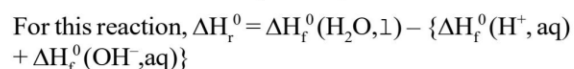$$= [-127 - 105 - (-167)] \text{ kJ mol}^{-1} \qquad = -65 \text{ kJ mol}^{-1}$$

ENTHALPY OF FORMATION OF IONS :

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state.

$$\frac{1}{2} Cl_2(g) + aq \longrightarrow Cl^-(aq) \quad \Delta H_r° = \Delta H_f° (Cl^-, aq)$$
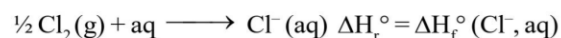
By convention, the standard enthlpy of formation of $H^+(aq)$ is taken to be zero.

We have seen that

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(1) \quad \Delta_r H^0 = -57.1 \text{ kJ mol}^{-1}$$

For this reaction, $\Delta H_r^0 = \Delta H_f^0(H_2O, 1) - \{\Delta H_f^0(H^+, aq) + \Delta H_f^0(OH^-, aq)\}$

Hence, at 25°C, we get $\Delta H_f^0 (H^+, aq) + \Delta H_f^0(OH^-, aq) = \Delta H_f^0(H_2O, 1) - \Delta H_r^0$

so $\Delta H_f^0(OH^-, aq) = \{-286.1 - (-57.1)\} \text{ kJ mol}^{-1}$
$$= -229.00 \text{ kJ mol}^{-1}$$

- With the enthalpies of formation of these two ions, the enthalpy of formation of any other ion can be found from the enthalpies of formation and solution of its pure compound with H^+ or OH^-. for example, the enthalpy of formation of Na^+ can be calculated from the enthalpy of formation and enthalpy of infinite dilute solution of NaOH. The two values are :

- The chemical equation for the formation of infinite dilute solution of NaOH(s) is

$$NaOH(s) + nH_2O(\ell) \longrightarrow Na^+(aq) + OH^-(aq)$$
$$\Delta_{aq} H°(NaOH, s) = -44.50 \text{ kJ mol}^{-1}$$
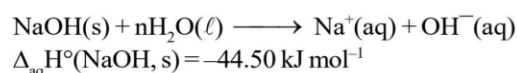
Since there are equal amounts of water on both sides of the above equation, the two enthalpies give no net effect and thus

$$\Delta_{aq} H°(NaOH, s) = \Delta_f H°(Na^+, aq) + \Delta_f H°(OH^-, aq)$$
$$- \Delta_f H°(NaOH, s)$$

or $\Delta_f H° (Na+, aq) = \Delta_{aq} H° (NaOH, s) - \Delta_f H°(OH°, aq)$
$$+ \Delta_f H°(NaOH, s)$$

$$= [-44.50 - (-229.99) + (-425.61)] \text{ kJ mol}^{-1}$$
$$= -240.12 \text{ kJ mol}^{-1}$$

- Similarly, from NaCl(aq) or HCl(aq), the enthalpy of formation of $Cl^-(aq)$ can be determined, and so on. The changes in enthalpy of any ionic reaction can

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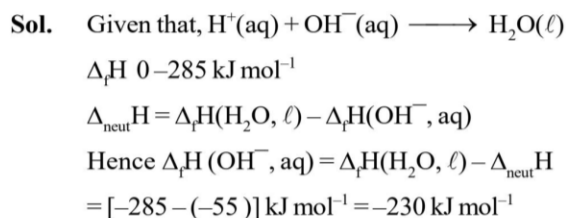then be found from these ionic enthalpies of formation and the usual enthalpies of formation of compounds.
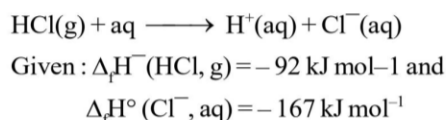
SOLVED EXAMPLE

Example-33

The enthalpy of formation of $H_2O(l)$ is -285 kJ mol^{-1} and enthalpy of neutralization of a strong acid and a strong base is -55 kJ mol^{-1}. What is the enthalpy of formation of OH^- ions ?
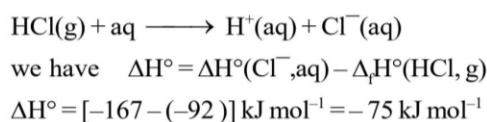
Sol. Given that, $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$

$\Delta_f H$ 0 -285 kJ mol^{-1}

$\Delta_{neut}H = \Delta_f H(H_2O, \ell) - \Delta_f H(OH^-, aq)$

Hence $\Delta_f H (OH^-, aq) = \Delta_f H(H_2O, \ell) - \Delta_{neut}H$

$= [-285 - (-55)]$ kJ mol^{-1} $= -230$ kJ mol^{-1}

Example-34

Calculate the enthalpy change when one mole of HCl(g) is dissolved in a very large amount of water at 25°C. The change in state is :

$HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$

Given : $\Delta_f H^- (HCl, g) = -92$ kJ mol–1 and

$\Delta_f H° (Cl^-, aq) = -167$ kJ mol^{-1}

Sol. For the reaction,

$HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$

we have $\Delta H° = \Delta H°(Cl^-, aq) - \Delta_f H°(HCl, g)$

$\Delta H° = [-167 - (-92)]$ kJ mol^{-1} $= -75$ kJ mol^{-1}

● **Bond Enthalpies :**

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While **bond dissociation enthalpy** is the enthalpy required to dissociate a given bond of some specific compound.for example the enthalpy of dissociation of the O–H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.

$H_2O(g) \rightarrow H(g) + OH(g)$ $\Delta H_r^0 = 501.87$ kJ mol^{-1}
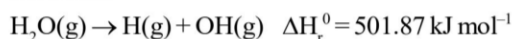
However, to break the O–H bond in the hydroxyl radical required a different quantity of heat :

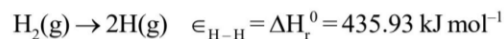$OH(g) \rightarrow O(g) + H(g)$ $\Delta H_r^0 = 423.38$ kJ mol^{-1}

The bond enthalpy, ϵ_{OH}, is defined as the average of these two values, that is :

$\epsilon_{OH} = \dfrac{501.87 kJmol^{-1} + 423.38 kJmol^{-1}}{2}$

$= 462.625$ kJ mol^{-1}

In the case of diatomic molecules, such as H_2, the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.

$H_2(g) \rightarrow 2H(g)$ $\epsilon_{H-H} = \Delta H_r^0 = 435.93$ kJ mol^{-1}

Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthaplies of the bond for a number of molecules in which the pair of atoms appears.

● **Estimation of Enthalpy of a reaction from bond Enthalpies :**

Let the enthalpy change for the gaseous reaction $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$ be required from the bond enthalpy data. This may be calculated as follows :

$\Delta H = \begin{pmatrix} Enthalpy \ required \ to \ break \ reactants \\ into \ gasesous \ atoms \end{pmatrix}$

$- \begin{pmatrix} Enthalpy \ released \ to \ form \ products \\ from \ the \ gasesous \ atoms \end{pmatrix}$

$= [4\epsilon_{C-H} + \epsilon_{C=C} + \epsilon_{H-Cl}] + [-5\epsilon_{C-H} - \epsilon_{C-C} - \epsilon_{C-Cl}]$

$= (\epsilon_{C=C} + \epsilon_{H-Cl}) - (\epsilon_{C-H} + \epsilon_{C-C} + \epsilon_{C-Cl})$

SOLVED EXAMPLE

Example-35

Using the bond enthalpy data given below, calculate the enthalpy change for the reaction

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

Data :
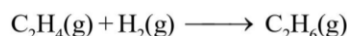
Bond	Bond enthalpy
C–C	336 kJ mol^{-1}
C=C	606 kJ mol^{-1}
C–H	410 kJ mol^{-1}
H–H	431 kJ mol^{-1}

Sol. Diagrammatically, we represent the given reaction as follows :
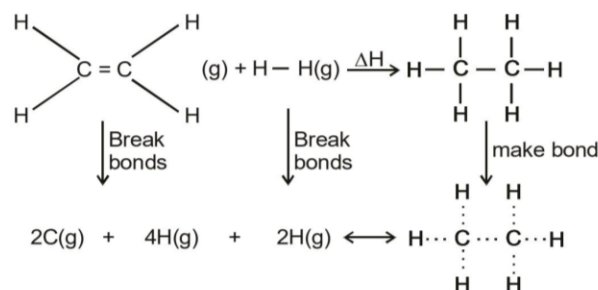
The heat required to dissociate $C_2H_4(g)$ and $H_2(g)$ into the gaseous atoms is

For breaking	1 C=C	606 kJ mol^{-1}
For breaking	4 C–H	4 x 410 kJ mol^{-1}
For breaking	1 H–H	431 kJ mol^{-1}
	Total	2677 kJ mol^{-1}

Thus, $\Delta H = -2802 \text{ kJ mol}^{-1} + 2677 \text{ kJ mol}^{-1}$
$= -125 \text{ kJ mol}^{-1}$

Example-36

Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene

$$CH_2 = C - CH = CH_2$$
$$\quad\quad\quad |$$
$$\quad\quad\quad CH_3$$
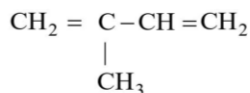
Data   Bond enthalpy of C – H bond $= 413.38 \text{ kJ mol}^{-1}$
Bond enthalpy of C – C bond $= 347.69 \text{ kJ mol}^{-1}$
Bond enthalpy of C = C bond $= 615.05 \text{ kJ mol}^{-1}$
Enthalpy of sublimation of carbon (graphite)
$$= 718.39 \text{ kJ mol}^{-1}$$
Enthalpy of dissociation of $H_2(g) = 435.97 \text{ kJ mol}^{-1}$

Sol.   For isoprene, we have to form
2C – C bonds ; 2C = C bonds and 8C – H bonds
For which energy released is
$[2(-347.69) + 2(-615.05) + 8(-413.38)] \text{ kJ mol}^{-1}$
$= 5\,232.52 \text{ kJ mol}^{-1}$
that is, ΔH (from gaseous atoms) $= -5\,232.52 \text{ kJ mol}^{-1}$
The reaction corresponding to this is
$5C(g) + 8H(g) \to C_5H_8(g) \quad \Delta_r H_1 = -5232.52 \text{ kJ mol}^{-1}$
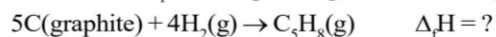But we want $\Delta_r H$ corresponding to the following equation
$5C(\text{graphite}) + 4H_2(g) \to C_5H_8(g) \quad \Delta_r H = ?$
This can be obtained by the following manipulations :
$5C(g) + 8H(g) \to C_5H_8(g) \quad \Delta_r H_2 = -5232.52 \text{ kJ mol}^{-1}$
$5C(\text{graphite}) \to 5C(g) \quad \Delta_r H_3 = 5 \times 718.39 \text{ kJ mol}^{-1}$
$4H_2(g) \to 8H(g) \quad \Delta_r H_4 = 4 \times 435.97 \text{ kJ mol}^{-1}$
Adding, we get
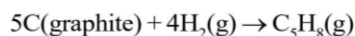
$5C(\text{graphite}) + 4H_2(g) \to C_5H_8(g)$
$\Delta_f H = 103.31 \text{ kJ mol}^{-1}$

Diagrammatically, the above calculations may be represented as follows.
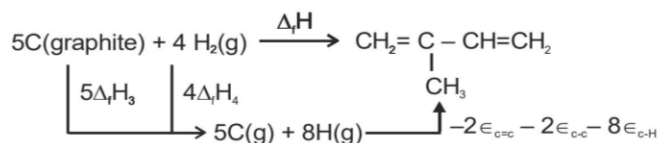
Applying Hess's law, we get
$\Delta_f H = 5\Delta H_3 + 4\Delta H_4 - 2\epsilon_{C=C} - 8\epsilon_{C-H}$
$= (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 - 8 \times 413.38) \text{ kJ mol}^{-1}$
$= 103.31 \text{ kJ mol}^{-1}$

- **LAW OF THERMO CHEMISTRY**

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

  (b) Hess's Law :- The total amount of heat evolved or absorbed in a chemical reaction is the same whether the reaction is carried out in one or several steps (by one or more methods).
  It also does not depend upon the manner in which the chemical reaction is carried out.

Ex.   Single step reaction $A \to B$; ΔH

Multi step reaction to produce B from A is given

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

According to Hess's law
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

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EXERCISE-I

Basic Definitions

Q.1 A well stoppered thermos flask contains some ice cubes. This is an example of a
(1) Closed system
(2) Open system
(3) Isolated system
(4) Non-thermodynamic system

Q.2 Which of the following is not a state function
(1) Internal energy (2) Enthalpy
(3) Work (4) Entropy

Q.3 Among them intensive property is
(1) Mass (2) Volume
(3) Surface tension (4) Enthalpy

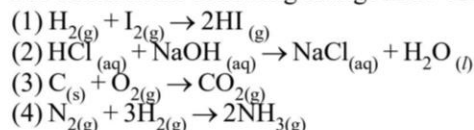### Thermodynamics Process and Graph and Work Calculation

Q.4 The process, in which no heat enters or leaves the system, is termed as
(1) Isochoric (2) Isobaric
(3) Isothermal (4) Adiabatic

Q.5 Which of the following is true for an adiabatic process
(1) $\Delta H = 0$ (2) $\Delta W = 0$
(3) $\Delta Q = 0$ (4) $\Delta V = 0$

Q.6 The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at $25^o C$ is
(1) $2.303 \times 298 \times 0.082 \log 2$
(2) $-298 \times 10^7 \times 8.31 \times 2.303 \log 2$
(3) $2.303 \times 298 \times 0.082 \log 0.5$
(4) $8.31 \times 10^7 \times 298 - 2.303 \log 0.5$
(5) $2.303 \times 298 \times 2 \log 2$

Q.7 An ideal gas expands in volume from $1 \times 10^{-3} m^3$ to $1 \times 10^{-2} m^3$ at $300\ K$ against a constant pressure of $1 \times 10^5\ Nm^{-2}$. The work done is
(1) $270\ kJ$ (2) $-900\ kJ$
(3) $-900\ J$ (4) $900\ kJ$

Work Heat capacity of Gases

Q.8 Find the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 15 to 50 litres is.
(1) -1426.87 calories.
(2) -142.587 calories.
(3) -1326.87 kilo calories.
(4) -14368.7 calories.

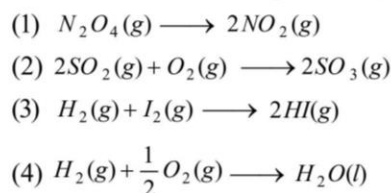**Q.9** For which of the following change $\Delta H \neq \Delta E$?
(1) $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
(2) $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
(3) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
(4) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

Heat and international energy and enthalphy

Q.10 The relation between ΔE and ΔH is
(1) $\Delta H = \Delta E - P\Delta V$ (2) $\Delta H = \Delta E + P\Delta V$
(3) $\Delta E = \Delta V + \Delta H$ (4) $\Delta E = \Delta H + P\Delta V$

Q.11 At constant T and P, which one of the following statements is correct for the reaction,

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

(1) ΔH is independent of the physical state of the reactants of that compound
(2) $\Delta H > \Delta E$
(3) $\Delta H < \Delta E$
(4) $\Delta H = \Delta E$

Q.12 Which is not the correct relation between enthalpy (ΔH) and inteanal energy (ΔE)
(1) $\Delta H = \Delta E + P\Delta V$ (2) $\Delta H = \Delta E + n\,RT$
(3) $\Delta H = \Delta E + \Delta(PV)$ (4) $\Delta E = \Delta H - P\Delta V$

Q.13 Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expression is true
(1) $\Delta H = 0$ (2) $\Delta H = \Delta U$
(3) $\Delta H < \Delta U$ (4) $\Delta H > \Delta U$

Q.14 In which of the following $\Delta E = \Delta H$
(1) $N_2O_4(g) \longrightarrow 2NO_2(g)$
(2) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
(3) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
(4) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

First law of thermo-dynamics

Q.15 Which of the following expressions represents the first law of thermodynamics
(1) $\Delta E = -q + W$ (2) $\Delta E = q - W$
(3) $\Delta E = q + W$ (4) $\Delta E = -q - W$

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Q.16 A system absorb $600 J$ of heat and work equivalent to $300 J$ on its surroundings. The change in internal energy is
(1) $300 J$ (2) $400 J$
(3) $500 J$ (4) $600 J$

Q.17 One mole of an ideal gas is allowed to expand reversibly and adiabatically from a temperature of $27°C$. If the work done during the process is $3\ kJ$, the final temperature will be equal to ($C_v = 20\ JK^{-1}$)
(1) $150\ K$ (2) $100\ K$
(3) $26.85°C$ (4) $295\ K$

Second law of thermodynamics and energy

Q.18 When disorder of a system increases, the change is said to be
(1) Exothermic   (2) Non-spontaneous
(3) Endothermic   (4) Spontaneous

Q.19 The spontaneous flow of heat is always
(1) From low to high pressure
(2) From high to high pressure
(3) Unidirectional from lower temperature to higher temperature
(4) Unidirectional from the higher to lower temperature

Q.20 An irreversible process occuring isothermally in an isolated system leads to
(1) Zero entropy
(2) An increase in the total entropy of the system
(3) A decrease in the total entropy of the system
(4) None of these

Q.21 For which reaction from the following, ΔS will be maximum
(1) $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$
(2) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(3) $C(s) + O_2(g) \rightarrow CO_2(g)$
(4) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

Q.22 The enthalpy change for the transition of liquid water to steam, $\Delta H_{vap} = 37.3\ kJ\ mol^{-1}$ at $373\ K$. The entropy change for the process is
(1) $111.9\ J\ mol^{-1}K^{-1}$ (2) $37.3\ J\ mol^{-1}\ K^{-1}$
(3) $100\ J\ mol^{-1}K^{-1}$ (4) $74.6\ J\ mol^{-1}K^{-1}$

Q.23 For which of the processes is ΔS negative
(1) $H_2(g) \rightarrow 2H(g)$
(2) $N_2(g) 1 atm \rightarrow N_2(g) 8\ atm$
(3) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$
(4) $C_{(diamond)} \rightarrow C_{(graphite)}$

Q.24 The unit of entropy is
(1) $J\ mol^{-1}$ (2) $JK\ mol^{-1}$
(3) $J\ mol^{-1}K^{-1}$ (4) $J^{-1}K^{-1}mol^{1}$

Third law of thermodynamics

Q.25 When enthalpy and entropy change for a chemical reaction are $-2.5 \times 10^3\ cal$ and $7.4\ cal\ deg^{-1}$ respectively. Predict the reaction at $298\ K$ is
(1) Spontaneous   (2) Reversible
(3) Irreversible   (4) Non-spontaneous

Q.26 The free energy change for a reversible reaction at equilibrium is
(1) Large positive   (2) Small negative
(3) Small positive   (4) 0

Q.27 For a spontaneous change, free energy change ΔG is
(1) Positive
(2) Negative
(3) Zero
(4) Can be positive or negative

Q.28 The relation between ΔG and ΔH is
(1) $\Delta H = \Delta G - T\Delta S$ (2) $\Delta G = \Delta H - T\Delta S$
(3) $T\Delta S - \Delta G = \Delta H$ (4) $\Delta H = T\Delta G + \Delta S$

Q.29 At $300\ K$, the reactions which have following values of thermodynamic parameters occur spontaneously
(1) $\Delta G° = -400\ kJ\ mol^{-1}$
(2) $\Delta H° = -200\ kJ\ mol^{-1}, \Delta S° = 4\ JK^{-1}mol^{-1}$
(3) $\Delta H° = 200\ J\ mol^{-1}, \Delta S° = 40\ JK^{-1}mol^{-1}$
(4) All of the above

Q.30 What is the free energy change ΔG when $1.0\ mole$ of water at $100°C$ and $1 atm$ pressure is converted into steam at $100°C$ and $1 atm$ pressure
(1) $540\ cal$ (2) $-9800\ cal$
(3) $9800\ cal$ (4) $0\ cal$

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Q.31 $\Delta G°$ for the reaction $X + Y \longrightarrow Z$ is $-4.606\ kcal$. The value of equilibrium constant of the reaction at $227°C$ is $(R = 2.0\ cal.mol^{-1}K^{-1})$

(1) 100   (2) 10
(3) 2   (4) 0.01

Q.32 Gibbs free energy G, enthalpy H and entropy S are interrelated as in

(1) $G = H + TS$ (2) $G = H - TS$
(3) $G - TS = H$ (4) $G = S = H$

Q.33 For a reaction $\Delta H = 9.08\ kJ\ mol^{-1}$ and

$\Delta S = 35.7\ JK^{-1}mol^{-1}$

Which of the following statements is correct for the reaction

(1) Reversible and Isothermal
(2) Reversible and Exothermic
(3) Spontaneous and Endothermic
(4) Spontaneous and Exothermic

Thermochemistry

Q.34 The enthalpy of neutralization of which of the following acids and bases is nearly $-13.6\ Kcal$

(1) HCN and NaOH   (2) HCl and KOH
(3) HCl and NaOH   (4) (2) & (3) both

Q.35 If $S + O_2 \to SO_2;(\Delta H = -298.2)$

$SO_2 + \frac{1}{2}O_2 \to SO_3;(\Delta H = -98.2)$

$SO_3 + H_2O \to H_2SO_4;(\Delta H = -130.2)$

$H_2 + \frac{1}{2}O_2 \to H_2O;(\Delta H = -287.3)$

then the enthalpy of formation of H_2SO_4 at 298K will be

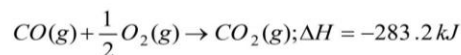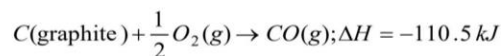(1) $-433.7\ kJ$ (2) $-650.3\ kJ$
(3) $+320.5\ kJ$ (4) $-813.9\ kJ$

Q.36 The heat evolved in the combustion of benzene is given by

$C_6H_{6(l)} + 7\frac{1}{2}O_{2(g)}$

$\to 6CO_2(g) + 3H_2O(l); \Delta H = -3264.6\ kJ$
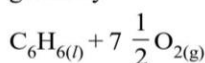
Which of the following quantities of heat energy will be evolved when $39\ g\ C_6H_6$ are burnt

(1) $816.15\ kJ$ (2) $1632.3\ kJ$
(3) $6528.2\ kJ$ (4) $2448.45\ kJ$

Q.37 Thermochemical reactions

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

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

From the above reaction, the heat of reaction for $C(graphite) + O_2(g) \to CO_2(g)$ will be

(1) $-393.7\ kJ$ (2) $+393.7\ kJ$
(3) $-172.7\ kJ$ (4) $+172.7\ kJ$

Q.38 Evaporation of water is

(1) An endothermic change
(2) An exothermic change
(3) A process where no heat change occurs
(4) A process accompanied by chemical reaction

Q.39 $\Delta H°_f$ (298 K) of methanol is given by the chemical equation

(1) $CH_4(g) + 1/2 O_2(g) \to CH_3OH(g)$
(2) $C (graphite) + 1/2 O_2(g) + 2H_2(g) \to CH_3OH(l)$
(3) $C (diamond) + 1/2 O_2(g) + 2H_2(g) \to CH_3OH(l)$
(4) $CO(g) + 2H_2(g) \to CH_3OH(l)$

Q.40 If ΔH^o_f for H_2O_2 and H_2O are $-188\ kJ/mole$ and $-286\ kJ/mole$. What will be the enthalpy change of the reaction $2H_2O_2(l) \to 2H_2O(l) + O_2(g)$

(1) $-196\ kJ/mole$ (2) $146\ kJ/mole$
(3) $-494\ kJ/mole$ (4) $-98\ kJ/mole$

Q.41 The heat of formations of $CO(g)$ and $CO_2(g)$ are $-26.4\ kcal$ and $-94.0\ kcal$ respectively. The heat of combustion of carbon monoxide will be

(1) $+26.4\ kcal$ (2) $-67.6\ kcal$
(3) $-120.6\ kcal$ (4) $+52.8\ kcal$

Q.42 Heat of neutralisation of NH_4OH and HCl is

(1) $13.7\ kcal$ (2) $>13.7\ kcal$
(3) $<13.7\ kcal$ (4) None of the above

Q.43 The difference between heats of reaction at constant pressure and at constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \to 12CO_2(g) + 6H_2O(l)$ at $25°C$ in kJ is
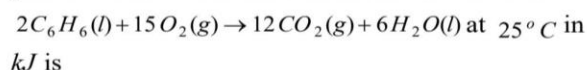
(1) -7.43 (2) $+3.72$
(3) -3.72 (4) $+7.43$

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Q.44 In an endothermic reaction, the value of ΔH is
(1) Zero (2) Positive
(3) Negative (4) Constant

Q.45 Standard molar enthalpy of formation of CO_2 is equal to
(1) Zero
(2) The standard molar enthalpy of combustion of gaseous carbon
(3) The sum of standard molar enthalpies of formation of CO and O_2
(4) The standard molar enthalpy of combustion of carbon (graphite)

Q.46 The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 $kcal$ respectively. The enthalpy of formation of HCl gas would be
(1) $-44\ kcal$ (2) $44\ kcal$
(3) $-22\ kcal$ (4) $22\ kcal$

Q.47 The $H-H$ bond energy is 430 $kJ\ mol$ and $Cl-Cl$ bond energy is 240 $kJ\ mol^{-1}$. ΔH_f for HCl is $-90\ kJ$. The $H-Cl$ bond energy is about
(1) $180\ kJ\ mol^{-1}$ (2) $360\ kJ\ mol^{-1}$
(3) $213\ kJ\ mol^{-1}$ (4) $425\ kJ\ mol^{-1}$

Q.48 If enthalpies of methane and ethane are respectively 320 and 360 calories then the bond energy of $C-C$ bond is
(1) $80\ calories$ (2) $40\ calories$
(3) $60\ calories$ (4) $120\ calories$

EXERCISE-II

Q.1 Out of boiling point (I), entropy (II), pH (III) and density (IV), Intensive properties are:
(1) I, II (2) I, II, III (3) I, III, IV (4) All of these

Q.2 Find the work done when 18 ml of water is getting vapourised at 373 K is open vessel
(Assume the ideal behaviour of water vapour.)
(1) – 30 litre atm (2) – 60 litre atm
(3) – 10 litre atm (4) – 20 litre atm

Q.3 Calculate work done for the expansion of a substance from 3m³ to 5m³ against. Constant pressure 10^5Pa.
(1) $-2 \times 10^5\ J$ (2) $2 \times 10^5\ J$
(3) $10^5\ J$ (4) None of these

Q.4 1 mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 100 litre. Which of the following is false for the process?
(1) $\Delta T = 0$ (2) $\Delta E = 0$
(3) $\Delta H = 0$ (4) heat supplied (q) = 0

Q.5 Molar heat capacity of water in equilibrium with ice at constant pressure is
(1) zero (2) ∞
(3) 40.45 kJ K⁻¹ mol⁻¹ (4) 75.48 JK⁻¹ mol⁻¹

Q.6 Difference between ΔH and ΔE for the combusion of liquid benzene at 27°C is -
(1) –7.48 kJ (2) –3.74 kJ
(3) –14.86 kJ (4) –5.73 kJ

Q.7 Heat of reaction for
$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(g)}$
at constant pressure is –651 Kcal at 17°C. Calculate the heat of reaction at constant volume at 17°C-
(1) – 554.5 Kcal (2) – 654.5 Kcal
(3) – 354.5 Kcal (4) – 154.5 Kcal

Q.8 For hypothetical reaction -
$A(g) + B(g) \rightarrow C(g) + D(g)$
Which of the following statements is correct -
(1) $\Delta H = \Delta E$ (2) $\Delta H > \Delta E$
(3) $\Delta H < \Delta E$ (4) unpredictable

Q.9 ΔH for $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$ is 176 kJ mol⁻¹ at 1240 K. The ΔU for the change is equal to :
(1) 160 kJ (2) 165.6 kJ (3) 186.3 kJ (4) 180.0 kJ

Q.10 Consider the reaction at 300 K
$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$; $\Delta H = -185$ kJ/mol
Calculate ΔU if 3 mole of H_2 completely react with 3 mole of Cl_2 to form HCl.
(1) 0 (2) – 185 kJ
(3) 555 kJ (4) None of these

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Q.11 A system does 100 J work on surroundings by absorbing 150 J of heat. Calculate the change in internal energy -
(1) 100 J   (2) 50 J   (3) 25 J   (4) 150 J

Q.12 A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre to 1.0 litre, Calculate the change in internal energy -
(1) 124 J   (2) 224 J   (3) 114 J   (4) 154 J

Q.13 One mole of an ideal gas expands from state-I (1 atm, 20 litre) to (2 atm, 10 litre) isothermally & reversibly. Calculate work done. (take ln2 = 0.7)
(1) 0 lit-atm   (2) 20 lit-atm
(3) – 7lit-atm   (4) 14 lit-atm

Q.14 Two mole of an ideal gas is expanded irreversibly & isothermally at 27°C until its volume is doubled and 3.3 kJ heat is absorbed from surrounding. Determine $\Delta S_{surrounding}$.
(1) –11 J/K   (2) 33 J/K   (3) –22 J/K   (4) None of these

Q.15 The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300°C reversibly and isochorically

(1) $\frac{3}{2} R \ln\left(\frac{300}{200}\right)$ (2) $\frac{5}{2} R \ln\left(\frac{573}{273}\right)$

(3) $3R \ln\left(\frac{573}{473}\right)$ (4) $\frac{3}{2} R \ln\left(\frac{573}{473}\right)$

Q.16 If $\Delta H_{vaporisation}$ of substance X (l) (molar mass : 30 g/mol) is 300 J/g at it's boiling point 300 K, then molar entropy change for reversible condensation process is
(1) 30 J/mol.K   (2) – 300 J/mol.K
(3) –30 J/mol.K   (4) None of these

Q.17 For the reaction at 300 K
$A(g) + B(g) \longrightarrow C(g)$
$\Delta U = -3.0$ kcal ; $\Delta S = -10.0$ cal/K
value of ΔG is
(1) –600 cal   (2) –6600 cal
(3) –6000 cal   (4) None

Q.18 The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is
(1) $-\Delta G° = RT \ln K$
(2) $\Delta G = RT \ln K$
(3) $-\Delta G = RT \ln K$
(4) $\Delta G° = RT \ln K$

Q.19 Calculate the standard enthalpy change for a reaction $CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$ given that ΔH_f^0 for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ as -393.5, -110.5 and -241.8 KJ/mol respectively.
(1) –31.2 KJ   (2) –21.2 KJ
(3) –11.2 KJ   (4) +41.2KJ

Q.20 If x_1, x_2 and x_3 are enthalpies of H – H, O = O and O – H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen

(1) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$

(2) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$

(3) $x_1 + \frac{x_2}{2} - x_3 + x_4$

(4) $2x_3 - x_1 - \frac{x_2}{2} - x_4$

Q.21 The enthalpy of neutralisation of HCl and NaOH is –57 kJ mol^{-1}. The heat evolved at constant pressure (in kJ) when 0.5 mole of H_2SO_4 react with 0.75 mole of NaOH is equal to

(1) $57 \times \frac{3}{4}$ (2) 57×0.5 (3) 57   (4) 57×0.25

Q.22 In the combustion of 4g of CH_4, 2.5 Kcal of heat is liberated. The heat of combustion of CH_4 is -
(1) 20 Kcal.   (2) 10 Kcal.   (3) 2.5 Kcal.   (4) 5 Kcal.

Q.23 Ammonium nitrate can decompose with explosion by the following reaction.
$NH_4NO_3 (s) \rightarrow N_2O (g) + 2H_2O$;
$\Delta H = -37.0$ KJ/mol
Calculate the heat produced when 2.50g of NH_4NO_3 decomposes -
(1) 1.06 kJ   (2) 0.96 kJ   (3) 1.16 kJ   (4) 1.26 kJ

Q.24 The reaction $CH_{4(g)} + Cl_{2(g)} \rightarrow CH_3Cl_{(g)} + HCl_{(g)}$ has $\Delta H = -25$ kcal.

Bond	Bond Energy kcal
C–Cl	84
H–Cl	103
C–H	x
Cl–Cl	y
x : y = 9 : 5	

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From the given data, what is the bond energy of $Cl-Cl$ bond
(1) 70 kcal   (2) 80 kcal
(3) 67.75 kcal   (4) 57.75 kcal

Q.25 Enthalpy of formation of compound is -
(1) always positive
(2) always negative
(3) can be either negative or zero
(4) can be positive or negative

Q.26 $HA + OH^- \rightarrow H_2O + A^- + q_1\ kJ$
$H^+ + OH^- \rightarrow H_2O + q_2\ kJ$
The enthalpy of dissociation of HA is
(1) $(q_1 + q_2)$ (2) $(q_1 - q_2)$ (3) $(q_2 - q_1)$ (4) $-(q_1 + q_2)$

Q.27 The value of $\Delta H_{sol.}$ of $BaCl_2(s)$ and $BaCl_2 \cdot 2H_2O(s)$ are $-a$ kJ and b kJ respectively. The value of $\Delta H_{Hydration}$ of $BaCl_2(s)$ is-
(1) $b - a$ (2) $a + b$ (3) $-a - b$ (4) $a - b$

Q.28 The net heat change in a chemical reaction is same whether it is brought about in two or more different ways in one or several steps. It is known as -
(1) Hess's law
(2) Law of conservation of energy
(3) Henry's law
(4) Joule's principle

Q.29 According to Hess's Law the thermal effect of a reaction depends on -
(1) initial concentration of reactants
(2) final condition of the reacting substance
(3) intermediate states of a reaction
(4) initial and final conditions of the reacting substances

Q.30 How many kcal of heat is evolved by the complete neutralisation of one mole sulphuric acid with NaOH -
(1) 13.7 kcal   (2) 27.4 kcal
(3) 6.85 kcal   (4) None of the above

Q.31 Heats of combustion of $CH_4, C_2H_6, C_3H_8, C_8H_{18}$ in K. cals mole^{-1} as $-210.8, -368.4, -526.3, -1302.7$ respectively. Decide which is a better rocket fuel -
(1) C_8H_{18} (2) CH_4 (3) C_3H_8 (4) C_2H_6

Q.32 The enthalpy of neutralization of NH_4OH and CH_3COOH is -10.5 kcal/mole and enthalpy of neutralization of strong base and CH_3COOH is -12.5 kcal/mole. Calculate the enthalpy of dissociation of NH_4OH -
(1) 3.0   (2) 4.0   (3) 2.0   (4) 10.0

Q.33 The heat of combustion of ethylene $C_2H_4(g)$ is -1420 kJ/mole. The volume of C_2H_4 at NTP that would evolve 355 kJ on combustion is -
(1) 2.8 lit   (2) 8.4 lit   (3) 5.6 lit   (4) 11.2 lit

Q.34 The lattice enthalpy and hydration enthalpy of four compounds are given below -

Compound	Lattice enthalpy (kJ/mol)	Hydration enthalpy (kJ/mol)
P	+780	−920
Q	+1012	−812
R	+828	−878
S	+632	−600

The pair of compounds which is soluble in water is -
(1) P and Q   (2) Q and R   (3) R and S   (4) P and R

Q.35 Heat evolved in the reaction $H_2 + Cl_2 \rightarrow 2HCl$ is 182 KJ. Bond energies H - H = 430 kJ/mole, Cl - Cl = 242 kJ/mole. The H - Cl bond energy is-
(1) 763 kJ mole^{-1} (2) 427 kJ mole^{-1}
(3) 336 kJ mole^{-1} (4) 154 kJ mole^{-1}

Q.36 Heat of neutralisation of HF is -
(1) -57.32 kJ   (2) > -57.32 kJ
(3) < -57.32 (4) None

Q.37 The heat of neutralisation is constant when dilute solution of -
(1) strong acid and strong base react
(2) strong acid and weak base react
(3) strong base and weak acid react
(4) in all the cases

Q.38 How much heat is liberated when 100 mL of 0.1 M NaOH are completely neutralised by 100 mL of 0.1 M HCl -
(1) -57 kJ   (2) -0.57 kJ
(3) -5.7 kJ   (4) -0.05 kJ

Q.39 The enthalpy of the reaction
$H_2O_2(\ell) \rightarrow H_2O(\ell) + 1/2\ O_2(g)$ is
-23.5 kcal mol^{-1} and the enthalpy of formation of H_2O (ℓ) is -68.3 kcal mol^{-1}. The enthalpy of formation of $H_2O_2(\ell)$ is
(1) -44.8 kcal mol^{-1}
(2) 44.8 kcal mol^{-1}
(3) -91.8 kcal mol^{-1}
(4) 91.8 kcal mol^{-1}

Q.40 Enthalpy change of the reaction
$2H(g) \rightarrow H_2(g)$ is - 104 kcal
The H - H bond dissociation energy is-
(1) 104 kcal   (2) -104 kcal
(3) -52 kcal   (4) $+52$ kcal

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EXERCISE-III

JEE-ADVANCED
MCQ/COMPREHENSION/MATCHING

Q.1 Which of the following statements is (are) correct
(A) The heat of neutralization of a strong acid with a strong base is always the same
(B) The enthalpy of combustion is always negative
(C) A spontaneous change involves a lowering of free energy
(D) The enthalpy of an element in the standard state is assumed to be unity at 298 K

Q.2 Which of the following statements is (are) true ?
(A) The evaporation of water is an endothermic change
(B) The conversion of white phosphorus to red phosphorus is an exothermic reaction
(C) The heat of neutralisation of a strong acid with a strong base is always the same
(D) ΔH is negative for endothermic reactions

Q.3 The standard heat of formation of U_3O_8 is -853.5 kcal mol^{-1} and standard heat of the reaction, $3UO_2 + O_2 \rightarrow U_3O_8$ is -76.01 kcal. The standard heat of formation of UO_2 is (are) :
(A) -1083 kJ mol^{-1}
(B) -1102 kJ mol^{-1}
(C) -259 kcal mol^{-1}
(D) -302 kcal mol^{-1}

Q.4 The enthalpy of formation of UF(g) is 22 kcal mol^{-1} and that of U(g) is 128 kcal mol^{-1}. The bond energy of the $F - F$ bond is 37 kcal mol^{-1}. The bond dissociation energy of UF(g) is (are) :
(A) 124.5 kcal mol^{-1}
(B) 131.1 kcal mol^{-1}
(C) 521 kJ mol^{-1}
(D) 623 kJ mol^{-1}

Q.5 For which of the following substances is the heat of formation in the standard state zero ?
(A) Aluminium
(B) $C_{diamond}$
(C) Zinc
(D) $C_{graphite}$

Q.6 The heat of combustion of ethanol was determined in a bomb calorimeter and was found to be -670.48 kcal mol^{-1} at 25°C. What will be ΔU for the same reaction at 298 K ?
(A) -2802.6 kJ
(B) -669.28 cal
(C) -670.48 kcal
(D) -280.26×10^4 J

Q.7 Which of the following pairs are correctly matched ?
(A) Arrhenius equation : Variation of enthalpy of a reaction with temperature
(B) Kirchoff equation : Variation of rate constant with temperature
(C) Second law of : Entropy of an isolated system tends to increase and reach a maximum value thermodynamics
(D) Hess's law of constant : Enthalpy change in a reaction is always constant and independent of the heat summation manner in which the reaction occurs

Comprehension # 01 (Q. No. 8 to 12)
Heat of reaction is the change in enthalpy or internal energy as represented by a balanced thermochemical equation. The amount of energy released during a chemical change depends upon the state of reactants and products, the conditions of pressure and volume at which reaction is carried out, and temperature. The variation of heat of reaction (ΔH or ΔE) with temperature is given as $\Delta H_2 - \Delta H_1 = \Delta C_p[T_2 - T_1]$ or $\Delta E_2 - \Delta E_1 = \Delta C_v(T_2 - T_1)$. Standard heat enthalpy of elements in their most stable state is assumed to be zero whereas standard heat enthalpy of compound is referred as heat of formation of that compound at 1 atm pressure and 25°C. Oxidation of N_2 to N_2O, NO, NO_2 shows absorption of energy whereas heat of combustion of N_2 is exothermic like other heat of combustion.

Q.8 Standard heat enthalpy has been assumed to be zero for :
(A) Graphite
(B) Diamond
(C) Charcoal
(D) Lamp black

Q.9 Which statements regarding the formation of NO and NO_2 respectively from N_2 and O_2 are correct :
(1) Heat of formation of NO is exothermic
(2) Heat of formation of NO_2 is exothermic
(3) The oxidation of N_2 to NO and NO_2 is favoured at high temperature.
(4) If heat of formation of NO and NO_2 are 21.55 and 8.50 kcal, heat of reaction for $NO + \frac{1}{2}O_2 \rightarrow NO_2$ is -13.05 kcal
(A) 1,2
(B) 3,4
(C) 1, 2, 4
(D) 1, 2, 3

Q.10 Heat of combustion of carbon in diamond and amorphous form are -94.3 and -97.6 kcal/mole. The heat required to convert 6 g carbon from diamond to amorphous form is :
(A) -1.65 kcal
(B) $+1.65$ kcal
(C) -3.3 kcal
(D) $+3.3$ kcal

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Q.11 Heat of vaporisation of H_2O is 627.78 cal/g. If heat of formation of $H_2O_{(l)}$ is –68.3 kcal, heat of formation of $H_2O_{(g)}$ is :
(A) –57.0 kcal
(B) 559.5 kcal
(C) 676.73 kcal
(D) Can not be calculated

Q.12 The specific heat of I_2 in vapour and solid state are 0.031 and 0.055 cal/g-°C respectively. If heat of sublimation of iodine is 6.096 kcal mol^{-1} at 200°C, the heat of sublimation of I_2 at 250°C is :
(A) 5.8 kcal mol^{-1}
(B) 2.28 kcal mol^{-1}
(C) 4.8 kcal mol^{-1}
(D) 3.8 kcal mol^{-1}

Comprehension # 2 (Q. No. 13 to 15)
Heat of neutralisation is amount of heat evolved or absorbed when 1 g-equivalent of an acid reacts with 1 g-equivalent of a base in dilute solution. If weak acid or weak base are neutralised, the heat released during neutralisation is some what lesser than –13.7 kcal or –57.27 kJ. Heat of neutralisation is also referred as heat of formation of water from H^+ and OH^- ions i.e.,
$H^+ + OH^- \rightarrow H_2O$; $\Delta H = -13.7$ kcal.

Q.16 Match the column
Column I
(A) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$
(B) $2KI_{(g)} + HgI_2(aq) \rightarrow K_2[HgI_4]_{(aq.)}$
(C) $PCl_3(g) + Cl_2(g) \rightarrow PCl_{5(g)}$
(D) $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$

Q.17 Match the column
Column I

(A) Kirchoff's equation

(B) ΔH

(C) $\dfrac{q_{rev}}{T}$

NUMERICAL VALUE BASED
Q.18 3 moles of ideal gas X ($C_{p,m} = 5/2R$) and 2 moles of ideal gas Y ($C_{p,m} = \dfrac{7}{2}R$) are taken in a vessel and compressed reversibly and adiabatically, during this process temperature of gaseous mixture increased from 300 K to 400 K. Calculate change in internal energy (ΔU) **in cal** of gaseous mixture. (**Given** R = 2 cal/mol.K)

Q.19 If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔU and ΔH of the process.

Q.13 Heat of neutralisation of HF and acetic acid respectively are (in kcal) :
(A) > –13.7, < –13.7
(B) > –13.7
(C) < –13.7
(D) < –13.7, > –13.7

Q.14 Which of the following statements are correct :
(1) $\Delta H = \Delta U + \Delta nRT$
(2) Heat changes measured by bomb calorimeter give change in heat enthalpy during the reaction.
(3) $\Delta H = \Delta U$ for the reaction :
$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
(4) Heat of formation for C_6H_6 can be directly measured
(A) 2, 3
(B) 1, 4
(C) 1, 2, 3
(D) 1, 3

Q.15 200 mL of 0.1 M NaOH is mixed with 100 mL of 0.1 M H_2SO_4 in 1 experiment. In II experiment 100 mL of 0.1 M NaOH is mixed with 50 mL of 0.1 M H_2SO_4. Select the correct statements :
(1) Heat liberated in each of the two reactions is 274 cal.
(2) Heat liberated in I is 274 cal and in II is 137 cal
(3) Temperature rise in I reaction is more than the temperature rise in II.
(4) Temperature rise in I reaction is equal to the temperature rise in II.
(A) 1, 3
(B) 2, 4
(C) 2, 3
(D) 1, 4

Column II
(P) $\Delta S > 0$
(Q) $\Delta S < 0$
(R) $\Delta H > 0$
(S) $\Delta H < 0$

Column II
(P) $\dfrac{d}{dt}(\Delta H) = \Delta C_p$
(Q) $\Delta U + \Delta n\,RT$
(R) ΔS
(S) $\dfrac{\Delta H_2 - \Delta H_1}{\Delta T} = \Delta C_p$

Q.20 At temperatures above 85 K, decarboxylation of acetic acid becomes a spontaneous process under standard state conditions. What is the standard entropy change (**in J/K-mol**) of the reaction.
$CH_3COOH\,(aq) \longrightarrow CH_4(g) + CO_2(g)$
[**Given :** ΔH_f^0 [$CH_3COOH\,(aq)$] = – 484 kJ/mole
ΔH_f^0 [$CO_2(g)$] = –392 kJ/mole
ΔH_f^0 [$CH_4(g)$] = –75 kJ/mole]

Q.21 When 2 moles of $C_2H_6(g)$ are completely burnt 3120 kJ of heat is liberated. Calculate the enthalpy of formation, of $C_2H_6(g)$. Given $\Delta_f H$ for $CO_2(g)$ & $H_2O(l)$ are – 395 & – 286 kJ respectively.
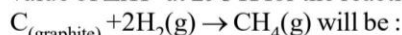
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Q.1 The heats of combustion of carbon and carbon monoxide are –393.5 and –283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is : **[JEE Main-2016]**
(1) 676.5   (2) – 676.5   (3) –110.5   (4) 110.5

Q.2 ΔU is equal to : **[JEE Main-2017]**
(1) Isochoric work   (2) Isobaric work
(3) Adiabatic work   (4) Isothermal work

Q.3 Given **[JEE Main-2017]**
$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$; $\Delta rH^\circ = -393.5$ kJ mol^{-1}

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta rH^\circ = -285.8$ kJ mol^{-1}
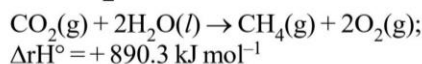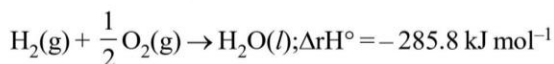
$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$;
$\Delta rH^\circ = +890.3$ kJ mol^{-1}
Based on the above thermochemical equations, the value of ΔrH° at 298 K for the reaction.
$C_{(\text{graphite})} + 2H_2(g) \rightarrow CH_4(g)$ will be :
(1) + 74.8 kJ mol^{-1} (2) + 144.0 kJ mol^{-1}
(3) – 74.8 kJ mol^{-1} (4) – 144.0 kJ mol^{-1}

Q.4 The combustion of benzene (l) gives CO_2 (g) and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25° C ; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be - (R = 8.314 JK^{-1} mol^{-1}] **[JEE Main-2018]**
(1) –452.46   (2) 3260
(3) –3267.6   (4) 4152.6

Q.5 For a disatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?
[JEE Main - 2019 (January)]
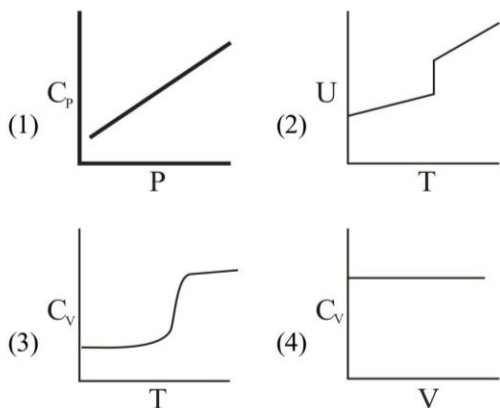
Q.6 The reaction
$MgO(s) + C(s) \rightarrow Mg(s) + CO$ (g), for which $\Delta_r H^0 = +491.1$ kJ mol^{-1} and $\Delta_r S^0 = 198.0$ JK^{-1} is not feasible at 298 K. Temperature above which reaction will befeasible is: **[JEE Main - 2019 (January)]**
(1) 2040.5K   (2) 1890.0K
(3) 2480.K   (4) 2380.K

Q.7 An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 NM^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol^{-1} K^{-1}, the temperature of Al is increased by : **[JEE Main - 2019 (January)]**
(1) $\dfrac{3}{2}$ K   (2) 2 K   (3) $\dfrac{2}{3}$ K   (4) 1 K

Q.8 Two blocks of the same metal having same mass and at temperature T_1 and T_2 respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is : **[JEE Main - 2019 (January)]**

(1) $C_p \ln\left[\dfrac{(T_1 + T_2)^2}{4T_1 T_2}\right]$ (2) $2C_p \ln\left[\dfrac{(T_1 + T_2)^{1/2}}{T_1 T_2}\right]$

(3) $2C_p \ln\left[\dfrac{(T_1 + T_2)}{4T_1 T_2}\right]$ (4) $2C_p \ln\left[\dfrac{(T_1 + T_2)}{2T_1 T_2}\right]$

Q.9 The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by
$\Delta_r G^0 = A - BT$
Where A and B are non – zero constant. Which of the following is TRUE about t his reaction?
[JEE Main - 2019 (January)]
(1) Endothermic if A > 0
(2) Exothermic if A > 0 and B < 0
(3) Endothermic if A < 0 and B > 0
(4) Exothermic if B < 0

Q.10 The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is: (Specific heat of water liquid and water vapours are 4.2 kJ K^{-1} kg^{-1} and 2.0 kJ K^{-1} kg^{-1}, heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJ kg^{-1}, respectively)(log 273 = 2.436, log 373 = 2.572, log 383 = 2.583) **[JEE Main - 2019 (January)]**
(1) 7.90 kJ K^{-1} kg^{-1} (2) 2.64 kJ K^{-1} kg^{-1}
(3) 8.49 kJ K^{-1} kg^{-1} (4) 9.26 kJ K^{-1} kg^{-1}

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Q.11 Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperature
[JEE Main - 2019 (January)]
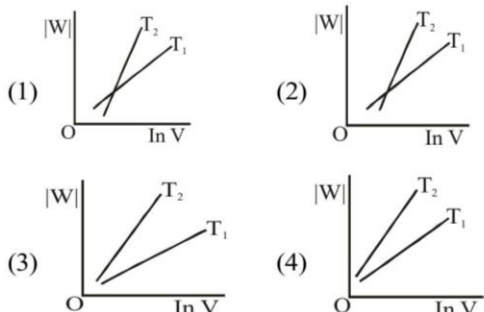
Q.12 A process that has $\Delta H = 200$ J mol^{-1} and $\Delta S = 40$ JK^{-1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous: **[JEE Main - 2019 (January)]**
(1) 20 K   (2) 12 K   (3) 5 K   (4) 4 K

Q.13 The process with negative entropy change is :
[JEE Main - 2019 (January)]
(1) Dissociation of $CaSO_4$ (s) to Ca O (s) and SO_3 (g)
(2) Sublimation of dry ice
(3) Dissolution of iodine in water
(4) Synthesis of ammonia from N_2 and H_2
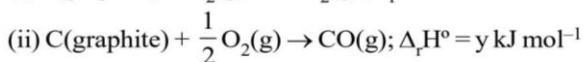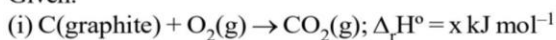
Q.14 The combination of plots which do not represent isothermal expansion of an ideal gas is :
[JEE Main - 2019 (January)]
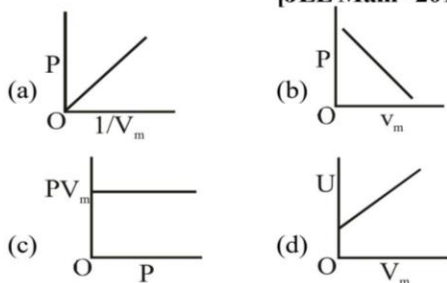
(1) (b) and (d)   (2) (a) and (c)
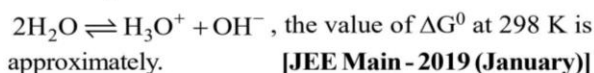(3) (b) and (c)   (4) (a) and (d)
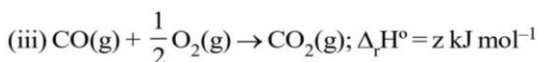
Q.15 Given:
(i) C(graphite) + O_2(g) → CO_2(g); $\Delta_r H^\circ = x$ kJ mol^{-1}
(ii) C(graphite) + $\frac{1}{2}O_2$(g) → CO(g); $\Delta_r H^\circ = y$ kJ mol^{-1}
(iii) CO(g) + $\frac{1}{2}O_2$(g) → CO_2(g); $\Delta_r H^\circ = z$ kJ mol^{-1}
Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct ? **[JEE Main - 2019 (January)]**
(1) x = y + z (2) z = x + y (3) y = 2z – x (4) x = y – z

Q.16 For the equilibrium
$2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of ΔG^0 at 298 K is approximately. **[JEE Main - 2019 (January)]**
(1) 100 kJ mol^{-1} (2) – 80 kJ mol^{-1}
(3) 80 kJ mol^{-1} (4) –100 kJ mol^{-1}

Q.17 Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas? (Assume non–expansion work is zero)
[JEE Main 2019 (April)]
(1) Cyclic process : q = – w
(2) Isothermal process : q = – w
(3) Adiabatic process : ΔU= – w
(4) Isochoric process : ΔU= – q

Q.18 For silver, C_p(JK^{-1}mol^{-1}) = 23 + 0.01 T. If the temperature (T) of 3 moles of silver is raised from 300k to 1000 K at 1 atm pressure, the value of Δ H will be colse to **[JEE Main 2019 (April)]**
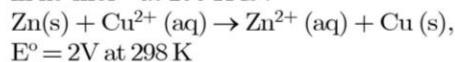(1) 21 KJ   (2) 16 KJ   (3) 13 KJ   (4) 62 KJ

Q.19 Among the following, the set of parameters that represents path function, is :
[JEE Main 2019 (April)]
(A) q + w   (B) q
(C) w   (D) H-TS
(1) (A) and (D)   (2) (B), (C) and (D)
(3) (B) and (C)   (4) (A), (B) and (C)

Q.20 The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is :
Zn(s) + Cu^{2+} (aq) → Zn^{2+} (aq) + Cu (s),
E° = 2V at 298 K
(Faraday's constant, F = 96000 C mol^{-1})
[JEE Main 2019 (April)]
(1) – 384   (2) – 192   (3) 192   (4) 384

Q.21 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If C_V = 28 JK^{-1} mol^{-1}, calculate ΔU and ΔpV for this process. (R= 8.0 KJ^{-1} mol^{-1}] **[JEE Main 2019]**
(1) ΔU = 14 kJ; Δ(pV) = 4 kJ
(2) ΔU = 14 kJ; Δ(pV) = 18 kJ
(3) ΔU = 2.8 kJ; Δ(pV) = 0.8 kJ
(4) ΔU = 14 kJ; Δ(pV) = 0.8 kJ

Q.22 The pair that has similar atomic radii is :
[JEE Main 2019 (April)]
(1) Sc and Ni   (2) Ti and HF
(3) Mo and W   (4) Mn and Re

Q.23 During compression of a spring the work done is 10kJ and 2kj escaped to the surroundings as heat. The change in internal energy, ΔU (inkJ) is:
[JEE Main 2019 (April)]
(1) 8   (2) 12   (3) –12   (4) –8

Q.24 An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is : **[JEE Main 2019 (April)]**
(1) –9.0   (2) +10.0   (3) –0.9   (4) –2.0

Q.25 Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200º C. If specific heat of $I_2(s)$ and $I_2(vap)$ are 0.055 and 0.031 cal g^{-1} K^{-1} respectively, then enthalpy of sublimation of iodine at 250ºC in cal g^{-1} is:**[JEE Main 2019 (April)]**
(1) 2.85 (2) 11.4 (3) 5.7 (4) 22.8

Q.26 A process will be spontaneous at all temperatures if :- **[JEE Main 2019 (April)]**
(1) $\Delta H > 0$ and $\Delta S < 0$ (2) $\Delta H < 0$ and $\Delta S > 0$
(3) $\Delta H > 0$ and $\Delta S > 0$ (4) $\Delta H < 0$ and $\Delta S < 0$

Q.27 The difference between ΔH and ΔU $(\Delta H - \Delta U)$, when the combustion of one mole of heptane (1) is carried out at a temperature T, is equal to:
[JEE Main 2019 (April)]
(1) 3RT (2) –3RT (3) – 4RT (4) 4RT

Q.28 For the reaction : **[JEE Main-2020 (January)]**
$A(l) \rightarrow 2B(g)$
$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K.
Hence ΔG in K. cal is _____

Q.29 The standard heat of formation $\left(\Delta_f H^{\circ}_{298}\right)$ of ethane (in kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are -1560, $- 393.5$ and -286kJ/mol, respectively is_____. **[JEE Main-2020 (January)]**

Q.30 The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is_____. **[JEE Main-2020 (January)]**

Q.31 At constant volume, 4 mol an ideal gas when heated from 300 K to 500 K changes its internal energy by 5000 J. The molar heat capacity at constant volume is_____.
[JEE Main-2020 (January)]

Q.32 If enthalpy of atomisation for $Br_{2(l)}$ is x kJ/mol and bond enthalpy for Br_2 is y kJ/mol the relation between them :
[JEE Main-2020 (January)]
(1) is x = y (2) is x < y
(3) does not exist (4) is x > y

Q.33 The true statement amongst the following is:
[JEE Main-2020 (January)]
(1) Both S and ΔS are not functions of temperature.
(2) S is not a function of temperature but ΔS is a function of temperature.
(3) Both ΔS and S are functions of temperature
(4) S is a function of temperature but ΔS is not a function of temperature

Q.34 The heat of combustion of ethanol into carbon dioxide and water is – 327 kcal at constant pressure. The heat evolved (in cal) at constant volume and 27°C (if all gases behave ideally) is (R = 2 cal mol^{-1} K^{-1})
[JEE Main-2020 (September)]

Q.35 The internal energy change (in J) when 90 g of water undergoes complete evaporation at 100°C is _____.
[To the nearest integer]
(Given : ΔH_{vap} for water at 373 K = 41 KJ/mol, R = 8.314 JK^{-1} mol^{-1})
[JEE Main-2020 (September)]

Q.36 Five moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to double the volume. The work done is
[JEE Main-2020 (September)]
(1) Zero (2) – RT ln V_2/V_1
(3) $C_V(T_2 - T_1)$ (4) – RT $(T_2 - T_1)$

Q.37 For one mole of an ideal gas, which of these statements must be true?
(a) U and H each depends only on temperature
(b) Compressibility factor z is not equal to 1
(c) $C_{P,m} - C_{V,m} = R$
(d) $dU = C_V dT$ for any process
[JEE Main-2020 (September)]
(1) (a) and (c) (2) (a), (c) and (d)
(3) (b), (c) and (d) (4) (c) and (d)

Q.38 For a dimerization reaction,
[JEE Main-2020 (September)]
$2A(g) \rightarrow A_2(g)$,
at 298 K, $\Delta U^{\circ} = -20$ kJ mol^{-1}, $\Delta S^{\circ} = -30$ JK^{-1} mol^{-1}, then the ΔG° will be _____ J.

Q.39 Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol^{-1} and 4 kJ mol^{-1}, respectively. The hydration enthalpy of NaCl is **[JEE Main-2020 (September)]**
(1) 784 kJ mol^{-1} (2) –780 kJ mol^{-1}
(3) 780 kJ mol^{-1} (4) –784 kJ mol^{-1}

Q.40 The variation of equilibrium constant with temperature is given below : **[JEE Main-2020 (September)]**
Temperature   Equilibrium Constant
$T_1 = 25$ºC $K_1 = 10$
$T_2 = 100$ºC $K_2 = 100$
The values of ΔH°, ΔG° at T_1 and ΔG° at T_2 (in kJ mol^{-1}) respectively, are close to [Use R = 8.314 J K^{-1} mol^{-1}]
(1) 28.4, –5.71 and –14.29
(2) 0.64, –7.14 and –5.71
(3) 28.4, –7.14 and –5.71
(4) 0.64, –5.71 and –14.29

Q.41 In an estimation of bromine by Carius method, 1.6 g of an organic compound gave 1.88 g of AgBr. The mass percentage of bromine in the compound is _____.(Atomic mass, Ag = 108, Br = 80 g mol^{-1})
[JEE Main-2020 (September)]

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Q.1 Among the following, the intensive property is (properties are) : **[JEE-2010]**

(A) molar conductivity   (B) electromotive force (C) resistance   (D) heat capacity

Q.2 One mole of an ideal gas is taken from **a** and **b** along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d, then the integer closest to the ratio w_d / w_s is : **[JEE-2010]**
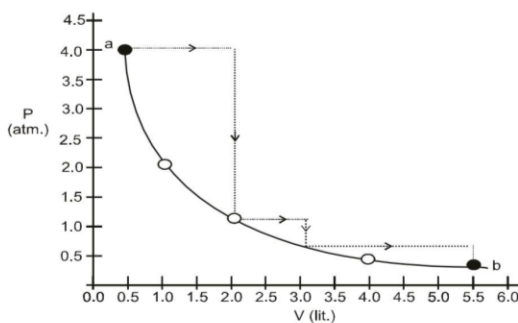
Q.3 The bond energy (in **kcal mol^{-1}**) of a C–C single bond is approximately : **[JEE-2010]**

(A) 1   (B) 10   (C) 100   (D) 1000

Q.4 Match the transformation in **column I** with appropriate options in **column II**. **[JEE-2011]**

| Column I	Column II
(A) $CO_2(s) \longrightarrow CO_2(g)$	(p) phase transition
(B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	(q) allotropic change
(C) $2H \bullet \longrightarrow H_2(g)$	(r) ΔH is positive
(D) $P_{(white, solid)} \longrightarrow P_{(red, solid)}$	(s) ΔS is positive
	(t) ΔS is negative

Q.5 For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [take ΔS as change in entropy and w as work done]. **[JEE-2012]**
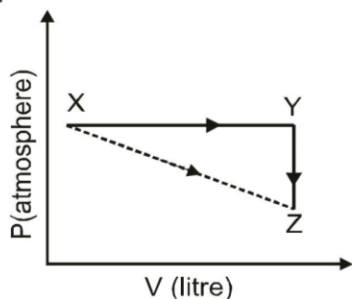
(A) $\Delta S_{x \to z} = \Delta S_{x \to y} + \Delta S_{y \to z}$
(B) $w_{x \to z} = w_{x \to y} + w_{y \to z}$
(C) $w_{x \to y \to z} = w_{x \to y}$
(D) $\Delta S_{x \to y \to z} = \Delta S_{x \to y}$

Q.6 Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C≡C bond C_2H_2. That energy is (take the bond energy of a C–H bond as 350 kJ mol^{-1}) **[JEE-2012]**

$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$
$\Delta H = 225$ kJ mol^{-1} $2C(s) \longrightarrow 2C(g)$
$\Delta H = 1410$ kJ mol^{-1} $H_2(g) \longrightarrow 2H(g)$
$\Delta H = 330$ kJ mol^{-1}

(A) 1165   (B) 837   (C) 865   (D) 815

Q.7 The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? **[JEE-2012]**
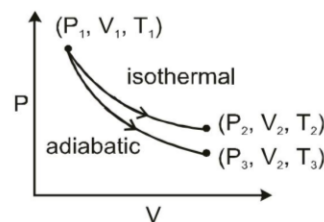
(A) $T_1 = T_2$ (B) $T_3 > T_1$
(C) $w_{isothermal} > w_{adiabatic}$ (D) $\Delta U_{isothermal} > \Delta U_{adiabati}$]

Q.8 The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is

[JEE Advance-2013]

(A) +2900 kJ
(B) –2900 kJ
(C) –16.11 kJ
(D) +16.11 kJ

Comprehension # 1 (Q. No. 9 to 10)

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (**Expt. 1**). Because the enthalpy of neutralization of a strong acid with a strong base is a constant ($-57.0 \text{ kJ mol}^{-1}$), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt. 2**), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1**) where a temperature rise of 5.6 °C was measured.

(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

Q.9 For the process, $H_2O(\ell) \rightarrow H_2O(g)$ at T = 100 °C and 1 atmosphere pressure, the correct choice is : **[JEE Advanced-2014]**

(A) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$
(B) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$
(C) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$
(D) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

Q.10 An ideal gas in a thermally insulated vessel at internal pressure = P_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2, V_2 and T_2, respectively. For this expansion, **[JEE Advanced-2014]**

(A) q = 0
(B) $T_2 = T_1$
(C) $P_2 V_2 = P_1 V_1$
(D) $P_2 V_2^\gamma = P_1 V_1^\gamma$

Q.11 Match the thermodynamic processes given under Column I with the expressions given under Column II.

[JEE Advanced-2015]

Column I

(A) Freezing of water at 273 K and 1 atm
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container
(D) Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm

Column II

(P) q = 0
(Q) w = 0
(R) $\Delta S_{sys} < 0$
(S) $\Delta U = 0$
(T) $\Delta G = 0$

Comprehension # 2 (Q. No. 12 to 13)

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (**Expt. 1**). Because the enthalpy of neutralization of a strong acid with a strong base is a constant ($-57.0 \text{ kJ mol}^{-1}$), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt. 2**), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1**) where a temperature rise of 5.6 °C was measured.

(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})
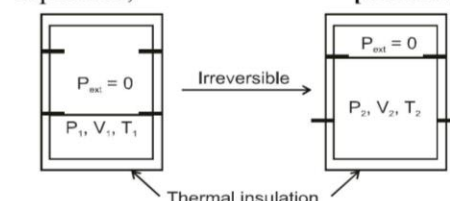
Q.12 Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt. 2** is : **[JEE Advance-2015]**

(A) 1.0
(B) 10.0
(C) 24.5
(D) 51.4

Q.13 The pH of the solution after **Expt. 2** is

[JEE Advance-2015]

(A) 2.8
(B) 4.7
(C) 5.0
(D) 7.0

Q.14 One mole of an ideal gas at 300K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ("S_{surr}) in JK^{-1} is **[JEE Advanced-2016]**

(A) 5.763
(B) 1.013
(C) –1.013
(D) –5.763

Q.15 The standard state Gibbs free energies of formation of C (graphite) and C (diamond) at T = 298 K are

$\Delta_f G^\circ [C(graphite)] = 0 \text{ kJ mol}^{-1}$
$\Delta_f G^\circ [C(diamond)] = 2.9 \text{ kJ mol}^{-1}$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by

2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C (diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[JEE Advanced-2017]

[Useful information : 1 J = 1 kg m^2 s^{-2} , 1 Pa = 1 kg m^{-1} s^{-2} ; 1 bar = 10^5 Pa]

(A) 58001 bar   (B) 1450 bar
(C) 14501 bar   (D) 29001 bar

Q.16 For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by   **[JEE Advanced-2017]**

(A) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

(B) With increase in temperature, the value of K for endothermic reaction increases because favourable change in entropy of the surroundings decreases

(C) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative

(D) With increase in temperature, the value of K for endothermic reaction decreases because the entropy change of the system is positive

Q.17 An ideal gas is expanded from (p_1, V_1 , T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are)   **[JEE Advanced-2017]**

(A) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions

(B) The change in internal energy of the gas is (i) zero , if it is expanded reversibly with $T_1 = T_2$ and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$

(C) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

(D) The work done on the gas is maximum when it is compressed irreversibly from (p_2,V_2) to (p_1, V_1) against constant pressure p_1

Q.18 A reversible cyclic process for an ideal gas is shown below. Here, P , V and T are pressure , volume and temperature , respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.
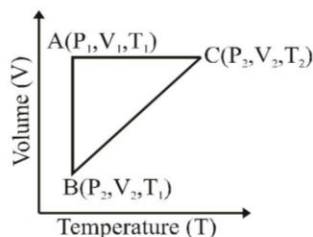
The correct option(s) is (are)

[JEE Advanced-2018]

(A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2 (V_2 - V_1)$
(B) $w_{BC} = P_2 (V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$
(C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$
(D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

Q.19 Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. **[JEE Advanced - 2019]**

(A) $\dfrac{3}{2} O_2 (g) \rightarrow O_3 (g)$

(B) $\dfrac{1}{8} S_8(s) + O_2(g) \rightarrow SO_2(g)$

(C) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(D) $2C(g) + 3H_2(g) \rightarrow C_2H_6(g)$

Q.20 In thermodynamics the P-V work done is given by

$w = -\int dV P_{ext}$.

For a system undergoing a particular process, the work done is ,

$w = -\int dV \left(\dfrac{RT}{V-b} - \dfrac{a}{V^2} \right)$ **[JEE Advanced- 2020]**

This equation is applicable to a

(A) System that satisfies the van der Waals equation of state.

(B) Process that is reversible and isothermal.

(C) Process that is reversible and adiabatic.

(D) Process that is irreversible and at constant isothermal.

Q.21 Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

At 298 K : $\Delta_f H^\circ(SnO_2(s)) = -581.0$ kJmol^{-1}, $\Delta_f H^\circ(CO_2(g)) = -394.0$ kJ mol^{-1}

$S^\circ(SnO_2(s)) = 56.0$ J K^{-1} mol^{-1}, $S^\circ(Sn(s)) 52.0$ J K^{-1} mol^{-1}, $S^\circ(C(s)) = 0.6$ J K^{-1}mol^{-1}, $S^\circ(CO_2(g)) = 210.0$ J K^{-1} mol^{-1}.

Assume that the enthalpies and the entropies are temperature independent.

[JEE Advanced- 2020]

Answer Key

EXERCISE-I

Q.1 (3)	Q.2 (3)	Q.3 (3)	Q.4 (4)	Q.5 (3)	Q.6 (2)	Q.7 (3)	Q.8 (1)	Q.9 (4)	Q.10 (2)
Q.11 (3)	Q.12 (3)	Q.13 (3)	Q.14 (3)	Q.15 (3)	Q.16 (1)	Q.17 (1)	Q.18 (4)	Q.19 (4)	Q.20 (2)
Q.21 (2)	Q.22 (3)	Q.23 (2)	Q.24 (3)	Q.25 (1)	Q.26 (4)	Q.27 (2)	Q.28 (2)	Q.29 (4)	Q.30 (4)
Q.31 (1)	Q.32 (2)	Q.33 (3)	Q.34 (4)	Q.35 (4)	Q.36 (2)	Q.37 (1)	Q.38 (1)	Q.39 (2)	Q.40 (1)
Q.41 (2)	Q.42 (3)	Q.43 (1)	Q.44 (2)	Q.45 (4)	Q.46 (3)	Q.47 (4)	Q.48 (4)		

EXERCISES-II

Q.1 (3)	Q.2 (1)	Q.3 (1)	Q.4 (4)	Q.5 (2)	Q.6 (2)	Q.7 (2)	Q.8 (1)	Q.9 (2)	Q.10 (4)
Q.11 (2)	Q.12 (1)	Q.13 (4)	Q.14 (1)	Q.15 (3)	Q.16 (3)	Q.17 (1)	Q.18 (1)	Q.19 (4)	Q.20 (2)
Q.21 (1)	Q.22 (2)	Q.23 (3)	Q.24 (4)	Q.25 (4)	Q.26 (3)	Q.27 (3)	Q.28 (1)	Q.29 (4)	Q.30 (2)
Q.31 (2)	Q.32 (3)	Q.33 (3)	Q.34 (4)	Q.35 (2)	Q.36 (2)	Q.37 (1)	Q.38 (2)	Q.39 (1)	Q.40 (1)

EXERCISES-III

Q.1 (A,B,C) Q.2 (A,B,C) Q.3 (A,C) Q.4 (A, C) Q.5 (A, C, D) Q.6 (A, C, D) Q.7 (C,D) Q.8 (A) Q.9 (B) Q.10 (B)

Q.11 (A) Q.12 (A) Q.13 (A) Q.14 (D) Q.15 (B) Q.16 A $\rightarrow$ (P,R), B $\rightarrow$ (Q,S), C $\rightarrow$ (Q,S), D $\rightarrow$ (Q,S)

Q.17 A $\rightarrow$ (P,S), B $\rightarrow$ (Q), C $\rightarrow$ (R) Q.18 [1900 cal] Q.19 $\Delta E = 0.993$ kcal, $\Delta H = 1$ kcal Q.20 [200 J/K mole]

Q.21 [-88 kJ/mol]

EXERCISES-IV

JEE-MAIN
PREVIOUS YEAR'S

Q.1 (3)	Q.2 (3)	Q.3 (3)	Q.4 (3)	Q.5 (1)	Q.6 (3)	Q.7 (3)	Q.8 (1)	Q.9 (1)	Q.10 (4)
Q.11 (1)	Q.12 (3)	Q.13 (4)	Q.14 (1)	Q.15 (1)	Q.16 (3)	Q.17 (3)	Q.18 (4)	Q.19 (3)	Q.20 (1)
Q.21 (1)	Q.22 (3)	Q.23 (1)	Q.24 (3)	Q.25 (4)	Q.26 (2)	Q.27 (3)	Q.28 [-2.70]		

Q.29 [-192.50 or -85.00] Q.30 [48.00] Q.31 [6.25] Q.32 (4) Q.33 (3) Q.34 [-326400]

Q.35 [189494] Q.36 (1) Q.37 (2) Q.38 [-13537.57] Q.39 (4) Q.40 (1) Q.41 [50]

JEE-ADVANCED
PREVIOUS YEAR'S

Q.1 (A,B) Q.2 [2] Q.3 (C) Q.4 (A $-$ p, r, s) ; (B $-$ r, s) ; (C $-$ t) ; (D $-$ p, q, t) Q.5 (A,C)

Q.6 (D) Q.7 (A,D) Q.8 (C) Q.9 (B) Q.10 (A,B,C) Q.11 (A-R,T) (B-P,Q,S) (C-P,Q,S) (D-P,Q,S,T)

Q.12 (A) Q.13 (B) Q.14 (C) Q.15 (C) Q.16 (A,B) Q.17 (ACD) Q.18 (B,C) Q.19 (A,B) Q.20 (A,B,C)

Q.21 [935.00]

EXERCISE Solution

EXERCISE-I

Q.1 (3) In isolated system neither exchange of matter nor exchange of energy is possible with surroundings.

Q.2 (3) Work is not a state function as during a process its value depends on the path followed. The value of enthalpy, internal energy and entropy depends on the state and not on the path followed to get that state, hence these are state functions.

Q.3 (3) Surface tension is an intensive property which do not depend upon the quantity of matter present in the system.

Q.4 (4)

Q.5 (3)

Q.6 (2) $W = -2.303\, nRT \log \dfrac{V_2}{V_1}$

$= -2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \dfrac{20}{10}$

$= -298 \times 10^7 \times 8.314 \times 2.303 \log 2$.

Q.7 (3) $W = -P\Delta V = -1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3})$

$= -1 \times 10^5 \times 9 \times 10^{-3} = -900\, J$

Q.8 (1) We have,

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

$= -2.303 \times 2 \times 2 \times 298 \times \log \dfrac{50}{15}$

$= -1426.87$ calories.

Q.9 (4) If $n_g = 0$ $\Delta H = \Delta E$

Q.10 (2) $\Delta H = \Delta E + P\Delta V$.

Q.11 (3) $\Delta n_g = 1 - \dfrac{3}{2} = \dfrac{-1}{2}$, As Δn_g is negative, thus

$\Delta H < \Delta E$.

Q.12 (3)

Q.13 (3) At constant P or T

$\Delta H = \Delta U + \Delta nRT \Rightarrow \Delta n = n_p - n_R = 2 - 4 = -2$

$\therefore \Delta H < \Delta U$.

Q.14 (3) Here $\Delta n = 0$ so, $\Delta E = \Delta H$.

Q.15 (3)

Q.16 (1) We know that $\Delta E = Q + W = 600 + (-300) = 300\, J$

Q.17 (1) We know that work done, $W = C_v(T_1 - T_2)$

$3 \times 1000 = 20\,(300 - T_2)$; $\therefore 3000 = 6000 - 20\,T_2$

$\therefore T_2 = \dfrac{3000}{20} = 150\, K$.

Q.18 (4) When $\Delta S = +ve$ the change is spontaneous.

Q.19 (4) Heat is always flow from the higher to lower temperature.

Q.20 (2) Entropy of the system increases as the process occur irreversibly and isothermally in an isolated system.

Q.21 (2) Solid $\longrightarrow$ Gas, ΔS is maximum.

Q.22 (3)

Q.23 (2)

Q.24 (3) $\Delta S = \dfrac{q_{rev}}{T}$ $\therefore$ unit of S is $JK^{-1}mol^{-1}$.

Q.25 (1) When $\Delta H = -ve$, $\Delta S = +ve$ and $\Delta G = -ve$ than reaction is spontaneous.

Q.26 (4) ΔG at equilibrium $= 0$.

Q.27 (2) For spontaneous change $\Delta G = -ve$.

Q.28 (2)

Q.29 (4) When $\Delta H = +ve$ and $\Delta S = -ve$ than the reaction is non-spontaneous.

Q.30 (4) At equilibrium $\Delta G = 0$.

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Q.31 (1) $\Delta G^o = -2.303\,RT \log K$

$-4.606 = -2.303 \times 0.002 \times 500 \log K$

$\log K = 2,\ K = 100$.

Q.32 (2)

Q.33 (3) ΔH and ΔS both are $+ve$ for spontaneous change, and $\Delta H = +ve$ for endothermic reaction.

Q.34 (4) Heat of neutralisation of a strong acid and strong base is equal to $-13.7\,kcal$.

Q.35 (4)

Q.36 (2) 78g of benzene on combustion produces heat $= -3264.6\,kJ$

$\therefore 39\,g$ will produce $= \dfrac{-3264.6}{2} = -1632.3\,kJ$.

Q.37 (1) $eq.\,(i) + eq.\,(ii)$ gives the required result.

Q.38 (1) Change of liquid to vapour takes energy in the form of heat so it is endothermic reaction.

Q.39 (2)

Q.40 (1) $H_2 + O_2 \rightarrow H_2O_2 \quad \Delta H_f^o = -188\,kJ/mole$
....(i)

$H_2 + \dfrac{1}{2}O_2 \rightarrow H_2O \quad \Delta H_f^o = -286\,kJ/mole$
....(ii)

eq. (i) − eq. (ii) × 2 gives the required result.

Q.41 (2) Aim: $CO + \dfrac{1}{2}O_2 \rightarrow CO_2$

$\Delta H = \Delta H_f^0(CO_2) - \left[\Delta H_f^0(CO) + \dfrac{1}{2}\Delta H_f^0(O_2)\right]$

$= -94.0 - (-26.4) = -67.6\ kcal.$

Q.42 (3) NH_4OH is a weak base. Heat of neutralisation < 13.7kcal.

Q.43 (1) $\Delta H - \Delta E = \Delta nRT = 3 \times 8.314 \times 298$

$= -7432\ J = -7.43\,kJ.$

Q.44 (2) $\Delta H = +ve$ for endothermic reaction.

Q.45 (4) Standard molar heat enthalpy (H^o) of a compound is equal to its standard heat of formation from most stable states of initial components.

Q.46 (3) Aim: $\dfrac{1}{2}H_2 + \dfrac{1}{2}Cl_2 \rightarrow HCl$

$\Delta H = \Sigma B.E._{(Products)} - \Sigma B.E._{(Reactants)}$

$= B.E.(HCl) - \left[\dfrac{1}{2}B.E.(H_2) + \dfrac{1}{2}B.E.(Cl_2)\right]$

$= -103 - \left[\dfrac{1}{2}(-104) + \dfrac{1}{2}(-58)\right]$

$= -103 - (-52 - 29) = -22\ kcal.$

Q.47 (4) $\dfrac{1}{2}H_2 + \dfrac{1}{2}Cl_2 \rightarrow HCl,\ \Delta H = -90\ KJ$

$\therefore \Delta H = \dfrac{1}{2}E_{H-H} + \dfrac{1}{2}E_{Cl-Cl}$

or $-90 = \dfrac{1}{2} \times 430 + \dfrac{1}{2} \times 240 - E_{HCl}$

$\therefore E_{H-Cl} = 425\ kJ\,mol^{-1}.$

Q.48 (4) $CH_4 \rightarrow C + 4H,\ \Delta H = 320$
$E_{C-H} = 80$ cal
$C_2H_6 \rightarrow 2C + 6H,\ \Delta H = 360$

$\therefore 360 = E_{C-C} + 6E_{C-H}$
$\therefore E_{C-C} = 360 - 6 \times 80 = 120$ cal

EXERCISE-II

Q.1 (3) Boiling point, pH & density are intensive properties. Entropy is an extensive property.

Q.2 (1) PV = nRT
[V in litre and T in Kelvin]
PV = 1 × 0.0821 × 373
PV = 30 litre
V = 30 litre
W = − PΔV
= − 1 (30 − V$_{gas}$)
[18 ml is negligible as compared to 30 litre]
= − 1 × 30 = − 30 litre atm.

Q.3 (1) $W = -10^5 \times 2 = -2 \times 10^5\,J$

Q.4 (4) For isothermal process involving ideal gas
$\Delta T = \Delta E = \Delta H = 0$

Q.5 (2) $C_P = \dfrac{q}{n\Delta T}$

$\Delta T = 0$

$C_P = \infty$

Q.6 (2)

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Q.7 (2) $\Delta H = \Delta E + \Delta n \, RT$

Given

$\Delta H = -651 \times 10^3$ cal., $R = 2$ cal,

$T = 290 \, K$ and $\Delta n = 6 + 6 - 6 = 6$

$\therefore \Delta E = -651 \times 10^3 - 6 \times 2 \times 290$

$= -654480$ cal $= -654.5$ Kcal

Q.8 (1)

Q.9 (2)

Q.10 (4) $\Delta n_g = 0$

$\Delta H = \Delta U$

$\Delta U = -185$ kJ/Mole

For three moles $= -185 \times 3 = -555$

Q.11 (2) $W = -100J$, $q = 150 \, J$

$\because q = \Delta E - W$

$\therefore 150 = \Delta E - (-100)$

$= 150 - 100$

$\Delta E = 50 \, J$

Q.12 (1) $W = -P\Delta V$

$= -1.5 \, (1 - 0.5)$

$= -0.75$ atm-litre $= -0.75 \times 101$ Joule

$q = 200 \, J$

$\because q = \Delta E - W$

$200 = \Delta E - (-0.75 \times 101)$

$\Delta E = 124.25$ Joule

Q.13 (4)

$U = 0, \ W = -nRT \ln\left(\dfrac{V_2}{V_1}\right) = -P_1 V_1 \ln\left(\dfrac{V_2}{V_1}\right)$

$= 20 \ln 2 = 14$ lit-atm

Q.14 (1) $\Delta S_{system} = nR \ln \dfrac{V_2}{V_1}$

$\Rightarrow 2 \times R \times \ln 2$

$\Rightarrow 11.52 \, J/K$

$\Delta S_{surrounding} = -\dfrac{3.3 \times 1000}{300} \Rightarrow -11 \, J/K$

Q.15 (3) $\Delta S = nC_v \ln \dfrac{T_2}{T_1}$

$= 2 \times \dfrac{3}{2} R \ln \dfrac{573}{473}$

Q.16 (3) $\Delta S_{vap} = +\dfrac{300 \times 30}{300} = -30 \, J/mol.K$

$\Delta S_{cond} = -30 \, J/mol\text{-}K$

Q.17 (1) $\Delta H = -3600$ cal

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

$\Delta G = -600$ cal

Q.18 (1) $\Delta G^{\circ} = -RT \ln k$

Q.19 (4) $\Delta H^{\circ} = \Sigma \Delta H^{\circ}_{f \, (products)} - \Sigma \Delta H^{\circ}_{f \, (Reactants)}$

$= [\Delta H^0_{f(H_2O)} + \Delta H^0_{f(CO)}] - [\Delta H^0_{f(CO_2)} + \Delta H^0_{f(H_2)}]$

$\Delta H^{\circ} = [-241.8 - 110.5] - [-393.5 + 0]$

$= -352.3 + 393.5 = +41.2$ KJ

Q.20 (2) $H_2 + O_2 \rightarrow H_2O \, (l)$

$H - H + 0 = 0 \ H_2O(g) \ H_2O \, (l)$
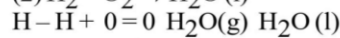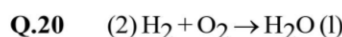
$X = X_1 + -2X_3 - X_4$

Q.21 (1) $H^+ = 1$ Mole ; $OH^- = 0.75$ Mole

$\Delta H = 0.75 \, (-57)$

Hear enolved $= 57 \dfrac{3}{4}$

Q.22 (2)

Q.23 (3)

Q.24 (4) $-25 = (4x + y) - (3x + 84 + 103)$

$x + y = 162$

$y = 57.85$

Q.25 (4)

Q.26 (3)

Q.27 (3)

Q.28 (1)

Q.29 (4)

Q.30 (2)

Q.31 (2)

Q.32 (3)

Q.33 (3)

Q.34 (4)

Q.35 (2)

Q.36 (2)

Q.37 (1)

Q.38 (2)

Q.39 (1)

Q.40 (1)

EXERCISE-III

JEE-ADVANCED
COMPREHENSION/STATEMENT/MATCHING/MCQ

Q.1 (A,B,C) $\Delta G < 0$ for spontaneous
(D) Assumed to zero not unity

Q.2 (A,B,C) $P_{white} < P_{red}$ (Stability)
$\Rightarrow$ Exothermic

Q.3 (A,C) $3UO_2 + O_2 \longrightarrow U_3O_8$
$-76.01 = -853.5 - (3 \times \Delta_f H(UO_2)$
$\Rightarrow \Delta_f H = \dfrac{-853.5 + 76.01}{3}$
$= -259.16 \, Kcal/Mole$

Q.4 (A, C) $UF(g) \longrightarrow U(g) + \dfrac{1}{2} F_2(g)$

$\Delta_r H = \Delta_f H(U,g) - \Delta_f H(UF,g)$
$\quad = 128 - 22 = 106$
or
$\Delta_r H = E_{U-F} - \dfrac{1}{2} E_{F-F} = 106$

$\Rightarrow E_{U-F} = 106 + \dfrac{1}{2} \times 37$

$= 124.5 \, Kcal/Mole$
or
521 kJ/Mole

Q.5 (A, C, D) C (diamond) ; $\Delta_f H \neq 0$

Q.6 (A, C, D)

Q.7 (C,D) Arrhenius equation ; $K = Ae^{-Ea/RT}$
Kirchaff's Equation ;
$d(\Delta_r H) = \Delta_r C_p dT$

Q.8 (A) Stable state had zero standard molar enthalpy

Q.9 (B) $N_2 + O_2 \longrightarrow 2NO$; $\Delta_r H > O$
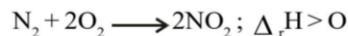
$N_2 + 2O_2 \longrightarrow 2NO_2$; $\Delta_r H > O$
Endothermic reactions are favourable High temperature.

Q.10 (B) (diamond) $+O_2 \longrightarrow CO_2$; -94.3
(Amorphous) $+ O_2 \longrightarrow CO_2$; -97.6
(diamond) $\longrightarrow$ (amorphous) ;
$\Delta_r H \; \Delta_r H = -94.3 + 97.6 = 3.3 \, KCal/Mole$

for $6g \, C \equiv \dfrac{1}{2} \, Mole \, C$

$\Delta_r H = \dfrac{3.3}{2} = 1.65 \, KCal$

Q.11 (A) $H_2O(l) \longrightarrow H_2O(g)$
$\Rightarrow 18 \times 0.62778 = \Delta_f H(H_2O, g) - \Delta_f H(H_2O, l)$
$= \Delta_f H(H_2O, g) + 68.3$
$\Rightarrow \Delta_f H(H_2O, g) = -68.3 + 11.3$
$= -57.0 \, KCal$

Q.12 (A) $I_2(s) \longrightarrow I_2(g)$
$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

$\Delta H_2 - 6.096 = (0.031 - 0.055) \dfrac{50}{1000} \times 254$

$\Delta H_2 = -0.3048 + 6.092$
$= 5.78$

Q.13 (A)
Acetic acid ; weak acid (Less than 13.7)
And HF is the exceptional case having langer value for Heat of neupralization than 13.7

Q.14 (D)
(i) True
(ii) Due to cont. volume it measure ΔU
(iii) $\Delta n_g = 0 \Rightarrow \Delta H = \Delta U$
(iv) False (due to involvement of R.E)

Q.15 (B)
Case I ; $H^+ = 0.1 \times 100 \times 2 = 20 \, m.eq.$
$OH^- = 0.1 \times 100 \times 2 = 20 \, m.eq.$
Case II ; $H^+ = 50 \times 0.1 \times 2 = 10 \, m.eq.$
$OH^- = 100 \times 0.1 = 10 \, m.eq.$
$\Rightarrow 2\Delta H_{II} = \Delta H_I$
$\Delta H_I = 274 \, cal$; $\Delta H_{II} = 137$
$\Delta T_I = \Delta T_{II}$ (Because amount of substasace in case I is double than case II)

Q.16 $A \to (P,R)$, $B \to (Q,S)$, $C \to (Q,S)$, $D \to (Q,S)$
If $\Delta n_g > 0 : \Delta S > 0$

Q.17 $A \to (P,S)$, $B \to (Q)$, $C \to (R)$

Kircaff's equation
$$d(\Delta_r H) = \Delta_r C_p dt$$
$$\Rightarrow \Delta H = \Delta U + \Delta ngRT$$
$$\Rightarrow \Delta s = \frac{q_{rev}}{T}$$

Q.18 [1900 cal]
$$\Delta U = \Delta U_1 + \Delta U_2$$
$$= n_1 C_{V_1m} \Delta T + n_2 C_{V_1m} \Delta T$$
$$= [3 \times \frac{3}{2} R \times 100] + [2 \times \frac{5R}{2} \times 100]$$
$$= 450 R + 500 R$$
$$= 950 R$$
$$= 1900 \text{ cal}$$

Q.19 $\Delta E = 0.993$ kcal, $\Delta H = 1$ kcal
$w = -P_{ext}(V_2 - V_1) = -1(1.5 - 1.2) = -0.3$ L atm $= -7.235$ cal
$\Delta U = q + w$
$= 1 - 0.007235 = 0.993$ kcal
$q = \Delta H = 1$ kcal

Q.20 [200 J/K mole]
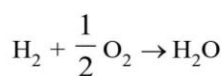$$\Delta S = \frac{\Delta H}{T} = \frac{-392 - 75 - (-484)}{85} = 200 \text{ J/K mole}$$

Q.21 [– 88 kJ/mol]

$$C_2H_6 + \frac{7}{2}O_2 \to 2CO_2 + 3H_2O \qquad \Delta H = -1560$$
$$.................(1)$$
$$C + O_2 \to CO_2 \qquad \Delta H = -395$$
$$..................(2)$$
$$H_2 + \frac{1}{2}O_2 \to H_2O$$
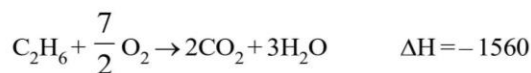
$$\Delta H = -286 \qquad ....(3)$$

Target reaction $2C + 3H_2 \to C_2H_6$ $\Delta H = ?$
ΔH can be obtained by $(2) \times 2 + (3) \times 3 - (1)$
$$\Delta H = -88 \text{ kJ mol}^{-1}$$

EXERCISE-IV

JEE-MAIN
PREVIOUS YEAR'S

Q.1 (3)
$$C(s) + O_2(g) \to CO_2(g) \qquad ;$$
$$\Delta H = -393.5 \text{ kJ/mol.}$$
$$CO(g) + \frac{1}{2}O_2(g) \to CO_2(g) ;$$
$$\Delta H = -283.5 \text{ kJ/mol.}$$
$$C(s) + \frac{1}{2}O_2(g) \to CO(g) \qquad ;$$
$$\Delta H = -393.5 + 283.5 \text{ kJ/mol} = -110 \text{ kJ/mol.}$$

Q.2 (3)
From 1st law :
$\Delta U = q + w$
For adiabatic process:
$q = 0$
$\therefore \Delta U = w$
Work involve in adiabatic process is at the expense of change in internal energy of the system.

Q.3 (3)
$$CO_2(g) + 2H_2O(l) \to CH_4(g) + 2O_2(g); \Delta rH° = +890.3 \text{ kJ mol}^{-1}$$
$$\quad -393.5 \quad -285.8 \qquad ? \qquad\qquad 0$$

$$\Delta_r H° = \sum (\Delta_f H°)_{Products} - \sum (\Delta_f H°)_{reactants}$$

$$890.3 = [1 \times (\Delta_f)H°)_{CH_4} + 2 \times 0] - [1 \times (-393.5) + 2(-285.8)]$$

$$(\Delta_f)H°)_{CH_4} = 890.3 - 965.1 = -74.8 \text{ kJ/mol}$$

Q.4 (3)
$C_6H_6(l) + 15/2O_2(g) \to 6CO_2(g) + 3H_2O(l)$
$\Delta n_g = 6 - 7.5 = -1.5$ (change in gaseous mole)
ΔU or $\Delta E = -3263.9$ kJ
$\Delta H = \Delta U + \Delta n_g RT$
$\Delta n_g = -1.5$
$R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$
$T = 298$ K
So, $\Delta H = -3263.9 + (-1.5)8.314 \times 10^{-3} \times 298$
$= -3267.6$ kJ
$\Delta H = $ Heat at constant pressure
$\Delta H/\Delta E = $ Heat at constant volume
$R = $ gas cosntant

Q.5 (1) C_P does not changes with change in pressure

Q.6 (3)

In order to be spontaneous $\Delta G°$ should be –ve

$\Delta G° = \Delta H° - T\Delta S°$

$0 = 491.1 \times 10^3 - T \times 198$

$T = \dfrac{491100}{198} = 2480$

If temp is above 2480 K, the reaction will be spontaneous.

Q.7 (3)

$q = P\Delta V$

$q = 16$

$C_p = 24$

$C_P = \dfrac{q_P}{\Delta T} \Rightarrow \Delta T = \dfrac{16}{24}K = \dfrac{2}{3}K$

Q.8 (1)

At the thermal equilibrium,

final temperature $T_f = \dfrac{T_1 + T_2}{2}$

$\Rightarrow$ for the 1st block, $\Delta S_I = C_P \ln \dfrac{T_f}{T_1}$

$\Rightarrow$ for the 2nd block, $\Delta S_{II} = C_P \ln \dfrac{T_f}{T_2}$

When brought in contact with each other,

$\Delta S = \Delta S_I + \Delta S_{II} = C_P \ln \dfrac{T_f}{T_1} + C_P \ln \dfrac{T_f}{T_2}$

$= C_P \ln \left(\dfrac{T_f}{T_1} \times \dfrac{T_f}{T_2} \right) = C_P \ln \left[\dfrac{T_f^2}{T_1 T_2} \right]$

$= C_P \ln \left[\dfrac{\left(\dfrac{T_1 + T_2}{2} \right)}{T_1 T_2} \right] = C_P \ln \left[\dfrac{(T_1 + T_2)^2}{4 T_1 T_2} \right]$

Q.9 (1) $\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = A - BT$

In endothermic reaction $\Delta H = +ve$. Hence, $A = +ve$

Q.10 (4)

$\underset{\substack{1\,kg \\ at\,273\,K}}{H_2O(s)} \rightarrow \underset{\substack{1\,kg \\ at\,273\,K}}{H_2O(\ell)} \rightarrow \underset{\substack{1\,kg \\ at\,373\,K}}{H_2O(\ell)} \rightarrow \underset{at\,373\,K}{H_2O(g)} \rightarrow \underset{at\,383\,K}{H_2O(g)}$

$\Delta s = \Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4$

$= \dfrac{334}{273} + 4.2 \ell n \dfrac{373}{273} + \dfrac{2491}{373} + 2 \ell n \dfrac{383}{373}$

$= 9.267 \, kJ \, Kg^{-1} K^{-1}$

Q.11 (1)

Let the gas is expanded form V_1 to V at T_1 and from V_2 to V at T_2.

$\therefore$ At T_1

$|W_1| = nRT_1 \ell n = \dfrac{V}{V} = nRT(\ell nV - \ell - nV_1)$

Similarly at T_2

$|W_2| = nRT_2 (\ell nV - \ell nV_2)$

$\therefore W_1 = nRT_1 \ell nV - nRT_1 \ell nV_1$

$W_2 = nRT_2 \ell nV - nRT_2 \ell nV_2$

Slope of W_2 > Slope of W_1

As $nRT_2 > nRT_1 (T_2 > T_1)$

$\therefore$ The intercept of W_2 is more negative than that of W_1 because $V_2 > V_1$.

Q.12 (3) $\Delta S = \dfrac{\Delta H}{T}$

Q.13 (4)

$CaSO_4(s) \rightarrow CaO(s) + SO_3(g)$

$CO_2(s) \rightarrow CO_2(s)$

$I_2 \rightarrow I_2(aq)$

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

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

$\Delta S = 2\Delta S_{NH_3} - \left[\Delta S_{N_2} + 3\Delta S_{H_2} \right]$

there is decrease in number of moles of NH_3 entropy is decreasing.

Q.14 (1)

The plot (b) and (d) are incorrect. The correct ones are given below:

[b]   [c]
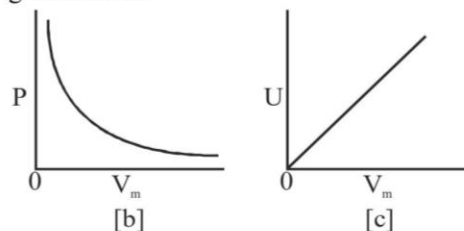
Q.15 (1)

(ii) + (iii) = (i)

Y + z = x

Q.16 (3)

$\Delta G° = -2.303 RT \log K_{eq}$

$= -2.303 \times 8.314 \times 298 \log 10^{-14}$

$= -2.303 \times 8.314 \times 298 \times -14$

$= 79,881.87$

$\simeq 80 \, KJ \, mol^{-1}$

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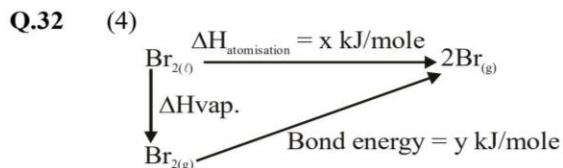
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Q.17 (3)

For cyclic process : $\Delta U = 0 \Rightarrow q = -w$
For isothermal process : $\Delta U = 0 \Rightarrow q = -w$
For adiabatic process : $q = 0 \Rightarrow \Delta U = W$
For isochoric process : $w = 0 \Rightarrow \Delta U = q$

Q.18 (4)

$$\Delta H = n\int_{T_1}^{T_2} C_{p,m}\,dT = 3 \times \int_{300}^{1000} (23 + 0.01T)dT$$

$$= 3[\ 23(1000 - 300) + \frac{0.01}{2}(1000^2 - 300^2)]$$

$$= 61950\,J \approx 62kJ$$

Q.19 (3)

(A) $q + w = \Delta U \leftarrow$ definite quantity
(B) $q \rightarrow$ Path function
(C) $w \rightarrow$ Path function
(D) $H - TS = G \rightarrow$ state function

Q.20 (1) $\Delta G^\circ = -nFE^\circ_{cell}$

$= -2 \times 96000 \times 2$
$= -384000\,J$
$= -384\,kJ$
∴ Ans. is (1)

Q.21 (1)

$n = 5$; $T_i = 100\,K$; $T_f = 200\,K$;
$C_v = 28\,J/mol\,K$;   Ideal gas
$\Delta U = nC_v\Delta T$
$= 5\,mol \times 28\,J/mol\,K \times (200 - 100)\,K$
$= 14{,}000\,J = 14\,kj$
$\Rightarrow C_p = C_v + R = (28 + 8)\,J/mol\,K$
$= 36\,J/mol\,K$
$\Rightarrow \Delta H = nC_p\Delta T = 5\,mol \times 36\,J/mol\,K \times 100\,K$
$= 18000\,J = 18\,kJ$
$\Delta H = \Delta U + \Delta(PV)$
$\Rightarrow \Delta(PV) = \Delta H - \Delta U = (18 - 14)\,kJ = 4\,kJ$

Q.22 (3)

Mo and W has nearly similar atomic radius due to lanthanoid contraction.

Q.23 (1)

$\Delta U = q + w$
$q = -2kJ$, $W = 10\,kJ$
$\Delta U = 8kJ$

Q.24 (3)

$W = -P_{ext}(V_2 - V_1)$
$= -1\,bar \times (10 - 1)lit$
$= -9\,bar - lit$
$= -900\,J$
$= -0.9\,kJ$

Q.25 (4)

$I_{2(s)} \rightarrow I_{2(g)}$: $\Delta H_1 = 24\,cal/g$ at $200^\circ\,C$
$\Delta H_2 = \Delta H_1 + \Delta C_{Prxn}(T_2 - T_1)$
$= 24 + (0.031 - 0.055) \times 50$
$= 24 - 1.2$
$= 22.8\,cal/g$

Q.26 (2)

$\Delta G = \Delta H - T\Delta S$
for spontaneous process at all temp. $\Delta G < 0$ and it is possible when $\Delta H < 0$ and $\Delta S > 0$.

Q.27 (3)

$C_7H_{16}(\ell) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(\ell)$
$\Delta n_g = n_p - n_r = 7 - 11 = -4$
∵ $\Delta H = \Delta U + \Delta n_g RT$
∴ $\Delta H - \Delta U = -4\,RT$

Q.28 [−2.70 to −2.70]

$\Delta H = \Delta U + \Delta\,ngRT$
$= 2.1 \times 10^3 + 2(2)(300)$
$= 2100 + 1200$
$= 3300\,cal$
$\Delta G = \Delta H - T\Delta S = 3300 - (300)(20) = 3300 - 6000 = -2700$
cals $= -2.7\,kcal$

Q.29 [−192.50 or −85.00]

$C_2H_6(g) + 3.5O_2(g) \rightarrow 2CO_2(g) + 3H_2O(I)$
From the given data
$2 \times (-286) + 3 \times (-393.5) - (-1560) = -572 - 1180.5 + 1560 = -192.50\,kJ/mol.$
         OR
$C_2H_6(g) + 3.5O_2(g) \rightarrow 2CO_2(g) + 3H_2O(I)$
$2 \times (-393.5) + 3 \times (-286) - (-1560) = -85\,kJ/mol$

Q.30 [48.00]

$$|W| = \frac{1}{2}(6 + 10) \times 6 = 48J$$

Q.31 [6.25 to 6.25]

$\Delta U = nC_v\Delta T$
$5000 = 4 \times C_V((500 - 300)$
$C_v = 6.25\,JK^{-1}\,mol^{-1}$

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Q.32 (4)

$$Br_{2(l)} \xrightarrow{\Delta H_{atomisation} = x \text{ kJ/mole}} 2Br_{(g)}$$

$\Delta H vap.$

$Br_{2(g)}$ Bond energy = y kJ/mole

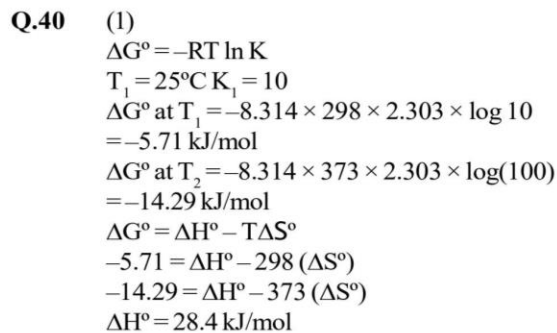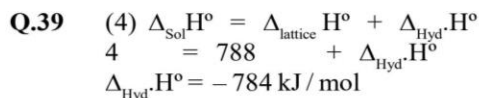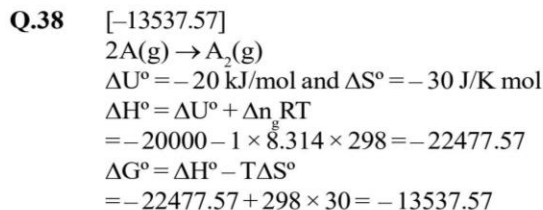$\Delta H_{atomisation} = \Delta H_{vap} + $ Bond energy
Hence $x > y$

Q.33 (3)

$$\Delta S = \int \frac{dq}{T}$$

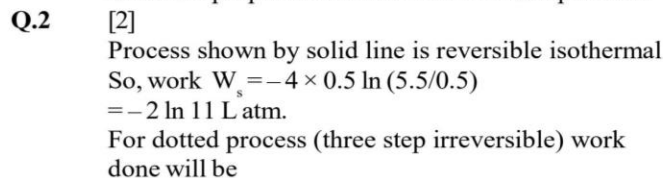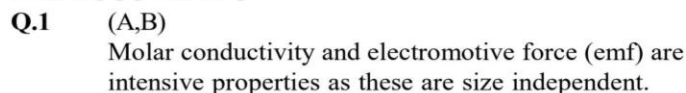$$S_T = \int_O^T \frac{ncdT}{T}$$

Q.34 [–326400]
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
$\Delta H = -327$ kcal; $\Delta n_g = -1$
$\Delta H = \Delta U + \Delta n_g RT$
$\Delta U = -327 + 2 \times 10^{-3} \times 300$
$= -326.4$ kcal
$= -326400$ cal

Q.35 [189494]
$H_2O(l) \rightarrow H_2O(g)$
$\Delta H_{vap} = \Delta U + \Delta n_g RT$
$\Delta U = \Delta H_{vap} - RT$
$= 41,000 - 8.314 \times 373$ J mol^{-1}
$= 37898.878$
For 5 moles, $\Delta U = 37898.878 \times 5$ J
$= 189494$ J

Q.36 (1)
$P_{ext} = 0$
$w = -P_{ext} \Delta V$
$= 0$

Q.37 (2)
For 1 mole of ideal gas.
• Both internal energy (U) and Enthalpy (H) depends on temperature
• Compressibility factor $Z = 1$
• $C_{P,m} - C_{V,m} = R$
and $dU = C_{V,m} dT$

Q.38 [–13537.57]
$2A(g) \rightarrow A_2(g)$
$\Delta U^o = -20$ kJ/mol and $\Delta S^o = -30$ J/K mol
$\Delta H^o = \Delta U^o + \Delta n_g RT$
$= -20000 - 1 \times 8.314 \times 298 = -22477.57$
$\Delta G^o = \Delta H^o - T\Delta S^o$
$= -22477.57 + 298 \times 30 = -13537.57$

Q.39 (4) $\Delta_{Sol}H^o = \Delta_{lattice}H^o + \Delta_{Hyd}H^o$
$4 = 788 + \Delta_{Hyd}.H^o$
$\Delta_{Hyd}.H^o = -784$ kJ / mol

Q.40 (1)
$\Delta G^o = -RT \ln K$
$T_1 = 25^oC$ $K_1 = 10$
ΔG^o at $T_1 = -8.314 \times 298 \times 2.303 \times \log 10$
$= -5.71$ kJ/mol
ΔG^o at $T_2 = -8.314 \times 373 \times 2.303 \times \log(100)$
$= -14.29$ kJ/mol
$\Delta G^o = \Delta H^o - T\Delta S^o$
$-5.71 = \Delta H^o - 298 (\Delta S^o)$
$-14.29 = \Delta H^o - 373 (\Delta S^o)$
$\Delta H^o = 28.4$ kJ/mol

Q.41 [50]
Mass of organic compound = 1.6 gm
Mass of AgBr = 1.88 gm

Moles of Br = Moles of AgBr = $\frac{1.88}{188} = 0.01$

Mass of Br = $0.01 \times 80 = 0.80$ gm
% of Br =
$\frac{0.80 \times 100}{1.60} = 50\%$

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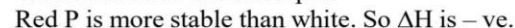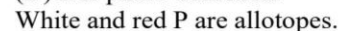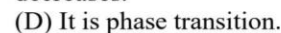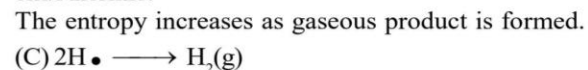## PREVIOUS YEAR'S

Q.1 (A,B)
Molar conductivity and electromotive force (emf) are intensive properties as these are size independent.

Q.2 [2]
Process shown by solid line is reversible isothermal
So, work $W_s = -4 \times 0.5 \ln (5.5/0.5)$
$= -2 \ln 11$ L atm.
For dotted process (three step irreversible) work done will be
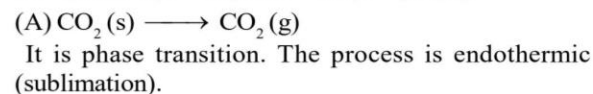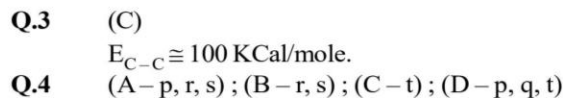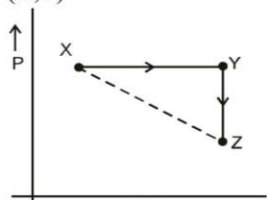
$$W_d = -\{4 \times 1.5 + 1 \times 1 + \frac{2}{3} \times 2.5\} \text{ L atm.}$$

$$= -\{6 + 1 + \frac{5}{3}\} \text{ L atm.} = -\frac{26}{3} \text{ L atm.}$$

so, $\frac{W_d}{W_s} = \frac{26}{3 \times 2 \ln 11} \approx 2.$

Q.3 (C)
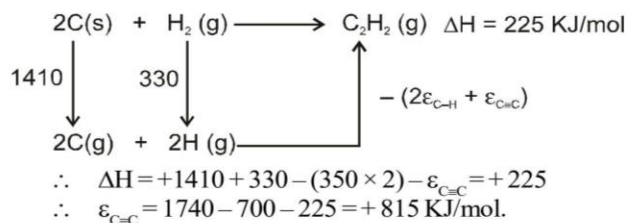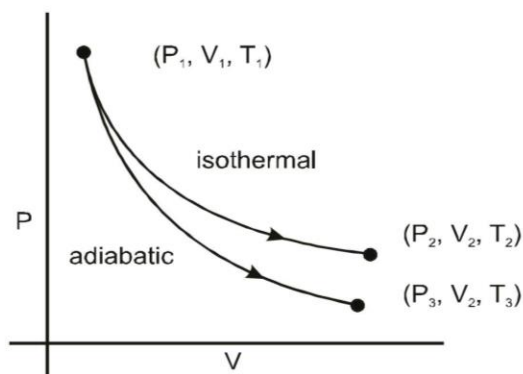$E_{C-C} \cong 100$ KCal/mole.

Q.4 (A – p, r, s) ; (B – r, s) ; (C – t) ; (D – p, q, t)
(A) $CO_2(s) \longrightarrow CO_2(g)$
It is phase transition. The process is endothermic (sublimation).
Gas is produced, so entropy increases.
(B) On heating $CaCO_3$ decomposes. So, process is endothermic.
The entropy increases as gaseous product is formed.
(C) $2H \bullet \longrightarrow H_2(g)$
Entropy decreases as number of gaseous particles decreases.
(D) It is phase transition.
White and red P are allotropes.
Red P is more stable than white. So ΔH is – ve.

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Q.5 (A,C)

(A) $\Delta S_{x \to z} = \Delta S_{x-y} + \Delta S_{y \to z}$
(Correct)

(B) $W_{x \to y} = W_{x-y} + W_{y \to z}$
(Incorrect)

(C) $W_{x \to y \to z} = W_{x-y}$
(Correct)

(D) $\Delta S_{x \to y \to z} = \Delta S_{x-y}$
(Incorrect)

Q.6 (D)

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g) \quad \Delta H = 225\ KJ/mol$$

$1410 \downarrow \qquad 330 \downarrow \qquad \qquad - (2\varepsilon_{C-H} + \varepsilon_{C \equiv C})$

$$2C(g) + 2H(g)$$

∴ $\Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{C \equiv C} = +225$

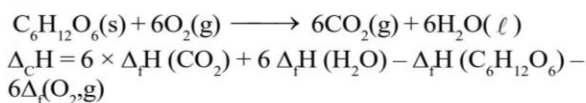∴ $\varepsilon_{C \equiv C} = 1740 - 700 - 225 = +815\ KJ/mol.$

Q.7 (A, D)

(A) $T_1 = T_2$ (due to isothermal)

(B) $T_3 > T_1$ (incorrect) cooling will take place in adiabatic expansion)

(C) $W_{isothermal} > W_{adiabatic}$ { with sign, this is incorrect}

(D) $\Delta U_{isothermal} = 0 > \Delta U_{adiabatic} = -ve$
So, answer is (A,D)

Q.8 (C)

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(\ell)$$
$\Delta_C H = 6 \times \Delta_f H\ (CO_2) + 6\ \Delta_f H\ (H_2O) - \Delta_f H\ (C_6H_{12}O_6) - 6\Delta_f (O_2, g)$

$= 6 \times (-400 - 300) - (-1300) - 0$
$= -4200 + 1300$
$= -2900\ KJ/mol$
For one gram of glucose, enthalpy of combustion = $-$
$\dfrac{2900}{180} = -16.11\ KJ/g.$

Q.9 (B)
For $H_2O(\ell) \to H_2O(g)$ at $T = 100ºC$, 1 atm
equilibrium exists. ∴ $\Delta G = 0$, $\Delta H - T\Delta S = 0$
$\Delta H = T\Delta S > 0$ for system, since evaporation is endothermic

∴ $(\Delta S)_{system} > 0$, also $(\Delta S)_{surrounding} = \dfrac{q_{surr}}{T_{surr}}$

Heat gained by system = heat lost by surroundings
∴ $q_{surr.} < 0$ ∴ $(\Delta S)_{surr.} < 0$

Q.10 (A,B,C)
Since the vessel is thermally insulated so
$q = 0$
$p_{ext} = 0$, so $w = 0$
so $\Delta U = 0$ (ideal gas)
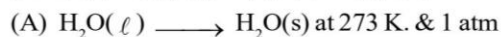Hence $\Delta T = 0$
$\Rightarrow \Delta T = 0$
$\Rightarrow T_2 = T_1$
$\Rightarrow P_2V_2 = P_1V_1$
The process is however adiabatic irreversible.
So we cannot apply $P_2V_2^{\gamma} = P_1V_1^{\gamma}$
Hence ans is (A), (B), (C)

Q.11 (A-R,T) (B-P,Q,S) (C-P,Q,S) (D-P,Q,S,T)

(A) $H_2O(\ell) \longrightarrow H_2O(s)$ at 273 K. & 1 atm
$\qquad \qquad \qquad \qquad \Delta H = -ve = q$
$\Delta S_{sys} < 0$, $\qquad \qquad \Delta G = 0.$
$w \neq 0$ (as water expands on freezing), $\Delta U \neq 0$

(B) Free expansion of ideal gas.
$q = 0 \qquad \qquad \qquad w = 0$
$\Delta U = 0 \qquad \qquad \qquad \Delta S_{sys} > 0$
$\Delta G < 0$

(C) Mixing of equal volume of ideal gases at constant pressure & temp in an isolated container
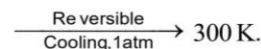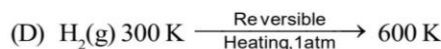$q = 0, \qquad \qquad \qquad w = 0,$
$\Delta U = 0, \qquad \qquad \qquad \Delta S_{sys} > 0$
$\Delta G < 0$

(D) $H_2(g)$ 300 K $\xrightarrow[\text{Heating,1atm}]{\text{Re versible}}$ 600 K
$\xrightarrow[\text{Cooling,1atm}]{\text{Re versible}}$ 300 K.
$q = 0, w = 0, \Delta U = 0, \Delta G = 0, \Delta S_{sys} = 0$

Q.12 (A)
Let the heat capacity of insulated beaker be C.
Mass of aqueous content in expt. 1 = $(100 + 100) \times 1$
$= 200\ g$
$\Rightarrow$ Total heat capacity = $(C + 200 \times 4.2)\ J/K$
Moles of acid, base neutralised in expt. $1 = 0.1 \times 1 = 0.1$
$\Rightarrow$ Heat released in expt. $1 = 0.1 \times 57 = 5.7\ KJ$

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$\Rightarrow 5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T.$

$5.7 \times 1000 = (C + 200 + 4.2) \times 5.7$

$\Rightarrow (C + 200 \times 4.2) = 1000$

In second experiment, $n_{CH_3COOH} = 0.2$, $n_{NaOH} = 0.1$

Total mass of aqueous content = 200 g

$\Rightarrow$ Total heat capacity = $(C + 200 \times 4.2) = 1000$

$\Rightarrow$ Heat released = $1000 \times 5.6 = 5600$ J.

Overall, only 0.1 mol of CH_3COOH undergo neutralization.

$\Rightarrow \Delta H_{neutralization}$ of $CH_3COOH = \dfrac{-5600}{0.1} = -56000$ J/mol

$= -56$ KJ/mol.

$\Rightarrow \Delta H_{ionization}$ of $CH_3COOH = 57 - 56 = 1$ KJ/mol

Q.13 (B)

Final solution contain 0.1 mole of CH_3COOH and CH_3COONa each.

Hence it is a buffer solution.

$pH = pK_a + \log \dfrac{[CH_3COO^-]}{[CH_3COOH]}$

$= 5 - \log 2 + \log \dfrac{0.1}{0.1} = 4.7$

Q.14 (C)

$\because$ Process is done against const. External P, process will be irreversible.

$\therefore "S_{sure}" = \dfrac{-P_{ext}(V_2 - V_1)}{T}$

$= \dfrac{-3 \times (2-1) \times 101.3}{300} = -1.013 J/K$

Q.15 (C)

$dG = VdP - SdT$

At 298 K, $SdT = 0$

$\therefore dG = VdP$

$\displaystyle\int_1^P dG = \int_1^P VdP \therefore G - G° = V(P-1)$

[$\because$ Solids involved $\therefore$ V almost constant]

$\therefore \Delta_r G = [G°_{diamond} + V_d(P-1)] - [G°_{graphite} + V_g(P-1)]$

$0 = 2.9 \times 10^3 + (P-1)10^5(-2 \times 10^{-6})$
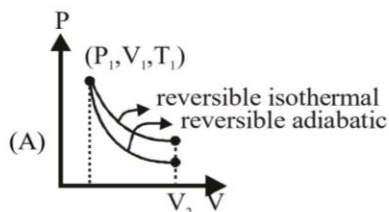
$\therefore P = 14501$ bat

Q.16 (A,B)

$\Delta S_{Surr} = \dfrac{-\Delta H}{T_{Surr}}$

For endothermic, if $T_{surr.}$ increases, ΔS_{surr} will increases.

For exothermic, if $T_{surr.}$ increases, $\Delta S_{surr.}$ will decreases.

Q.17 (A,C,D)

Area under curve in reversible isothermal is more. So, more work will be done by gas.

(B) $T_1 = T_2 \Rightarrow \Delta U = nC_V\Delta T = 0$

In reversible adiabatic expansion, $T_2 < T_1$
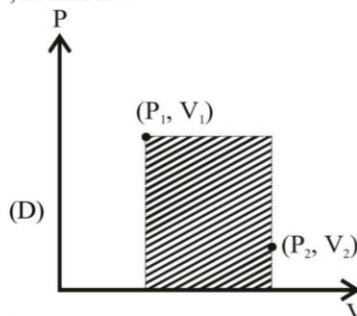
$\therefore \Delta T = -ve \therefore \Delta U = -ve$

(C) In Free expansion, $P_{ext} = 0 \therefore W = 0$

If carried out isothermally ($\Delta U = 0$) $\Rightarrow q = 0$ (Adiabatic) ; From I law

If carried out adiabatically ($q = 0$) $\Rightarrow \Delta U = 0$ (isothermal) ; From I law

(D)

During irreversible compression, maximum work is done on the gas (corresponding to shaded area)

Q.18 (B,C) AC $\to$ Isochoric

AB $\to$ Isothermal

BC $\to$ Isobaric

\# $q_{AC} = \Delta U_{BC} = nC_V(T_2 - T_1)$

$W_{AB} = nRT_1 \ln\left(\dfrac{V_2}{V_1}\right)$ A (wrong)

\# $q_{BC} = \Delta H_{AC} = nC_P(T_2 - T_1)$

$W_{BC} = -P_2(V_1 - V_2)$ B (correct)

\# $nC_P(T_1 - T_2) < nC_V(T_1 - T_2)$ C (correct)

$\Delta H_{CA} < \Delta U_{CA}$

\# D (wrong)

Q.19 (A,B) Enthalpy of formation is defined as enthalpy change for formation of 1 mole of substance from its elements, present in their natural most stable form.

Q.20 (A,B,C) For 1 mole Vander Waal's gas

$P = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$

If $P_{ext} = P$, means process is reversible. For Vanderwaal gas, expression is correct for all reversible process.

Q.21 [935.00] $SnO_{2(S)} + C_{(S)} \to Sn_{(S)} + CO_{2(g)}$

$\Delta H°_{rxn} = [-394] - [-581] = 187$ kJ/mole

$\Delta S°_{rxn} = [52 + 210] - [56 + 6]$

$= 200$ J/k–mole

$T = \dfrac{\Delta H°}{\Delta S°} = \dfrac{187 \times 1000}{200} = 935K$