



Ranjan Singh
Chemistry Classes

JEE (Main & Advanced) • NEET • XI • XII

Study Package



Ranjan Singh

M.Sc. Bio-Chemistry(P.U)

Ex-Faculty : Narayana & Goal

PHYSICAL CHEMISTRY

Thermodynamics



Director's Message



Ranjan Singh
M.Sc.(Biochemistry), P.U.

Chemistry plays a central and important role in all competitive examinations as well as in day to day life. For last so many years, I have constantly been in touch with students, guiding them in Chemistry and looking into their difficulties for them to succeed in their board as well as competitive examinations (JEE(Mains & Advance) | NEET).

I have felt a need for a good coaching centre to fulfil the requirements of students. Students need a highly experienced and qualified faculty in chemistry, who can guide them well, clear their doubts, provide them the effective & tricky notes, and make them do much needed practice. More importantly they should also be provided Classroom Monitoring, Periodical & Surprise Tests to guide them in the proper direction. I realize that, it is very important to diagnose the basic weaknesses and problems of students not succeeding in JEE(Mains & Advance) | NEET and Board exams. In fact, as question patterns are changing, now they need to have a different approach for these Examinations.

At RANJAN SINGH CHEMISTRY CLASSES, we have our own way to prepare students for Competitive Examinations as well as Board Examination at a time so they can crack the entrance exam like JEE(Mains & Advance) and NEET as well as 12th Board simultaneously. We act as a medium to provide the simplest, easiest and a comfortable way to make students achieve their target. At RANJAN SINGH CHEMISTRY CLASSES(RSCC), we guide our students with the best motivational classes so weak students are also able to believe that, They can do it.

When you join RANJAN SINGH CHEMISTRY CLASSES you become a part of the powerful force which propels you towards your goal and if you get a position among the rankers with my excellent guidance, I will think that our efforts have borne fruits.

M.Sc(Biochemistry), P.U.
Ex-faculty : Narayana IIT Academy
& Goal Institute

Ranjan Singh



Introduction

Thermodynamics : The branch of science which deals with different forms of energy & their interconversion is called Thermodynamics.

In chemistry using Thermodynamics.

- ◆ We can predict that if two substances are mixed then the reaction between them will take place or not. (feasibility of the reaction)
- ◆ If a reaction does take place then what are the energy changes involved during the reaction.
- ◆ If in a chemical reaction, equilibrium is going to get attained then what will be the equilibrium concentrations of different reactants & products, can be calculated with thermodynamics.

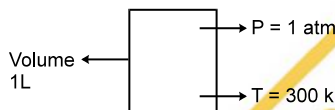
Limitations of Thermodynamics :

- ◆ Laws of thermodynamics are applicable to matter in bulk or on a system as a whole, these can not be applied on individual particles (temperature, pressure, enthalpy etc have meanings only for a system as a whole).
- ◆ Using thermodynamics we cannot calculate the time taken for completion of a reaction or for attainment of chemical equilibrium.

Some Important terms to be used in Thermodynamics :

- ◆ **System, surroundings and boundary.**

(i) **System** : Part of the universe which is under study for energy changes.



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

(ii) **Surrounding** : Rest of the universe.

System + Surroundings = universe.

(iii) **Boundary** : Anything which separates system & surroundings is called boundary.

Boundary can be real or imaginary.

Boundary can be flexible or rigid (for example - air in a flexible balloon (flexible boundary) while air in a room (fixed boundary)).

Boundary can be adiabatic (non-conducting) or diathermic (conducting).

(iv) **Types of system** :

(1) **Open system** : System which can exchange energy & matter both with the surroundings.

Ex. Living systems (any living organism) are open systems, air in an open room.

(2) **Closed system** : System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.

Ex. any matter in a closed container.

(3) **Isolated system** : System which cannot exchange energy and matter both with the surroundings.

Ex. (1) Water in a thermos flask. (Though not a perfectly isolated system but can be taken as, for a small interval of time as the energy exchanges are negligible).

(2) Whole of universe is a perfect isolated system.

- ◆ **State of a system** :

It means the condition in which the system is present and it can be specified/defined by measuring/specifying some observable/measurable properties of the system.

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

For other systems we may have to specify more properties of the system depending on the complexity of the system.



◆ **State functions & path functions :**

State function : Any property of the system which is dependent only on the state of the system and not on the way that state has been achieved.

Ex. (In Mechanics, Displacement of any object will be 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), Enthalpy(H), Gibbs free energy (G), Entropy (S) are all state functions.

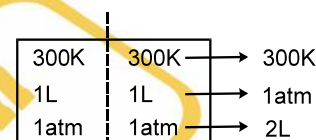
Path function : Quantities which are dependent on the path/way the system has achieved a particular state.

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

◆ **Extensive & intensive functions :**

Extensive functions : Functions or properties of the system which are dependent on mass or on size of the system.

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 two equal halves

Ex. Volume, Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S).

Extensive functions are additive in nature(The addition of the volumes of the two parts equals the volume of the whole of the room.)

Intensive functions : Functions or properties which are not mass dependent or size dependent are called intensive function.

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

Intensive properties are not additive in nature.

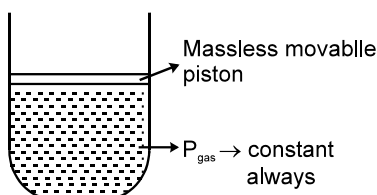
◆ **Thermodynamic equilibrium :** When there is no change in any observable or measurable property of a system with time then the system is said to be in thermodynamic equilibrium.



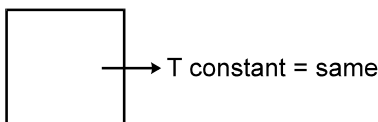
Thermodynamic equilibrium consist of three types of equilibrium.

- (a) Mechanical equilibrium (b) Thermal equilibrium (c) Chemical equilibrium

(a) Mechanical equilibrium : There should not be any pressure gradient (with time or with space(for any ideal gaseous system, for a liquid system there can be pressure gradient with space as pressure at the bottom of the container in which a liquid is filled will be greater than the pressure at the surface of the liquid.)) in the system.



(b) Thermal equilibrium : There should not be any temperature gradient.



Temperature may have different values at different places/locations in a system but it should remain constant with time

(c) Chemical equilibrium : There should not be any concentration gradient of any of the species in the system.

◆ **Thermodynamic process** : Any method/process by which system can change its state from one state of thermodynamic equilibrium to another state of thermodynamic equilibrium.

There can be infinite type of thermodynamic processes, out of these the following are important ones:

1. **Isothermal process** : $T = \text{constant}$

$$dT = 0$$

$$\Delta T = 0$$

2. **Isochoric process** : $V = \text{constant}$

$$dV = 0$$

$$\Delta V = 0$$

3. **Isobaric process** : $P = \text{constant}$

$$dP = 0$$

$$\Delta P = 0$$

4. **Adiabatic process** : $q = 0$

or heat exchange with the surrounding = 0(zero)

Classification of thermodynamics processes on the basis of the way these processes are carried out:

1. **Reversible process**

2. **Irreversible process/spontaneous process/Natural process.**

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

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

Irreversible process : If a process is carried out in such a manner so that the system is in thermodynamic equilibrium only at initial & final state of the process but not at the intermediate stages. (or system should be in thermodynamic equilibrium state at some finite number of intermediate stages only - for example - n step irreversible expansion of a gas)

Irreversible processes will get completed in finite time .

◆ **Heat & work** : These are two ways by which a system can interact or can exchange energy with its surroundings.

Heat & work both are forms of energy.

Heat : When the energy transfer between system & surroundings takes place because of temperature difference.

Work : Any energy transfer which is not heat or which is not because of temperature difference is called work. Work can be of many types such as Mechanical work, Electrical work, Magnetic work, Gravitational work etc.

The same energy transfer can be called work or can also be called heat depending on choice of the system.

Work Done (w) :

Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved. This definition is consistent with our understanding of work as $dw = Fdx$. The force F can arise from electrical, magnetic, gravitational & other sources . It is a **path function**

Note : You will frequently encounter (litre. atmosphere) term which has units of energy . It is useful to remember the conversion : 1 litre. atm = 101.3 Joules = 24.206 cal

Units :

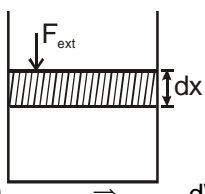
Heat & work both are forms of energy . Hence, their units are units of energy. i.e.SI system: Joule (J). Much data is available in the old units of calories (cal) as well. Hence it is also used sometimes.

Convention :

According to IUPAC, heat added to the system & work done on the system are assigned positive values as both these modes increase the internal energy of the system.

Work : $dW = F_{\text{ext}} dx$

P-V Work :



$$dW = \frac{F_{\text{ext}}}{A} (A dx) \Rightarrow dW = P_{\text{ext}} (dV)$$

As the work done in the above case by the external agent is +ve and as the expression conveys otherwise, hence a -ve sign is introduced.

$$\therefore dW = -P_{\text{ext}} dV$$

Electrical work : $W = Q \times V = I \cdot Vt$

Work calculations for Isothermal Process

Single stage expansion :

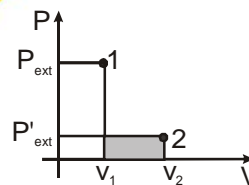
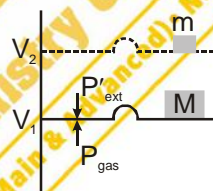
$$P_{\text{gas}} = P_{\text{atm}} + Mg/A = P_{\text{ext}}$$

$$P'_{\text{ext}} = P_{\text{atm}} + \frac{mg}{A} < P_{\text{ext}}$$

$$\therefore P'_{\text{ext}} < P_{\text{gas}}$$

$$W = -\int P'_{\text{ext}} dv$$

$$= P'_{\text{ext}} [V_2 - V_1]$$



Infinite stage process

Let initial pressure of gas be P_i and initial mass of sand placed to keep equilibrium be m_0 , so

$$P_i = P_{\text{atm}} + \left(\frac{m_0 g}{A} \right)$$

A = Area of cross section of piston

Now at some intermediate stage of expansion let the volume has become V and mass of remaining sand be m , then as process is reversible, so there is equilibrium (always). so

$$P_{\text{ext}} = P_{\text{atm}} + \frac{mg}{A} = P_{\text{gas}} = P$$

As process is isothermal so $P = \frac{nRT}{V}$

where 'n' is mo. of moles of gas enclosed and T = temperature of gas = temp. of constant temp. both Now if volume of system is increased by dv amount by displacing a small mass of sand from above the piston so

$$P_{\text{ext}} - P_{\text{gas}} = dp \rightarrow 0$$

then work done in this slight expansion



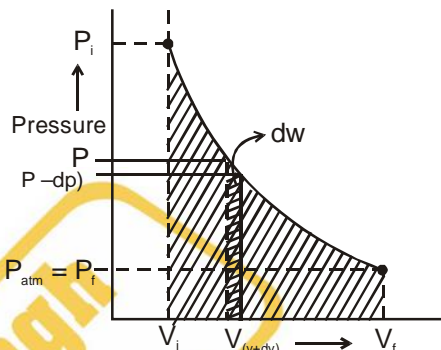
$$dw = -P_{\text{ext}} \cdot dv = -P_{\text{gas}} \cdot dv \text{ (with IUPAC sign convention)}$$

To obtain the total work done. We have to do the integration so

$$W = \int dw = -\int_{V_i}^{V_f} P_{\text{ext}} dv = -\int_{V_i}^{V_f} P_{\text{gas}} dv = -\int_{V_i}^{V_f} P dv \text{ so } W = -\int_{V_i}^{V_f} \frac{nRT}{V} \cdot dv$$

$$W = -nRT \ln(V_f/V_i)$$

This process can also be represented in a PV diagram as follows

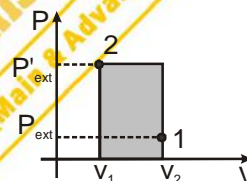
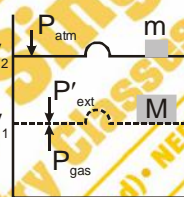


Single Stage Compression

$$P_{\text{ext}} = P_{\text{atm}} + \frac{mg}{A} = P_{\text{gas}}$$

$$P'_{\text{ext}} = P_{\text{atm}} + Mg/A > P_{\text{gas}}$$

$$\text{Work} = \int_{V_2}^{V_1} P'_{\text{ext}} dV = -P'_{\text{ext}} (V_1 - V_2)$$



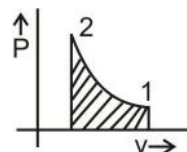
Infinite Stage Compression

at any instant

$$P_{\text{ext}} = P_{\text{int}} + dp$$

$$w = -\int_{V_2}^{V_1} P_{\text{ext}} \cdot dp = -\int_{V_2}^{V_1} P_{\text{int}} dv$$

$$= -\int_{V_2}^{V_1} \frac{nRT}{V} dv = -nRT \int_{V_2}^{V_1} \frac{dv}{V} = -nRT \ln\left(\frac{V_1}{V_2}\right)$$



Temperature is constant.

Que. Calculate W and ΔE for the conversion of 1 mole of water into 1 mole of steam at a temperature of 100°C and at a pressure of 1 atmosphere. Latent heat of vaporisation of water is 9720 cal/mole .

Sol. $P = 1 \text{ atm}$

$V_1 =$ volume of 1 mole of water at $100^\circ\text{C} = 18 \text{ mL}$.

$V_2 =$ volume of 1 mole of steam at 100°C

$$= \frac{373}{273} \times 22400 = 30605 \text{ mL.} \quad (\text{Charles's law})$$



Now we have,

$$W = -p (V_2 - V_1) = -1 (30605 - 18) = -30587 \text{ atm ml} = -\frac{30587}{1000} \times \frac{101.3}{4.2} \text{ cal} = -741 \text{ calories}$$

Again we have,

$$\Delta E = q + W = 9720 + (-741) = 8979 \text{ calories.}$$

Que. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 15 to 50 litres.

Sol. We have,

$$W = -2.303 n RT \log \frac{V_2}{V_1} = -2.303 \times 2 \times 2 \times 298 \times \log \frac{50}{15} = -1436 \text{ calories.}$$

Que. If a gas at a pressure of 10 atm at 300 K expands against a constant external pressure of 2 atm from a vol. of 10 litres to 20 litres find work done ? [Isothermal process]

Sol Process is irreversible

$$w = -\int_{10}^{20} 2dv = -2[20 - 10] = -20 \text{ litre atm}$$

$$1 \text{ litre atm} = 101.3 \text{ J}$$

(a) Internal Energy (E, also denoted by U) :

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy .

$$E = E_{\text{Translational}} + E_{\text{Rotational}} + E_{\text{Vibrational}} + E_{\text{bonding}} + \dots$$

$$\Delta E = E_{\text{Final}} - E_{\text{Initial}} .$$

$\Delta E = q_v$, heat supplied to a gas at constant volume, since all the heat supplied goes to increase the internal energy of the gas .

It is an extensive property & a state function . It is exclusively a function of temperature.

If $\Delta T = 0$; $\Delta E = 0$ as well.

(b) Heat Supplied (q) :

The energy which crosses the system boundary on account of temperature difference between the system & its surroundings . It is a path function .

First Law Of Thermodynamics :

It is simply law of conservation of energy . Whenever energy of a particular form disappears, an exactly equivalent amount of another form must appear .

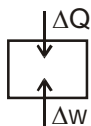
Mathematically, it is written as :

These three terms are of crucial importance & are defined as :

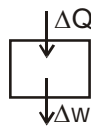
$$\Delta U = \Delta Q + \Delta W$$

Law of conservation of energy says that the total energy of the universe is constant.

According to Chemistry :



$$\Delta U = \Delta Q + \Delta W$$



$$\Delta U = \Delta Q - \Delta W$$

IUPAC convention

1. Heat given to the system = +ve

2. Heat coming out of the system = -ve
3. Work done on the system = +ve
4. Work done by the system = -ve

Application of 1st Law

$$\Delta U = \Delta Q + \Delta W \quad \Rightarrow \quad \Delta W = -P \Delta V$$

$$\therefore \Delta U = \Delta Q - P \Delta V$$

(i) Constant vol. Process

$$\Delta U = \Delta Q - P (\Delta V) \quad C_V = \text{molar heat capacity of constant volume}$$

$$\Delta U = \Delta Q_V \quad \Rightarrow \quad \Delta U = nC_V \Delta T$$

$$\Delta U = nC_V \Delta T \quad \Rightarrow \quad C_V = \frac{1}{n} \cdot \frac{dU}{dT} = \frac{1}{n} \left[\frac{dQ}{dT} \right]_V$$

(ii) Constant pressure Process

$$\Delta U = \Delta Q + \Delta W \quad \text{or} \quad \Delta U = \Delta Q - P \Delta V$$

Introducing a new thermodynamics

$$H = U + PV \quad H : \text{enthalpy}$$

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

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

$\Delta H = \Delta Q$ at constant pressure

$$\Delta H = (\Delta Q)_P = (n.C. \Delta T)_P \quad \Rightarrow \quad \Delta H = n.C_p. \Delta T$$

Que. Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 to 1 atm at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy? Also, calculate 'q'.

Sol. We have,

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

$$n = \text{number of moles of hydrogen} = \frac{\text{wt. in grams}}{\text{mol. wt.}} = \frac{10}{2} = 5 \text{ moles.}$$

$$\text{Thus } W = -2.303 \times 5 \times 2 \times 273 \times \log \frac{20}{1} = -8180 \text{ calories.}$$

further, the change in state of the system is from a gas to a gas and therefore, at constant temperature, internal energy will not change i.e.,

$$\Delta E = 0.$$

$$\text{Again, } q = \Delta E - W = 0 - (-8180) = 8180 \text{ calories.}$$

Reversible and irreversible isochoric processes.

$$\text{Since } dV = 0$$

$$\text{So } dW = -P_{\text{ext}} \cdot dV = 0.$$

Reversible isobaric process :

$$\text{Isobaric, } P_{\text{gas}} = \text{constant}$$

Since pressure of gas is defined during whole of the process and hence the process must be reversible

$$\text{So due} = -P_{\text{ext}} dV = -P_{\text{gas}} dV$$

$$= - \int_{V_i}^{V_f} dV \quad W = P (V_f - V_i)$$



Adiabatic Process :

Adiabatic reversible expansion –

$dQ = 0$ (no heat changed b/w) system and sorrods

$$du = dQ + dW$$

$$\Rightarrow nC_v d_T = -PdV$$

$$\Rightarrow \int nC_v d_T = \int -\frac{nRT}{V} \cdot dv$$

$$\Rightarrow \int_{T_1}^{T_2} \frac{C_v \cdot dT}{T} = - \int_{V_1}^{V_2} \frac{R}{V} \cdot dT$$

$$\Rightarrow C_v \ln \frac{T_2}{T_1} = -P \ln \frac{V_2}{V_1}$$

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{V_2}{V_1} \right)^{-R/C_v}$$

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

$$\text{or } T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$PV^\gamma = \text{constant}$$

Operation of adiabatic process

(i) Reversible Adiabatic

operation wise adiabatic process and isothermal process are similar hence all the criteria that is used for judging an isothermal irreversible processes are applicable to adiabatic process also volume in case of isothermal volume is more than that of adiabatic at contant pressure and no of moles, $V \propto T$

$$w = - \int P_{\text{ext}} \cdot dv$$

$$\text{but } P_{\text{ext}} = P_{\text{int}} = \frac{K}{V^\gamma}$$

$$\therefore w = - \int \frac{K}{V^\gamma} \cdot dv$$

$$\Rightarrow -K \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right] / (1-\gamma)$$

$$\text{as } K = P_2 V_2^\gamma = P_1 V_1^\gamma$$

$$= \frac{P_2 V_2^\gamma \cdot V_2^{1-\gamma} - P_1 V_1^\gamma \cdot V_1^{1-\gamma}}{\gamma-1}$$

$$\Rightarrow \frac{P_2 V_2 - P_1 V_1}{\gamma-1} = \text{work done}$$

(ii) Irreversible Adiabatic

$$W = \int -P_{\text{ext}} \cdot dv$$



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

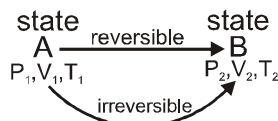
$$\text{or } \int du = \int dw$$

$$\therefore w = \Delta u$$

$$w = nC_v (T_2 - T_1)$$

$$= \frac{nR(T_2 - T_1)}{\gamma - 1}$$

$$= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$



If the two states are linked by an adiabatic reversible and irreversible path then

$$w_{\text{rev.}} = \Delta u_{\text{rev.}}$$

But as u is a state function

$$\therefore \Delta u_{\text{rev.}} = \Delta u_{\text{irrev.}}$$

$$\Rightarrow w_{\text{irrev.}} = w_{\text{rev.}}$$

Enthalpy (H) :

The term $(E + PV)$ is frequently encountered in thermodynamics. It is useful to group these terms together & called it enthalpy. Enthalpy is defined as $H = E + PV$.

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

$\Delta H = q_p$, heat supplied at constant pressure.

Also remember $\Delta E = q_v$, heat supplied at constant volume.

For any reaction in general, if heat is supplied at constant pressure then it is equal to ΔH and if heat is supplied at constant volume then it is equal to ΔE .

Also note that at a given temperature : $\Delta(PV) = \Delta(nRT) = (\Delta n) RT$.

Thus $\Delta H = \Delta E + (\Delta n)_{\text{gas}} RT$.

Since we used $PV = nRT$, the ideal gas law, n refers to the number of moles of gases only and $\Delta n = (\text{total number of moles of gases})_{\text{final}} - (\text{total number of moles of gases})_{\text{initial}}$.

Thus ΔH can be greater than, equal to or less than ΔE depending upon Δn .

For solids & liquids, $\Delta H \cong \Delta E$.

For exothermic reactions, $\Delta H < 0$, since energy is lost by the system ;

For endothermic reactions, $\Delta H > 0$, since energy is gained by the system .

Temperature Dependence of ΔH : (Kirchoff's Law)

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p \cdot dT.$$

where $\Delta C_p = C_p (\text{products}) - C_p (\text{reactants})$.

e.g. for $aA + bB = cC + dD$; $\Delta C_p = cC_p(C) + dC_p(D) - aC_p(A) - bC_p(B)$

Molar Heat Capacity :

The amount of heat required to raise one mole of a substance by one celsius degree .

It is a path function. Two special cases are used, when heating is done at constant pressure (C_p) or at constant volume (C_v) .

$$C_p = \frac{dq_p}{dT} = \frac{dH}{dT} \quad ; \quad C_v = \frac{dq_v}{dT} = \frac{dE}{dT}$$

In general, heat capacity $c = \frac{dq}{dT}$.

For n moles $q = nC\Delta T$. $C_p - C_v = R$.

Important : It is useful to remember the value of R in different units.

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

$$= 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 0.082 \text{ (lit. atm) mol}^{-1} \text{ K}^{-1} . \quad \frac{C_p}{C_v} = \gamma , \text{ the Poisson's ratio .}$$

Note : Since heat capacity varies with temperature, in some cases a mean value is given which can be taken to be constant over the required temperature ranges . This is called **mean molar heat capacity** .

Dulong And Petit's Law : Molar heat capacity of any metallic element is $\cong 6 \text{ cal/mol}$.

Thermochemistry :

Deals primarily with the transfer of heat between a chemical system and its surroundings when a change of phase or a chemical reaction takes place with the system.

Enthalpy of a substance :

Every substance has a fixed value of enthalpy under any particular state. Through 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

Enthalpy of formation :

The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value. The specified temperature is usually taken as 25 °C.

A few examples are $\Delta H_f^\circ (\text{O}_2, \text{g}) = 0$

$$\Delta H_f^\circ (\text{C, graphite}) = 0 \quad \Delta H_f^\circ (\text{C, diamond}) \neq 0$$

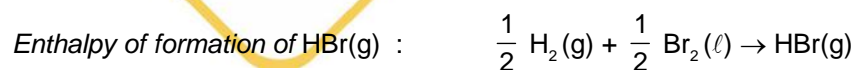
$$\Delta H_f^\circ (\text{Br}_2, \ell) = 0$$

$$\Delta H_f^\circ (\text{S, rhombic}) = 0 \quad \Delta H_f^\circ (\text{S, monoclinic}) \neq 0$$

$$\Delta H_f^\circ (\text{P, white}) = 0 \quad \Delta H_f^\circ (\text{P, black}) \neq 0$$

The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation.

The chemical equations corresponding to enthalpy of formation of few substances are given below.



$$\Delta H_f^\circ(\text{HBr, g}) = \sum n_B H_m^\circ(\text{B}) = H_f^\circ(\text{HBr, g}) - \frac{1}{2} H_f^\circ(\text{H}_2, \text{g}) - \frac{1}{2} H_f^\circ(\text{Br}_2, \ell) \quad \dots(1)$$



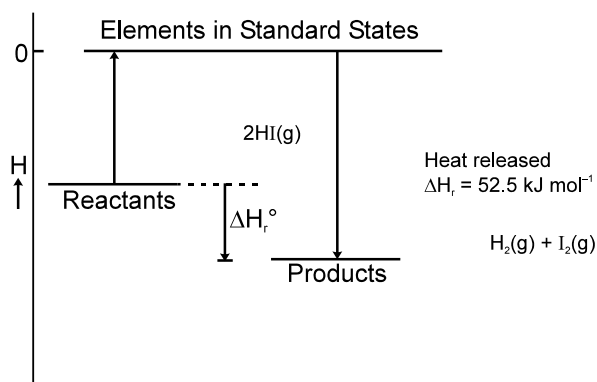
$$\Delta H_f^\circ(\text{SO}_2, \text{g}) = H_f^\circ(\text{SO}_2, \text{g}) - H_f^\circ(\text{S, rhombic}) - H_f^\circ(\text{O}_2, \text{g}) \quad \dots(2)$$

Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

$$\Delta H_r^\circ = \sum n_B \Delta H_f^\circ \text{ , products} - \sum n_B \Delta H_f^\circ \text{ , reactants} \quad n_B \text{ is the stoichiometric coefficient}$$

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

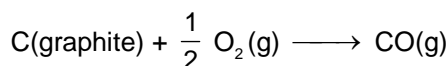


Enthalpy of Reaction

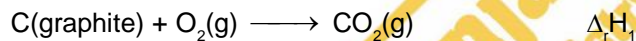
Hess's Law of Constant Heat Summation :

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

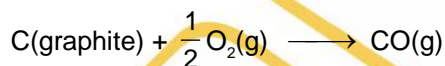
One of the important applications of Hess's law is to determine enthalpy of reaction which is difficult to determine experimentally. For example, the value $\Delta_r H$ for the reaction



which is difficult to determine experimentally, can be estimated from the following two reactions for which $\Delta_r H$ can be determined experimentally.



Subtracting the latter from the former, we get

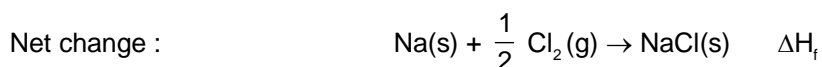


Consequently, $\Delta_r H = \Delta_r H_1 - \Delta_r H_2$

Lattice Energy of a Crystal (Born-Haber Cycle) :

The lattice energy is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous ions. The larger the lattice energy, the more stable the ionic compound and the more tightly the ions held. Consider the following sequence of steps for the formation of NaCl crystals from Na(s) and Cl₂(g)

(i)	Vaporization of Na(s)	$\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g})$	ΔH_{sub}
(ii)	Ionization of Na(g)	$\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$	ΔH_{ion}
(iii)	Dissociation of chlorine	$\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$	ΔH_{diss}
(iv)	Formation of Cl ⁻ (g)	$\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$	$\Delta H_{\text{electron gain}}$
(v)	Condensation of Na ⁺ (g) and Cl ⁻ (g)	$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$	$\Delta H_{\text{lattice}}$



Hess's law, we can write $\Delta H_f = \Delta H_{\text{sub}} + \Delta H_{\text{ion}} + \Delta H_{\text{diss}} + \Delta H_{\text{electron gain}} + \Delta H_{\text{lattice}}$

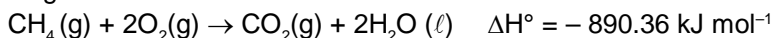
All other enthalpies can be determined experimentally. Hence, $\Delta H_{\text{lattice}}$ can be determined from the above relation. The lattice energy is the negative of $\Delta H_{\text{lattice}}$ value.



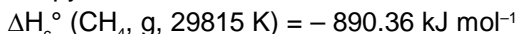
Enthalpy of Combustion :

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.

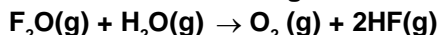
For example, the standard enthalpy of combustion of methane at 298.15 K is $-890.36 \text{ kJ mol}^{-1}$. This implies the following reaction :



The standard enthalpy of combustion of methane at 298.15 K may be written as

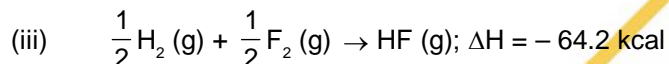
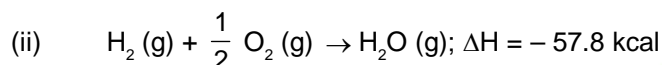
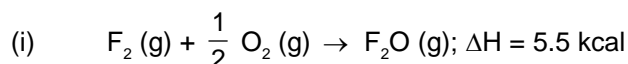


Que. Calculate heat of the following reaction at constant pressure,



The heats of formation of $\text{F}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and $\text{HF}(\text{g})$ are 5.5 kcal, -57.8 kcal and 64.2 kcal respectively.

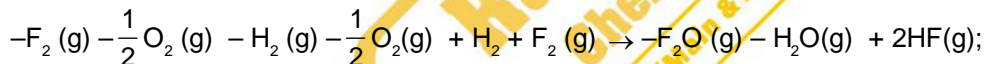
Sol. Given that



F_2O and H_2O in equation (i) and (ii) and in the equation given in the problem are on the opposite sides, while HF in equation (iii) and in the equation given in the problem is on the same sides.

Thus applying,

[- Eqn. (i) - Eqn. (ii) + 2 × Eqn. (iii)], we get

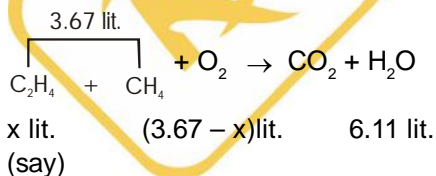


$$\Delta H = -5.5 - (-57.8) + 2 \times (-64.2)$$

$$\text{or } \text{F}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{O}_2(\text{g}) + 2\text{HF}(\text{g}); \Delta H = -76.1 \text{ kcal.}$$

Que. A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2 . find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol^{-1} at 25°C . [IIT 1991]

Sol.



or x moles $(3.67 - x)$ moles 6.11 moles

Applying POAC for C atoms,

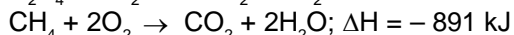
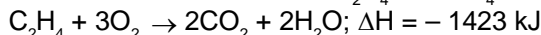
$$2 \times x + 1 \times (3.67 - x) = 1 \times 6.11; x = 2.44 \text{ lit.}$$

Thus, the volume of $\text{C}_2\text{H}_4 = 2.44$ lit., and volume of $\text{CH}_4 = 1.23$ lit.

$$\therefore \text{volume of } \text{C}_2\text{H}_4 \text{ in a 1-litre mixture} = \frac{2.44}{3.67} = 0.665 \text{ lit.}$$

and volume of CH_4 in a 1-litre mixture = $1 - 0.665 = 0.335$ lit.

Now, thermochemical reactions for C_2H_4 and CH_4 are



As ΔH values given are at 25°C , let us first calculate the volume occupied by one mole of any gas at 25°C

(supposing pressure as 1 atm)

$$\text{Volume per mole at } 25^{\circ}\text{C} = \frac{298}{273} \times 22.4 = 24.45 \text{ lit.}$$

$$\text{Thus, heat evolved in the combustion of } 0.665 \text{ lit. of } \text{C}_2\text{H}_4 = -\frac{1423}{24.45} \times 0.665 = -38.70 \text{ kJ}$$

$$\text{and heat evolved in the combustion of } 0.335 \text{ lit. of } \text{CH}_4 = \frac{891}{24.45} \times 0.335 = -12.20 \text{ kJ.}$$

\therefore total heat evolved in the combustion of 1 litre of the mixture = $-38.70 + (-12.20) = -50.90 \text{ kJ.}$

Enthalpy of Dilution :

The enthalpy of dilution is the change in enthalpy when a solution containing 1 mole of solute is diluted from one concentration to another for example for the reaction

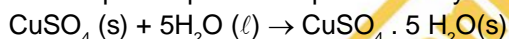
$\text{HCl} \cdot 40 \text{ H}_2\text{O} + \text{aq} \rightarrow \text{HCl} (\text{aq}),$ the enthalpy change can be calculated as follows



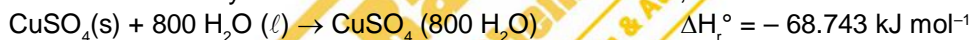
Subtracting, we have $\text{HCl} \cdot 40 \text{ H}_2\text{O} + \text{aq} \rightarrow \text{HCl} (\text{aq}) \quad \Delta H_r = -2.122 \text{ kJ mol}^{-1}$

Enthalpy of Hydration :

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



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



by subtraction, we get $\text{CuSO}_4 (\text{s}) + 5 \text{ H}_2\text{O} (\ell) \rightarrow \text{CuSO}_4 \cdot 5 \text{ H}_2\text{O} (\text{s}) \Delta H_r^{\circ} = -78.868 \text{ kJ mol}^{-1}$

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.

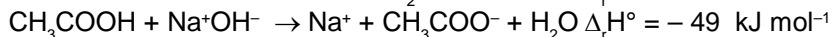
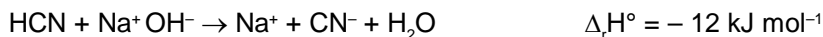


for $\text{SA} + \text{SB}$ this heat of neutralisation is always equal to -13.7 kcal/mole or -57.1 kJ/mole .

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

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 these acids and bases this heat is known as enthalpy of ionization. Examples are :



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

- (i) Ionization $\text{HCN} \longrightarrow \text{H}^+ + \text{CN}^- \quad \Delta H_1^\circ = x$
 (ii) Neutralization $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} \quad \Delta H_2^\circ = -57.1 \text{ kJ/mole}$
 The complete reaction is obtained by adding the above two steps. Thus



Obviously,

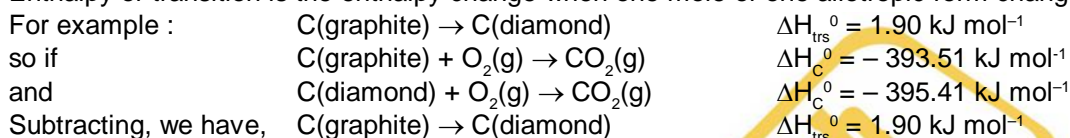
$$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ$$

$$\Delta H_1^\circ = \Delta H^\circ - \Delta H_2^\circ = [-12 - (-57.1)] = 45.1 \text{ kJ/mole}$$

Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.

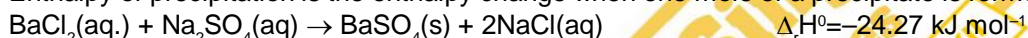
Enthalpy of Transition :

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



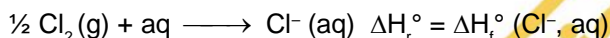
Enthalpy of Precipitation :

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

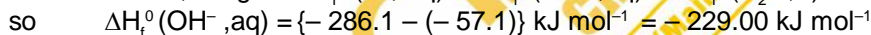
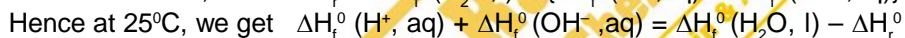
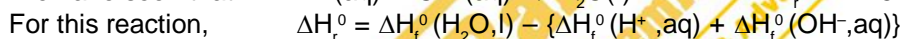
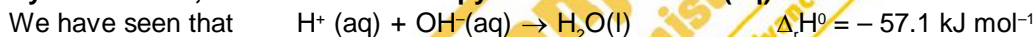


Enthalpy of Formation of ions :

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



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



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.



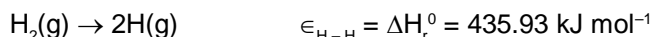
However, to break the O-H bond in the hydroxyl radical required a different quantity of heat :



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

$$\epsilon_{\text{OH}} = \frac{501.87 \text{ mol}^{-1} + 423.38 \text{ kJ mol}^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

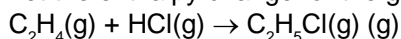
In the case of diatomic molecules, such as H_2 , the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.



Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthalpies 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



be required from the bond enthalpy data. This may be calculated as follows :

$$\Delta H = \left(\begin{array}{l} \text{Enthalpy required to} \\ \text{break reactants into} \\ \text{gaseous atoms} \end{array} \right) - \left(\begin{array}{l} \text{Enthalpy released to} \\ \text{form products from the} \\ \text{gaseous atoms} \end{array} \right)$$



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

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

Resonance Energy :

$$\Delta H^{\circ}_{\text{resonance}} = \Delta H^{\circ}_{f, \text{experimental}} - \Delta H^{\circ}_{f, \text{calculated}}$$

$$= \Delta H^{\circ}_{c, \text{calculated}} - \Delta H^{\circ}_{c, \text{experimental}}$$

Que. Calculate the heat of formation of benzene from the following data, assuming no resonance.

Bond energies :

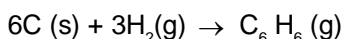
$$C - C = 83 \text{ kcal} \quad C = C = 140 \text{ kcal}$$

$$C - H = 99 \text{ kcal}$$

Heat of atomisation of C = 170.9 kcal

Heat of atomisation of H = 52.1 kcal

Sol. We have to calculate ΔH for the reaction



For reactants :

Heat of atomisation of 6 moles of C = 6×170.9 kcal

Heat of atomisation of 6 moles of H = 6×52.1 kcal

For products :

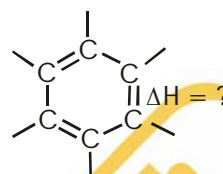
Heat of formation of 6 moles of C - H bonds = -6×99

Heat of formation of 3 moles of C-C = -3×83

Heat of formation of 3 moles of C = C bonds = -3×140

on adding, we get heat of formation of C_6H_6 , i.e.,

$$\Delta H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = 75.0 \text{ kcal}$$



Relation between Energy and Enthalpy of a Reaction :

$$\Delta_r H = \Delta_r U + (\Delta n_g)RT$$

where Δn_g is the change in the stoichiometric number of gaseous species in going from reactants to products.

It should be noted that while computing Δn_g of a reaction, only the stoichiometric numbers of gaseous is counted and those of liquids and solids are completely ignored.

Spontaneous /Natural /Irreversible Processes :

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

Second law of thermodynamics :

Entropy of the universe is constantly increasing.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \quad \text{for a spontaneous process.}$$

Where (**S**) = entropy is the measure of randomness or disorder. It is a state function and extensive property.

Mathematically

$$ds = \frac{dq_{\text{rev}}}{T} \quad \text{or} \quad \Delta S = \int \frac{dq_{\text{rev}}}{T}$$

dq is state function only for reversible process

$$dS \propto dq_{rev}, dS \propto \frac{1}{T}$$

At Higher T - entropy is already high. Therefore heat addition will not introduce much change in the entropy.

Entropy calculation :

- ◆ **For calculating $\Delta S_{\text{surrounding}}$** : As the surrounding is an infinite heat reservoir hence no. amount of heat given to the surrounding can cause turbulence in it, hence all heat exchanges with surroundings are considered to be reversible.

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

For surrounding T is constant

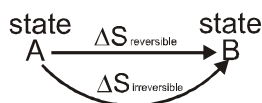
$$\begin{aligned} \therefore \Delta S_{\text{surr}} &= \frac{1}{T} \int dq_{\text{surr}} \\ &= \frac{q_{\text{surrounding}}}{T} \end{aligned}$$

By the law of conservation of energy

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

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

- ◆ **For ΔS_{system}**



As 'S' is a state function 'ΔS' will not depend on path.

$$\therefore \Delta S_{\text{irrev}} = \Delta S_{\text{rev}}$$

$$\Delta S = \int_A^B \frac{dq_{\text{rev}}}{T} \text{ reversible path}$$

- ◆ **For Phase Transformations**

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

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

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

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

$$\text{for constant Pressure, } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\text{for constant Volume, } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$



◆ Entropy calculation for an ideal gas undergoing a process.

State A $\xrightarrow[\Delta S_{\text{irr}}]{\text{irr}}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

As 's' is a state function ΔS will not depend upon path

$$\Delta S_{\text{irr}} = \Delta S_{\text{rev, system}} = \int_A^B \frac{dq_{\text{rev}}}{T} \text{ rev path.}$$

from the first law

$$du = dQ + dw$$

$$dQ = du - dw$$

for reversible path

$$dq = dq_{\text{rev}}$$

$$dQ_{\text{rev}} = du + P_{\text{gas}} dv \quad \{P_{\text{ext}} = P_{\text{gas}} \text{ reversible}\}$$

$$\Delta S_{\text{rev, system}} = \int_A^B \frac{du + P_{\text{gas}} dv}{T}$$

for an ideal gas

$$\frac{P_{\text{gas}}}{T} = \frac{nR}{V} \quad \& \quad du = nc_v dT$$

$$\therefore \Delta S_{\text{sys}} = \int_{T_1}^{T_2} \frac{nc_v dT}{T} + \int_{V_1}^{V_2} \frac{nR dv}{V}$$

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

Isothermal process :

(a) Reversible

State A $\xrightarrow{\text{Rev}}$ State B

P_1, V_1, T P_2, V_2, T

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

↓
0

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

FLOT $du = dq + dw$

$$\therefore dq = -dw$$

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

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

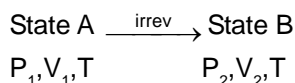


$$\therefore \Delta S_{\text{sys.}} = \frac{-nRT \ln \frac{V_2}{V_1}}{T} = -nR \ln \frac{V_2}{V_1}$$

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

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

(b) **Irreversible** →



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

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

q_{system} is calculated using FLOT

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

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

$$\Delta S_{\text{universe}} = nR \ln \frac{V_2}{V_1} - \frac{-P_{\text{ext}}(V_2 - V_1)}{T} > 0$$

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

As irreversible work of gas is less than reversible work.

Adiabatic Process

(a) **Reversible Adiabatic**



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

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

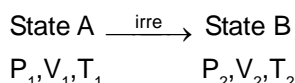
$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

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

$$\Delta S_{\text{surr}} = -\frac{\Delta q}{T} = 0$$

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

(b) **Irreversible Adiabatic**



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



$$\Delta S_{\text{system}} = nC_V \ln \frac{T_2}{T_1} + nr \ln \frac{V_2}{V_1} > 0 \quad [(T_2)_{\text{irrev}} > (T_2)_{\text{rev}}]$$

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

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

Que. (a) One mole of an ideal gas expands isothermally and reversibly at 25°C from a volume of 10 litres to a volume of 20 litres.

(i) What is the change in entropy of the gas?

(ii) How much work is done by the gas?

(iii) What is q (surroundings)?

(iv) What is the change in the entropy of the surroundings?

(v) What is the change in the entropy of the system plus the surroundings?

(b) Also answer the questions opening a stopcock and allowing the gas to rush into an evacuated bulb of 10-L volume.

Sol. (a) (i) $\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76 \text{ J/K.}$

(ii) $W_{\text{rev}} = -2.303nRT \log \frac{V_2}{V_1}$

$$= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10} = -1781 \text{ J.}$$

(iii) For isothermal process, $\Delta E = 0$ and heat is absorbed by the gas,

$$q_{\text{rev}} = \Delta E - W = 0 - (-1718) = 1718 \text{ J.}$$

∴ $q_{\text{rev}} = 1718 \text{ J.}$ (∴ process is reversible)

(iv) $\Delta S_{\text{surr}} = -\frac{1718}{298} = -5.76 \text{ J/K.}$

As entropy of the system increases by 5.76 J, the entropy of the surroundings decreases by 5.76J, since the process is carried out reversibly.

(v) $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ for reversible process

(b) (i) $\Delta S = 5.76 \text{ J/K,}$ which is the same as above because S is a state function

(ii) $W = 0$ (∴ $p_{\text{ext}} = 0$)

(iii) No heat is exchanged with the surroundings.

(iv) $\Delta S_{\text{surr}} = 0.$

(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increase in an irreversible process.

Third Law Of Thermodynamics :

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

Gibb's free energy (G) :

A system parameter to predict the spontaneity of chemical reaction was introduced by Gibb's so that entropy calculation for the surrounding need not be carried out.



for a spontaneous change

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{surr}} = \frac{-Q_{\text{system}}}{T} = -\frac{-\Delta H_{\text{system}}}{T}$$

$$T\Delta S_{\text{univ}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}}$$

Introducing a new thermodynamic function $G =$ Gibbs's free energy (State function and an extensive property)

$$\begin{aligned} G_{\text{system}} &= H_{\text{system}} - TS_{\text{system}} \\ \therefore \Delta G &= \Delta H - T\Delta S \\ \Delta G_{\text{system}} &= \Delta H_{\text{system}} - T\Delta S_{\text{system}} \dots\dots\dots (ii) \end{aligned}$$

Comparing equation (i) and (ii)

$$\Delta G_{\text{system}} = -T\Delta S_{\text{universe}}$$

New criteria of spontaneity :

- (i) If ΔG_{system} is $(-ve) < 0 \Rightarrow$ process is spontaneous
- (ii) If ΔG_{system} is $> 0 \Rightarrow$ process is non spontaneous
- (iii) If $\Delta G_{\text{system}} = 0 \Rightarrow$ system is at equilibrium

So at every temperature $\Delta G \neq 0$

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

+ Ve	- Ve	+	
- Ve	+ Ve	-	
+ Ve	+ Ve	-	at high temperature
- Ve	- Ve	+	at high temperature

Physical interpretation of ΔG .

The free energy change of a process symbolises the maximum amount of non-expansional (compression) work which can be performed.

$$\begin{aligned} du &= dq + dw \\ \therefore du &= dq + dw_{\text{expon}} + dw_{\text{exp}} \\ dw_{\text{non-exp}} &= du - dq - dw_{\text{exp}} \\ \Rightarrow dw_{\text{non-exp}} &= du - dq + PdV \quad \Rightarrow \quad dw_{\text{non-exp}} = dH - dq \end{aligned}$$

For maximum work of non expansion the process should be reversible isobaric.

$$\begin{aligned} \therefore dq &= dq_{\text{rev}} = T.dS \\ dw_{\text{non-exp}} &= dH - TdS = \Delta G \end{aligned}$$





TOPIC WISE MCQS

Enthalpy change & Internal energy change

01. The heat of reaction at constant volume (ΔE) and that at constant pressure (ΔH) are related as -
(A) $\Delta E = \Delta H + \Delta nRT$
(B) $\Delta H = \Delta E - \Delta nRT$
(C) $\Delta H = \Delta E + \Delta nRT$
(D) $\Delta H = \Delta E + nRT$
02. For hypothetical reaction -
 $A(g) + B(g) \rightarrow C(g) + D(g)$
Which of the following statements is correct -
(A) $\Delta H = \Delta E$ (B) $\Delta H > \Delta E$
(C) $\Delta H < \Delta E$ (D) unpredictable
03. When two ideal liquids are mixed, the enthalpy of the system -
(A) Decreases (B) Increase
(C) Remains unaffected
(D) May increase or decrease
04. Select the correct order in the following :
(A) 1 erg > 1 joule > 1 cal
(B) 1 cal > 1 joule > 1 erg
(C) 1 erg > 1 cal > 1 joule
(D) 1 joule > 1 cal > 1 erg
05. Which among the following is not a state function -
(A) Internal energy (B) Free energy
(C) Work (D) Enthalpy
06. A state function is that -
(A) Which is used in thermochemistry
(B) Which obeys all the laws of thermodynamics
(C) Quantity whose value depends only on the state of the system
(D) Quantity which is used in measuring thermal change
07. Difference between ΔH and ΔE for the combustion of liquid benzene at 27°C is -
(A) 7.48 kJ (B) 3.74 kJ
(C) 14.86 kJ (D) 5.73 kJ
08. For a chemical reaction,
 $2A_2(g) + 5B_2(g) \longrightarrow 2A_2B_5(g)$,
at 27°C the difference between ΔH and ΔE is X. Then the ratio X/R -
(A) Zero (B) Unity (C)
(C) -5×10^0 (D) -1.5×10^3

09. One litre-atmosphere is approximately equal to -
(A) 19.2 J (B) 101 J
(C) 8.31 J (D) 831 J

Heat of reactions

10. In the combustion of 4g. of CH_4 , 2.5 K cal of heat is if liberated. The heat of combustion of CH_4 is -
(A) 20 K. cal (B) 10 K. cal
(C) 2.5 K. cal (D) 5 K. cal
11. Ammonium nitrate Can decompose with explosion by the following reaction.
 $\text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}$;
 $\Delta H = -37.0 \text{ KJ/mol}$
Calculate the heat produced when 2.50g of NH_4NO_3 decomposes -
(A) 1.06 KJ (B) 0.96KJ
(C) 1.16 KJ (D) 1.26 KJ
12. When ammonium chloride is dissolved in water, the solution becomes cold. The change is -
(A) Endothermic (B) Exothermic
(C) Supercooling (D) None of the above
13. The enthalpies of all elements in their standard states are -
(A) unity (B) zero
(C) < 0 (D) > 0
14. For the process, melting of ice at 260 K the ΔH is -
(A) Negative (B) Positive
(C) Zero (D) Cannot be predicted
15. Enthalpy of formation of compound is -
(A) always positive
(B) always negative
(C) can be either negative or zero
(D) can be positive or negative
16. The enthalpy of combustion of a substance -
(A) is always positive
(B) is always negative
(C) can be either zero or greater than zero
(D) is unpredictable till calculations are done.
17. $\text{HA} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{A}^- + q_1 \text{ kJ}$
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + q_2 \text{ kJ}$
The enthalpy of dissociation of HA is
(A) $(q_1 + q_2)$ (B) $(q_1 - q_2)$
(C) $(q_2 - q_1)$ (D) $-(q_1 + q_2)$



18. For which of the following processes will energy be absorbed -
(A) Separating an electron from an electron
(B) Separating proton from a proton
(C) Separating a neutron from neutron
(D) Separating an electron from neutral atom
19. The value of ΔH_{sol} of $\text{BaCl}_2(\text{s})$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ are $-a$ kJ and b kJ respectively. The value of $\Delta H_{\text{Hydration}}$ of $\text{BaCl}_2(\text{s})$ is -
(A) $b - a$ (B) $a + b$
(C) $-a - b$ (D) $a - b$
20. The heats of neutralisation of four acids a, b, c and d when neutralised against a common strong base are 13.7, 9.4, 11.2 and 12.4 kcal respectively. The weakest among these acids is
(A) a (B) b (C) c (D) d
21. The heat of neutralization of HCN by NaOH is 13.3 KJ/mole, the energy of dissociation of HCN is -
(A) 43.8 KJ (B) -43.8 KJ
(C) -68 KJ (D) 68 KJ
22. A solution of 500 ml of 0.2 M KOH and 500 ml of 0.2 M HCl is mixed and stirred; the rise in temperature is T_1 . The experiment is repeated using 250 ml each of solution, the temperature raised is T_2 . Which of the following is true -
(A) $T_1 = T_2$ (B) $T_1 = 2T_2$
(C) $T_1 = 4T_2$ (D) $T_2 = 9T_1$
23. In decomposition reactions enthalpy of products is mostly.....than the enthalpy of reactants?
(A) Greater (B) Lesser
(C) Constant (D) Infinite
24. The enthalpy of formation of ammonia is -46.0 kJ mol^{-1} . The enthalpy for the reaction $2\text{N}_2(\text{g}) + 6\text{H}_2(\text{g}) \rightarrow 4\text{NH}_3(\text{g})$ is equal to -
(A) -46.0 kJ (B) 46.0 kJ
(C) 184.0 kJ (D) -184.0 kJ
- ### Hess's Law
25. 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 -
(A) Hess's law (B) Law of conversion of energy
(C) Henry's law (D) Joule's principle
26. According to Hess's Law the thermal effect of a reaction depends on -
(A) initial concentration of reactants
(B) final condition of the reacting substance
(C) intermediate states of a reaction
(D) initial and final conditions of the reacting substances
- ### Entropy & Free energy change
27. When the egg is hard boiled, there is -
(A) Increase in disorder
(B) Decrease in disorder
(C) No change in disorder
(D) ΔG is negative
28. Free energy change of reversible reaction at equilibrium is -
(A) Infinite (B) Zero
(C) Positive (D) Negative
29. Which one of the following is correct -
(A) $-\Delta G = \Delta H - T\Delta S$ (B) $\Delta H = \Delta G - T\Delta S$
(C) $\Delta S = \frac{1}{T}[\Delta G - \Delta H]$ (D) $\Delta S = \frac{1}{T}[\Delta H - \Delta G]$
30. Which of the following has highest entropy -
(A) Water (B) Graphite
(C) Mercury (D) Hydrogen
31. For the reversible vapourisation of water at 100°C and 1 atmospheric pressure. ΔG is equal to?
(A) ΔH (B) ΔS
(C) Zero (D) $\Delta H/T$
32. The least random state of H_2O system is -
(A) Ice
(B) liquid water
(C) Steam
(D) Randomness is same in all
33. For the process -
 $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$
(A) Both ΔH and ΔS are positive
(B) ΔH is negative and ΔS is positive
(C) ΔH is positive and ΔS is negative
(D) Both ΔH and ΔS are negative
34. Calculate the temperature at which $\Delta G = -5.2$ kJ mol^{-1} $\Delta H = 145.6$ kJ mol^{-1} and $\Delta S = 216$ JK $^{-1}$ mol^{-1} for a chemical reaction -
(A) 698°C (B) 425°C
(C) 650 K (D) 650°C
35. If the enthalpy of vapourisation of water is 186.5 J mol^{-1} , the entropy of its vaporisation will be -
(A) 0.5 JK $^{-1}$ mol^{-1} (B) 1.0 JK $^{-1}$ mol^{-1}
(C) 1.5 JK $^{-1}$ mol^{-1} (D) 2.0 JK $^{-1}$ mol^{-1}
36. For the reaction
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ the entropy-
(A) increases
(B) decreases
(C) remains unchanged
(D) change cannot be predicted

**Laws of thermodynamics**

37. A gas is allowed to expand at constant pressure from a volume of 1.0 litre to 10.0 litre against an external pressure of 0.50 atm. If the gas absorbs 250 J of heat from the surroundings, what are the values of q , w and ΔE ? (Given 1 L atm = 101 J)

q	w	ΔE
(A) 250 J	-455 J	-205 J
(B) -250 J	-455 J	-710 J
(C) 250 J	455 J	710 J
(D) -250 J	455 J	205 J

38. Which law of thermodynamics introduces the concept of entropy?

- (A) First law (B) Zeroth law
(C) Third law (D) Second law

39. The total entropy change for a system and its surroundings increases, if the process is

- (A) Reversible (B) Irreversible
(C) Exothermic (D) Endothermic

40. Which of the following state function is not zero at standard state -

- (A) Enthalpy
(B) Entropy
(C) Free energy
(D) Entropy and enthalpy

41. In any natural process -

- (A) The entropy of the universe remains constant
(B) The entropy of universe tends towards maximum.
(C) The entropy of universe tends towards minimum.
(D) Any of the above can happen

42. Which law of thermodynamics helps in calculating the absolute entropies of various substances at different temperatures -

- (A) First law (B) Second law
(C) Third law (D) Zeroth law

43. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is ($R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$) -

- (A) 163.7 cal (B) zero
(C) 138.1 cal (D) 9 lit atm.

44. An ideal gas expands in volume from $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work done is -

- (A) -900 J (B) -900 kJ
(C) 270 kJ (D) 900 kJ

Spontaneity

45. For the reaction between CO_2 and graphite
 $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightarrow 2\text{CO}(\text{g})$

$\Delta H = +170.0 \text{ kJ}$ and $\Delta S = 170 \text{ JK}^{-1}$. The reaction is spontaneous at -

- (A) 298 K (B) 500 K
(C) 900 K (D) 1200 K.

46. An exothermic reaction has a large positive entropy change. The reaction will be -

- (A) Possible at all temperatures
(B) Possible at low temperatures only
(C) impossible at all temperatures
(D) Possible at high temperatures only

47. For precipitation reaction of Ag^+ ions with AgCl -

- (A) $\Delta H = 0$ (B) $\Delta G = 0$
(C) $\Delta G = -ve$ (D) $\Delta H = \Delta G$

48. For the spontaneity of a reaction, which is true-

- (A) $\Delta G = +ve$, $\Delta H = +ve$
(B) $\Delta H = +ve$, $\Delta S = -ve$
(C) $\Delta G = +ve$, $\Delta H = -ve$
(D) $\Delta H = -ve$, $\Delta S = +ve$

49. Which of the following is not a spontaneous process?

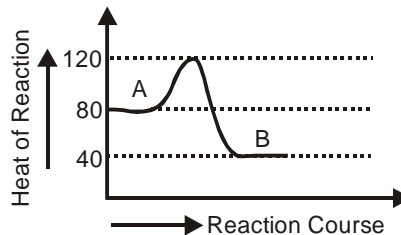
- (A) Dissolution of CuSO_4 in water
(B) Water flowing down hill
(C) Flow of current from low potential to high potential
(D) Reaction between H_2 and O_2 to form H_2O

50. The occurrence of reaction is impossible if

- (A) ΔH is +ve ; ΔS is also +ve
(B) ΔH is -ve ; ΔS is also -ve
(C) ΔH is -ve ; ΔS is +ve
(D) ΔH is +ve ; ΔS is -ve

MISCELLANEOUS QUESTIONS

01. A hypothetical reaction, $A \rightarrow 2B$, proceed through following sequence of steps -
 $A \rightarrow C$; $\Delta H = q_1$ $C \rightarrow D$; $\Delta H = q_2$
 $\frac{1}{2}D \rightarrow B$; $\Delta H = q_3$
 The heat of reaction is :
 (A) $q_1 - q_2 + 2q_3$ (B) $q_1 + q_2 - 2q_3$
 (C) $q_1 + q_2 + 2q_3$ (D) $q_1 + 2q_2 - 2q_3$
02. In a change from state A to state B -
 (A) 'q' depends only on the initial and final state
 (B) 'w' depends only on the initial and final state
 (C) ΔE depends only on the initial and final state
 (D) ΔE depends upon the path adopted by A to change into B
03. The heat of combustion of benzene determined in a bomb calorimeter is $-870 \text{ K.cal. mol}^{-1}$ at 298 K. The value of ΔE for the reaction is -
 (A) $-1740 \text{ K. cal mol}^{-1}$
 (B) $+870 \text{ K. cal mol}^{-1}$
 (C) $-870 \text{ K. cal mol}^{-1}$
 (D) $+1740 \text{ K. cal mol}^{-1}$
04. How many kcal of heat is evolved by the complete neutralisation of one mole sulphuric acid with NaOH -
 (A) 13.7 kcal (B) 27.4 kcal
 (C) 6.85 kcal (D) None of the above
05. The enthalpy of formation for $\text{C}_2\text{H}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at 25°C and 1 atm pressure by 52, -394 and -286 kJ mol^{-1} respectively. The enthalpy of combustion of $\text{C}_2\text{H}_4(\text{g})$ will be -
 (A) $+1412 \text{ kJ mol}^{-1}$ (B) $-1412 \text{ kJ mol}^{-1}$
 (C) $+141.2 \text{ kJ mol}^{-1}$ (D) $-141.2 \text{ kJ mol}^{-1}$
06. X g of ethanal (CH_3CHO) was subjected to combustion in a bomb calorimeter and the heat produced is Y joules. Then which of following is correct -
 (A) $\Delta E_{(\text{comb.})} = -Y \text{ kJ}$
 (B) $\Delta E_{(\text{comb.})} = -\frac{44Y}{X} \text{ J mol}^{-1}$
 (C) $\Delta H_{(\text{comb.})} = -\frac{44Y}{X} \text{ J mol}^{-1}$
 (D) $\Delta H_{(\text{comb.})} = -Y \text{ J mol}^{-1}$
07. Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10.00 kcal/mol . What will be the change in internal energy (ΔE of 3 mol of liquid at same temperature)-
 (A) 13.0 kcal (B) -13.0 kcal
 (C) 27.0 kcal (D) -27.0 kcal
08. Give that $\Delta H_{\text{comb.}}$ of cyclopropane is $-4000 \text{ kJ mol}^{-1}$. The amount of cyclopropane that needs to be burnt in oxygen for producing $2 \times 10^5 \text{ kJ}$ of heat is -
 (A) 20 kg (B) 2.1 kg
 (C) 21 g (D) 210 mg
09. The latent heats of fusion in J g^{-1} of five substances a (mol.mass = 18) ; b (mol. mass = 20) ; c (mol. mass = 30), d (mol. mass = 60) and e (mol. mass = 30) are respectively 80, 45, 90, 45, 45. Which of the following pair has same value of ΔH_{fusion} -
 (A) a,c (B) b,e
 (C) d,e (D) c, d
10. Given heats of combustion of CH_4 , C_2H_6 , C_3H_8 , C_8H_{18} in K. cal. mole $^{-1}$ as -210.8 , -368.4 , -526.3 , -1302.7 respectively. Decide which is a better rocket fuel -
 (A) C_8H_{18} (B) CH_4
 (C) C_3H_8 (D) C_2H_6
11. $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$; $\Delta H = -44 \text{ K. cal}$. In this reaction heat of formation of 1 mole of HCl in K. cal is -
 (A) -44.0 (B) $+44.0$
 (C) -22.0 (D) $+22.0$
12. The enthalpies of combustion of carbon and carbon monoxide are -390 KJ and -278 KJ respectively. The enthalpy of formation of CO in kJ is -
 (A) 668 (B) 112
 (C) -112 (D) -668
13. According to the diagram given below, the value of ΔH for conversion of A to B is -



- (A) -40 (B) $+40$
 (C) -120 (D) $+120$

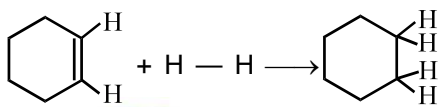


14. Heat evolved in the reaction $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ is 182 KJ. Bond energies H - H = 430 KJ/ mole, Cl - Cl = 242 KJ/ mole. The H - Cl bond energy is -
(A) 763 kJ mole⁻¹ (B) 427 kJ mole⁻¹
(C) 336 kJ mole⁻¹ (D) 154 kJ mole⁻¹
15. The work done on the system when one mole of an ideal gas at 500 K is compressed isothermally and reversibly to 1/10th of its original volume ($R = 2 \text{ cal}$) -
(A) 500 kcal (B) 1.51 kcal
(C) - 23.03 kcal (D) 2.303 kcal
16. For a certain reaction the change in enthalpy and change in entropy are 40.63 kJ mol⁻¹ and 100 JK⁻¹. What is the value of ΔG at 27°C and indicate whether the reaction is spontaneous or not -
(A) +10630 J mol⁻¹; spontaneous
(B) + 10630 J mol⁻¹; non spontaneous
(C) - 7990 J mol⁻¹; spontaneous
(D) + 7900 J mol⁻¹; spontaneous
17. Heat of neutralisation of HF is -
(A) 57.32 kJ (B) > 57.32 kJ
(C) < 57.32 (D) None
18. The heat of neutralisation is constant when dilute solution of -
(A) strong acid and strong base react
(B) strong acid and weak base react
(C) strong base and weak acid react
(D) in all the cases
19. For an endothermic reaction ΔS is positive. The reaction is -
(A) Feasible at all temperatures
(B) Feasible when $T\Delta S > \Delta H$
(C) Feasible when $\Delta H > T\Delta S$
(D) Not feasible at all
20. How much heat is liberated when 100 mL of 0.1 M NaOH are completed neutralised by 100 mL of 0.1 M HCl -
(A) - 57 kJ (B) - 0.57 kJ
(C) - 5.7 kJ (D) - 0.05 kJ
21. Calculate the bond energy of C-H bond from the following data :
(a) $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$; $\Delta H = -74.8 \text{ KJ}$
(b) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$; $\Delta H = 435.4 \text{ KJ}$
(c) $\text{C(s)} \rightarrow \text{C}(\text{g})$; $\Delta H = 718.4 \text{ KJ}$.
(A) 316.0 KJ/mol (B) 416 KJ/mol
(C) 516 KJ/mol (D) 616.0 KJ/mol
22. The heat of combustion of solid benzoic acid at constant volume is - 321.30 kJ at 27°C. The heat of combustion at constant pressure is -
(A) - 321.30 - 300 R
(B) - 321.30 + 300 R
(C) - 321.30 - 150 R
(D) - 321.30 + 900 R
23. The enthalpy of the reaction $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + 1/2 \text{O}_2(\text{g})$ is - 23.5 kcal mol⁻¹ and the enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ is - 68.3 kcal mol⁻¹. The enthalpy of formation of $\text{H}_2\text{O}_2(\text{l})$ is -
(A) - 44.8 kcal mol⁻¹ (B) 44.8 kcal mol⁻¹
(C) - 91.8 kcal mol⁻¹ (D) 91.8 kcal mol⁻¹
24. The heat of combustion of ethanol determined in a bomb calorimeter is - 670.48 K. cal mole⁻¹ at 25°C. What is ΔE at 25°C for the reaction -
(A) - 335.24 K cal (B) - 669.28 K cal
(C) - 670.48 K cal (D) + 670.48 K cal
25. The difference between ΔH and ΔE at constant volume is equal to -
(A) R (B) $P\Delta V$ (C) $V\Delta P$ (D) $3/2 R$.
26. Enthalpy change of the reaction $2\text{H}(\text{g}) \rightarrow \text{H}_2(\text{g})$ is - 104 kcal. The H - H bond dissociation energy is
(A) 104 kcal (B) -104 kcal
(C) - 52 kcal (D) + 52 kcal
27. If for $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$; ΔH_1 is enthalpy of reaction and for $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ ΔH_2 is enthalpy of reaction. Then magnitude of -
(A) $\Delta H_1 > \Delta H_2$ (B) $\Delta H_1 = \Delta H_2$
(C) $\Delta H_1 < \Delta H_2$ (D) $\Delta H_1 + \Delta H_2 = 0$.
28. The heat change for the reaction $\text{C}(\text{s}) + 2\text{S}(\text{s}) \rightarrow \text{CS}_2(\text{l})$ is called -
(A) Heat of transition
(B) Heat of fusion
(C) Heat of formation
(D) Heat of combustion.
29. The solubility of NaCl in water at 25°C is about 6 moles per litre. Suppose you add 1 mole of NaCl to a litre of water. For the reaction, $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{Salt solution}$ -
(A) $\Delta G > 0$, $\Delta S > 0$ (B) $\Delta G < 0$, $\Delta S > 0$
(C) $\Delta G > 0$, $\Delta S < 0$ (D) $\Delta G < 0$, $\Delta S < 0$



30. For a reversible reaction at equilibrium ΔG is -
(A) positive
(B) negative
(C) zero
(D) may be positive or negative
31. The work done by the system in the conversion of 1 mol of water at 100°C and 760 torr to steam is 3.1 KJ. Calculate the ΔE for the conversion (Latent heat of vaporisation of water is 40.65 kJ mol^{-1})
(A) 43.75 KJ (B) 101.35 KJ
(C) 37.55 KJ (D) -40.65 KJ
32. $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2 + X\text{ kJ}$
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + Y\text{ kJ}$
The enthalpy of formation of NO is
(A) $(2X - 2Y)$ (B) $X - Y$
(C) $\frac{1}{2}(Y - X)$ (D) $\frac{1}{2}(X - Y)$
33. For which of the following equations is the enthalpy change is likely to be negative -
(A) $\text{Cl}^-_{(\text{g})} + \text{aq} \rightarrow \text{Cl}^-_{(\text{aq})}$
(B) $\text{Cl}_{(\text{g})} \rightarrow \text{Cl}^+_{(\text{g})} + \text{e}^-$
(C) $\frac{1}{2}\text{Cl}_{2(\text{g})} \rightarrow \text{Cl}_{(\text{g})}$
(D) $\text{Cl}_{2(\text{l})} \rightarrow \text{Cl}_{2(\text{g})}$
34. Bond energy of a substance -
(A) Is always negative
(B) Is always positive
(C) Either positive or negative
(D) Depends upon the physical state of the system
35. (i) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) ; \Delta H = -x\text{ kJ}$
(ii) $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl} ; \Delta H = -y\text{ kJ}$
(iii) $2\text{H}_2\text{O} + 2\text{Cl}_2 \rightarrow 4\text{HCl} + \text{O}_2 ; \Delta H = -z\text{ kJ}$
From the above equations, the value of ΔH_f of HCl is -
(A) $-x\text{ kJ}$ (B) $-y\text{ kJ}$
(C) $-z\text{ kJ}$ (D) $-x/2\text{ kJ}$
36. For a reaction
 $\text{A}(\text{g}) + 3\text{B}(\text{g}) \rightarrow 2\text{C}(\text{g}) ; \Delta H^\circ = -24\text{ kJ}$
The value of ΔG° is -9 kJ. The standard entropy change of reaction is:
(A) 5 JK^{-1} (B) -50 JK^{-1}
(C) 500 JK^{-1} (D) 0.5 JK^{-1}
37. The work done by the system in a cyclic process involving one mole of an ideal monoatomic gas is -50 kJ/cycle . The heat absorbed by the system per cycle is -
(A) Zero (B) 50 kJ
(C) -50 kJ (D) 250 kJ
38. The reaction with maximum evolution of heat is -
(A) $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$
(B) $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
(C) $\text{C}_2\text{H}_5\text{OH} + 1/2\text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$
(D) $2\text{C} + 3\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{OH}$
39. The heat change accompanying the reaction
 $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) ; \Delta H = -136\text{ kcal}$
is called -
(A) heat of combustion of hydrogen
(B) heat of reaction
(C) heat of formation of water
(D) none of these
40. Enthalpy of neutralisation of NaOH with H_2SO_4 is $-57.3\text{ kJ mole}^{-1}$ and ethanoic acid -55.2 kJ mol^{-1} . which of the following is the best explanation of this difference -
(A) Ethanoic acid is a weak acid and thus requires less NaOH for neutralisation
(B) Ethanoic acid is only partly ionised, neutralisation is there for incomplete
(C) Ethanoic acid is monobasic while H_2SO_4 is di basic
(D) Some heat is used to ionized ethanoic acid completely
41. For a reversible process -
(A) $\Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} > 0$
(B) $\Delta G > 0$
(C) $\Delta S_{\text{sys.}} = -\Delta S_{\text{surr.}}$
(D) $\Delta G < 0$
42. For the process $2\text{F}(\text{g}) \rightarrow \text{F}_2(\text{g})$, the sign of ΔH and ΔS respectively are -
(A) +, - (B) +, +
(C) -, - (D) -, +
43. For the process :
 $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s}) ;$
Which one is correct ?
(A) $\Delta H > 0 ; \Delta S > 0$ (B) $\Delta H < 0 ; \Delta S > 0$
(C) $\Delta H > 0 ; \Delta S < 0$ (D) $\Delta H < 0 ; \Delta S < 0$



44. Work done in vaporisation of one mol of water at 373 K against the pressure of 1 atmosphere is approximately -
 (A) - 3100.0 J (B) 31.20 J
 (C) - 20.2 J (D) +20.2 J
45. The enthalpies of formation of N_2O and NO are 82 and 90 kJ mol^{-1} , respectively. The enthalpy [kJ] of the reaction :
 $2N_2O(g) + O_2(g) \rightarrow 4NO(g)$ would be -
 (A) - 16 (B) 196
 (C) 8 (D) 88
46. A mixture of 2 mole of carbon monoxide gas and one mole of dioxygen gas is enclosed in a vessel and is ignited to convert carbon monoxide into carbon dioxide. If the enthalpy change is ΔH and internal energy change is ΔU , then for the above process -
 (A) $\Delta H = \Delta U$ (B) $\Delta H + \Delta U = 1$
 (C) $\Delta H - \Delta U > 0$ (D) $\Delta H < \Delta U$
47. 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 bond dissociation of base NH_4OH -
 (A) 3.0 (B) 4.0
 (C) 2.0 (D) 10.0
48. Given that
 $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g); \Delta H^\circ = -x \text{ kJ}$
 which of the following is correct -
 (A) $\Delta H^\circ \text{ comb. of C} = -x \text{ kJ mol}^{-1}$
 (B) $\Delta H_f^\circ \text{ of } CO_2 = -x \text{ kJ mol}^{-1}$
 (C) $\Delta H_{\text{comb.}} \text{ of } CO(g) = -x \text{ kJ mol}^{-1}$
 (D) $\Delta H_f^\circ \text{ of } CO = +x \text{ kJ mol}^{-1}$
49. For the reaction,

 bond energies are given as under -
 (i) C—C, 346 kJ/mol
 (ii) C—H, 413 kJ/mol
 (iii) H—H, 437 kJ/mol and
 (iv) C = C, 611 kJ/mol
 What will be the value of ΔH 25°C for the above reaction ?
 (A) -289 kJ mol^{-1} (B) - 124 kJ mol^{-1}
 (C) + 124 kJ mol^{-1} (D) + 289 kJ mol^{-1}
50. Latent heat of vaporisation of water is 540 cal g^{-1} . The entropy change during the evaporation of 1 mole of water at 100°C is -
 (A) $5.4 \text{ cal K}^{-1} \text{ mol}^{-1}$
 (B) $20 \text{ cal K}^{-1} \text{ mol}^{-1}$
 (C) $25 \text{ cal K}^{-1} \text{ mol}^{-1}$
 (D) $26.06 \text{ cal K}^{-1} \text{ mol}^{-1}$





ANSWER KEY

TOPIC WISE MCQS

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	A	C	B	C	C	B	D	B	B	C	A	B	B	D
Q.No.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	B	C	D	C	B	A	A	A	D	A	D	A	B	D	D
Q.No.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	C	A	A	B	A	B	A	D	B	B	B	C	B	A	D
Q.No.	46	47	48	49	50										
Ans.	A	C	D	C	D										

MISCELLANEOUS QUESTIONS

Ques.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	C	C	B	B	B	C	B	D	B	C	C	A	B	D
Ques.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	B	B	A	B	B	B	C	A	C	C	A	A	C	B	C
Ques.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	C	C	A	C	D	B	B	B	B	D	C	C	D	A	B
Ques.	46	47	48	49	50										
Ans.	D	C	C	B	D										

24x7
Doubt Support

Online Motivational classes

Ranjan Singh
Chemistry Classes
JEE (Main & Advanced) • NEET • XI • XII

Our INFRASTRUCTURE

CLASSROOM



Individual interaction with Ranjan Singh Sir

DOUBT



Library for Boys & Girls In Our Premises

LIBRARY



Help Desk with complete care

RECEPTION

PROJECTOR

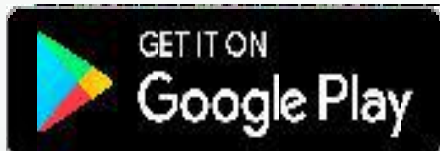


CCTV SECURITY



Ranjan Singh Chemistry Classes

MOBILE APP available on



Our **YouTube Channel** **Ranjan Singh Chemistry Classes**



Ranjan Singh Chemistry Classes

JEE (Main & Advanced) • NEET • XI • XII

HEAD OFFICE

1/11, Vivekanand Marg, Opp. A.N. College, Boring Road, Patna-13

  **9334366815, 7463829757**

 www.chemistrybyranjansingh.com  info@chemistrybyranjansingh.com