ALLEN CAREER INSTITUTE KOTA (RAJASTHAN)

CHEMICAL THERMODYNAMICS AND ENERGETICS

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NEET SYLLABUS

CHEMICAL THERMODYNAMICS : *First law of thermodynamics-internal energy and enthalpy, heat capacity and specific heat, measurement of ΔU and ΔH, Hess's law of constant heat summation, enthalpy of : bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Introduction of entropy as state function, Second law of thermodynamics, Gibbs energy change for spontaneous and non-spontaneous process, criteria for equilibrium and spontaneity. Third law of thermodynamics- Brief introduction.*

OBJECTIVES

After studying this unit, we will be able to :

- *explain the terms : system and surroundings;*
- *discriminate between close, open and isolated systems;*
- *explain internal energy, work and heat;*
- *state first law of thermodynamics and express it mathematically;*
- *calculate energy changes as work and heat contributions in chemical systems;*
- *explain state functions: U, H.*
- *correlate ΔU and ΔH;*
- *define standard states for ΔH;*
- *calculate enthalpy changes for various types of reactions;*
- *state and apply Hess's law of constant heat summation;*
- *differentiate between extensive and intensive properties;*
- *define spontaneous and nonspontaneous processes;*
- *explain entropy as a thermodynamic state function and apply it for spontaneity;*
- *explain Gibbs energy change (ΔG);*
- *establish relationship between ΔG and spontaneity, ΔG and equilibrium constant.*

"Thermodynamics cannot be fathomed in all its profundity in a single pass"

Joseph Kestin

CHEMICAL THERMODYNAMICS

5.0 INTRODUCTION :

Thermo (Heat/energy) + Dynamics (Flow/motion)

Thermodynamics is the branch of science which deals with the energy changes taking place in all physical and chemical processes but **Chemical thermodynamics** is the branch of thermodynamics which deals with the study of energy changes taking place in chemical processes.

Advantages of thermodynamics :

(i) It gives information about various **thermodynamic laws.**

(ii) It helps us to predict whether a given **chemical reaction will take place or not** under the given set of conditions.

(iii) It gives information about various **energy changes**.

Limitations of thermodynamics :

(i) Thermodynamics deals with the properties like temperature, pressure, volume, etc of matter in bulk but doesn't tell us anything about the individual properties of atoms or molecules.

or

Thermodynamics deals with **macroscopic system** but not with **microscopic system.**

(ii) It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the **rate of reaction.**

5.1 SOME IMPORTANT TERMS :

- **System** : A system is defined as a specific part of universe or specified portion of the matter which is under experimental investigation
- **Surrounding** : The rest part of the universe excluding the system is called surrounding.

  Universe = System + Surrounding
- **Boundary** : Anything which separates system and surrounding is called boundary.

  Types of boundary :

  (i) Boundary can be conducting or non-conducting.

  (ii) Boundary can be rigid or non-rigid.

  (iii) Boundary can be real or imaginary.

For example :

A reaction is carried out in a beaker. The contents of beaker constitute the system, beaker serves as boundary and anything which is outside the beaker is called surroundings.

5.2 TYPES OF SYSTEM :

System are of 3 types :

Open system : This type of system can exchange energy as well as matter with the surrounding. The boundary is neither sealed nor insulated. Total mass will not remain constant.

Eg.1 Coffee in open glass. Hot water in open glass.

Eg.2 All living systems. human being, plants, animals.

Eg.3 Classroom, earth.

Closed system : This type of systems can exchange energy, (in the form of heat, work or radiations) but not matter with its surroundings. The boundary is sealed but not insulated. Amount of the system will remain constant.

Eg.1 Coffee in closed vessel. Hot water in closed vessel.

Eg.2 Glowing bulb, tube light.

Eg.3 A satellite in orbit.

Isolated system : This type of system are perfectly insulated systems and cannot interact in any way with its surrounding i.e. neither matter nor energy can be exchanged with the surrounding. The boundary is sealed and insulated. Universe can be considered as an isolated system.

Eg.1 Coffee in thermosflask.

5.3 STATE OF THE SYSTEM :

- Properties which define state of any system are called its state variables or thermodynamic variables or thermodynamic quantities.
- The state of the system is defined by their measurable properties like temperature, pressure, volume etc.
- If any of these properties change, state of the system is said to be changed.

State Function :

- Those state variables which depend only upon initial and final state of the system but doesn't depend upon the path or mechanism followed by the system to achieve final state are called state function.
- State functions are denoted by capital letters.

Ex. E, H, S, G, T, P, V etc.

Path function :

- Properties of the system which depend upon the initial and final state of the system as well as the path or mechanism followed by the system to achieve final state are called path function.
- Path functions are denoted by small letters.

Eg. Work done (w), heat (q)

Thermodynamic properties :

(i) Intensive properties : The properties of the system which are independent of matter (size and mass) present in system are called intensive properties.

(ii) Extensive properties : The properties of the system which are dependent on matter (size and mass) present in system are called extensive properties

Extensive Properties	Intensive Properties
Volume (V)	Molar volume (V_m)
Number of moles (n)	Density (d)
Mass (m)	Gibb's energy per mole (G_m)
Gibb's Energy (G)	Specific heat
Entropy (S)	Pressure (P)
Enthalpy (H)	Temperature (T)
Internal energy (E or U)	All concentration terms (M,N)
Heat capacity (C)	Boiling point, freezing point (T_b, T_f)
Force (F)	Cell potential (E_{cell})
Surface Area (A)	Specific conductance (κ)
	Refractive index
	Surface tension, Viscosity
	pH value
	Vapour pressure

Special Points :

(i) The ratio of two extensive properties indicates the intensive property Eg. $d = \frac{\text{mass}}{\text{volume}}$

(ii) An extensive property can be converted into intensive property when it is defined for unit amount of the substance.

Eg. Mass per unit volume = density; $\left(d = \frac{m}{V}\right)$

(iii) Intensive properties of a substance are non-additive in nature while extensive properties are additive in nature.

	$\boxed{H_2O}$	$\boxed{H_2O}$	On adding	
Vessel	**A**	**B**		
Mass	m_1	m_2	$m_1 + m_2$ (Total mass)	Extensive
Moles	n_1	n_2	$n_1 + n_2$ (Total moles)	Extensive
Volume	V_1	V_2	$V_1 + V_2$ (Total volume)	Extensive
Density	d	d	Remains same (d)	Intensive
Boiling point	T	T	Remains same (T)	Intensive

5.4 TYPES OF THERMODYNAMIC PROCESSES :

When a system changes from one state to another, the operation is called a thermodynamic process. Thermodynamic processes may be in form of expansion or compression.

(a) Isothermal Process (n,T = constant)

Isothermal processes are those processes in which

(a) Temperature of system during entire process remains constant i.e. $\Delta T = 0$

(b) Heat is exchanged with surroundings

(c) Volume and pressure are variable

- For ideal gas in Isothermal process $\Delta E = 0$ and $\Delta H = 0$
- All phase transitions are isothermal process but $\Delta E \neq 0$ and $\Delta H \neq 0$

(b) Isobaric Process (n,P=constant) :

Isobaric processes are those processes in which

(a) Pressure of system during entire process remains const i.e. $\Delta P = 0$

(b) Volume and temperature are variable.

(c) Process in open system is isobaric in nature.

(c) Isochoric Process (n,V = constant) :

Isochoric processes are those processes in which

(a) Volume remains constant i.e. $\Delta V = 0$

(b) Pressure and temperature are variable

(c) Work, $w = -P\Delta V$, $\because \Delta V = 0$, $\therefore w = 0$ (Zero)

(d) Process in closed system is isochoric in nature.

(d) Adiabatic Process (n = constant, q = 0)

Adiabatic processes are those processes in which

(a) No exchange of heat between system and surrounding takes place durint entire process i.e. $q = 0$

(b) The temperature pressure, volume of the system varies.

(c) The system is thermally insulated by keeping the system in an insulated container.

(e) Cyclic Process :

When a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.

In cyclic process change in all state function will be zero. i.e. $\Delta E = 0,\ \Delta H = 0,\ \Delta P = 0,\ \Delta T = 0$

(f) Reversible Process (quasi-static) :

(1) Process in which all changes occuring at any part of the system are exactly reversed when small changes in variables are carried out in opposite direction.

(2) Driving force should be infinitesimally greater than opposing force.

(3) Process takes place in infinitesimal small steps or in many steps and takes infinite time to complete the process.

(4) It is an ideal process.

(5) Work obtained in expansion is maximum.

(6) System is in virtual equilibrium at any state.

(7) $P_{ext} = P_{int} \pm dP$; P_{ext} is variable.

Irreversible Process :

(1) Process in which direction of change cannot be reversed by small changes in variables.

(2) Driving force is much greater than opposing force.

(3) It takes finite time and finite/usually single step.

(4) Process takes place in short time

(5) All natural processes are irreversible

(6) System is in equilibrium only at initial and final state

(7) $P_{ext} = P_{int} \pm \Delta P$; P_{ext} is constant.

5.5 WORK AND HEAT :

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

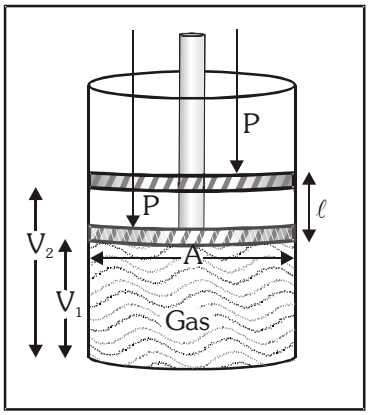
work (w) = force (F) × displacement (ℓ)

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) = $w = F.\ell$

$\because P = \frac{F}{A} \quad \therefore F = P \times A$

$w = P \times A \times \ell$ (change in volume = $A \times \ell = V_2 - V_1$)

$w = P \times (V_2 - V_1)$

$w = P\Delta V$ (According to Physics)

In general $\boxed{w = -P_{external}\ DV}$ (According to Chemistry)

SIGN CONVENSIONS :

- According to latest sign conventions

(a) Work done is taken negative if it is done by the system since energy of system is decreased.

Eg. Expansion of gas.

$\because V_2 > V_1$; ΔV = positive; w = negative

(b) Work done is taken positive if it is done on the system, since energy of system is increased.

Eg. Compression work.

$\because V_1 > V_2$; ΔV = negative ; w = positive

(B) Heat exchange (q) :

Heat is defined as the energy that flow in or out of a system because of a difference in temprature between the thermodynamic system and its surrounding. It is a path function.

According to IUPAC convention, heat given by the system is expressed with negative sign and heat given to the system is expressed with positive sign.

- Heat always flows from high temperature to low temprature.
- Heat flowing into the system q = positive
- Heat flowing out of the system q = negative

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 cal = 4.184 J $\simeq$ 4.2 J

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

1 L-atm > 1 Cal > 1 J > 1 erg

GOLDEN KEY POINTS

- Molar properties like ΔH_m, ΔG_m, ΔS_m, ΔU_m are intensive properties.
- In cyclic process change in all state function will be equal to zero.

  $\Delta E = 0$; $\Delta H = 0$ $\Delta P = 0$, $\Delta T = 0$ etc.
- For ideal gases $\Delta E = 0$ (For isothermal process)
- All natural process are irreversible in nature.
- Both q and w are (+) **to** system.
- Both q and w are (–) **by** the system.

Illustrations

Illustration 1. Find the work done in each case :

(a) When one mol of ideal gas in 10 litre container at 1 atm is allowed to enter a **vacuum bulb** of capacity 100 litre.

(b) When 1 mol of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

Solution (a) $W = -P\Delta V$ but since gas enters the vacuum bulb and pressure in vacuum is zero. This type of expansion is called **free expansion** and work done is zero.

Note :- Work done in free expansion is always zero.

(b) $W = -P\Delta V = -1(5 - 1) = -4$ L-atm.

Illustration 2. A 5 litre cylinder contained 10 mol of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escapped into the atmosphere and the cylinder got empty. If the atmosphere pressure is 1.0 atm. Calculate the work done by the gas ? ($R = 0.083$ lit atm mol^{-1} K^{-1})

Solution $V_{initial} = 5$ L

$T = 27°C = 27 + 273 = 300$ K

$$V_{final} = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$\Delta V = V_{final} - V_{initial} = 249 - 5 = 244$ L

$W_{exp} = -P\Delta V = -1 \times 244$ L-atm. $= -244$ L-atm.

BEGINNER'S BOX–1

1. Which of the following open system

(1) Animals and plants (2) A fridge (3) A solar cooker (4) None of these

2. One mole of gas occupying 3 litre volume is expanded against a constant external pressure of one atm to a volume of 15 litre. The work done by the system is :-

(1) -1.215×10^3 J (2) $+12.15 \times 10^3$ J (3) $+121.5 \times 10^3$ J (4) $+1.215 \times 10^3$ J

3. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is :-

(1) –608 J (2) +304 J (3) –304 J (4) –6 J

4. The work done during the expansion of a gas from a volume of 14 dm^3 to 16 dm^3 against a constant external pressure of 2 atm is :-

(1) –405.2 J (2) +304 J (3) –304 J (4) –6 J

5.6 INTERNAL ENERGY (E/U) :

Internal energy of a system is defined as the sum of different energies associated with its atoms and molecules like Potential energy, Kinetic energy (due to translatory, rotatory and vibratory motion), electronic energy, nuclear energy etc.

$E = E_{PE} + E_T + E_R + E_V + E_e + E_N$

(i) Internal energy is an **extensive property**.

(ii) We can **never find out the absolute value** of internal energy (E) of system.

We can only calculate the change in internal energy of the system (ΔE) by using an instrument which is called as Bomb calorimeter. In Bomb calorimeter reactions are carried out at constant volume.

(iii) Internal energy is a **state function**.

$\Delta E = E_f - E_i$

(In reaction) $\Delta E = E_P - E_R$

ΔE is + ve if $E_f > E_i$

ΔE is – ve if $E_f < E_i$

5.7 LAWS OF THERMODYNAMICS :

GENERAL POINT :

Laws of thermodynamics are based on human experiences there is no formal proof for them.

FIRST LAW OF THERMODYNAMICS (FLOT) :

- This law is based on law of conservation of energy and was given by **Robert Mayer and Helmholtz.**
- Energy can neither be created nor destroyed but can be transformed from one form to another.
- The total energy of the universe is always constant. i.e. total energy of an isolated system is always conserved.
- The mathematical form of first law of thermodynamics can be expressed as follows

$\boxed{\Delta E = q + w}$: where q, w are path function and E is state function.

Here q is the energy given to the 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 proper sign.

CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS :

(a) During isothermal process of an ideal gas :

During an isothermal process the temperature of the system remains constant and hence

$\Delta E = 0$

Therefore FLOT : $\Delta E = q + w$

$\therefore \boxed{+q = -w}$ or $-q = +w$

In isothermal process –

(I) Heat absorbed by the system is equal to work done by the system.

OR

(II) Heat evolved by the system is equal to work done on the system.

(b) During isochoric process :

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

Hence $W = -P\Delta V = 0$ ..... No work done at constant volume therefore,

FLOT: $\Delta E = q + w$ $\boxed{\Delta E = q_v}$

(i) In isochoric process

- At constant volume, heat absorbed by the system is equal to increase in internal energy of the system.

OR

- At constant volume, heat evolved by the system is equal to decrease in internal energy of the system.

(ii) Heat at constant volume $(q_v) = \Delta E$

(iii) **In isochoric process heat is idependent of path.**

(c) During adiabatic process :

During adiabatic process the system acts an isolated system and hence **q = 0** in such cases. Therefore

FLOT : $\Delta E = q + w$ $\quad \because q = 0$ $\quad \boxed{\Delta E = w}$

(i) Work done on the system is equal to increase in internal energy of the system i.e., when a gas is compressed adiabatically its internal energy increases.

OR

Work done by the system is equal to decrease in internal energy of the system, i.e., when a gas is expanded adiabatically its internal energy decreases.

(ii) **In adiabatic process work is independent of path.**

(d) During Cyclic Process :

$\Delta E = 0$ $\quad$ FLOT ; $\Delta E = q + w$ $\quad \boxed{+q = -w}$

In cyclic process.

(I) Work done by the system is equal to heat absorbed by the system.

OR

(II) Work done on the system is equal to heat evolved by the system.

(e) During Isobaric process :

P – constant

FLOT : $\Delta E = q + W$

$\Delta E = q + (-P\Delta V)$

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

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

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

$\because$ Enthalpy $H = E + PV$

$\therefore$ $q_P = H_2 - H_1$ $\quad \boxed{q_P = \Delta H}$

(i) **In isobaric process :**

• At constant pressure, heat absorbed by the system is equal to increase in enthalpy of the system.

OR

• At constant pressure, heat evolved by the system is equal to decrease in enthalpy of the system.

(ii) Heat at constant pressure (q_p) = ΔH

(iii) **In isobaric process heat is idependent of path.**

Illustrations

Illustration 3. 1g of water changes from liquid to vapour phase at constant pressure of 1 atmosphere, the volume increases from 1 mL to 1671 mL. The heat of vaporisation at this pressure is 540 Cal g Find the increase in internal energy of water. (1 L atm = 101 J)

Solution Work done $w = -P\Delta V = -P(V_2 - V_1)$

$$= -1(1671 - 1) \times \frac{1}{1000} = \frac{-1670}{1000}\text{L–atm}$$

$$= \frac{-1670}{1000} \times 101\,\text{J} = -168.67\ \text{J}$$

given that $q = 540\ \text{Cal} = 540 \times 4.2\ \text{J} = 2268\ \text{J}$

$\therefore\ \Delta E = q + w = 2268 - 168.67 = 2099.33\ \text{J}$

Illustration 4. A gas occupies 2 L at STP. It is provided 300 J heat so that its volume becomes 2.5 L at 1 atm. Calculate change in its internal energy.

Solution $w = -P\Delta V = -1 \times (2.5 - 2) = -0.5$ L-atm or $w = -0.5 \times 101.3 = -50.65$ J.

$\Delta E = q + w = 300 + (-50.65)$

$\Delta E = 249.35$ J

Illustration 5. A sample of gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2L to 12L. During the process, it absorbs 600 J of heat from the surroundings. Calculate the change in internal energy of the system.

Solution During the process,

$q = 600$ J, $\Delta V = 12 - 2 = 10$ L, $P = 1$ atm

$w = -P\Delta V$

$= -1 \times 10 = -10$ L atm

Now, 1 L atm = 101.3 J

$\therefore\ w = -10 \times 101.3 = -1013$ J

According to first law of thermodynamics,

$\Delta E = q + w = 600 - 1013 = -413$ J

Illustration 6. Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one half of its volume by a constant external pressure of 4 atm. Calculate q, w &ΔE. ($R = 0.082$ L atm mol^{-1} K^{-1})

Solution Work done on the system,

$w = -P_{ext}\Delta V = -P_{ext}(V_f - V_i)$

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

$n = 2$ mol and $R = 0.082$ atm L mol^{-1} K^{-1},

$T = 273 + 27 = 300$ K, $P = 2$ atm

$$V_i = \frac{2 \times 0.082 \times 300}{2} = 24.6\ \text{L} \quad \text{and} \quad V_f = \frac{V_i}{2} = \frac{24.6}{2} = 12.3\ \text{L}$$

$w = -4 \text{ atm} \times (12.3 - 24.6)L = 49.2 \text{ L atm} = 49.2 \times 101.3 \text{ J} = 4984 \text{ J}.$

Since, it is isothermal compression, $\Delta E = 0$

Now , $\Delta E = q + w$

$0 = q + 4984 \text{ J}$ or $q = -4984 \text{ J}$

Illustration 7 A system is provided with 100 J of heat. Work done on the system is 20 J. What is the change in internal energy.

Solution $q = 100 \text{ J}$ and $w = +20 \text{ J}$

$\Delta E = q + w = 100 + 20 \text{ J} = 120 \text{ J}$

Illustration 8. An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T, while the other portion is a perfect Vacuum. If a hole is opened between the two portions, Calculate the –

(i) Change in internal energy of the gas (ii) Change in temperature of the gas

Solution For insulated system, $q = 0$

The gas is allowed to expand against vacuum, the process of free expansion and thus

$w = -P\Delta V = 0$ (for vacuum = $P_{ext} = 0$)

Thus from I law of thermodynamics, $\Delta E = q + w$ or $\Delta E = 0$

i.e. internal energy change is zero or internal energy of gas remains constant during free expansion. Also $E \alpha T$ and thus temperature of the gas will also remains constant.

BEGINNER'S BOX–2

1. A system absorb 300 cal of heat with the result of that, the volume of the system becomes double of its initial volume and temperature changes from 273K to 546K. The work done by the system on the surroundings is 200.0 Cal Calculate ΔE :-

(1) 273 kCal (2) 500 Cal (3) 100 Cal (4) –500 Cal

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

(1) 163.7 Cal (2) 1381.1 Cal (3) 9 L-atm (4) Zero

3. In an adiabatic process which of the following is true :-

(1) $q = +w$ (2) $-\Delta E = -w$ (3) $P\Delta V = 0$ (4) $q = \Delta E$

4. In an isochoric process, the increase in internal energy is :-

(1) Equal to the heat absorbed (2) Equal to the heat evolved

(3) Equal to the work done (4) Equal to zero

5.8 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.

$\because H = E + PV$

$$\therefore \quad \boxed{\Delta H = \Delta E + \Delta(PV)} \quad ...(i)$$

(when P, V and T are variables)

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

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

For chemical reactions at constant temprature and pressure $\because P.\Delta V = \Delta n_g RT$

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

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

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

GOLDEN KEY POINTS

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

Illustrations

Illustration 9. The heat of reaction for $C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(\ell)$ at constant volume is – 1228.2 kCal at 25°C. Calculate the heat of reaction at constant pressure and at 25°C.

Solution

$\Delta n_g = [10] - [12] = -2$

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

$= -1228.2 \times 10^3 + (-2)(2) \times 298$

$= -1229392$ Cal

$\Delta H = -1229.392$ kCal

Illustration 10. For the reaction at 25°C

$$NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \; ; \; \Delta H^\circ = 11.04 \text{ kCal.}$$

Calculate ΔE° of the reaction at the given temperature.

Solution $\Delta H^\circ = \Delta E^\circ + \Delta n_g RT$

$\Delta n_g = 2 - 1 = 1$ mol

$\Delta E^\circ = \Delta H^\circ - \Delta n_g RT$

$= 11.04 \text{ Kcal} - 1 \text{ mol} \times \frac{2}{1000} \text{ kCal mol}^{-1}\text{K}^{-1} \times 298\text{K}$

$= 11.04 - 0.596 = 10.44$ kCal

Illustration 11 At 27°C the internal energy change of reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ is 2Cal. What is the enthalpy change of this reaction.

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

$\Delta H = \Delta E + 0 \times RT$

$\Delta H = \Delta E$

$\Delta H = 2$Cal

Illustration 12 The heat of combustion of gaseous methane (CH_4) at constant volume is measured in bomb calorimeter at 298K is found to be –885.4 kJ mol^{-1}. Find the value of enthalpy change at the same temperature.

Solution Combustion of methane gives $CO_2(g)$ and $H_2O(\ell)$ as

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$

$\Delta E = -885.4 \text{ kJ mol}^{-1} = -885400 \text{ J mol}^{-1}$

$\Delta n_g = 1-(1 + 2) = -2$ mol

$T = 298\text{K}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

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

$= -885400 + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1}\text{K}^{-1}) \times (298\text{K})$

$= -885400 - 4955$

$= -890355 = -890.355$ kJ

Illustration 13. 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 ΔE at 298 K ?

Solution ΔH and ΔE are related as $\Delta H = \Delta E + \Delta n_g RT$

for the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$\Delta n_g = 2 - (1 + 3) = -2$ mol, T = 298 K

$\Delta H = -92.38 \text{ kJ} = -92380 \text{ J}, \quad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

$-92380 = \Delta E + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$

$-92380 = \Delta E - 4955$

$\Delta E = -92380 + 4955$

$= -87425 \text{ J} = -87.425 \text{ kJ}.$

Illustration 14 The enthalpy change for the reaction $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ at 1000K is 176 kJ mol^{-1}. Calculate the change in internal energy.

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

$176 = \Delta E + (+1) \times 8{\cdot}314 \times 10^{-3} \times 1000$

$\Delta E = 167{\cdot}686$ kJ

BEGINNER'S BOX–3

1. When a solid melts, there is :-

(1) No increase in enthalpy (2) Increase in enthalpy

(3) Decrease in enthalpy (4) Anything can happen

2. For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ which of the following is valid :-

(1) $\Delta H = \Delta E$ (2) $\Delta H < \Delta E$

(3) $\Delta H > \Delta E$ (4) None of these

3. Heat exchanged in a chemical reaction at constant pressure is called :-

(1) Internal energy (2) Enthalpy

(3) Enthropy (4) Free energy

4. Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10.0 kCal mol^{-1}. What will be the change in internal energy of 3 mol of liquid at same temperature and pressure

(1) 13.0 kCal (2) –13.0 kCal

(3) 27.0 kCal (4) –27.0 kCal

5. What is the value of Δn_g if we consider the combustion of 1 mol of liquid ethanol if reactants and products are at 298 K :-

(1) –1 (2) –2 (3) +1 (4) +2

6. If a reaction involves only solids and liquids, which of the following is true

(1) $\Delta H < \Delta E$ (2) $\Delta H = \Delta E$

(3) $\Delta H > \Delta E$ (4) $\Delta H = \Delta E + RT\Delta n_g$

7. The value of $\Delta H - \Delta E$ for the following reaction at 27°C will be, $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$:-

(1) $8.314 \times 273 \times (-2)$ J

(2) $8.314 \times 300 \times (-2)$ J

(3) $8.314 \times 27\ (+2)$ J

(4) $8.314 \times 300\ (+2)$ J

8. At constant temperature for the reaction $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(\ell)$, $\Delta E - \Delta H$ is :-

(1) +RT (2) –3RT (3) +3RT (4) –RT

5.9 HEAT CAPACITY / MOLAR HEAT CAPACITY / SPECIFIC HEAT CAPACITY :

(i) Heat capacity (C) : Amount of heat required to raise the temperature of given amount of a substance by 1℃ or 1K is called heat capacity.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temp.}}$$

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

Units :- JK^{-1}, Cal K^{-1}, J $℃^{-1}$, Cal $℃^{-1}$

- Heat capacity is extensive property.

(ii) Molar heat capacity (C_m) : Amount of heat required to raise the temperature of 1 mole of substance by 1℃ or 1 K is called as molar heat capacity.

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

Units :- $Jmol^{-1}\ K^{-1}$, Cal $mol^{-1}\ K^{-1}$, J $mol^{-1}\ ℃^{-1}$, Cal $mol^{-1}\ ℃^{-1}$

- Molar heat capacity is an intensive property.

(iii) Spcific heat capacity (c) : Amount of heat required to raise the temperature of 1 g of substance by 1℃ or 1K is called as specific heat capacity.

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

Units :- $Jg^{-1}\ K^{-1}$, Cal $g^{-1}\ K^{-1}$, J $g^{-1}\ ℃^{-1}$, Cal $g^{-1}\ ℃^{-1}$

- Specific heat capacity is an intensive property.

- If heat is suppplied at constant pressure, then $C_p = \left(\frac{dq}{dT}\right)_P = \frac{dH}{dT}$ ...(i)

- If heat is supplied at cosntatn volume, then $C_V = \left(\frac{dq}{dT}\right)_V = \frac{dE}{dT}$ ...(ii)

From equation (i) and (ii) :

From equation (i)	Unit	From equation (ii)
• $\Delta H = C_p dT$ [Here 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 $\Delta H = mC_p dT$ [Here C_p is gram specific heat (specific heat capacity) at constant P]	J $g^{-1}\ K^{-1}$	$\Delta E = mC_V dT$ [Here C_V is gram specific heat (specific heat capacity) at constant V]

Relation between C_P and C_V for 1 mole of an ideal gas :

$\because$ $H = E + PV$

for ideal gas,

$PV = nRT$

$PV = RT$ for 1 mole

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

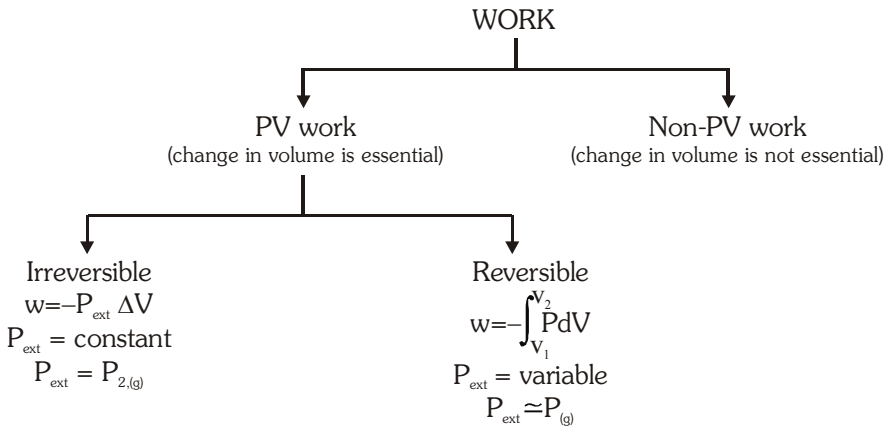
$$\left(\frac{dH}{dT}\right)=\left(\frac{dE}{dT}\right)+R$$

$$C_P = C_V + R$$

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

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

5.10 WORK DONE IN DIFFERENT PROCESS :



Here $P_{2(g)}$ = Pressure of gas outside piston.

$P_{(g)}$ = Pressure of gas inside piston.

(a) Work done in reversible isothermal process :

$P_{external}$ = Variable

For reversible process

$P_{ext} = P_{gas} \pm dP$

$\because$ $w_{rev.} = -\int_{V_1}^{V_2} P_{ext.}dV$

$$w_{rev.} = -\int_{V_1}^{V_2} (P_{gas} \pm dP).dV$$

Both dP and dV are very small so, (dP.dV) is negligible.

$$w_{rev.} = -\int_{V_1}^{V_2} P_{gas}.dV$$

$$w_{rev.} = -\int_{V_1}^{V_2} \frac{nRT}{V}.dV$$

$$w_{rev.} = -nRT\int_{V_1}^{V_2}\frac{dV}{V}$$

$$w_{rev.} = -nRT\ell n\left(\frac{V_2}{V_1}\right)$$

or, $$\boxed{w_{rev.} = -2.303nRT\log_{10}\left(\frac{V_2}{V_1}\right)} \quad ...(i)$$

according to Boyle's law at constant temperature $P \propto \frac{1}{V}$ or PV = constant

$$\therefore \quad P_1V_1 = P_2V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\boxed{w_{rev.} = -2.303nRT\log\left(\frac{P_1}{P_2}\right)} \quad ...(ii)$$

(b) Work done in reversible adiabatic process :

In adiabatic process $q = 0$

FLOT : $\Delta E = q + w$

$$\Rightarrow \boxed{w = \Delta E} \Rightarrow w = nC_V\Delta T$$

$$\boxed{w = nC_V(T_2 - T_1)} \quad .....(i)$$

$\because \quad C_P - C_V = R$

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\gamma - 1 = \frac{R}{C_V} \quad \left(\because \gamma = \frac{C_P}{C_V}\right) \Rightarrow C_V = \frac{R}{\gamma - 1} \quad .....(ii)$$

From equation (i) and (ii) $\boxed{w = \frac{nR}{\gamma\text{-}1}(T_2 - T_1)} = \boxed{w = \frac{P_2V_2 - P_1V_1}{(\gamma - 1)}}$

State equations of reversible adiabatic processes are :

PV^{γ} = constant

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

$T^{\gamma}P^{1-\gamma}$ = constant

GOLDEN KEY POINTS

- Work in closed vessel is zero because volume remains constant.
- Work during free expansion of an ideal gas in vacuum is zero, because P_{ext} is zero.
- Work in a chemical reaction $w = -P\Delta V = -\Delta n_g.RT$

Illustrations

Illustration 15 5 moles of oxygen are heated at constant volume from 10°C to 20°C. What will be the change in the internal energy of gas? The molar heat capacity of oxygen at constant pressure,

$$Cp = 7.03 \ \frac{Cal}{mol\,K} \text{ and } R=2 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

Solution We know mayer's relation is $C_P - C_v = R$

$C_v = C_p - R = 7.03 - 2 = 5.03$ Cal mol^{-1} K^{-1}

As we know $\Delta E = nC_vdT = 5 \times 5.03 \times 10 = 251.5$ Cal

Illustration 16 At 27°C, one mole of an ideal gas compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate ΔE and q in calorie.

Solution For isothermal process $\Delta E = 0$ and $w = -2.303\ nRT \log_{10}\frac{P_1}{P_2}$

$$w = -2.303 \times 1 \times 2 \times 300 \times \log \frac{2}{10}$$

$w = +\ 2.303 \times 600 \times \log 5$

$w = +\ 2.303 \times 600 \times 0.699$

$w = +\ 965.87$ Cal

For isothermal process $\because w = -q$

$\therefore q = -\ 965.87$ Cal

Illustration 17 A gas expands from $3dm^3$ to $5\ dm^3$ against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mol of water of temperature 290 K. Calculate final temperature of water (if specific heat of water is 4.184 $Jg^{-1}K^{-1)}$

Solution Since work is done aganist constant P and thus, irreversible

$\Delta V = 5 - 3 = 2dm^3 = 2$ L, P = 3 atm

$w = -P\Delta V = -\ 3 \times 2$ L atm $= -\ 6 \times 101.3$ J $= -\ 607.8$ Joule

Now this work is used up in heating water

$w = n \times C \times \Delta T$

$607.8 = 10 \times (4.184 \times 18) \times \Delta T$

$\Delta T = 0.81 = T_2 - T_1$

$\therefore$ Final temperature $= T_1 + \Delta T = 290 + 0.81 = 290.81$ K

Illustration 18 A sample of 3 mol of an ideal gas at 200K and 2 atm is compressed reversibly and adiabatically until the temperature reaches 250K, given that molar heat capacity is 27.5 Jk^{-1} mol^{-1} at constant volume, calculate w.

Solution $C_v = 27.5\ Jk^{-1}mol^{-1}$

During reversible adiabatic process

$w = nC_V (T_2 - T_1) = 3 \times 27.5 \times 50 = 4125$ Joule

Illustration 19 10 moles of an ideal gas at 27°C and 10 atm., pressure occupying a volume of 24.6 L undergoes the following changes.

(i) Isothermal & reversible expansion to 246 L

(ii) Isothermal and irreversible expansion to 246 L.

(iii) Isochoric heating to 177°C.

Calculate the work done in each transformation in kJ.

Solution (i) Work done in isothermal reversible expansion

$$w = -2.303 \times nRT \log \frac{v_2}{v_1} = -2.303 \times 10 \times 8.31 \times 300 \times \log \frac{246}{24.6}$$

$$= -57413.79\ J = -57.41\ kJ$$

(ii) Work done in isothermal irreversible expansion

$w = -P (V_2 - V_1) = -1\ (246 - 24.6) = -221.4$ L-atm $= -221.4 \times 101.3\ J = -22.43$ kJ

(iii) Work done in isochoric change

Since $\Delta V = 0$ $\quad \therefore \quad w = 0$

Illustration 20 Find the work done when 2 mol of a gas expands isothermally from $5dm^3$ to $40dm^3$ against a constant external pressure of 2 atm at 298K. Also calculate w_{rev} for the change.

Solution (i) $w = -P\Delta V$

$w = -2 \times (40 - 5)$

$w = -70\ \ell$ atm $= -70 \times 101.3\ J$

$w = -7091\ J$

(ii) $w = -2.303\ nRT \log \frac{V_2}{V_1}$

$w = -2.303 \times 2 \times 8.314 \times 298 \log \frac{40}{5}$

$w = -10.3 \times 10^3\ J$

BEGINNER'S BOX–4

1. Calculate w for the isothermal reversible expansion of 1mol of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K :-

(1) –5227.2 J (2) +5227.2 J (3) –2257 J (4) +2257 J

2. When 229 J of energy is supplied as heat at constant pressure to 3 mol Ar(g), the temperature of the sample is increased by 2.55K. Calculate the molar heat capacity at constant volume :-

(1) 30 kJ K^{-1} mol^{-1} (2) 30 J K^{-1} mol^{-1} (3) 21.7 J K^{-1} mol^{-1} (4) 21.7 kJ K^{-1} mol^{-1}

5.11 SPONTANEOUS PROCESS AND NON–SPONTANEOUS PROCESS :

(i) Spontaneous process :

- The process which has a natural tendency to occur in a particular direction either of its own or after proper initiation under the given set of conditions.
- All natural processes are ir-reversible and spontaneous processes. The natural processes take place of their own in one direction only.

(ii) Non–spontaneous process :

- The process which does not occur of its own in a particular direction i.e. a process which does not have a natural tendency to occur in a particular direction either of its own or after initiation is called as non-spontaneous process.
- Non-spontaneous process may be made to occur when energy from some external source is supplied continuously throughout the process.

Examples of spontaneous process that need no initiation :

Ex.1 Flow of water from high level to low level.
Flow of heat from hot body to cold body.
Flow of charge from high potential to low potential.
Flow of gas from high pressure to low pressure.

Ex.2 Melting of ice at 25° C
Evapouration of water at 25° C
Dissolution of common salt in water.

Ex.3 Mixing of different non reacting gases

Examples of spontaneous process that need initiation :

Ex.1 Burning of fuel (coal, petrol)

$$C(s) + O_2 \longrightarrow CO_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Ex.2 Lighting of candle

Criteria for a process to be spontaneous :

(i) Tendency to attain minimum energy or maximum stability (Energy Factor).

(ii) Tendency to attain maximum randomness (Entropy Factor)

5.12 ENTROPY (S) :

(i) The thermodynamic quantity, which is used to measure **degree of randomness** or **disorderness** of the system is called as entropy.
Entropy (s) $\propto$ Randomness or disorderness

(ii) More is the disorderness, higher is the entropy.

(iii) The ratio of heat absorbed by the system in isothermal and reversible manner to the temperature at which heat is absorbed is equals to the change in entropy.

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

Where q_{rev}= heat absorbed by the system in a reversible manner at the temperature T

Unit : J K^{-1} or Cal K^{-1}

(iv) $\Delta S = S_{final} - S_{inital}$

If $S_{final} > S_{initial}$: Then ΔS = positive

If $S_{final} < S_{initial}$: Then ΔS = negative

(v) Entropy is an extensive property and state function.

(vi) Entropy change in a chemical reaction $\boxed{\Delta S = \Sigma S_{product} - \Sigma S_{reactant}}$

(vii) Entropy change for a process : $\Delta S = \frac{q_{rev}}{T}$ $\boxed{\Delta S = nC_V \ell n \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}}$ or $\boxed{\Delta S = nC_P \ell n \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}}$

Case I : For an ideal gas reversible isothermal process; : $T_2 = T_1$

$$\boxed{\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}}$$

$$\boxed{\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 nR \log \frac{P_1}{P_2}}$$

Case II : For an isochoric process $V_2 = V_1$

$$\boxed{\Delta S = nC_V \ln \frac{T_2}{T_1}} \; ; \; \boxed{\Delta S = 2.303 \; nC_v \log \frac{T_2}{T_1}}$$

(viii) **For reversible adiabatic process :**

Entropy remains constant so process is also known as **isoentropic process**.

Factors affecting entropy of system :

(I) If $\Delta n_g > 0$ then $\Delta S > 0$

If $\Delta n_g < 0$ then $\Delta S < 0$

(II) Physical state : $S_{solid} < S_{liquid} < S_{gas}$

(III) On increasing gaseous moles entropy increases.

(IV) On increasing temperature, S will increase.

Ex. $Fe(s) \rightarrow Fe(s)$: ΔS=positive
300K 400K

(V) On decreasing pressure, S increases.

Ex. $N_2(g) \rightarrow N_2(g) : \Delta S$ = positive
5atm 2 atm

(VI) Mixture : Solid + solid, liquid + liquid, gas + gas } $S \uparrow$

Entropy change during phase transition :

(I) Entropy of fusion [$(\Delta S)_f$] mole :

The entropy change, when 1 mol solid changes into liquid at its melting point temperature.

$$\text{solid} \rightleftharpoons \text{liquid}$$

$$(\Delta S)_f = \frac{\Delta H_{fusion}}{T}$$

(II) Entropy of vapourisation [$(\Delta S)_{vap}$] mole :

The entropy change, when 1 mol liquid changes into vapour at its boiling point temperature.

$$\text{liquid} \rightleftharpoons \text{vapour}$$

$$(\Delta S)_{vap} = \frac{\Delta H_{vap}}{T}$$

(III) Entropy of sublimation [$(\Delta S)_{sub}$] mole :

The entropy change, when 1 mol solid changes into vapour at a particular temperature.

$$\text{solid} \rightleftharpoons \text{vapour}$$

$$(\Delta S)_{sub} = \frac{\Delta H_{sub}}{T}$$

Some famous or extra ordinary examples of entropy change :

(i) Entropy of graphite > Entropy of diamond.

(ii) In rusting of iron entropy increases.

(iii) $NH_4Cl(s) + aq \longrightarrow NH_4^+(aq) + Cl^-(aq)$

In this process NH_4^+ and Cl^- ions are free to move in solution where as they are not free to move in solid NH_4Cl. Hence ΔS is positive for this type of dissolution process.

(iv) On addition of HCl in the aqueous solution of Ag^+ ions entropy decreases due to precipitation of AgCl.

(v) **On boiling of egg :** Denaturation of proteins occur. Thus entropy increases.

(vi) **Stretching of rubber :** During stretching of rubber band its long flexible macromolecules get uncoiled. The uncoiled form has more specific geometry and more ordered arrangement. Thus entropy decreases.

Total entropy change in reversible process :

In reversible process, at every step system and surroundings remain in thermal equilibrium with each other. Let a system, releases q heat to the surroundings at temperature T.

$$\Delta S_{system} = \frac{-q}{T}; \qquad \Delta S_{surroundings} = \frac{+q}{T}$$

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

$$\Delta S_{total} = \frac{-q}{T} + \frac{q}{T} \Rightarrow \boxed{\Delta S_{total} = 0}$$

Total entropy change in irreversible process :

Let a system is at high temperature T_1 and surroundings are at low temperature T_2.

Let q amount of heat is released by the system.

$$\Delta S_{system} = \frac{-q}{T_1}, \qquad \Delta S_{surroundings} = \frac{+q}{T_2}$$

$$\because \quad \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = \frac{-q}{T_1} + \frac{q}{T_2}$$

$$\therefore \quad \boxed{\Delta S_{total} = +ve} \qquad (\because T_1 > T_2)$$

Total entropy change for irreversible spontaneous process is always greater than zero.

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

Illustrations

Illustration 21 The enthalpy change for transition of liquid water to steam is 40.8 kJ mol^{-1} at 373K. Calculate ΔS for the process.

Solution The entropy change for the vapourization of water is given by $\Delta S = \frac{\Delta H_{Vap.}}{T}$

Given $\Delta H_{vap.} = 40.8$ kJ $mol^{-1} = 40.8 \times 1000$ J mol^{-1} and T = 373 K

$$\Delta S = \frac{40.8 \times 1000 \text{ Jmol}^{-1}}{373\text{K}} = 109.38 \text{ JK}^{-1} \text{ mol}^{-1}$$

Illustration 22 Calculate the change in entropy for the fusion of 1 mol of ice. The melting point of ice is 273K and molar enthalpy of fusion of ice = 6 kJ mol^{-1}

Solution $\Delta S_f = \frac{\Delta H_f}{T} = \frac{6 \times 10^3}{273} = 21.97 \text{ JK}^{-1} \text{ mol}^{-1}$

Illustration 23 The enthalpy of vapourisation of liquid diethyl ether $(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate ΔS for conversion of :-

(i) Liquid to vapour and (ii) Vapour to liquid at 35°C

Solution (i) $\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T} = \frac{26 \times 10^3}{308} = 84.41 \text{ JK}^{-1}\text{mol}^{-1}$

(ii) $\Delta S_{cond.} = \frac{\Delta H_{cond.}}{T} = \frac{-26 \times 10^3}{308} = -84.41 \text{ JK}^{-1}\text{mol}^{-1}$

Illustration 24 Which of the following processes are accompanied by increase of entropy :

(i) Dissolution of iodine in a solvent $[I_2(s) \longrightarrow I_2(aq.)]$

(ii) HCl is added to $AgNO_3$ and a precipitate of AgCl is obtained.

(iii) A partition is removed to allow two gases to mix.

Solution Increase of entropy : (i) and (iii)

BEGINNER'S BOX–5

1. In any natural process, occuring in the universe :-

(1) Entropy is conserved (2) Entropy increases

(3) Entropy decreases (4) Entropy remains unchanged

2. The most random state of H_2O system is :-

(1) Ice (2) $H_2O(\ell)$ at 80°C ; 1 atm

(3) Steam (4) H_2O (ℓ) at 25°C ; 1 atm

3. Change in entropy is negative for :-

(1) $Br_2(\ell) \longrightarrow Br_2(g)$ (2) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

(3) $M_2(g, 10\ atm) \longrightarrow M_2(g,\ 1atm)$ (4) Fe (at 400K) $\longrightarrow$ Fe (at 300K)

4. Entropy change in spontaneous adiabatic process is :-

(1) Zero (2) < 0

(3) > 0 (4) None of these

5. 5 mole of an ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27°C. The change in entropy is :-

(1) 41.57 JK^{-1} (2) –95.73 JK^{-1}

(3) 95.73 JK^{-1} (4) –41.57 JK^{-1}

6. The latent heat of vapourisation of water at 100°C is 540 Cal g^{-1}. Calculate the entropy increase when one mole of water at 100°C is evaporated :-

(1) 26 Cal K^{-1} mol^{-1} (2) 1.45 Cal K^{-1} mol^{-1}

(3) 367 Cal K^{-1} mol^{-1} (4) 1.82 Cal K^{-1} mol^{-1}

7. Calculate enthalpy of vapourization per mole of ethanol. Given ΔS = 109.8 J K^{-1} mol^{-1} and B.P. of ethanol is 78.5°C :-

(1) Zero (2) 38.594 kJ mol^{-1}

(3) 3.85 kJ mol^{-1} (4) None of these

5.13 SECOND LAW OF THERMODYNAMICS (SLOT) :

(i) It states about the direction of flow of heat

(ii) All natural processes in universe are ir-reversible process or natural processes are spontaneous process.

(iii) Due to spontaneous process entropy of universe is increasing continuously i.e. entropy of an isolated system increases.

$(\Delta S)_T$ = + ve or $(\Delta S)_T > 0$ or $(\Delta S)_{system} + (\Delta S)_{surr.} > 0$

5.14 GIBB'S ENERGY (G or F) :

- Gibb's energy is defined at constant temperature and pressure to predict spontaneity of a process.
- Gibb's energy is a thermodynamic quantity which is used to measure the capacity of system to do useful work or Gibb's energy is that part of the total energy of system which can be converted into useful work.
- The term Gibbs energy was introduced to explain criteria of spontaneity in terms of system.
  - Since ; energy = useful work + randomness energy

    H = G + TS

    $\boxed{G = H - TS}$ ...(i)

    So the function that takes both enthalpy and entropy of system into account is called Gibbs energy.
  - Gibbs energy is an extensive property and state function.
  - Absolute value of G can't be measured but change can be measured, So we discuss (ΔG)

    $\Delta G = G_{final} - G_{initial}$

    From eq. (i) $\boxed{\Delta G = \Delta H - T\Delta S}$

    Where ΔG = Change in Gibb's energy

    ΔH = Change in enthalpy

    ΔS = Change in entropy

Relation between 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.

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

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

Put W in equation (i)

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

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

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

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

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

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

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

$\therefore$ $q = q_P = \Delta H$

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

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

$$\Delta S_{surr.} = \frac{\Delta H_{surr.}}{T}$$

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

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

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

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

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

or $\boxed{\Delta G_{sys.} = -T\Delta S_{total}}$

(i) If, ΔS_{total} = +ve $\Rightarrow$ ΔG_{system} = –ve $\Rightarrow$ spontaneous process

(ii) If, ΔS_{total} = –ve $\Rightarrow$ ΔG_{system} = +ve $\Rightarrow$ non spontaneous process

(iii) If, $\Delta S_{total} = 0 \Rightarrow \Delta G_{system} = 0 \Rightarrow$ process is at equilibrium.

$\Delta_r H^-$	$\Delta_r S^-$	$\Delta_r G^-$	**Description**
–	+	–	Reaction spontaneous at all temperature
–	–	–	(at low T) Reaction spontaneous at low temperature
–	–	+	(at high T) Reaction nonspontaneous at high temperature
+	+	+	(at low T) Reaction nonspontaneous at low temperature
+	+	–	(at high T) Reaction spontaneous at high temperature
+	–	+	(at all T) Reaction nonspontaneous at all temperatures

Relationship between standard Gibb's energy change (ΔG°) and Equilibrium constant (K_{eq}) :-

For a reaction $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$\Delta G = \Delta G^\circ + RT\ \ell nQ$$

At equilibrium – $\Delta G = 0$ and $Q = K_{eq}$

$$0 = \Delta G^\circ + RT\ \ell n\ K_{eq}$$

$\therefore \quad \boxed{\Delta G^\circ = -RT\ell nK_{eq}}$ ...(i)

or $\boxed{\Delta G^\circ = -2.303RT\log_{10}K_{eq}}$ ...(ii)

from equation (i)

$$\log K_{eq} = -\frac{\Delta G^\circ}{RT}$$

$\therefore \quad \boxed{K_{eq} = e^{-\Delta G^\circ/RT}}$ ...(iii)

Illustrations

Illustration 25. 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 possible or not ?

Solution We know that :

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

$T = 27 + 273 = 300K$

$\Delta H = 40.63 \times 10^3$ J $mol^{-1} = 40630$ J mol^{-1}

$\Delta S = 100\ JK^{-1}$

$\Delta G = 40630 - 300 \times 100 = 40630 - 30000 = + 10630$ J

Positive value of ΔG indicates that the reaction is not possible.

Illustration 26 For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are -11.7×10^3 J mol^{-1} and -105 J mol^{-1} K^{-1} respectively. Find out whether this reaction is spontaneous or not.

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

$= - 11700 - 298 \times (- 105)$

$= + 19590$ J

ΔG = + ve, so reaction is non-spontaneous.

Illustration 27 Calculate the equilibrium constant for the reaction given below at 400K.

If $\Delta H°=77.2$kJmol^{-1} and $\Delta S° = 122\ JK^{-1}\ mol^{-1}$

$PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$

Solution $\Delta G^0 = \Delta H^0 - T\Delta S^0 = 77200 - 400 \times 122 = 28400$ J

$\Delta G^0 = - 2.303\ RT \log K_c$

or $28400 = -2.303 \times 8.31 \times 400 \log K_c$

or $K_c = 1.958 \times 10^{-4}$

Illustration 28 For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H = -95.4$ kJ and $\Delta S = -198.3\ Jk^{-1}$. Calculate the temperature at which the reaction will proceed in forward direction.

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

$\because$ At equilibrium $\Delta G = 0$

$\therefore\ \Delta H = T\Delta S$ so $T = \dfrac{\Delta H}{\Delta S} = \dfrac{-95.4 \times 1000J}{-198.3JK^{-1}} = 481$ K

For this reaction ΔH is –ve and ΔS is –ve, so it will be spontaneous at low temperature.

$\therefore$ Below 481K the reaction would be spontaneous.

Illustration 29 Enthalpy and entropy changes of a reaction are 40.63 kJ mol^{-1} and 108.8 J K^{-1} mol^{-1} respectively. Analyse the feasibility of the reaction at 27°C.

Solution $\Delta H = 40.63$ kJ $mol^{-1} = 40630$ J K^{-1} mol^{-1}

$\Delta S = 108.8$ J K^{-1} mol^{-1}

$T = 27°C = 27 + 273 = 300$ K

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

$= 40630$ J $mol^{-1} - (300\text{ K}) \times (108.8$ J K^{-1} $mol^{-1})$

$\Delta G = 7990$ J mol^{-1}.

Since ΔG is positive, the reaction is not feasible in the forward direction.

Illustration 30 For a certain reaction the change in enthalpy and change in entropy are 40·63 kJ mol^{-1} and 100 JK^{-1}. Show that the reaction at 27°C is possible or not.

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

$\Delta G = 40.63 - 300 \times 100 \times 10^{-3}$

$\Delta G = +\ 10{\cdot}630$ kJ

ΔG is positive so reaction is not possible.

Illustration 31 Zinc reacts with dilute hydrochloric acid to give hydrogen at 17°C. The enthalpy of the reaction is –12.55 kJ mol^{-1} and entropy change is 5JK^{-1} mol^{-1} for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.

Solution Given $\Delta H = -12.55$ kJmol^{-1} and $\Delta S = 5$ JK^{-1} mol^{-1}

$T = 17+273 = 290$ K

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

$$= -12.55\ \frac{\text{kJ}}{\text{mol}} - 290\text{K} \times \frac{5}{1000}\ \frac{\text{kJ}}{\text{Kmol}}$$

$$= -12.55 - 1.45$$

$$= -14\ \frac{\text{kJ}}{\text{mol}}$$

Since ΔG is negative, the reaction will be spontaneous

Illustration 32 For a reaction both ΔH and ΔS are positive under what condition will the reaction occur spontaneously.

Solution The reaction will occurs spontaneously only when $T\Delta S > \Delta H$.

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

For ΔG to be negative, $T\Delta S$ must be $> \Delta H$

Illustration 33 Which of the following are state function ?

(i) q (ii) Entropy (iii) Specific heat capacity (iv) H (v) w

Solution **Ans.** (ii), (iii) and (iv)

BEGINNER'S BOX–6

1. If $\Delta G^\circ > 0$ for a reaction then :-

(1) $Kp > 1$ (2) $Kp < 1$ (3) $Kp = 1$ (4) None

2. For an endothermic reaction to be spontaneous :-

(1) ΔG must be +ve (2) ΔS must be > 0

(3) $T\Delta S$ must be –ve (4) $T\Delta S$ must be equal to ΔG

3. The value of ΔG for the process $H_2O(s) \longrightarrow H_2O(\ell)$ at 1 atm and 260 K is :-

(1) < 0 (2) $= 0$ (3) > 0 (4) Unpredictable

4. In a certain chemical reaction $\Delta H = 150$ KJ and $\Delta S = 10\ JK^{-1}$ at 300 K. The value of ΔG would be :-

(1) –2850 J (2) Zero

(3) +2850 J (4) 147 kJ

5. The standard Gibb's energy change for a gaseous reaction at 27°C is X kCal. If equilibrium constant for a reaction is 100 and R is 2 Cal K^{-1} mol^{-1}. Then X is :-

(1) –2.7636 (2) +2.7636 (3) + 807 (4) – 807

6. The favourable conditions for a spontaneous reaction are :-

(1) $T\Delta S > \Delta H$, ΔH = +ve, ΔS = +ve (2) $T\Delta S > \Delta H$, ΔH = +ve, ΔS = –ve

(3) $T\Delta S = \Delta H$, ΔH = –ve, ΔS = –ve (4) $T\Delta S = \Delta H$, ΔH = +ve, ΔS = +ve

5.15 THIRD LAW OF THERMODYNAMICS (TLOT)

At zero kelvin (absolute zero temperature), the entropy of pure perfect crystalline solid is taken as zero.

Exceptions :

(i) NO, N_2O (ii) CO, CO_2 (iii) Mixture of isotopes (iv) Ice

ENERGETICS

5.16 INTRODUCTION :

Thermochemistry is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or chemical reaction takes place within the system.

Depending upon the conditions under which the reaction is carried out, the quantity of heat transferred is related to energy or enthalpy change due to changes of states which occur in the system.

In this chapter we will introduced enthalpies of some specific reaction. Like, Enthalpy of formation (ΔH_f), Enthalpy of combustion (ΔH_{comb}), Bond dissociation enthalpy (ΔH_{BDE}) & Enthalpy of Neutralisation ($\Delta H_{neutralization}$)

THERMOCHEMICAL REACTION :

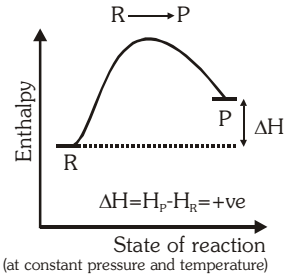
The balanced chemical reaction which give information about the physical states of reactants & products and heat change is called as thermo chemical reaction.

eg. $2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$, $\Delta H = +$ xcal

Thermo chemical reaction are of 2 types.

(i) Endothermic reaction :

The reaction which absorbs heat is called as endothermic reaction.



$\boxed{\Delta H = +ve}$

$\Delta H = H_P - H_R = +ve$ i.e. $\boxed{H_P > H_R}$

(a) Stability of reactant > Stability of product because more heat is required to break the bonds of reactant.

(b) The product formed in the endothermic reaction is called endothermic compound.

(c) If more heat is absorbed then the product formed in the reaction will be less stable or the reactant is more stable.

Representation of endothermic reaction :

$A + B + xCal \longrightarrow C + D$ (endo)

$A + B \longrightarrow C + D - xcal$ (endo)

$A + B \longrightarrow C + D,\ \Delta H = +xcal$ (endo)

Examples :

(I) Dissociation reactions (mostly)

(II) Fusion reactions

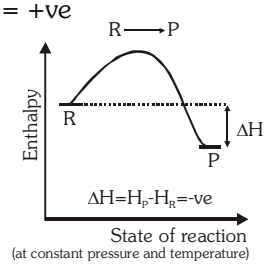
(III) Vaporization reactions

(IV) Sublimation reactions

(V) Photosynthesis $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$, $\Delta H = +ve$

(ii) Exothermic reaction :

The reaction which evolves heat is called as exothermic reaction.



$\boxed{\Delta H = -ve}$ $\Delta H = H_P - H_R = -ve$ i.e. $\boxed{H_P < H_R}$

(a) Stability of reactant < Stability of product because less heat is required to break the bonds of reactant.

(b) The product formed in the exothermic reaction is called exothermic compound.

(c) If more heat is released then the product formed in the reaction will be more stable or the reactant is less stable.

Representation of exothermic reaction.

$A + B \longrightarrow C + D + xcal$ (exo)

$A + B - xcal \longrightarrow C + D$ (exo)

$A + B \longrightarrow C + D, \quad \Delta H = -xcal$ (exo)

Examples :

(I) Combustion reactions (II) Neutralisation reactions

(III) Respiration reaction **eg.** $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

(IV) Formation reaction $\overset{\text{endo}}{\underset{\text{exo (generally)}}{\lessgtr}}$

Exceptions of formation reaction :

$$\left[\begin{array}{l} C + 2S \longrightarrow CS_2 \\ \frac{1}{2}N_2 + \frac{3}{2}Cl_2 \longrightarrow NCl_3 \\ N_2 + O_2 \longrightarrow NO/N_2O/NO_2/N_2O_4 \\ O_2 + F_2 \longrightarrow OF_2/O_2F_2 \end{array}\right] \Delta H = +ve \text{ (endothermic)}$$

GOLDEN KEY POINTS

(i) If conditions are not given then, ΔH is considered to be $\Delta H°$.

(ii) If thermochemical reaction is multiplied by a coefficient then, ΔH of reaction is also multiplied by that coefficient.

e.g. $H_2(g) + ½\ O_2(g) \longrightarrow H_2O\ (\ell)$ $\Delta H = -285\ kJ\ mol^{-1}$

$2H_2(g) + O_2 \longrightarrow 2H_2O\ (\ell)$ $\Delta H = -2 \times 285\ kJ$

(iii) If reaction is reversed then numerical value of ΔH remains same but sign is changed.

$H_2(g) + ½\ O_2(g) \longrightarrow H_2O\ (\ell)$ $\Delta H = -285\ kJ\ mol^{-1}$

$H_2O\ (\ell) \longrightarrow H_2(g) + ½\ O_2(g)$ $\Delta H = +285\ kJ\ mol^{-1}$

BEGINNER'S BOX–7

1. An endothermic reaction is one in which :
(1) heat is converted into electricity (2) heat is asborbed
(3) heat is evolved (4) heat is converted into mechanical work

2. If heat of reaction $A + 5B \longrightarrow 2C + 3D$, is –50 kJ. What is the heat of the reaction $2A + 10B \longrightarrow 4C + 6D$.
(1) – 50 kJ (2) – 25 kJ (3) – 100 kJ (3) + 100 kJ

3. The process $CH_3COOH \longrightarrow CH_3COO^- + H^+$, should be :
(1) exothermic (2) endothermic
(3) neither exothermic nor endothermic (4) exothermic or endothermic depending upon temperature

4. For the given reaction :

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$; $\Delta H = 40$ kJ

The ΔH is specifically called
(1) Heat of formation of CO (2) Heat of combustion
(3) Heat of reaction (4) Heat of hydrogenation of C = O bond

5.17 HEAT OF REACTION OR (ENTHALPLY OF REACTION) OR (ΔH_R) :

The amount of heat evolved or absorbed when number of moles of the reactant according to the balanced chemical reaction had completely reacted is called as heat of reaction.

Example : $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$, $\Delta H_R = \checkmark$

$H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{(g)}$, $\Delta H_R = \times$

$H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{2(g)}$, $\Delta H_R = \checkmark$

Note : Heat of reaction at constant pressure is ΔH and heat of reaction at constant volume is ΔE.

Factors affecting heat of reaction :

(i) Reaction condition :

(a) The chemical reactions are carried out at constant temperature with either pressure or volume constant.

At constant pressure $q_p = \Delta H_{reactin}$

At constant volume $q_v = \Delta E_{reaction}$

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

(ii) Quantity of reactant :

Example : $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H_1 = -x$ lCal mol^{-1}

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta H_2 = 2 \times (-x$ Kcal)

If equation is multiplied by coefficient then value of ΔH is also multiplied by that coefficient.

(iii) Physical state of products and reactants :

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$, $\Delta H = -285.8$ kJ $mole^{-1}$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$, $\Delta H = -242$ kJ/$mole^{-1}$

If the physical state of product is different then the value of ΔH is different.

Note : For H_2O (liq.), ΔH is more negative in comparison to the formation of H_2O(vap.) because when vapours convert into liquid then some heat is released.

(iv) Allotropic form : (Physical nature of reactant)

$C_{graphite} + O_2 \longrightarrow CO_2$, $\Delta H_R = -393.5$ kJ $mole^{-1}$

$C_{diamond} + O_2 \longrightarrow CO_2$, $\Delta H_R = -399.5$ kJ $mole^{-1}$

(v) Temperature :

Effect of temperature on heat of reaction is given by **Kirchoff equation**

(i) at constant pressure : $\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_{Pm}$

$\Delta C_{Pm} = \Sigma(C_{Pm})_P - \Sigma(C_{Pm})_R$

ΔH_{T_1} = Heat of reaction at T_1 temperature

ΔH_{T_2} = Heat of reaction at T_2 temperature

(ii) at constant volume : $\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_{Vm}$

$\Delta C_{Vm} = \Sigma(C_{Vm})_P - \Sigma(C_{Vm})_R$

5.18 TYPES OF HEAT OF REACTION :

(A) Heat of formation, Enthalpy of formation (ΔH_f) or (Δ_f H) :

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states).

The reference state of oxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$, respectively some reactions with standard molar enthalpies of formation are :

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f \quad ✓$$

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow \underset{1\text{mole}}{HNO_3} \qquad \Delta H_f \quad ✓$$

$$Na_{(s)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \longrightarrow \underset{1\text{mole}}{NaOH} \qquad \Delta H_f \quad ✓$$

APPLICATION OF ΔH_f :

Calculation of ΔH of any general reaction.

Let us considered a general reaction $aA + bB \rightarrow cC + dD$

$$\Delta H_{reaction} = \Sigma\Delta H_{f(products)} - \Sigma\Delta H_{f(reactant)} = \left[c\Delta H_{f(C)} + d\Delta H_{f(D)}\right] - \left[a\Delta H_{f(A)} + b\Delta H_{f(B)}\right]$$

GOLDEN KEY POINTS

- Standard condition means, P = 1 atm, T = 25°C or 298 K
  Standard heat of formation is represent by ΔH_f°.
- If no condition is given then value of ΔH_f is considerd as ΔH_f°.
- Standard heat of formation of all the elements in stable standard state is taken to be zero.
- The reference state of commonly used elements are

Elements	Reference state	
C	$C_{(graphite)}$	
S	$S_{8(Rhombic)}$	(Rhombic sulphur is energy wise more stable as compared to monoclinic sulphur)
P	$P_{4(white)}$	
O	$O_{2(g)}$	
H	$H_{2(g)}$	
Br	$Br_{2(\ell)}$	
Metal	$M_{(s)}$[except $Hg_{(\ell)}$]	

- The formation reaction may be exothermic or endothermic.

Illustrations

Illustration 34 Since enthalpy of elements in their natural state is taken as zero. The value of ΔH_f of compounds :
(1) is always negative (2) is always positive
(3) may be positive or negative (4) is zero

Solution **Ans. (3)**

Illustration 35 The enthalpy of formation of ammonia at 298K is given as $\Delta H_f^\circ = -46.11$ kJ per mol of $NH_3(g)$. To which of the following equation does this value apply ?

(1) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ (2) $N(g) + 3H(g) \longrightarrow NH_3(g)$

(3) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ (4) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(\ell)$

Solution **Ans. (1)**

Illustration 36 Which of the following equation represents the standard heat of formation :

(1) C(diamond) + $2H_2(g) \longrightarrow CH_4(g)$ (2) C(graphite) + $2H_2(g) \longrightarrow CH_4(g)$

(3) C(diamond) + $4H(g) \longrightarrow CH_4(g)$ (4) C(graphite) + $4H(g) \longrightarrow CH_4(g)$

Solution **Ans. (2)**

Illustration 37 Which of the following reaction defines ΔH_f°

(1) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$ (2) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$

(3) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ (4) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

Solution **Ans. (2)**

Illustration 38 How much heat will be required at constant pressure to form 1.28 kg of CaC_2 from CaO(s) & C(s)?

Given : $\Delta_f H^\circ$ (CaO, s) = – 152 kCal mol^{-1}

$\Delta_f H^\circ$ (CaC_2, s) = – 14 kCal mol^{-1}

$\Delta_f H^\circ$ (CO, g) = – 26 kCal mol^{-1}

(1) + 112 kCal (2) 224 kCal (3) 3840 kCal (4) 2240 kCal

Solution. $CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$

$\Delta_f H^\circ = (-14 - 26) - (-152) = +112$ kCal mol^-

Total heat required = $\left(\frac{1280}{64}\right) \times 112 \quad \Rightarrow \quad 2240$ kCal

Illustration 39 The $\Delta_f H^\circ$ (N_2O_5, g) in kJ mol^{-1} on the bases of the following data is :

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\Delta_r H^\circ = -114$ kJ mol^{-1}

$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$ $\Delta_r H^\circ = -102.6$ kJ mol^{-1}

$\Delta_f H^\circ$ (NO,g) = 90.2 kJ mol^{-1}

(1) 15.1 (2) 30.2 (3) – 36.2 (4) none of these

Solution $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$ $\Delta_f H^\circ = 90.2$

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\Delta_r H^\circ = 90.2 \times 2$ ... (1)

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\Delta_r H^\circ = -114$ ... (2)

$2NO_2(g) + \frac{1}{2}O_2(g) \longrightarrow N_2O_5(g)$ $\Delta_r H^\circ = \frac{-102.6}{2} = -51.3$... (3)

From Equations (1) + (2) + (3)

$N_2(g) + \frac{5}{2}O_2(g) \longrightarrow N_2O_5(g)$ $\Delta_f H^\circ(N_2O_5, g) = 15.1$ kJ mol^{-1}

Illustration 40 Calculate ΔH° for $2Al_{(s)} + Fe_2O_3 \longrightarrow 2Fe_{(s)} + Al_2O_3$ given that standard enthalpy of Fe_2O_3 and Al_2O_3 are –196.5 and –399.1 kCal.

Solution $\Delta H^0_{Reaction} = \Sigma \Delta H_P^\circ - \Sigma \Delta H_R^\circ$

$= \left[2 \times \Delta H^0_{Fe(s)} + \Delta H^0_{Al_2O_3}\right] - \left[2 \times \Delta H^0_{Al(s)} + \Delta H^0_{Fe_2O_3}\right] = 2 \times 0 + (-399.1) - [2 \times 0 + (-196.5)]$

$\Delta H^0_{Reaction} = -202.6$ kCal

Illustration 41 The heat of formation of the compound in the following reaction is :

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)} + 44 \text{ Kcal}$$

(1) –44 kCal mol^{-1} (2) – 22 kCal mol^{-1} (3) +11 kCal mol^{-1} (4) –88 kCal mol^{-1}

Solution **Ans. (2)**

For the formation of 1 mol of HCl from elements $\Delta H_f^\circ = -\frac{44}{2} = -22$ Kcal

(B) Heat of combustion (ΔH_{comb}) :

Amount of heat evolved when 1 mole of substance is completely burnt (or oxidised) in excess of oxygen.

Example :

$\underset{1\text{mole}}{C_{\text{graphite}}} + O_2 \longrightarrow CO_2, \Delta H_{comb}$ ✓ and ΔH_f ✓

$\underset{1\text{mole}}{C_{\text{diamond}}} + O_2 \longrightarrow CO_2, \Delta H_{comb}$ ✓ and ΔH_f ×

$\underset{1\text{mole}}{C} + \frac{1}{2}O_2 \longrightarrow CO, \quad \Delta H_{comb}$ × and ΔH_f ✓

$\underset{1\text{mole}}{CO} + \frac{1}{2}O_2 \longrightarrow CO_2, \quad \Delta H_{comb}$ ✓ and ΔH_f ×

Note :

(I) Heat of combustion reaction is always exothermic

(II) If conditions are not given then ΔH_{comb} considered as ΔH°_{comb}.

(III) If in a reaction heats of combustion of reactants and products are given then heat of that reaction can be measured as follows

$$\boxed{\Delta H = \Sigma (\Delta H_{comb})_R - \Delta(\Delta H_{comb})_P}$$

APPLICATION OF HEAT OF COMBUSTION :

Calorific value or fuel value (C.V.) :

The amount of heat evolved when 1 g of a substance (food or fuel) is completely burnt (or oxidised)

$$\boxed{\text{Calorific value} = \frac{\Delta H_{comb}}{\text{Molecular weight}}}$$

Unit :- kJ g^{-1} or kCal g^{-1}

GOLDEN KEY POINTS

- Heat of combustion reaction is always exothermic
- If conditions are not given then ΔH_{comb} is considered as ΔH°_{comb}.
- Maximum value of calorific value = Maximum efficiency or best fuel
- H_2 has the highest calorific value (150 kJ/g) but it is not used as domestic or industrial fuel due to some technical problems.

Illustrations

Illustration 42 1 mole of methanol, when burnt in oxygen, gives out –723 kJ mol^{-1} heat. If 1 mole of oxygen is used what will be the amount of heat evolved?

(1) 723 kJ (2) 964 kJ (3) 482 kJ (4) 241 kJ

Solution **Ans. (3)**

$CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O, \quad \Delta H = -723$ kJ

with 1 mole of O_2, $\Delta H = -\frac{2}{3} \times 723 = -482$ kJ

Illustration 43 Combustion of methane :

(1) is an exothermic reaction (2) is an endothermic reaction

(3) requires a catalyst (4) gives H_2

Solution **Ans. (1)**

Combustion is always exothermic

Illustration 44 The heat evolved in the combustion of glucose is given by the equation

$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g), \quad \Delta H = -680$ kCal

The wt. of $CO_2(g)$ produced when 170 kCal of heat is evolved in the combustion of glucose is

(1) 264 g (2) 66 g (3) 11 g (4) 44 g

Solution **Ans. (2)**

Evolution of 680 Kcal is accompanied by $CO_2 = 6 \times 44 = 264$ g

Evolution of 170 Kcal is accompanied by $CO_2 = \frac{264}{680} \times 170 = 66$ g

Illustration 45 Find out the calorific value of Glucose

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; $\Delta H = -2900$ kJ mol^{-1}

Solution $\because$ Heat evolved from 1 mol glucose = 2900 kJ

or Heat evolved from 180 gram glucose = 2900 kJ

$\therefore$ Heat evolved from 1 gram glucose = $\frac{2900}{180} = 16.11$ kJ g

or another method C.V. = $\frac{\Delta H_{comb}}{M_w} = \frac{2900}{180} = 16.11$ kJ g

Illustration 46 Enthalpy of combustion of a substance is always :

(1) > 0 (2) ≥ 0 (3) ≤ 0 (4) < 0

Solution **Ans. (4)**

Illustration 47 The heat change for a reaction : $CO(g) + \frac{1}{2}O_2 \longrightarrow CO_2(g)$ refers to

(1) enthalpy of formation of carbon dioxide (2) enthalpy of combustion of carbon dioxide

(3) enthalpy of vapourisation (4) enthalpy of combustion of carbon monoxide

Solution **Ans. (4)**

(C) Heat of neutralisation (ΔH_{neut}) :

The heat evolved when one equivalent of an acid is completely neutralised by one equivalent of a base in dilute solution is called as heat of neutralisation.

$$SA + SB \longrightarrow Salt + Water$$

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

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

$$\boxed{H^+ + OH^- \longrightarrow H_2O}$$

Note :

(i) When one equivalent of SA is neutralised by one equivalent of SB then evolve heat remain constant and its value is – 13.7 kCal/equivalent or – 57.2 kJ equivalent^{-1}.

eg. SA		SB		
HCl (aq)	+	NaOH (aq)	$\longrightarrow$	$NaCl + H_2O + 13.7$ kCal
NV = 1 eq.		NV = 1 eq.	$\longrightarrow$	$\Delta H = -13.7$ kCal
NV = 2 eq.		NV = 2 eq.	$\longrightarrow$	$\Delta H = 2\ (-13.7)$ kCal
NV = 3 eq.		NV = 3 eq.	$\longrightarrow$	$\Delta H = 3\ (-13.7)$ kCal
NV = 4 eq.		NV = 5 eq. = (4 + 1) eq.	$\longrightarrow$	$\Delta H = 4\ (-13.7)$ kCal
NV = 5 eq. = (3+2)eq		NV = 3 eq.	$\longrightarrow$	$\Delta H = 3\ (-13.7)$ kCal

(ii) If one of the acid or base or both are weak then heat of neutralization is usually less than –13.7 KCal eq^{-1} or –57.3 kJ eq^{-1} because some part of the heat released in neutralization is absorbed to dissociate the weak electrolyte completely.

eg. $\overset{WA}{CH_3COOH}(aq) + \overset{SB}{NaOH}(aq) \rightarrow CH_3COONa(aq) + H_2O;\ \Delta H = -13.4$ kCal eq^{-1}

Exception :

For a reaction HF + NaOH $\rightarrow$ NaF + H_2O; ΔH=–16.7 Kcal; this is because of hydration of F^- ion.

(D) Heat of hydrogenation ($\Delta H_{Hydrogenation}$) :

The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.

Unsaturated organic compound $\xrightarrow{\text{Change}}$ Saturated organic compound

(= or ≡ Bond)			**(– Bond)**	
$C_2H_2 + 2H_2$	$\longrightarrow$	C_2H_6,	ΔH_{hydro}	✓
$C_2H_2 + H_2$	$\longrightarrow$	C_2H_4,	ΔH_{hydro}	×
$C_2H_4 + H_2$	$\longrightarrow$	C_2H_6,	ΔH_{hydro}	✓

Note : Heat of hydrogenation is exothermic process.

(E) Heat of atomization (ΔH_{atom}) :

The amount of heat required to dissociate 1 mol substance into gaseous atoms is called as heat of atomization.

Example :

$\frac{1}{2}H_{2(g)} \longrightarrow 1\ H_{(g)}$	ΔH_{atom}	×
$H_{2(g)} \longrightarrow 2\ H_{(g)}$	ΔH_{atom}	✓
$\frac{1}{2}Cl_{2(g)} \longrightarrow 1\ Cl_{(g)}$	ΔH_{atom}	×
$Cl_{2(g)} \longrightarrow 2Cl_{(g)}$	ΔH_{atom}	✓

Note : It is an endothermic reaction.

(F) HEAT OF TRANSFORMATION :

(i) Heat of fusion (ΔH_{fusion}) : The required amount of heat to convert 1 mole solid into liquid at its melting point is called as heat of fusion.

Example : $1\ H_2O_{(s)} \longrightarrow H_2O_{(l)}$ ΔH_{fusion} ✓

Note : Heat of fusion is always endothermic reaction i.e. (ΔH = + ve)

(ii) Heat of vapourization (ΔH_{Vapour}) : The required amount of heat to convert 1 mole liquid into gas at its boiling point is called as heat of vapourization.

Example : $1\ H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$ ΔH_{Vapour} ✓

Note : Heat of vapourization is always endothermic reaction i.e. (ΔH = +ve)

(iii) Heat of sublimation (ΔH_{Sub}) :

The required amount of heat to convert 1 mole solid into gas at a certain termperature is called as heat of sublimation.

Example : $H_2O_{(s)} \longrightarrow H_2O_{(g)}$, ΔH_{Sub} ✓

Note : Heat of sublimation is always endothermic reaction i.e. (ΔH = + ve)

Illustrations

Illustration 48 Heat of neutralisation of an acid by a base is maximum when :
(1) Both the acid and base are weak
(2) Both the acid and base are strong
(3) The acid is strong and the base is weak
(4) The acid is weak and the base is strong

Solution **Ans. (2)**
Heat of neutralisation is maximum (57.2 kJ eq^{-1} or 13.7 kCal eq^{-1}) when both acid and base are strong.

Illustration 49 The enthalpy change for the process $C_{(s)} \longrightarrow C_{(g)}$ corresponds to the enthalpy of
(1) fusion (2) vapourization (3) combustion (4) sublimation

Solution **Ans. (4)**
Solid ⟶ gas, is sublimation.

Illustration 50 If $H^+ + OH^- \longrightarrow H_2O$ + 13.7 kCal, then heat of complete neutralisation of 1 gm mol of H_2SO_4 with base in excess will be :
(1) –13.7 kCal (2) –27.4 kCal (3) –6.85 kCal (4) –3.425 kCal

Solution **Ans. (2)**
Moles of H_2SO_4 = 1 mol
g eq. of H_2SO_4 = moles ×V.F. = 1 ×2 = 2 g eq.
Heat evolve due to 2 g eq. = – 13.7 ×2 = – 27.4 kCal

Illustration 51 200 cm^3 of 0.1 M H_2SO_4 is mixed with 150 cm^3 of 0.2 M KOH. Find the value of evolved heat.

Solution

H_2SO_4	KOH
eq. = NV = (0.1 ×2) ×0.2	(0.2 ×1) ×(0.15)
= 0.04	= 0.03

Heat liberated by 1 eq. = 57.2 kJ
So heat liberated by 0.03 eq. = 57.2 ×0.03 = 1.7 kJ

BEGINNER'S BOX–8

1. Enathalpy of neutralisation of acetic acid with KOH will be numerically :
(1) = 57.2 kJ (2) > 57.2 kJ (3) < 57.2 kJ (4) unpredictable

2. The vapourisation process is always :
(1) exothermic (2) endothermic
(3) can be exothermic or endothermic (4) none of these

3. One mol of H_2SO_4 is completely neutralised with 2 mole of NaOH in dilute solutions. The amount of heat **evolved** during the process is :
(1) 57.2 kJ (2) $\frac{57.2\,kJ}{2}$ (3) 13.7 kCal (4) 114.4 kJ

4. Which of the following data represents the value of heat of neutralisation of strong acid against strong base ?
(1) – 13.7 kCal (2) – 57.2 kJ (3) -5.72×10^4 J (4) All the above

5. Fusion of ice is :
(1) exothermic change (2) endothermic change
(3) a process that does not involve any heat change (4) unpredictable

---

(G) Heat of hydration (ΔH_{hydra}) :

Amount of heat evolved when **one mole** of anhydrous salt combines with fixed number of water molecules to convert into its specific hydrated crystal is called as heat of hydration.

Example :

- $1\ CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5\,H_2O(s)$ $\Delta H = -ve$
  anhydrous salt hydrated salt
- $1\ MgSO_4(s) + 7H_2O(\ell) \longrightarrow MgSO_4.7H_2O(s)$ $\Delta H = -ve$
  anhydrous salt hydrated salt
- $1\ CaCl_2(s) + 6H_2O(\ell) \longrightarrow CaCl_2.6\,H_2O(s)$ $\Delta H = -ve$
  anhydrous salt hydrated salt

Special Note : Heat of hydration is exothermic

(H) Heat of solution ($\Delta H_{sol.}$) :

Amount of heat absorbed or evolved when **one mol** of substance is dissolved in such a large volume of solvent that further addition of solvent does not produce any more heat change is called as **'Heat of solution'**.

Example 1: $1\ CuSO_{4(s)} + aq \longrightarrow CuSO_4(aq)$ $\Delta H_{solution}$ ✓

$1\ CuSO_{4(s)} + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s)$ $\Delta H_{hydration}$ ✓

Example 2: $MgSO_{4(s)} + 7H_2O(\ell) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

$MgSO_4.7H_2O(s) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

Sp. Note : Heat of solution may be endothermic or exothermic.

(I) Bond energy / Bond dissociation energy :

The required amount of energy to dissociate **one mole gaseous bond** into separate **gaseous atoms** is called as **bond dissociation energy.**

Example :

$1H - H_{(g)} \longrightarrow 2H_{(g)}$	ΔH_{H-H}	✓
$1Cl - Cl_{(g)} \longrightarrow 2Cl_{(g)}$	ΔH_{Cl-Cl}	✓
$1H - Cl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)}$	ΔH_{H-Cl}	✓
$1H - Cl_{(g)} \longrightarrow H^+_{(g)} + Cl^-_{(g)}$	ΔH_{H-Cl}	×
$1H - Cl_{(g)} \longrightarrow \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)},$	ΔH_{H-Cl}	×
$1H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)}$	ΔH_{H-O}	×

GOLDEN KEY POINTS

- The **bond energy** may be defined as the **average** amount of energy required to dissociate one mole gaseous bond into separate gaseous atoms.
- Bond dissociation process is an endothermic process.
- If bond energy of various bonds present in the reactants and products are given then ΔH of that reaction can be calculate as follows.

$$\boxed{\Delta H = \Sigma (B.E.)_R - \Sigma (B.E.)_P}$$

- **In the case of poly atomic molecule** we calculate the average bond energy.

$$\boxed{(BE)_{av} = \text{Average bond energy} = \frac{\text{Total energy required with all bonds}}{\text{Number of bond dissociation}}}$$

Example :

$$H - O - H_{(g)} + 112\ KJ \longrightarrow H - O_{(g)} + H_{(g)}$$

$$H - O_{(g)} + 108\ KJ \longrightarrow H_{(g)} + O_{(g)}$$

$$(BE)_{av} = \text{Average bond energy} = \frac{112+108}{2} = 110\ \text{kJ mol}^{-1}$$

Illustrations

Illustration 52 Given the bond energy of N ≡ N, H – H and N – H bonds are 945, 436 and 391 kJ mol^{-1} respectively, the enthalpy of the reaction $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ is :

(1) – 93 kJ (2) 102 kJ (3) 90 kJ (4) 105 kJ

Solution **Ans. (1)**

$$N \equiv N_{(g)} + 3H - H_{(g)} \longrightarrow 2\,\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{N}}}}\!-\!H_{(g)}$$

$945 + 3 \times 436$ $2 \times (3 \times 391)$

$= 2253$ kJ $= 2346$ kJ

$\Delta H = \Sigma (B.E.)_R - \Sigma (B.E.)_P = 2253 - 2346 = -93$ kJ

Illustration 53 The enthalpy changes at 298 K in successive breaking of O – H bonds of H – O – H are

$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)}$, $\Delta H = 498$ kJ mol^{-1}

$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)}$, $\Delta H = 428$ kJ mol^{-1}

The bond enthalpy of the O – H bond is

(1) 498 kJ mol^{-1} (2) 463 kJ mol^{-1} (3) 428 kJ mol^{-1} (4) 70 kJ mol^{-1}

Solution **Ans. (2)**

$$(B.E.)_{av} = \frac{498 + 428}{2} = 463 \text{ kJ}$$

Illustration 54 The required heat for dissociation of 1 mol H_2O into its atoms (H and oxygen) is $\Delta H_{Dis.}$. Then calculate the bond energy of O – H bond.

$H_2O\,(g) \rightarrow O(g) + 2H(g)$; $\Delta H_{Dissociation}$

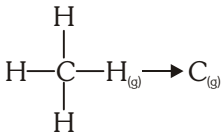
Solution $H - O - H(g) \longrightarrow O(g) + 2H(g)$; $\Delta H_{Dissociation}$

$\because$ required energy for breaking the 2 mol O – H bond = $\Delta H_{Dis.}$

$\therefore$ required energy for 1 mole $= \frac{\Delta H_{Dis.}}{2}$; $\Delta H_{O-H} = \frac{\Delta H_{Dis.}}{2}$

Illustration 55 Calculate the bond energy of C – H Bond in methane.

Solution $CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}$; $\Delta H_{Dis.}$

or  ; $\Delta H_{Dis.}$

$\because$ Bond energy of 4 mol C – H= ΔH_{Dis}

$\therefore$ Bond energy of 1 mol C – H bond $= \frac{\Delta H_{Dis.}}{4}$

Illustration 56 The energy change of reaction $C_2H_{6(g)} \longrightarrow 2C_{(g)} + 6H_{(g)}$ is X kJ. The bond energy of C – H bond is:

(1) $\frac{X}{6}$ kJ mol^{-1} (2) $\frac{X}{3}$ kJ mol^{-1} (3) X kJ /mol^{-1} (4) unpredictable from data

Solution **Ans. (4)**

Illustration 57 $CuSO_4(\ell) + 5H_2O(s) \longrightarrow CuSO_4.\,5H_2O(s)$; $\Delta H = -x$ kJ

The value of ΔH represents :

(1) enthalpy of solution of copper (II) sulphate

(2) enthalpy of hydration of copper (II) sulphate

(3) enthalpy of hydrolysis of copper (II) sulphate

(4) lattice energy of copper (II) sulphate

Solution **Ans. (2)**

Illustration 58 The bond energy of hydrogen is 103 kCal mol^{-1}. This means that :

(1) 103 kCal are required to break 6.023×10^{23} gaseous H_2 molecules into gaseous atoms

(2) 103 kCal are required to break the bonds in one gram of hydrogen

(3) 103 kCal are required to break one bond to form two atoms of hydrogen

(4) 103 kCal are required to break one mole of gaseous hydrogen molecules into ions.

Solution **Ans. (1)**

5.19 LAWS OF THERMOCHEMISTRY :

(I) LAVOISIER AND LAPLACE LAW :

Enthalpy of formation of compound is **numerically equal** to the enthalpy of decomposition of that compound with **opposite sign**.

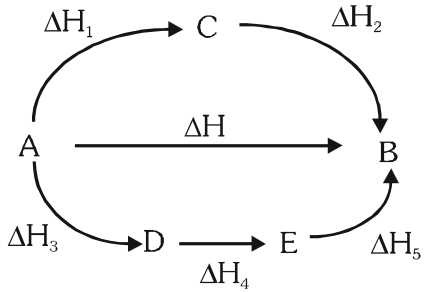
Example : $C + O_2 \longrightarrow CO_2, \quad \Delta H = -94$ kCal

$CO_2 \longrightarrow C + O_2, \quad \Delta H = +94$ kCal

(II) HESS LAW OF CONSTANT HEAT SUMMATION :

The heat change in a complete chemical reaction always remain same whether reaction completes in one step or more.

Example - 1 :

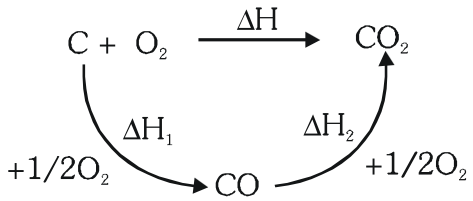


$\Delta H = \Delta H_1 + \Delta H_2$

or $\Delta H = \Delta H_3 + \Delta H_4 + \Delta H_5$

or $\mathbf{\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5}$

Example - 2 :



$\mathbf{\Delta H = \Delta H_1 + \Delta H_2}$

GOLDEN KEY POINTS

- Heat change of a reaction does not depend on the **number of steps** used in the reaction.
- Heat change of a reaction does not depend on **intermediate position**, it depend only on initial and final state.
- Heat change of a chemical reaction does not depend on **time of reaction**.

Illustrations

Illustration 59 Single step reaction $A \rightarrow B$; $\Delta H = ?$

Multi step reaction to produce B from A is given

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

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

Illustration 60 Calculate the heat of formation of Benzene. The reaction is given below :

$6C(s) + 3H_{2(g)} \rightarrow C_6H_6(\ell)$ and –3268, –393.5 and –285.8 kJ mol^{-1} are the heats of combustion of benzene, heat of formation of CO_2 and heat of formation of $H_2O(\ell)$ respectively.

Solution Target reation $6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(\ell)}$

Given

(i) $C_6H_{6(\ell)} + 7\frac{1}{2}\ O_{2(g)} \rightarrow 6CO_2\,(g) + 3H_2O\,(\ell)$ $\Delta H = -3268$ kJ

(ii) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kJ

(iii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$; $\Delta H = -285.8$ kJ

6 ×eq. (ii) + 3 ×eq. (iii) – eq. (i)

$\Delta H = 6 \times -393.5 + 3 \times -285.8 - (-3268) = +49.6$ kJ mol^{-1}

Illustration 61 The heats of formation of $CO_{2\,(g)}$ and $H_2O_{(\ell)}$ are – 97 and – 68 kCal mol^{-1}. The heat of combustion of benzene is –783 kCal mol^{-1}. What will be the heat of formation of benzene ?

Solution Given :

(i) $C_6H_6\,(\ell) + \frac{7}{2}O_2\,(g) \longrightarrow 6CO_2\,(g) + 3H_2O\,(\ell)$; $\Delta H = -783$ kCal.

(ii) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta H = -97$ kCal.

(iii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(\ell)$; $\Delta H = -68$ kCal.

Target reaction $6C\,(s) + 3H_2\,(g) \longrightarrow C_6H_6(\ell)$; $\Delta H = -3$ kCal.

6 ×eq. (ii) + 3 ×eq. (iii) – eq. (i)

$\Delta H = 6 \times -97 + 3 \times -68 - (-783) = -3$ kCal mol^{-1}

Illustration 62 Calculate the enthalpy of combustion of ethylene (gas) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of $CO_{2\,(g)}$, $H_2O_{(g)}$ and $C_2H_{4(g)}$ are –393.7, –241.8, + 52.3 kJ per mol respectively.

Solution We are given :

(i) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta H = -393.7$ kJ mol^{-1}

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

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

Target reaction $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g)$, $\Delta H = ?$

2 × Equation (i) + 2 × Equation (ii) – Equation (iii) gives

$\Delta H = 2(-393.7) + 2\,(-241.8) - (52.3) = -1323.3$ kJ mol^{-1}

Illustration 63 The heat of solution of anhydrous $CuSO_{4(s)}$ is –15.9 kCal mol^{-1} and that of $CuSO_4.5H_2O_{(s)}$ is 2.8 kCal mol^{-1}. Calculate the heat of hydration of $CuSO_{4(s)}$.

Solution Given $CuSO_{4(s)} + aq. \longrightarrow CuSO_4\,(aq)$ $\Delta H = -15.9$ kCal ....(i)

$CuSO_4.5H_2O_{(s)} + aq. \longrightarrow CuSO_4(aq)$ $\Delta H = +2.8$ kCal .....(ii)

Subtracting Eq. (ii) from Eq.(i)

$CuSO_{4(s)} + 5H_2O \longrightarrow CuSO_4.5H_2O_{(s)}$; $\Delta H = -15.9 - 2.8 = -18.7$ kCal

Heat of hydration of $CuSO_4 = -18.7$ kCal mol^{-1}

BEGINNER'S BOX–9

1. A hypothetical reaction, $X \longrightarrow 2Y$ proceeds by the following sequence of steps

(i) $\frac{1}{2} X \longrightarrow Z$; $\Delta H = q_1$

(ii) $Z \longrightarrow 2W$; $\Delta H = q_2$

(iii) $W \longrightarrow \frac{1}{2} Y$; $\Delta H = q_3$

The value of ΔH of reaction is :

(1) $q_1 + q_2 + q_3$ (2) $2q_1 + 2q_2 + 3q_3$ (3) $2(q_1 + q_2 + 2q_3)$ (4) $2(q_1 + q_2 + q_3)$

2. Consider two paths of a certain reaction

(i) $A + B \xrightarrow{\Delta H_1} AB$; $AB \xrightarrow{\Delta H_2} P + Q$

(ii) $A + B \xrightarrow{\Delta H_3} C$; $C \xrightarrow{\Delta H_4} P + Q$ then,

(1) $(\Delta H_1 + \Delta H_2) > (\Delta H_3 + \Delta H_4)$ (2) $(\Delta H_1 + \Delta H_2) = (\Delta H_3 + \Delta H_4)$

(3) $(\Delta H_2 + \Delta H_3) = (\Delta H_1 + \Delta H_4)$ (4) $(\Delta H_1 + \Delta H_2) < (\Delta H_3 + \Delta H_4)$

ANSWER KEY

BEGINNER'S BOX-1	**Que.**	1	2	3	4						
	Ans.	**1**	**1**	**1**	**1**						
BEGINNER'S BOX-2	**Que.**	1	2	3	4						
	Ans.	**3**	**4**	**2**	**1**						
BEGINNER'S BOX-3	**Que.**	1	2	3	4	5	6	7	8		
	Ans.	**2**	**2**	**2**	**3**	**1**	**2**	**4**	**3**		
BEGINNER'S BOX-4	**Que.**	1	2								
	Ans.	**1**	**3**								
BEGINNER'S BOX-5	**Que.**	1	2	3	4	5	6	7			
	Ans.	**2**	**3**	**4**	**3**	**3**	**1**	**2**			
BEGINNER'S BOX-6	**Que.**	1	2	3	4	5	6				
	Ans.	**2**	**2**	**3**	**4**	**1**	**1**				
BEGINNER'S BOX-7	**Que.**	1	2	3	4						
	Ans.	**2**	**3**	**2**	**3**						
BEGINNER'S BOX-8	**Que.**	1	2	3	4	5					
	Ans.	**3**	**2**	**4**	**4**	**2**					
BEGINNER'S BOX-9	**Que.**	1	2								
	Ans.	**3**	**2**								

EXERCISE-I (Conceptual Questions) — Build Up Your Understanding

INTRODUCTION

1. Thermodynamics is concerned with :-
(1) Total energy of a system
(2) Energy changes in a system
(3) Rate of a chemical change
(4) Mass changes in nuclear reactions

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

3. Identify the intensive quantity from the following -
(1) Enthalpy and temperature
(2) Volume and temperature
(3) Enthalpy and volume
(4) Temperature and refractive index

4. Which of the following is an extensive property
(1) Mass (2) Enthalpy
(3) Energy (4) All of these

5. For an adiabatic process which of the following relations is correct
(1) $\Delta E = 0$ (2) $P\Delta V = 0$
(3) $q = 0$ (4) $q = + W$

6. In which of the following process work is independent of path :
(1) Isothermal (2) Isochoric
(3) Adiabatic (4) Isobaric

7. When a gas is compressed adiabatically and reversibly, the final temperature is-
(1) Higher than the initial temperature
(2) Lower than the initial temperature
(3) The same as initial temperature
(4) Dependent upon the rate of compression

8. Which one is dependent only on initial and final state ?
(1) Heat supplied at constant pressure
(2) Heat supplied at constant volume
(3) Enthalpy
(4) All of the above

9. Out of boiling point (I), entropy (II), pH (III) and emf of a cell (IV), intensive properties are :
(1) I, III, IV (2) I, II
(3) I, II, III (4) All of these

10. The work done by a weightless piston in causing an expansion ΔV (at constant temperature), when the opposing pressure P is variable, is given by :
(1) $W = -\int PdV$ (2) $W = 0$
(3) $W = -P\Delta V$ (4) None

11. The work done by 100 calorie of heat in isothermal expansion of ideal gas is :-
(1) 418.4 J (2) 4.184 J
(3) 41.84 J (4) None

12. Temperature and volume are not :-
(1) Extensive properties
(2) Intensive properties
(3) Intensive and extensive properties respectively
(4) Extensive and intensive properties respectively

13. $q = -w$ is not true for :-
(1) Isothermal process (2) Adiabatic process
(3) Cyclic process (4) 1 and 3 both

14. The temperature of an ideal gas increase in an -
(1) Adiabatic compression (2) Adiabatic expansion
(3) Isothermal expansion (4) Isothermal compression

15. Enthalpy of 1 mole monoatomic ideal gas is equals to :–
(1) $\frac{3}{2}RT$ (2) $\frac{5}{2}RT$
(3) RT (4) 2 RT

16. Which statement is true for reversible process :–
(1) It takes place in single step
(2) Driving force is much greater than opposing force
(3) Work obtain is minimum
(4) None

FIRST LAW OF THERMODYNAMICS ($\Delta E = q + W$)

17. Both q & w are_ _ _ _ _ function :-
(1) State (2) State, Path
(3) Path, State (4) Path

18. If work done by the system is 300 joule when 100 cal. heat is supplied to it. The change in internal energy during the process is :-
(1) – 200 Joul (2) 400 Joul
(3) 720 Joul (4) 120 Joul

19 A system has internal energy equal to E_1, 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -
(1) (E_1 + 150) (2) (E_1 + 1050)
(3) (E_1 – 150) (4) None of these

20. The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :
(1) 32 J (2) 40 J
(3) 48 J (4) –32 J

21. If a gas absorbs 100 J of heat and expands by 500cm^3 against a constant pressure of 2×10^5 Nm^{-2}, the change in internal energy is:-
(1) - 300 J (2) - 100 J
(3) + 100 J (4) None of these

ENTHALPY [$\Delta H = \Delta E + P\Delta V/\Delta H = \Delta E + \Delta n_g RT$]

22. Internal energy change during a reversible isothermal expansion of an ideal gas is :-
(1) Always negative
(2) Always positive
(3) Zero
(4) May be positive or negative

23. Under which of the following conditions is the relation, $\Delta H = \Delta E + P\Delta V$ valid for a system :–
(1) Constant pressure
(2) Constant temperature
(3) Constant temperature and pressure
(4) Constant temperature, pressure and composition

24. The difference between heats of reaction at constant pressure and constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ at 25^{0}C in KJ is
(1) + 7.43 (2) +3.72
(3) – 7.43 (4) – 3.72

25. For a gaseous reaction,
$A(g) + 3B(g) \longrightarrow 3C(g) + 3D(g)$
ΔE is 17 kCal at 27^{0}C assuming R = 2 Cal K^{-1} mol^{-1}, the value of ΔH for the above reaction is:
(1) 15.8 Kcal (2) 18.2 Kcal
(3) 20.0 Kcal (4) 16.4 Kcal

26. Which of the following statements is correct for the reaction ; $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ at constant temperature and pressure
(1) $\Delta H = \Delta E$ (2) $\Delta H < \Delta E$
(3) $\Delta H > \Delta E$ (4) None of the above

27. For the reaction $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$, which one of the following is true :
(1) $\Delta H = \Delta E$ (2) $\Delta H = \frac{1}{2}\Delta E$
(3) $\Delta H < \Delta E$ (4) $\Delta H > \Delta E$

28. A mixture of 2 moles of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If ΔH is the enthalpy change and ΔE is the change in internal energy, then :–
(1) $\Delta H > \Delta E$ (2) $\Delta H < \Delta E$
(3) $\Delta H = \Delta E$ (4) Not definite

29. For the gaseous reaction involving the complete combustion of isobutane -
(1) $\Delta H = \Delta E$ (2) $\Delta H > \Delta E$
(3) $\Delta H = \Delta E = 0$ (4) $\Delta H < \Delta E$

30. For the reversible isothermal expansion of one mole of an ideal gas at 300 K, from a volume of 10 dm^3 to 20 dm^3, ΔH is -
(1) 1.73 kJ (2) –1.73 kJ
(3) 3.46 kJ (4) Zero

31. For $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ at 977°C, ΔH = 174 KJ/mol ; then ΔE is :-
(1) 160 kJ (2) 163.6 kJ
(3) 186.4 kJ (4) 180 kJ

32. Heat of reaction for , $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at constant V is –67.71 K cal at 17°C. The heat of reaction at constant P at 17°C is :-
(1) –68.0 kCal (2) + 68.0 kCal
(3) – 67.42 kCal (4) None

33. The reaction :-

$$NH_2CN_{(S)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$$

was carried out in a bomb caloriemeter. The heat released was 743 kJ mol^{-1}. The value of ΔH_{300k} for this reaction would be :-
(1) – 740.5 kJ mol^{-1} (2) – 741.75 kJ mol^{-1}
(3) – 743.0 kJ mol^{-1} (4) – 744.25 kJ mol^{-1}

34. The enthalpy of vaporisation of water at 100^{0}C is 40.63 kJ mol^{-1}. The value ΔE for this process would be:-
(1) 37.53 kJ mol^{-1} (2) 39.08 kJ mol^{-1}
(3) 42.19 kJ mol^{-1} (4) 43.73 kJ mol^{-1}

35. For the system $S(s) + O_2(g) \rightarrow SO_2(g)$:–
(1) $\Delta H = \Delta E$ (2) $\Delta H > \Delta E$
(3) $\Delta E > \Delta H$ (4) $\Delta H = 0$

36. For the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

Which one of the statement is correct at constant T and P ?
(1) $\Delta H = \Delta E$
(2) $\Delta H < \Delta E$
(3) $\Delta H > \Delta E$
(4) ΔH is Independent of physical state of reactants

37. Which is true for the combustion of sucrose ($C_{12}H_{22}O_{11}$) at 25°C :-
(1) $\Delta H > \Delta E$ (2) $\Delta H < \Delta E$
(3) $\Delta H = \Delta E$ (4) None

38. For which change $\Delta H \neq \Delta E$:-

(1) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(2) $HCl(\ell) + NaOH(\ell) \rightarrow NaCl(s) + H_2O(\ell)$
(3) $C(s) + O_2(g) \rightarrow CO_2(g)$
(4) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

39. The heat of combustion of ethanol determined in a bomb calorimeter is – 670.48 kCal $mole^{-1}$ at 27°C. What is ΔH at 27°C for the reaction :–
(1) – 335.24 kCal (2) – 671.08 kCal
(3) – 670.48 kCal (4) + 670.48 kCal

40. The difference in ΔH and ΔE for the combustion of methane at 25°C would be :–
(1) Zero (2) $2 \times 298 \times -2$ Cals.
(3) $2 \times 298 \times -3$ Cals. (4) $2 \times 25 \times -3$ Cals.

41. For which of the following reactions ΔH is less than ΔE :–
(1) $C_{12}H_{22}O_{11}(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(\ell)$
(2) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
(3) $N_2O_4(g) \rightarrow 2NO_2(g)$
(4) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

42. For a reaction $2X(s) + 2Y(s) \rightarrow 2C(\ell) + D(g)$
The q_p at 27°C is – 28 kCal mol^{-1}.
The q_V is ---------- kCal mol^{-1} :–
(1) – 27.4 (2) + 27.4
(3) – 28.6 (4) 28.6

WORK DONE IN DIFFERENT PROCESS

43. The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25^0C is :
(1) $-2.303 \times 8.31 \times 10^7 \times 298 \log 2$
(2) $-2.303 \times 0.0821 \times 298 \log 2$
(3) $-2.303 \times 0.0821 \times 298 \log 0.5$
(4) $-2.303 \times 2 \times 298 \log 2$

44. 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 ?
(1) –504.2 Joule (2) –405.2 Joule
(3) +810.4 Joule (4) –810.4 Joule

45. Two moles of an ideal gas expand spontaneouly into vacuum. The work done is :–
(1) Zero (2) 2 J
(3) 4 J (4) 8 J

46. One mole of a gas occupying $3dm^3$ expands against a constant external pressure of 1 atm to a volume of 13 lit. The workdone is :–
(1) – 10 atm dm^3 (2) – 20 atm dm^3
(3) – 39 atm dm^3 (4) – 48 atm dm^3

ENTROPY/SECOND LAW OF THERMODYNAMICS

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

48. An adiabatic reversible process is one in which :-
(1) Temperature of the system does not change
(2) The system is not closed to heat transfer
(3) There is no entropy change
(4) None of these

49. Entropy means
(1) Disorderness (2) Randomness
(3) Orderness (4) both 1 & 2

50. ΔS for the reaction;
$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$ will be :
(1) 0 (2) –ve (3) +ve (4) ∞

51. Change in entropy is negative for
(1) Bromine (ℓ) $\longrightarrow$ Bromine (g)
(2) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$
(3) N_2(g, 10 atm) $\longrightarrow$ N_2 (g, 1 atm)
(4) Fe(at 400 K) $\longrightarrow$ Fe(at 300 K)

52. In which reaction ΔS is positive :-
(1) $H_2O(\ell) \rightarrow H_2O(s)$
(2) $3O_2(g) \rightarrow 2O_3(g)$
(3) $H_2O(\ell) \rightarrow H_2O(g)$
(4) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

53. When the egg is hard boiled, there is-
(1) Increase in disorder
(2) Decrease in disorder
(3) No change in disorder
(4) ΔG is negative

54. If S^0 for H_2, Cl_2 and HCl are 0.13, 0.22 and 0.19 kJ K^{-1} mol^{-1} respectively. The total change in standard entropy for the reaction
$H_2 + Cl_2 \longrightarrow 2HCl$ is :
(1) 30 JK^{-1} mol^{-1} (2) 40 JK^{-1} mol^{-1}
(3) 60 JK^{-1} mol^{-1} (4) 20 JK^{-1} mol^{-1}

55. Which has the least entropy :
(1) Graphite (2) Diamond
(3) $N_2(g)$ (4) $N_2O(g)$

56. When two gases are mixed the entropy :–
(1) Remains constant (2) Decreases
(3) Increases (4) Becomes zero

57. The enthalpy of vaporization for water is 186.5 kJ mol^{-1}, the entropy of its vaporization will be-
(1) 0.5 kJK^{-1} mol^{-1} (2) 1.0 kJK^{-1} $mole^{-1}$
(3) 1.5 kJ K^{-1} $mole^{-1}$ (4) 2.0 kJK^{-1} $mole^{-1}$

58. The enthalpy of vaporisation of per mole of ethanol (b.p. = 79.5^0C and ΔS = 109.8 JK^{-1} mol^{-1}) is :–
(1) 27.35 kJ mol^{-1} (2) 32.19 kJ mol^{-1}
(3) 38.70 kJ mol^{-1} (4) 42.37 kJ mol^{-1}

59. If 900J/g of heat is exchanged at boiling point of water, then what is increase in entropy?
(1) 43.4 $JK^{-1}mole^{-1}$
(2) 87.2 $JK^{-1}mole^{-1}$
(3) 900 $JK^{-1}mole^{-1}$
(4) Zero

60. 5 mole of an ideal gas expand reversibly from a volume of 8 dm^3 to 80dm^3 at a temperature of 27^0C. The change in entropy is :–
(1) 41.57 JK^{-1} (2) – 95.73 JK^{-1}
(3) 95.73 JK^{-1} (4) – 41.57 JK^{-1}

61. In a spontaneous irreversible process the total entropy of the system and surroundings
(1) Remains constant (2) Increases
(3) Decreases (4) Zero

62. The total entropy change for a system & its surroundings increases if the process is :
(1) Reversible (2) Irreversible
(3) Exothermic (4) Endothermic

63. Calculate the entropy of $Br_2(g)$ in the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, $\Delta S° = 20.1 JK^{-1}$ given, entropy of H_2 and HBr is 130.6 and 198.5 J mol^{-1} K^{-1} :-
(1) 246.3 JK^{-1} (2) 123.15 JK^{-1}
(3) 24.63 JK^{-1} (4) 20 KJK^{-1}

64. Ammonium chloride when dissolved in water leads to cooling sensation. The dissolution of NH_4Cl at constant temperature is accompanied by :–
(1) Increase in entropy
(2) Decrease in entropy
(3) No change in entropy
(4) No change in enthalpy

65. In which of the following case entropy decreases–
(1) Solid changing to liquid
(2) Expansion of a gas
(3) Crystals dissolve
(4) Polymerisation

66. Which of the following state function is not zero at standard state :–
(1) Enthalpy (2) Entropy
(3) Free energy (4) Work

67. Entropy of an adiabatic reversible process is:-
(1) Positive (2) Zero
(3) Negative (4) Constant

GIBBS FREE ENERGY

68. A gas is allowed to expand under reversible adiabatic conditions then what is zero for such a process:-
(1) $\Delta G = 0$ (2) $\Delta T = 0$
(3) $\Delta S = 0$ (4) None of these

69. For a reaction at 25^0C enthalpy change (ΔH) and entropy change (ΔS) are -11.7×10^3 $Jmol^{-1}$ and -105 J mol^{-1} K^{-1} respectively. The reaction is :
(1) Spontaneous
(2) Non spontaneous
(3) At equilibrium
(4) Can't say anything

70. The spontaneous nature of a reaction is impossible if :
(1) ΔH is +ve, ΔS is also +ve
(2) ΔH is – ve; ΔS is also – ve
(3) ΔH is –ve ; ΔS is +ve
(4) ΔH is +ve; ΔS is –ve

71. If $\Delta H > 0$ and $\Delta S > 0$, the reaction proceeds spontaneously when :-
(1) $\Delta H > 0$ (2) $\Delta H < T\Delta S$
(3) $\Delta H = T\Delta S$ (4) None

72. The temperature at which the reaction
$Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$
is at equilibrium is ……..;
Given $\Delta H = 30.5$ kJ mol^{-1}
and $\Delta S = 0.066$ kJK^{-1} mol^{-1} :
(1) 462.12 K (2) 362.12 K
(3) 262.12 K (4) 562.12 K

73. The enthalpy change for a given reaction at 298 K is –x cal mol^{-1}. If the reaction occurs spontaneously at 298 K, the entropy change at that temperature
(1) Can be negative but numerically larger than x/298 Cal K^{-1} mol^{-1}
(2) Can be negative but numerically smaller than x/298 Cal K^{-1} mol^{-1}
(3) Cannot be negative
(4) Cannot be positive

74. Which of the following is true for the reaction $H_2O(\ell) \rightleftharpoons H_2O(g)$ at 100^0C and 1 atmosphere
(1) $\Delta S = 0$ (2) $\Delta H = 0$
(3) $\Delta H = \Delta E$ (4) $\Delta H = T\Delta S$

75. For the reaction $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2} O_2(g)$ the value of $\Delta H = 30.56$ kJ mol^{-1} and ΔS=66 JK^{-1} mol^{-1}. The temperature at which the free energy change for the reaction will be zero is :–
(1) 373 K (2) 413 K
(3) 463 K (4) 493 K

76. For hypothetical reversible reaction
$\frac{1}{2}A_2(g) + \frac{3}{2}B_2(g) \longrightarrow AB_3(g)$; $\Delta H = -20$ kJ if standard entropies of A_2, B_2 and AB_3 are 60, 40 and 50 JK^{-1} $mole^{-1}$ respectively. The above reaction will be in equilibrium at :–
(1) 400 K (2) 500 K
(3) 250 K (4) 200 K

77. For the precipitation of AgCl by Ag^+ ions and HCl
(1) $\Delta H = 0$ (2) $\Delta G = 0$
(3) $\Delta G = -ve$ (4) $\Delta H = \Delta G$

78. What is the sign of ΔG for the process of ice melting at 283 K ?
(1) $\Delta G > 0$ (2) $\Delta G = 0$
(3) $\Delta G < 0$ (4) None of these

79. 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

80. A reaction A + B $\longrightarrow$ C + D + q is found to have a positive entropy change, the reaction will be -
(1) Possible at high temperature
(2) Possible only at low temperature
(3) Not possible at any temperature
(4) Possible at any temperature

81. Equilibrium constant of a reaction is related to :
(1) Standard free energy change ΔG^0
(2) Free energy change ΔG
(3) Entropy change
(4) None

82. The Vant Hoff equation is :
(1) $\Delta G° = RT \log_e K_p$ (2) $-\Delta G° = RT \log_e K_p$
(3) $\Delta G° = RT^2 \ell n K_p$ (4) None

83. If $\Delta G^0 > 0$ for a reaction then :
(1) $K_p > 1$
(2) $K_p < 1$
(3) The products predominate in the equilibrium mixture
(4) None

84. If the equilibrium constant for a reaction is 10, then the value of ΔG^0 will be
(R = 8JK^{-1} mol^{-1}, T = 300 K)
(1) + 5.527 kJ mol^{-1}
(2) – 5.527 kJ mol^{-1}
(3) +55.27 kJ mol^{-1}
(4) – 55.27 kJ mol^{-1}

85. The process of evaporation of a liquid is accompanied by :
(1) Increase in enthalpy
(2) Decrease in free energy
(3) Increase in entropy
(4) All

86. For the process, $CO_2(s) \longrightarrow CO_2(g)$:
(1) Both ΔH and ΔS are +ve
(2) ΔH is negative and ΔS is +ve
(3) ΔH is +ve and ΔS is –ve
(4) Both ΔH and ΔS are –ve

87. Which of the following provide exceptions to third law of thermodynamics
(1) CO (2) ice
(3) CO_2 (4) All the above

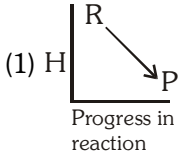
88. The Gibbs free energy change of a reaction at 27°C is –26 kCal. and its entropy change is – 60 Cals K. ΔH for the reaction is :–
(1) – 44 kCals. (2) – 18 kCals.
(3) 34 kals. (4) – 24 kCals.

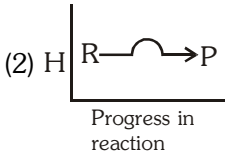
89. Which of the following reaction is expected never to be spontaneous :–
(1) $2O_3(g) \rightarrow 3O_2(g)$ $\Delta H = -Ve$, $\Delta S = +Ve$
(2) $Mg(s) + H_2(g) \rightarrow MgH_2$ $\Delta H = -Ve$, $\Delta S = -Ve$
(3) $Br_2(l) \rightarrow Br_2(g)$ $\Delta H = +Ve$, $\Delta S = +Ve$
(4) $2Ag(s) + 3N_2(g) \rightarrow 2AgN_3$ $\Delta H = +Ve$, $\Delta S = -Ve$

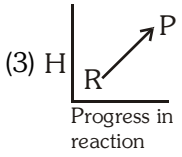
THERMOCHEMICAL REACTION

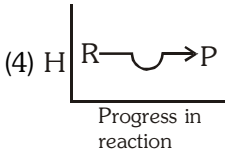
90. The formation of water from $H_2(g)$ and $O_2(g)$ is an exothermic process because :
(1) The chemical energy of $H_2(g)$ and $O_2(g)$ is more than that of water
(2) The chemical energy of $H_2(g)$ and $O_2(g)$ is less than that of water
(3) The temperature of $H_2(g)$ and $O_2(g)$ is higher than that of water
(4) The temperature of $H_2(g)$ and $O_2(g)$ is lower than that of water

91. Which plot represents for an exothermic reaction:

(1) 

(2) 

(3) 

(4) 

92. Which one of the following is not applicable for a thermochemical equation :
(1) It tells about physical state of reactants and products
(2) It tells whether the reaction is spontaneous
(3) It tells whether the reaction is exothermic or endothermic
(4) It tells about the allotropic form (if any) of the reactants

93. The correct thermochemical equation is :
(1) $C + O_2 \longrightarrow CO_2$; $\Delta H = -94$ kCal
(2) $C + O_2 \longrightarrow CO_2$; $\Delta H = +94.0$ kCal
(3) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -94$ kCal
(4) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = +94$ kCal

94. The enthalpy changes of formation of the gaseous oxide of nitrogen (N_2O and NO) are positive because of :
(1) The high bond energy of the nitrogen molecule
(2) The high electron affinity of oxygen atoms
(3) The high electron affinity of nitrogen atoms
(4) The tendency of oxygen to form O^{2-}

95. ΔH for transition of carbon from diamond form to graphite form is – 453.5 Cal. This suggests that :
(1) Graphite is chemically different from diamond
(2) Graphite is as stable as diamond
(3) Graphite is more stable than diamond
(4) Diamond is more stable than graphite

96. Which of the following values of heat of formation indicates that the product is least stable
(1) – 94 kCal (2) – 231.6 kCal
(3) + 21.4 kCal (4) + 64.8 kCal

97. Heat of formation, ΔH_f° of an explosive compound like NCl_3 is –
(1) Positive (2) Negative
(3) Zero (4) Positive or negative

98. According to the following reaction
$C(s) + 1/2\ O_2(g) \rightarrow CO(g)$, $\Delta H = -26.4$ kCal
(1) CO is an endothermic compound
(2) CO is an exothermic compound
(3) The reaction is endothermic
(4) None of the above

99. Which of the following represents an exothermic reaction:-
(1) $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H = 180.5$ kJ
(2) $H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$, $\Delta E = 131.2$kJ
(3) $2HgO(s) + 180.4$ KJ $\rightarrow 2Hg(\ell) + O_2(g)$
(4) $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$, $\Delta E = -693.8$ kJ

100. The heat change during the reaction 24g C and 128g S following the change $C+S_2 \rightarrow CS_2$; $\Delta H=22$ kCal
(1) 22 kCal (2) 11 kCal
(3) 44 kCal (4) 32 kCal

101. Consider the reaction $3O_2 \rightarrow 2O_3$; $\Delta H = +Ve$, from the reaction, we can say that :–
(1) Ozone is more stable then oxygen
(2) Ozone is less stable then oxygen and ozone decomposes forming oxygen readily
(3) Oxygen is less stable than ozone and oxygen decomposes forming ozone readily
(4) None of the above

102. From the reaction P(White) $\rightarrow$ P(Red) ; $\Delta H = -18.4$ kJ, it follows that :-
(1) Red P is readily formed from white P
(2) White P is readily formed from red P
(3) White P can not be converted to red p
(4) White P can be converted into red P and red P is more stable

FACTORS AFFECTING HEAT OF REACTION

103. In Kirchoff's equation which factor affects the heat of reaction :
(1) Pressure (2) Temperature
(3) Volume (4) Atomicity

104. For the reaction; $H_2(g) + \frac{1}{2} O_2(g) = H_2O(\ell)$, $\Delta C_p = 7.63$ Cal deg; $\Delta H_{25^0C} = 68.3$ kCal, what will be the value (in kCal) of ΔH at 100^0C :
(1) $7.63 \times (373 - 298) - 68.3$
(2) $7.63 \times 10^{-3} (373 - 298) - 68.3$
(3) $7.63 \times 10^{-3} (373 - 298) + 68.3$
(4) $7.63 \times (373 - 298) + 68.3$

105. The enthalpy of a reaction at 273 K is – 3.57 kJ. what will be the enthalpy of reaction at 373 K if ΔC_p = zero :–
(1) – 3.57 (2) Zero
(3) $-3.57 \times \frac{373}{273}$ (4) – 375

106. For the reactions,
(i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) + xkJ$
(ii) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(\ell) + ykJ$
Which one of the following statement is correct :
(1) x > y (2) x < y
(3) x = y (4) More data required

HEAT OF FORMATION

107. Since the enthalpy of the elements in their standard states is taken to be zero. The heat of formation (ΔH_f) of compounds :
(1) Is always negative
(2) Is always positive
(3) Is zero
(4) May be positive or negative

108. Reaction $H_2(s) + I_2(g) \longrightarrow 2HI$; $\Delta H = 12.40$ kCal. According to this, heat of formation of HI will be –
(1) 12.40 kCal (2) – 12.40 kCal
(3) – 6.20 kCal (4) 6.20 kCal

109. At 300K the standard enthalpies of formation of $C_6H_5COOH_{(s)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ are –408, –393 and –286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at contant volume :
(1) +3201 kJ
(2) +3199.75 kJ
(3) –3201 kJ
(4) –3199.75 kJ

110. Enthalpy of a compound is equal to its :- (When it is formed from constituent particles)
(1) Heat of combustion
(2) Heat of formation
(3) Heat of reaction
(4) Heat of solution

111. Which of the following equations respresents standard heat of formation of CH_4 ?
(1) $C_{(diamond)} + 2H_{2\,(g)} \longrightarrow CH_{4\,(g)}$
(2) $C_{(graphite)} + 2H_{2\,(g)} \longrightarrow CH_{4\,(g)}$
(3) $C_{(diamond)} + 4H_{(g)} \longrightarrow CH_{4\,(g)}$
(4) $C_{(graphite)} + 4H_{(g)} \longrightarrow CH_{4\,(g)}$

112. The enthalpy of formation of ammonia is –46.0 kJ mol^{-1}. The enthalpy change for the reaction $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ is :
(1) 46.0 kJ mol^{-1} (2) 92.0 kJ mol^{-1}
(3) – 23.0 kJ mol^{-1} (4) – 92.0 kJ mol^{-1}

113. Given enthalpy of formation of $CO_2(g)$ and CaO(s) are – 94.0 kJ and – 152 kJ respectively and the enthalpy of the reaction :
$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ is 42 kJ. The enthalpy of formation of $CaCO_3(s)$ is
(1) – 42 KJ (2) – 202 KJ
(3) +202 KJ (4) – 288KJ

114. Given that standard heat enthalpy of CH_4, C_2H_4 and C_3H_8 are –17.9, 12.5, –24.8 kCal mol^{-1}. The ΔH for $CH_4 + C_2H_4 \rightarrow C_3H_8$ is :
(1) – 55.2 kCal (2) – 30.2 kCal
(3) 55.2 kCal (4) – 19.4 kCal

115. The standard molar heat of formation of ethane, CO_2 and water(ℓ) are respectively –21.1, –94.1 and – 68.3 kCal. The standard molar heat of combustion of ethane will be
(1) –372 kCal (2) –162 kCal
(3) – 240 kCal (4) –183.5 kCal

116. Two atoms of hydrogen combine to form a molecule of hydrogen gas, the energy of the H_2 molecule is :
(1) Greater than that of seperate atoms
(2) Equal to that of seperate atoms
(3) Lower than that of seperate atoms
(4) Some times lower and some times higher

117. The ΔH_f° for $CO_{2(g)}$, $CO_{(g)}$ and $H_2O_{(g)}$ are –393.5, –110.5 and –241.8 kJ mol^{-1}respectively the standard enthalpy change (in kJ) for the reaction $CO_{2(g)} + H_{2\,(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$ is -
(1) 524.1 (2) 41.2 (3) –262.5 (4) –41.2

118. The enthalpies of combustion of carbon and carbon monoxide are –393.5 kJ and –283 kJ, respectively the enthalpy of formation of carbon monoxide is :
(1) –676.5 kJ (2) –110.5 kJ
(3) 110.5 kJ (4) 676.5 kJ

119. The standard heat of formation of $CS_2(\ell)$ will be; given that the standard heat of combustion of carbon (s), sulphur(s) and $CS_2(\ell)$ are –393.3, –293.72 and –1108.76 kJ mol^{-1} respectively is
(1) –128.02 kJ $mole^{-1}$
(2) +12.802 kJ mol^{-1}
(3) +128.02 kJ mol^{-1}
(4) –12.802 kJ mol^{-1}

120. The heat of combustion of $CH_{4\,(g)}$, $C_{(s)}$ and $H_{2\,(g)}$ at 25 °C are –212.4 K Cal, –94.0 K Cal and –68.4 K Cal respectively, the heat of formation of CH_4 will be -
(1) +54.4 K Cal (2) –18.4 K Cal
(3) –375.2 K Cal (4) +212.8 K Cal

121. Standard enthalpy of formation is zero for .
(1) $C_{diamond}$ (2) $Br_{(g)}$
(3) $C_{graphite}$ (4) $O_{3(g)}$

122. The standard heats of formation of $NO_2(g)$ and $N_2O_4(g)$ are 8.0 and 2.0 kCal mol^{-1} respectively the heat of dimerization of NO_2 in kCal is

(1) 10.0 (2) –6.0 (3) –12.0 (4) –14.0

123. M is a metal that forms an oxide

M_2O, $\frac{1}{2}M_2O \rightarrow M + \frac{1}{4}O_2$ $\Delta H = 120$ kCal.

When a sample of metal M reacts with one mole of oxygen what will be the ΔH in that case
(1) 240 kCal. (2) – 240 kCal.
(3) 480 kCal. (4) – 480 kCal.

HEAT OF COMBUSTION

124. According to equation,
$C_6H_6(\ell) + 15/2\ O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell)$; $\Delta H = -3264.4$ kJ mol^{-1} the energy evolved when 7.8 g benzene is burnt in air will be -
(1) 163.22 kJ (2) 32.64 kJ
(3) 3.264 kJ (4) 326.4 kJ

125. Heat of combustion of CH_4,C_2H_6, C_2H_4 and C_2H_2 gases are –212.8, –373.0, –337.0 and –310.5 kCal respectively at the same temperature. The best fuel among these gases is :
(1) CH_4 (2) C_2H_6 (3) C_2H_4 (4) C_2H_2

126. Given standard enthalpy of formation of CO (–110 kJ mol^{-1}) and CO_2(–394 kJ mol^{-1}). The heat of combustion when one mole of graphite burns is
(1) – 110 kJ (2) – 284 kJ
(3) – 394 kJ (4) – 504 kJ

127. The enthalpy of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(\ell)$ at 25°C and 1 atm. pressure are 52, - 394 and - 286 kJ $mole^{-1}$ respectively. The enthalpy of combustion of C_2H_4 will be:-
(1) + 1412 kJ $mole^{-1}$ (2) –1412 kJ $mole^{-1}$
(3) + 142.2 kJ $mole^{-1}$ (4) –141.2 kJ $mole^{-1}$

128. The heat of combustion of carbon and carbon monoxide are – 394 and –285 kJ mol^{-1} respectively. The heat of formation of CO in kJ mol^{-1} is:-
(1) + 109 (2) – 109
(3) + 218 (4) – 218

129. If heat of combustion of ethylene is 1411 kJ when a certain amount of ethylene was burnt 6226 kJ heat was evolved. Then the volume of O_2 (at NTP) that entered into the reaction is :–
(1) 296.5 ml (2) 296.5 litre
(3) 6226 × 22.4 litre (4) 22.4 litre

130. The heat evolved during the combustion of 112 litre of water gas at STP (mixture of equal volume of H_2 and CO) is : Given
$H_2(g) + ½\ O_2(g) = H_2O\ (g)$; $\Delta H = -241.8$ kJ
$CO(g) + ½\ O_2(g) = CO_2(g)$; $\Delta H = -283$ kJ
(1) 241.8 kJ (2) 283 kJ
(3) 1312 kJ (4) 1586 kJ

131. A person requires 2870 kCal of energy to lead normal daily life. If heat of combustion of cane sugar is –1349 kCal, then his daily consumption of sugar is :
(1) 728 g (2) 0.728 g
(3) 342 g (4) 0.342 g

132. On complete combustion of 2 gm methane 26575 Cal heat is generated. The heat of formation of methane will be (given heat of formation of CO_2 and H_2O are –97000 and –68000 Cal respectively) :
(1) + 20400 Cal (2) + 20600 Cal
(3) – 20400 Cal (4) – 2000 Cal

133. X gm of ethanal was subjected to combustion in a bomb calorimeter and the heat produced is YJoules. Then -

(1) $\Delta E_{(combustion)} = -XJ$

(2) $\Delta E_{(combustion)} = -YJ$

(3) $\Delta E_{(combustion)} = -\frac{44Y}{X}$ J mol^{-1}

(4) $\Delta H_{(combustion)} = -\frac{44Y}{X}$ J mol^{-1}

134. The following are the heats of reactions -

(i) ΔH_f° of $H_2O_{(\ell)} = -68.3$ kCal mol^{-1}

(ii) $\Delta H_{comb.}^\circ$ of $C_2H_2 = -337.2$ kCal mol^{-1}

(iii) $\Delta H_{comb.}^\circ$ of $C_2H_4 = -363.7$ kCal mol^{-1}

Then heat change for the reaction $C_2H_2 + H_2 \rightarrow C_2H_4$ is -

(1) –716.1 kCal (2) + 337.2 kCal
(3) –41.8 kCal (4) –579.5 kCal

135. The heat of combustion of a substance is :-

(1) Always positive
(2) Always negative
(3) Numerically equal to the heat of formation
(4) 1 and 3 both

136. The value of ΔH for the combustion of C(s) is –94.4 kCal. The heat of formation of CO_2(g) is :-

(1) –49.5 kCal (2) –94.4 kCal
(3) –188.0 kCal (4) More data required

137. In the combustion of 0.4 g. of CH_4, 0.25 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

138. If $C_6H_{12}O_6(s) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$; $\Delta H = -680$ kCal The weight of CO_2(g) produced when 170 kCal of heat is evolved in the combustion of glucose is:-

(1) 265 g (2) 66 g
(3) 11 g (4) 64 g

139. Which of the following equations corresponds to the enthalpy of combustion at 298 K :-

(1) $C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

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

(3) $C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$

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

140. Heat of formation of CO_2 is - 94.0 kCal. What would be the quantity of heat liberated, when 3 g of graphite is burnt in excess of oxygen:-

(1) 23.5 kCal (2) 2.35 kCal
(3) 94.0 kCal (4) 31.3 kCal

HEAT OF NEUTRALIZATION

141. The amount of heat liberated when one mole of NH_4OH reacts with one mole of HCl is

(1) 13.7 kCal (2) More than 13.7 kCal
(3) Less than 13.7 kCal (4) Cannot be predicted

142. If $H^+ + OH^- = H_2O + 13.7$ kCal, then heat of complete neutralisation of one gram mole of H_2SO_4 with strong base will be :

(1) 13.7 Kcal (2) 27.4 Kcal
(3) 6.85 Kcal (4) 3.425 KCal

143. Heat of neutralisation of a strong dibasic acid in dilute solution by NaOH is nearly :

(1) – 27.4 kCal eq^{-1} (2) – 13.7 kCal eq^{-1}
(3) 13.7 kCal eq^{-1} (4) – 13.7 kCal mol^{-1}

144. The temperature of a 5 ml of strong acid increases by 5^{0}C when 5 ml of a strong base is added to it. If 10 ml of each are mixed temperature should increase by :

(1) 5^0 C (2) 10^{0}C
(3) 15^{0}C (4) Cannot be known

145. The heat of neutralization of HCl by NaOH is –55.9 kCal mol^{-1}. If the heat of neutralization of HCN by NaOH is – 12.1 kCal mol^{-1}. The energy of dissociation of HCN is

(1) – 43.8 kJ (2) 43.8 kJ
(3) 68 kJ (4) – 68 kJ

146. If water is formed from H^+ ions and OH^- the heat of formation of water is :

(1) – 13.7 kCal (2) 13.7 kCal
(3) –63.4 kCal (4) More data required

147. The change in the enthalpy of $NaOH + HCl \longrightarrow NaCl + H_2O$ is called :

(1) Heat of neutralisation (2) Heat of reaction
(3) Heat of hydration (4) Heat of solution

148. Heat of neutralisation of oxalic acid is –106.7 kJ mol^{-1} using NaOH hence ΔH of :

$H_2C_2O_4 \longrightarrow C_2O_4^{2-} + 2H^+$ is :-

(1) 5.88 kJ mol^{-1} (2) –5.88 kJ mol^{-1}
(3) –13.7 kCal mol^{-1} (4) 7.5 kJ mol^{-1}

HEAT OF HYDROGENATION

149. The heat of combustion of C_2H_4, C_2H_6 and H_2 are –1409.5 kJ, –1558.3 kJ and –285.6 kJ. The heat of hydrogenation of ethene is -
(1) –136.8 kJ (2) –13.68 kJ
(3) 273.6 kJ (4) 1.368 kJ

150. The enthalpy of combustion of cyclohexane, cyclohexene and H_2 are respectively –3920, –3800 and –241 kJ mol^{-1}. The heat of hydrogenation of cyclohexene is:-
(1) –121 kJ mol^{-1} (2) 121 kJ mol^{-1}
(3) –242 kJ mol^{-1} (4) 242 kJ mol^{-1}

BOND ENERGY/RESONANCE ENERGY

151. Bond energy of a molecule :
(1) Is always negative
(2) Is always positive
(3) Either positive or negative
(4) Depends upon the physical state of the system

152. Among the following for which reaction heat of reaction represents bond energy of HCl
(1) $HCl(g) \longrightarrow H^+(g) + Cl^-(g)$
(2) $HCl(g) \longrightarrow \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g)$
(3) $2HCl(g) \longrightarrow H_2(g) + Cl_2(g)$
(4) $HCl(g) \longrightarrow H(g) + Cl(g)$

153. The bond energies of F_2, Cl_2, Br_2 and I_2 are 155.4, 243.6, 193.2 and 151.2 kJ mol^{-1} respectively. The strongest bond is :
(1) F – F (2) Cl – Cl
(3) Br – Br (4) I – I

154. Energy required to dissociate 4g of gaseous hydrogen into free gaseous atoms is 208 kCal at 25^0C. The bond energy of H—H bond will be :
(1) 1.04 kCal (2) 10.4 kCal
(3) 104 kCal (4) 1040 kCal

155. Heat evolved in the reaction $H_2 + Cl_2 \longrightarrow 2HCl$ is 182 kJ. Bond energies of H–H and Cl–Cl are 430 and 242 kJ mol^{-1} respectively. The H–Cl bond energy is :
(1) 245 kJ mol^{-1}
(2) 427 kJ mol^{-1}
(3) 336 kJ mol^{-1}
(4) 154 kJ mol^{-1}

156. The enthalpy change for the reaction $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$ is..... . The bond energies are,
H – H = 103, C – H = 99, C – C = 80 &
C = C =145 kCal mol^{-1}
(1) –10 kCal mol^{-1} (2) +10 kCal mol^{-1}
(3) – 30 kCal mol^{-1} (4) +30 kCal mol^{-1}

157. Bond dissociation enthalphies of $H_2(g)$ and $N_2(g)$ are 436.0 kJ mol^{-1} and 941.8 kJ mol^{-1} respectively and enthalpy of formation of $NH_3(g)$ is –46 kJ mol^{-1}. What is enthalpy of atomization of $NH_3(g)$?
(1) 390.3 kJ mol^{-1} (2) 1170.9 kJ mol^{-1}
(3) 590 kJ mol^{-1} (4) 720 kJ mol^{-1}

158. From the reactions :
$C(s) + 2H_2(g) \rightarrow CH_4(g)$ ΔH = - X Kcal
$C(g) + 4H(g) \rightarrow CH_4(g)$, ΔH = - X_1 Kcal
$CH_4(g) \rightarrow CH_3(g) + H(g)$ ΔH = + Y(Kcal)
Bond energy of C–H bond is –
(1) $\frac{X}{4}$ kCal mol^{-1}
(2) Y kCal mol^{-1}
(3) $\frac{X_1}{4}$ kCal mol^{-1}
(4) X_1 kCal mol^{-1}

159. The enthalpy changes at 298 K in successive breaking of O–H bonds of water are
$H_2O \longrightarrow H(g) + OH(g)$; ΔH = 498 kJ mol^{-1}
$OH(g) \longrightarrow H(g) + O(g)$; ΔH = 428 kJmol^{-1}
the bond enthalpy of O–H bond is
(1) 498 kJ mol^{-1} (2) 428 kJ mol^{-1}
(3) 70 kJ mol^{-1} (4) 463 kJ mol^{-1}

160. If ΔH_f° of $ICl_{(g)}$, $Cl_{(g)}$, and $I_{(g)}$ is 17.57, 121.34 and 106.96 J mol^{-1} respectively. Then bond dissociation energy of ICl bond is -
(1) 35.15 J mol^{-1} (2) 106.69 J mol^{-1}
(3) 210.73 J mol^{-1} (4) 420.9 J mol^{-1}

161. Heat of dissociation of benzene to elements is 5535 kJ mol^{-1}. The bond enthalpies of C–C, C=C and C–H are 347.3, 615.0 and 416.2 kJ respectively. Magnitude resonance energy of benzene is
(1) 1.51 kJ (2) 15.1 kJ
(3) 151 kJ (4) 1511 kJ

SOME OTHER HEAT OF REACTIONS

162. The enthalpy change for the reaction $2C(graphite) + 3H_2(g) \longrightarrow C_2H_6(g)$ is called
(1) Enthalpy of formation
(2) Enthalpy of combustion
(3) Enthalpy of hydrogenation
(4) Enthalpy of vaporisation

163. $Cl_2(g) \longrightarrow 2Cl(g)$, In this process value of ΔH will be -
(1) Positive
(2) Negative
(3) Zero
(4) Nothing can be predicted

164. The magnitude of heat of solution ..... on addition of solvent to solution
(1) Decreases
(2) Increases
(3) Remains constant
(4) Increases or decreases

165. If $H_2(g) = 2H(g)$; $\Delta H = 104$ kCal, than heat of atomisation of hydrogen is :
(1) 52 kCal (2) 104 kCal
(3) 208 kCal (4) None of these

166. $S_{(rhombic)} + O_{2(g)} \longrightarrow SO_{2(g)}$; $\Delta H = -297.5$ kJ

$S_{(monoclinic)} + O_{2(g)} \longrightarrow SO_2$; $\Delta H = -300$ kJ

The data can predict that –
(1) Rhombic sulphur is yellow in colour
(2) Monoclinic sulphur has metallic lusture.
(3) Monoclinic sulphur is more stable
(4) ΔH transition of S_R to S_M is endothermic

167. The heat of combustion of yellow phosphorous and red phosphorous are – 9.91 kJ and –8.78 kJ respectively. The heat of transition of yellow phosphorous to red phosphorous is
(1) –18.69 kJ (2) +1.13 kJ
(3) +18.69 kJ (4) –1.13 kJ

168. For the change C (diamond) $\longrightarrow$ C(graphite) ; $\Delta H = -1.89$ KJ, if 6 g of diamond and 6g of graphite are seperately burnt to yield CO_2 the heat liberated in first case is :
(1) Less than in the second case by 1.89 kJ
(2) Less than in the second case by 11.34 kJ
(3) Less than in the second case by 14.34 kJ
(4) More than in the second case by 0.945 kJ

169. $2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)} + X$ kJ
In the above equation X kJ refers to :
(1) Heat of formation of CO_2
(2) Heat of vapourisation
(3) Heat of reaction
(4) Heat of sublimation

170. Which of the following reactions represents ΔH (hydration) :–
(1) $CuSO_4(s) + (aq) \rightarrow CuSO_4(aq)$; $\Delta H = -x$ kJ
(2) $BaCl_2(s) + 2H_2O(\ell) \rightarrow BaCl_2 . 2H_2O(s)$; $\Delta H = -x'$ kJ
(3) $CuSO_4(s) + 5H_2O(\ell) + (aq) \rightarrow CuSO_4 . 5H_2O(aq)$; $\Delta H = -y'$ kJ
(4) None of the above

171. ΔH for the reaction, $I_{(g)} + I_{(g)} \rightarrow I_2(g)$ will be:-
(1) Zero (2) – ve (3) + ve (4) ∞

172. Given that :
$A(s) \rightarrow A(\ell)$; $\Delta H = x$, $A(\ell) \rightarrow A(g)$ - y
The heat of sublimation of A will be:-
(1) x + y (2) x - y
(3) x or y (4) - (x + y)

HESS LAW

173. The enthalpy change of a reaction does not depend on
(1) State of reactants and products
(2) Nature of reactants and products
(3) Different intermediate reactions
(4) Initial and final enthalpy change of reaction

174. From the thermochemical reactions,
$C(graphite) + \frac{1}{2} O_2 \longrightarrow CO$; $\Delta H = -110.5$ kJ
$CO + \frac{1}{2} O_2 \longrightarrow CO_2$; $\Delta H = -283.2$ kJ
the heat of reaction of $C(graphite) + O_2 \longrightarrow CO_2$ is :
(1) 393.7 kJ
(2) – 393.7 kJ
(3) – 172.7 kJ
(4) + 172.7 kJ

175. If $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -68.39$ kCal
$K + H_2O$ + water $\longrightarrow$ KOH(aq) + $\frac{1}{2} H_2$; $\Delta H = -48.0$ kCal
KOH + water $\longrightarrow$ KOH (aq) $\Delta H = -14.0$ kCal
the heat of formation of KOH is -
(1) – 68.39 + 48 – 14.0
(2) – 68.39 – 48.0 +14.0
(3) +68.39 – 48.0 + 14.0
(4) + 68.39 + 48.0 – 14.0

176. Given $C(s) + O_2(g) \longrightarrow CO_2(g) + 94.2$ kCal
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell) + 68.3$ kCal
$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) + 210.8$ kCal
The heat of formation of methane in Kcal will be
(1) –45.9 (2) –47.8
(3) –20.0 (4) –47.3

177. From the following data, the heat of formation of $Ca(OH)_2(s)$ at 18^0C is ..... kCal.
(i) $CaO(s) + H_2O(\ell) = Ca(OH)_2(s)$;
$\Delta H_{18^0C} = -15.26$ kCal.....
(ii) $H_2O(\ell) = H_2(g) + \frac{1}{2}O_2(g)$;
$\Delta H_{18^0C} = 68.37$ kCal ...
(iii) $Ca(s) + \frac{1}{2}O_2(g) = CaO(s)$;
$\Delta H_{18^0C} = -151.80$ kCal .....
(1) – 98.69 (2) – 235.43
(3) 194.91 (4) 98.69

178. If, $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$; $\Delta H^0 = -44$ kCal
$2Na(s) + 2HCl(g) \longrightarrow 2NaCl(s) + H_2(g)$;
$\Delta H = -152$ kCal
Then, $Na(s) + 0.5\ Cl_2(g) \longrightarrow NaCl(s)$; $\Delta H^0 = ?$
(1) 108 kCal (2) 196 kCal
(3) – 98 kCal (4) 54 kCal

179. (i) $S(s) + 3/2\ O_2(g) = SO_3(g) + 2x$ kCal
(ii) $SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g) + y$ kCal
Calculate the heat of formation of SO_2 :
(1) (2x + y) (2) –(2x – y)
(3) x + y (4) 2x / y

180. If $S + O_2 \longrightarrow SO_2$; $\Delta H = -298.2$
$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$; $\Delta H = -98.7$
$SO_3 + H_2O \longrightarrow H_2SO_4$; $\Delta H = -130.2$
$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -287.3$
Then the enthalpy of formation of H_2SO_4 at 298 K is -
(1) –814.4 kJ (2) –650.3 kJ
(3) –320.5 kJ (4) –433.5 kJ

181. Given that :
$Zn + \frac{1}{2}O_2 \rightarrow ZnO + 84000$ Cal 1
$Hg + \frac{1}{2}O_2 \rightarrow HgO + 21700$ Cal 2
The heat of reaction (ΔH) for,
$Zn + HgO \rightarrow ZnO + Hg$ is :-
(1) 105700 Cal
(2) 62300 Cal
(3) –105700 Cal
(4) – 62300 Cal

182. Given that -
$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$ $\Delta H = -787$ kJ
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -286$ kJ
$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(\ell)\ \Delta H = -1310$ kJ
Heat of formation of acetylene is :-
(1) + 1802 kJ (2) – 1802 kJ
(3) – 800 kJ (4) + 237 kJ

183. Find the heat change in the reaction : $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
from the following data
$NH_3(g) + aq \rightarrow NH_3(aq)$, $\Delta H = -8.4$ kCal
$HCl(g) + aq \rightarrow HCl(aq)$, $\Delta H = -17.3$ kCal
$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$, $\Delta H = -12.5$ kCal
$NH_4Cl(s) + aq \rightarrow NH_4Cl(aq)$, $\Delta H = +3.9$ kCal
(1) – 42.1 (2) – 34.3
(3) + 34.3 (4) + 42.1

184. The heat of reaction for
$A + \frac{1}{2}O_2 \rightarrow AO$ is - 50 kCal and
$AO + \frac{1}{2}O_2 \rightarrow AO_2$ is 100 kCal. The heat of reaction for $A + O_2 \rightarrow AO_2$ is:-
(1) – 50 kCal (2) + 50 kCal
(3) 100 kCal (4) 150 kCal

185. $C(s) + O_2(g) \rightarrow CO_2(g) + 94.0$ kCal
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H = -67.7$ kCal
from the above reactions find how much heat (kCal $mole^{-1}$) would be produced in the following
reaction: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
(1) 20.6 (2) 26.3
(3) 44.2 (4) 161.6

186. Using the following thermochemical data:
$C(S) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -94.0$ kCal
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(\ell)$, $\Delta H = -68.0$ kCal
$CH_3COOH(\ell) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(\ell)$, $\Delta H = -210.0$ kCal
The heat of formation of acetic acid is:-
(1) 116.0 kCal (2) - 116.0 kCal
(3) - 114.0 kCal (4) + 114.0 kCal

187. The enthalpy of vapourisation of liquid water using the data:

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$; $\Delta H = -285.77$ kJ mol^{-1}

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$; $\Delta H = -241.84$ kJ mol^{-1}

(1) + 43.93 kJ mol^{-1} (2) - 43.93 kJ mol^{-1}
(3) + 527.61 kJ mol^{-1} (4) - 527.61 kJ mol^{-1}

188. $H_2(g) + ½O_2(g) = H_2O(\ell)$; $\Delta H_{298K} = -68.32$kCal. Heat of vapourisation of water at 1 atm and 25^{0}C is 10.52 kCal. The standard heat of formation (in kCal) of 1 mole of water vapour at 25^{0}C is
(1) 10.52 (2) –78.84
(3) +57.80 (4) –57.80

189. The heat of solution of anhydrous $CuSO_4$ and $CuSO_4.5H_2O$ are – 15.89 and 2.80 kCal mol^{-1} respectively. What will be the heat of hydration of anhydrous $CuSO_4$?
(1) –18.69 kCal (2) 18.69 kCal
(3) –28.96 kCal (4) 28.96 kCal

190. One mole of anhydrous salt AB dissolves in water and librates 21.0 J mol^{-1} of heat. The value of $\Delta H_{(hydration)}$ of AB is –29.4 J mol^{-1}. The heat of dissolution of hydrated salt $AB.2H_2O_{(s)}$ is -
(1) 50.4 J mol^{-1}
(2) 8.4 J mol^{-1}
(3) –50.4 J mol^{-1}
(5) –8.4 J mol^{-1}

191. Which of the following expressions is true:-

(1) H_f^0 (CO,g) = $\frac{1}{2} \Delta H_f^0 (CO_2,g)$

(2) ΔH_f^0 (CO,g)=ΔH_f^0 (C,graphite) + $\frac{1}{2}$ $\Delta H_f^0(O_2,g)$

(3) ΔH_f^0 (CO,g)=$\Delta H_f^0 (CO_2,g)$ - $\frac{1}{2}$ $\Delta H_f^0 (O_2,g)$

(4) ΔH_f^0 (CO,g)=ΔH_{comb}^0 (C,graphite)-ΔH_{comb}^0 (CO,g)

EXERCISE-I (Conceptual Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**2**	**3**	**4**	**4**	**3**	**3**	**1**	**4**	**1**	**1**	**1**	**4**	**2**	**1**	**2**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**4**	**4**	**4**	**1**	**1**	**4**	**3**	**1**	**3**	**2**	**2**	**4**	**2**	**2**	**4**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**2**	**1**	**2**	**1**	**1**	**2**	**3**	**4**	**2**	**2**	**2**	**3**	**1**	**4**	**1**
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	**1**	**2**	**3**	**4**	**3**	**4**	**3**	**1**	**1**	**2**	**3**	**1**	**3**	**1**	**3**
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	**2**	**2**	**1**	**1**	**4**	**2**	**4**	**3**	**2**	**4**	**2**	**1**	**2**	**4**	**3**
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	**2**	**3**	**3**	**4**	**4**	**1**	**2**	**2**	**2**	**4**	**1**	**4**	**1**	**4**	**1**
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	**1**	**2**	**3**	**1**	**3**	**4**	**1**	**2**	**4**	**3**	**2**	**4**	**2**	**3**	**1**
Que.	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
Ans.	**2**	**4**	**4**	**4**	**2**	**2**	**2**	**4**	**4**	**1**	**3**	**2**	**2**	**3**	**2**
Que.	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135
Ans.	**3**	**4**	**4**	**4**	**1**	**3**	**2**	**2**	**2**	**3**	**1**	**3**	**3**	**3**	**2**
Que.	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150
Ans.	**2**	**2**	**2**	**3**	**1**	**3**	**2**	**2**	**1**	**2**	**1**	**1**	**4**	**1**	**1**
Que.	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165
Ans.	**2**	**4**	**2**	**3**	**2**	**3**	**2**	**3**	**4**	**3**	**3**	**1**	**1**	**3**	**2**
Que.	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180
Ans.	**4**	**4**	**4**	**3**	**2**	**2**	**1**	**3**	**2**	**2**	**3**	**2**	**3**	**2**	**1**
Que.	181	182	183	184	185	186	187	188	189	190	191				
Ans.	**4**	**4**	**1**	**2**	**2**	**3**	**1**	**4**	**1**	**2**	**4**				

AIPMT 2006

1. Identify the correct statement for change of Gibbs energy for a system (ΔG_{system}) at constant temperature and pressure.
(1) If $\Delta G_{system} > 0$, the process is spontaneous.
(2) If $\Delta G_{system} = 0$, the system has attained equilibrium.
(3) If $\Delta G_{system} = 0$, the system is still moving in a particular direction.
(4) If $\Delta G_{system} < 0$, the process is not spontaneous.

2. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?
(1) $H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$
(2) $C(s) + 2\,H_2O(g) \rightarrow 2\,H_2(g) + CO_2(g)$
(3) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
(4) $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$

3. The enthalpy and entropy change for reaction $Br_2(\ell) + Cl_2(g) \rightarrow 2\,BrCl(g)$ are 30 kJ mol^{-1} and 105 JK^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is
(1) 285.7 K (2) 273 K
(3) 450 K (4) 300 K

4. The enthalpy of hydrogenation of cyclohexene is -119.5 kJ mol^{-1}. If resonance energy of benzene is -150.4 kJ mol^{-1}, its enthalpy of hydrogenation would be
(1) – 508.9 kJ mol^{-1} (2) – 208.1 kJ mol^{-1}
(3) – 269.9 kJ mol^{-1} (4) – 358.5 kJ mol^{-1}

AIIMS 2006

5. When you make ice cubes, the entropy of water
(1) Does not change
(2) Increases
(3) Decreases
(4) May either increase or decrease depending on the process used

6. For a phase change $H_2O(\ell) \underset{0^\circ C\ 1\,bar}{\rightleftharpoons} H_2O(s)$
(1) $\Delta G = 0$ (2) $\Delta S = 0$
(3) $\Delta H = 0$ (4) $\Delta U = 0$

7. For a spontaneous process the correct statement is –
(1) Entropy of the system always increase
(2) Free energy of the system always increases
(3) Total entropy change is always negative
(4) Total entropy change is always positive

8. The enthalpy change (ΔH) for the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ is $-92{\cdot}38$ kJ at 298 K. The internal energy change ΔU at 298 K is
(1) $-92{\cdot}38$ kJ (2) $-87{\cdot}42$ kJ
(3) $-97{\cdot}34$ kJ (4) $-89{\cdot}9$ kJ

AIPMT 2007

9. Consider the following reactions :
(a) $H^+_{(aq)} + OH^-_{(aq)} = H_2O_{(l)}$, $\Delta H = -X_1$ kJ mol^{-1}
(b) $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(l)}$, $\Delta H = -X_2$ kJ mol^{-1}
(c) $CO_{2(g)} + H_{2(g)} = CO_{(g)} + H_2O_{(l)} - X_3$ kJ mol^{-1}
(d) $C_2H_{2(g)} + \frac{5}{2}O_{2(g)} = 2CO_{2(g)} + H_2O_{(l)} + X_4$ kJ mol^{-1}
Enthalpy of formation of $H_2O_{(l)}$ is :
(1) $+X_1$ kJ mol^{-1} (2) $-X_2$ kJ mol^{-1}
(3) $+X_3$ kJ mol^{-1} (4) $-X_4$ kJ mol^{-1}

10. Given that bond energies of H–H and Cl–Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and $\Delta_f H$ for HCl is -90 kJ mol^{-1}. Bond enthalpy of HCl is :
(1) 245 kJ mol^{-1}
(2) 290 kJ mol^{-1}
(3) 380 kJ mol^{-1}
(4) 425 kJ mol^{-1}

AIPMT 2008

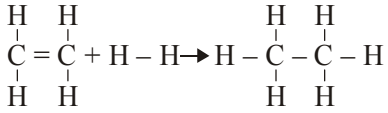
11. Bond dissociation enthalpy of H_2,Cl_2 and HCl are 434, 242 and 431 kJmol^{-1} respectively.Enthalpy of formation of HCl is:-
(1) -93 kJmol^{-1}
(2) 245 kJmol^{-1}
(3) 93 kJmol^{-1}
(4) -245 kJmol^{-1}

12. For the gas phase reaction,
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
Which of the following conditions are correct ?
(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 $\Delta S > 0$

13. Which of the following are not state functions ?
(I) q + w (II) q
(III) w (IV) H-TS
(1) (I),(II) and (III)
(2) (II) and (III)
(3) (I) and (IV)
(4) (II), (III) and (IV)

AIPMT 2009

14. From the following bond energies :-
H – H bond energy : 431.37 kJ mol^{-1}
C = C bond energy : 606.10 kJ mol^{-1}
C – C bond energy : 336.49 kJ mol^{-1}
C – H bond energy : 410.50 kJ mol^{-1}
Enthalpy for the reaction,



will be :-
(1) 553.0 kJ mol^{-1} (2) 1523.6 kJ mol^{-1}
(3) –243.6 kJ mol^{-1} (4) –120.0 kJ mol^{-1}

15. The values of ΔH and ΔS for the reaction, $C_{(graphite)} + CO_{2(g)} \rightarrow 2CO_{(g)}$ are 170 kJ and 170JK^{-1}, respectively. This reaction will be spontaneous at :-
(1) 510 K (2) 710 K
(3) 910 K (4) 1110 K

AIPMT 2010

16. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are 40.63 kJ mol^{-1} and 108.8 $JK^{-1}mol^{-1}$, respectively. The temperature when Gibbs energy change (ΔG) for this transformation will be zero, is :-
(1) 393.4 K (2) 373.4 K
(3) 293.4 K (4) 273.4 K

17. Three moles of an ideal gas expanded spontaneously into vacuum. The work done will be :-
(1) 3 Joule (2) 9 Joule
(3) Zero (4) Infinite

18. The following two reactions are known :
$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$;
$\Delta H = -26.8$ kJ
$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$;
$\Delta H = -16.5$ kJ
Correct target equation is
$Fe_2O_3(s) + CO(g) \rightarrow 2FeO(s) + CO_2(g)$, ΔH = ?
(1) –43.3 kJ (2) –10.3 kJ
(3) + 6.2 kJ (4) + 10.3 kJ

19. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1} respectively. For the reaction $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$, $\Delta H = -30$ kJ to be at equilibrium, the temperature should be :-
(1) 500 K (2) 750 K
(3) 1000 K (4) 1250 K

AIIMS 2010

20. Intensive property is :-
(1) Moles (2) Volume
(3) Enthalpy (4) Temperature

21. In which of following there is decrease in entropy :-
(1) When temperature is raised from 30 K to 150 K.
(2) When $NaHCO_3$ changes into Na_2CO_3 (s) and CO_2(g)
(3) $H_2(g) \longrightarrow 2H(g)$
(4) Liquid crystalises into a solid

22. Which of the following is not a state function:-
(1) Pressure (2) Volume
(3) Temperature (4) Heat

AIPMT Pre. 2011

23. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C, the entropy changes for the process would be:
(1) 10 J mol^{-1} K^{-1}
(2) 1.0 J mol^{-1} K^{-1}
(3) 0.1 J mol^{-1} K^{-1}
(4) 100 J mol^{-1} K^{-1}

24. Enthalpy change for the reaction,
$4H_{(g)} \rightarrow 2H_{2(g)}$ is –869.6 kJ
The dissociation energy of H–H bond is :
(1) –434.8 kJ (2) 869.6 kJ
(3) +434.8 kJ (4) +217.4 kJ

25. Which of the following correct option for free expansion of an ideal gas under adiabatic condition ?
(1) q = 0, $\Delta T \neq 0$, w = 0
(2) $q \neq 0$, ΔT = 0, w = 0
(3) q = 0, ΔT = 0, w = 0
(4) q = 0, $\Delta T < 0$, $w \neq 0$

AIPMT Msins 2011

26. Consider the following processes :-

	ΔH(kJ mol^{-1})
$\frac{1}{2}$ A $\rightarrow$ B	+150
3B $\rightarrow$ 2C + D	–125
E + A $\rightarrow$ 2D	+350

For B + D $\rightarrow$ E + 2C, ΔH will be :
(1) 325 kJ mol^{-1}
(2) 525 kJ mol^{-1}
(3) –175 kJ mol^{-1}
(4) –325 kJ mol^{-1}

AIIMS 2011

27. The enthalpy of formation of CO(g), CO_2(g), N_2O(g) and N_2O_4(g) is –110, –393, +81 and 10 kJ mol^{-1} respectively. For the reaction $N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$. ΔH_r is
(1) –212 (2) +212
(3) +778 (4) –778

28. For adiabatic process which is correct-
(1) $\Delta T = 0$ (2) $w = 0$
(3) $q = 0$ (4) $\Delta U = 0$

29. Which of the following is not thermodynamic function-
(1) Internal energy (2) work done
(3) Enthalpy (4) Entropy

30. Which of the following is intensive property-
(1) Enthalpy (2) Entropy
(3) specific heat (4) volume

AIPMT Pre. 2012

31. In which of the following reactions, standard reaction entropy change (ΔS°) is positive and standard Gibb's energy change (ΔG°) decreases sharply with increasing temperature?

(1) $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

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

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

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

32. Standard enthalpy of vapourisation $\Delta_{vap}H^\ominus$ for water at 100°C is 40.66 $kJmol^{-1}$. The internal energy of vaporisation of water at 100°C (in $kJmol^{-1}$) is
(1) +43.76 (2) +40.66
(3) +37.56 (4) –43.76

33. The enthalpy of fusion of water is 1.435 kCal mol^{-1}. The molar entropy change for the melting of ice at 0°C is:
(1) 5.260 Cal mol^{-1} K^{-1}
(2) 0.526 Cal mol^{-1} K^{-1}
(3) 10.52 Cal mol^{-1} K^{-1}
(4) 21.04 Cal mol^{-1} K^{-1}

AIIMS 2012

34. At equilibrium which is correct :-
(1) $\Delta G = 0$ (2) $\Delta S = 0$
(3) $\Delta H = 0$ (4) $\Delta G^\circ = 0$

35. Heat of atomisation of CH_4 is 360 kJ mol^{-1} and C_2H_6 has 620 kJ mol^{-1}. Then bond dissociation energy of C–C bond is :-
(1) 170 kJ mol^{-1}
(2) 50 kJ mol^{-1}
(3) 80 kJ mol^{-1}
(4) 220 kJ mol^{-1}

AIIMS 2013

36. Which thermodynamic parameter does not depend only on initial and final state ?
(1) q at constant pressure
(2) q at constant volume
(3) w at adiabatic
(4) w at isothermal

AIPMT 2014

37. For the reaction : $X_2O_4(\ell) \longrightarrow 2XO_2(g)$
$\Delta U = 2.1$ kCal, $\Delta S = 20$ cal K^{-1} at 300 K
Hence ΔG is :-
(1) 2.7 kCal (2) – 2.7 kCal
(3) 9.3 kCal (4) – 9.3 kCal

AIIMS 2014

38. $\Delta S_{Total} = -40$ kJ $mol^{-1} \times K^{-1}$
$\Delta H_{sys} = 2000$ kJ mol^{-1}
T = 400 K
Calculate value of ΔS_{system} ?
(1) – 35 kJ $mol^{-1} \times K$
(2) – 5 kJ $mol^{-1} \times K$
(3) – 40 kJ $mol^{-1} \times K$
(4) + 5 kJ $mol^{-1} \times K$

AIPMT 2015

39. Which of the following statements is **correct** for a reversible process in a state of equilibrium ?
(1) $\Delta G = 2.30\ RT \log K$
(2) $\Delta G^\circ = -2.30\ RT \log K$
(3) $\Delta G^\circ = 2.30\ RT \log K$
(4) $\Delta G = -2.30\ RT \log K$

Re-AIPMT 2015

40. The heat of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is:
(1) –630 kJ (2) –3.15 kJ
(3) –315 kJ (4) +315 kJ

AIIMS 2015

41. $A_{2(g)} \rightarrow 2A(g)$ and for this reaction on increasing T value of K_{eq} increases then for this reaction is
(1) ΔH = positive; ΔS = positive
(2) ΔH = negative; ΔS = negative
(3) ΔH = positive; ΔS = negative
(4) ΔH = negative ; ΔS = positive

42. For endothermic reaction when change in entropy is negative, then reaction is
(1) not possible at any temperature
(2) possible at low temperature
(3) possible at all temperature
(4) possible at high temperature

43. For the formation of CH_4 of $\Delta U^0 = -x$ kJ mol^{-1} then what will be value of ΔH^0 kJ mol^{-1}.
(1) $-x - RT$ (2) $-x + 2RT$
(3) $-x + RT$ (4) $-2x - 4RT$

NEET-I 2016

44. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
(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 $\Delta S < 0$

NEET-II 2016

45. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by
(1) $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$ (2) $\Delta S = RT \ln\left(\frac{p_i}{p_f}\right)$
(3) $\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$ (4) $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$

AIIMS 2016

46. For a given reaction at 298K

$$2A_{(g)} + B_{(g)} \longrightarrow 2C_{(g)}$$

If $\Delta U^\circ = -10 kJ\,mol^{-1}$ $\Delta S^\circ = -45 J\,K^{-1}mol^{-1}$

Then what will be value of ΔG° for above reaction?
(1) +930 J mol^{-1} (2) –25890 J mol^{-1}
(3) 2000 J mol^{-1} (4) 8500 J mol^{-1}

47. Calculate work done during isothermal reversible process when 5 mol ideal gas is expanded so that its volume is doubled at 400K?
(1) –11.5 kJ (2) –344 kJ
(3) 0 (4) –2.8 kJ

48. For a reaction

$$2A_{(g)} + B_{(g)} \longrightarrow C_{(g)} + D_{(g)} - q$$

Where ΔS is –ve; then which of the following is correct?
(1) reaction is possible only at low temperature
(2) reaction is possible only at high temperature
(3) reaction is never possible
(4) reaction is possible at all temperature

49. If 400 kJ work is done by the system and 150 kJ heat is given to system then what will be effect on internal energy?
(1) Increases by 250 kJ (2) Decreases by 250 kJ
(3) Increases by 600 kJ (4) Decreases by 600 kJ

50. For gas 'A' in a calorimeter heat evolved is 250 kJ mol^{-1}. For 0.2 mol of A, temperature rise from 298 K to 300 K. Find out heat capacity of calorimeter:-
(1) 12.5 kJ K^{-1} (2) 25 kJ K^{-1}
(3) 50 kJ K^{-1} (4) 100 kJ K^{-1}

NEET(UG) 2017

51. For a given reaction, ΔH = 35.5 kJ mol^{-1} and ΔS = 83.6 $JK^{-1}mol^{-1}$. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with tempearature)
(1) T > 425 K (2) All temperatures
(3) T > 298 K (4) T < 425 K

52. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be:-
(1) –500 J (2) –505 J
(3) +505 J (4) 1136.25 J

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53. For an isolated system :-
(1) q = 0 and w = 0
(2) $q \neq 0$ and w = 0
(3) q = 0 and $w \neq 0$
(4) $q \neq 0$ and $w \neq 0$

54. An ideal gas is expanded against 42 Pascal external pressure by 10 m^3. If 350 J heat is given to the system then ΔU of system (in J) will be :-
(1) –50 J (2) –70 J
(3) +50 J (4) +70 J

55. The heat of combustion of C_4H_{10} is –2878 kJ mol^{-1}. If the heats of formation of CO_2 and H_2O are –393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} then the heat of formation of C_4H_{10} is :-
(1) –125.0 kJ mol^{-1} (2) 126.75 kJ mol^{-1}
(3) –402.5 kJ mol^{-1} (4) 402.5 kJ mol^{-1}

56. During adiabatic expansion of an ideal gas in vacuum :-
(1) q = 0 and $\Delta U \neq 0$ (2) q ≠ 0 and $\Delta U \neq 0$
(3) q ≠ 0 and $\Delta U \neq 0$ (4) q = 0 and $\Delta U = 0$

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57. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be
(1) 200 kJ mol^{-1} (2) 100 kJ mol^{-1}
(3) 800 kJ mol^{-1} (4) 400 kJ mol^{-1}

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58. Which of the following pair is an example of extensive property :-
(1) P and T (2) C_p and E
(3) E and V (4) T and V

59. An ideal gas expands from 2 L to 10 L adiabatically against a constant external pressure of 10 atm. Then find the change in internal energy:-
(1) –80 L-atm (2) Zero
(3) 80 L-atm (4) 40 L-atm

60. The correct set of intensive properties :-
(1) P, T (2) V, T (3) P, V (4) V, E

61. Which of the following always increases for spontaneous process :-
(1) ΔH_{system} (2) ΔS_{system}
(3) $\Delta S_{system} - \frac{\Delta H_{system}}{T}$
(4) $\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$

62. 1 mole of ideal gas (A) expands from 2 lit to 4 lit through reversible isothermal process. 3 mol of another ideal gas (B) expands from 2 lit to x lit and does the same amount of work as done by gas (A) the value of x is :- (Consider that both the gases temperature is same)
(1) 2 (2) 8 (3) $(8)^{1/3}$ (4) $(4)^{2/3}$

63. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ $\Delta H = -2220$ kJ mol^{-1}
$C_3H_6 + H_2 \rightarrow C_3H_8$ $\Delta H = -124$ kJ mol^{-1}
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H = -285$ kJ mol^{-1}
Then find heat of combustion of C_3H_6
(1) –2059 kJ mol^{-1} (2) 2059 kJ mol^{-1}
(3) –4118 kJ mol^{-1} (4) +4118 kJ mol^{-1}

64. A rigid container contain 1 kg N_2 gas at 400 K if final temeprature is 800 K then find change in entropy (J K^{-1}) [Given : C_P = 29.099 joule)
(1) 512.86 (2) 1025.736
(3) 256.43 (4) 170.9

65. Heat of formation of ethane –20.2 kCal mol^{-1} and heat of atomisation of C and H_2 are 179.2 kCal mol^{-1} and 52.1 kCal mol^{-1} respectively. If bond energy of C–H bond is 73.3 kCal mol^{-1}. Then caculate approx. B.E. of C–C :-
(1) 96 kCal mol^{-1} (2) 230 kCal mol^{-1}
(3) 88 kCal mol^{-1} (4) 540 kCal mol^{-1}

EXERCISE-II (Previous Year Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**2**	**1**	**1**	**2**	**3**	**1**	**4**	**2**	**2**	**4**	**1**	**4**	**2**	**4**	**4**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	**2**	**3**	**3**	**2**	**4**	**4**	**4**	**4**	**3**	**3**	**3**	**4**	**3**	**2**	**3**
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	**3**	**3**	**1**	**1**	**3**	**4**	**2**	**1**	**2**	**3**	**1**	**1**	**1**	**3**	**4**
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	**1**	**1**	**3**	**2**	**2**	**1**	**2**	**1**	**2**	**1**	**4**	**3**	**3**	**1**	**1**
Que.	61	62	63	64	65										
Ans.	**3**	**4**	**1**	**1**	**1**										

EXERCISE-III (Analytical Questions) — Check Your Understanding

1. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and w correspond to :–
(1) $\Delta U < 0$, w=0 (2) $\Delta U < 0$, w < 0
(3) $\Delta U > 0$, w=0 (4) $\Delta U > 0$, w > 0

2. 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 expressions is true ?
(1) $\Delta H < \Delta U$ (2) $\Delta H > \Delta U$
(3) $\Delta H = 0$ (4) $\Delta H = \Delta U$

3. For a reversible process at T = 300K, the volume is increased from V_i = 1L to V_f = 10L. Calculate ΔH if the process is isothermal -
(1) 11.47 kJ (2) 4.98 kJ
(3) 0 (4) –11.47 kJ

4. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1} will be) :-
(1) 4.100 kJ mol^{-1} (2) 3.7904 kJ mol^{-1}
(3) 37.904 kJ mol^{-1} (4) 41.00 kJ mol^{-1}

5. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :-
(R = 8.314 J mol^{-1} K^{-1}) (ln 7.5 = 2.01)
(1) q = + 208 J, w = – 208 J
(2) q = – 208 J, w = – 208 J
(3) q = – 208 J, w = + 208 J
(4) q = + 208 J, w = + 208 J

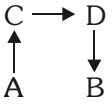
6. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is :-
(1) 32.3 J mol^{-1} K^{-1} (2) 42.3 J mol^{-1} K^{-1}
(3) 38.3 J mol^{-1} K^{-1} (4) 35.8 J mol^{-1} K^{-1}

7. The value of enthalpy change (ΔH) for the reaction
$C_2H_5OH_{(\ell)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$
at 27°C is –1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be :-
(1) –1371.5 kJ (2) –1369.0 kJ
(3) –1364.0 kJ (4) –1361.5 kJ

8. For the process $H_2O(\ell)$ (1 bar , 373K) $\rightarrow$ $H_2O(g)$ (1 bar , 373K), the correct set of thermodynamic parameters is :
(1) $\Delta G = 0$, ΔS =+ve
(2) $\Delta G = 0$, ΔS = –ve
(3) ΔG = +ve, ΔS=0
(4) ΔG = –ve, ΔS = +ve

9. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction.?
(1) endothermic and decreasing disorder
(2) exothermic and increasing disorder
(3) endothermic and increasing disorder
(4) exothermic and decreasing disorder

10. The conversion A to B is carried out by the following path :



Given : $\Delta S_{(A \rightarrow C)}$ = 50 e.u. ,
$\Delta S_{(C \rightarrow D)}$ = 30 e.u., $\Delta S_{(B \rightarrow D)}$ = 20 e.u.
where e.u. is entropy unit then $\Delta S_{(A \rightarrow B)}$ is
(1) + 100 e.u.
(2) + 60 e.u.
(3) – 100 e.u.
(4) – 60 e.u.

11. In conversion of lime-stone to lime,
$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
the values of $\Delta H°$ and $\Delta S°$ are +179.1 kJ mol^{-1} and 160.2 J K^{-1} respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-
(1) 1008 K
(2) 1200 K
(3) 845 K
(4) 1118 K

12. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$CH_3OH(\ell) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$

At 298 K standard Gibb's energies of formation for $CH_3OH(\ell)$, $H_2O(\ell)$ and $CO_2(g)$ are –166.2, –237.2 and –394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is –726 kJ mol^{-1}, efficiency of the fuel cell will be
(1) 90% (2) 97% (3) 80% (4) 87%

13. Identify the correct statement regarding a sponateous process :-
(1) For a spontaneous process in an isolated system, the change in entropy is positive
(2) Endothermic processes are never spontaneous
(3) Exothermic processes are always spontaneous
(4) Lowering of energy in the reaction process is the only criterion for spontaneity

14. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction,

$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be
(1) 1250 K (2) 500 K (3) 750 K (4) 1000 K

15. The absolute enthalpy of neutralisation of the reaction for MgO(s) :
$MgO(s) + 2HCl(aq) \longrightarrow Mg\,Cl_2(aq) + H_2O(\ell)$ will be :
(1) 57.33 kJ mol^{-1}
(2) – 57.33 kJ mol^{-1}
(3) Greater than –57.33 kJ mol^{-1}
(4) Less than –57.33 kJ mol^{-1}

16. The enthalpy changes for the following processes are listed below :
$Cl_2(g) \rightarrow 2Cl(g)$, 242.3 kJ mol^{-1}
$I_2(g) \rightarrow 2I(g)$, 151.0 kJ mol^{-1}
$ICl(g) \rightarrow I(g) + Cl(g)$, 211.3 kJ mol^{-1}
$I_2(s) \rightarrow I_2(g)$, 62.76 kJ mol^{-1}
Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for ICl(g) is :-
(1) –16.8 kJ mol^{-1} (2) +16.8 kJ mol^{-1}
(3) +244.8 kJ mol^{-1} (4) –14.6 kJ mol^{-1}

17. Consider the reaction :
$4NO_{2(g)} + O_{2(g)} \rightarrow 2N_2O_{5(g)}$, $\Delta_rH = -111$kJ.
If $N_2O_{5(s)}$ is formed instead of $N_2O_{5(g)}$ in the above reaction, the Δ_rH value will be :-
(given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1})
(1) –165 kJ (2) +54 kJ
(3) +219 kJ (4) –219 kJ

18. For complete combustion of ethanol, $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion, Δ_cH, for the raction will be :- (R = 8.314 kJ mol^{-1})
(1) –1460.50 kJ mol^{-1}
(2) – 1350.50 kJ mol^{-1}
(3) – 1366.95 kJ mol^{-1}
(4) – 1361.95 kJ mol^{-1}

19. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and Δ_fH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be :-
(1) 200 kJ mol^{-1} (2) 100 kJ mol^{-1}
(3) 800 kJ mol^{-1} (4) 300 kJ mol^{-1}

20. The standard enthlapy of formation ($\Delta_fH°$) at 298K for methane, $CH_4(g)$, is –74.8 kJ mol^{-1}. The additional information required to determine the average energy for C–H bond formation would be:-
(1) Latent heat of vapourization of methane
(2) The first four ionization energies of carbon and electron gain enthalpy of hydrogen
(3) The dissociation energy of hydrogen molecule H_2
(4) The dissociation energy of H_2 and enthalpy of sublimation of carbon

21. The standard enthalphy of formation of NH_3 is –46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is –436 kJ mol^{-1} and that of N_2 is –712kJ mol^{-1}, the average bond enthalpy of N–H bond in NH_3 is :-
(1) –1102 kJ mol^{-1}
(2) –964 kJ mol^{-1}
(3) + 352 kJ mol^{-1}
(4) +1056 kJ mol^{-1}

22. The incorrect expression among the following is :-

(1) $K = e^{-\Delta G°/RT}$

(2) $\frac{\Delta G_{system}}{\Delta S_{total}} = -T$

(3) In isothermal process, $W_{reversible} = -nRT \ln \frac{V_f}{V_i}$

(4) $\ln K = \frac{\Delta H° - T\Delta S°}{RT}$

23. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^\ominus} Cl(g) \xrightarrow{\Delta_{eg}H^\ominus} Cl^-(g) \xrightarrow{\Delta_{hyd}H^\ominus} Cl^-(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq)$

(using the data $\Delta_{diss}\ H^\ominus_{Cl_2} = 240$ kJ mol^{-1}, $\Delta_{eg}\ H^\ominus_{Cl} = -349$ kJ mol^{-1}, $\Delta_{hyd}H^\ominus_{Cl^-} = -381$ kJ mol^{-1}) will be:-

(1) –610 kJ mol^{-1} (2) –850 kJ mol^{-1}

(3) +120 kJ mol^{-1} (4) +152 kJ mol^{-1}

24. On the basis of the following thermochemical data : $\left[\Delta H^0_f\left(H^+_{(aq)} = 0\right)\right]$

$H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$; $\Delta H = 57.32$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$; $\Delta H = -286.20$ kJ

The value of enthalpy of formation of OH^- ion at 25°C is :-

(1) +228.88 kJ (2) –343.52 kJ

(3) –22.88 kJ (4) –228.88 kJ

EXERCISE-III (Analytical Questions) ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	1	3	3	1	3	3	1	2	2	4	2	1	3	3
Que.	16	17	18	19	20	21	22	23	24						
Ans.	2	4	3	3	4	3	4	1	4						

EXERCISE-IV (Assertion & Reason) — Target AIIMS

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.

(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.

(C) If Assertion is True but the Reason is False.

(D) If both Assertion & Reason are false.

1. ***Assertion :–*** There is no reaction known for which ΔG is positive, yet it is spontaneous.
Reason :– For photochemical reactions, ΔG is negative.
(1) A (2) B (3) C (4) D

2. ***Assertion :–*** Absolute value of enthalpy cannot be determined.
Reason :– Enthalpy is defined as H=E+PV, and value of internal energy cannot be determined absolutely therefore absolute value of enthalpy can not be determined.
(1) A (2) B (3) C (4) D

3. ***Assertion :–*** When a rubber band is stretched entropy increases.
Reason :– During expansion entropy increases.
(1) A (2) B (3) C (4) D

4. ***Assertion :–*** At constant pressure for the change $H_2O(s) \rightarrow H_2O(g)$ work done is negative.
Reason :– During phase transition work done is always negative.
(1) A (2) B (3) C (4) D

5. ***Assertion :–*** Enthalpy of graphite is lower than that of diamond.
Reason :– Entropy of graphite is greater than that of diamond.
(1) A (2) B (3) C (4) D

6. ***Assertion :–*** The enthalpy of formation of gaseous oxygen molecules at 298K and under a pressure of one atm. is zero.
Reason :– The entropy of formation of gaseous oxygen molecules under the same condition is zero.
(1) A (2) B (3) C (4) D

7. ***Assertion :–*** Many endothermic reactions that are not spontaneous at room temp. becomes spontaneous at high temp.
Reason :– Entropy of the system increases with increase in temperature.
(1) A (2) B (3) C (4) D

8. ***Assertion :–*** Mass, Volume and pressure are extensive properties.
Reason :– Extensive properties depend upon the amount of the substance.
(1) A (2) B (3) C (4) D

9. ***Assertion :–*** For a particular reaction, heat of combustion at constant pressure (q_p) is always greater than that at constant volume (q_v).
Reason :– Combustion reactions are invariably accomplished by increase in no. of moles.
(1) A (2) B (3) C (4) D

10. ***Assertion :–*** At constant temp 0°C and 1atm, the change $H_2O(s) \rightarrow H_2O(l)$ ΔH and ΔE both are zero.
Reason :– During isothermal process H and E both remains constant.
(1) A (2) B (3) C (4) D

11. ***Assertion :-*** The change in internal energy (ΔE) for the vapourization of one mole of water at 1 atm and 373 K is zero.
Reason :- For all isothermal processes $\Delta E=0$
(1) A (2) B (3) C (4) D

12. ***Assertion:–*** Water in liquid state is more stable than ice at room temperature.
Reason:– Water in liquid from has higher entropy than ice.
(1) A (2) B (3) C (4) D

13. ***Assertion:–*** In an isolated system the entropy increases due to spontaneous process.
Reason:– The processes in an isolated system are isothermal.
(1) A (2) B (3) C (4) D

14. **Assertion :-** Entropy is always constant for a closed system.
Reason :- Closed system is always reversible
(1) A (2) B (3) C (4) D

15. ***Assertion :-*** For an isolated system q is zero.
Reason :- In an isolated system change in U is zero.
(1) A (2) B (3) C (4) D

16. ***Assertion :-*** Entropy of system always increases for a spontaneous reaction.
Reason :- Enthalpy of reaction always decreases for spontaneous reaction.
(1) A (2) B (3) C (4) D

17. ***Assertion :-*** Catalyst changes Gibbs free energy of system.
Reason :- Catalyst changes preexponential factor of a chemical reaction.
(1) A (2) B (3) C (4) D

18. ***Assertion :-*** Entropy increases with increase in temperature of gas.
Reason :- If q_{rev} is same, then entropy of that system is higher for which temperature is higher.
(1) A (2) B (3) C (4) D

19. ***Assertion :-*** The value of specific heat at constant pressure is more than that at constant volume.
Reason :- The energy required to raise temperature by a unit at constant pressure is greater because some amount of heat is used in doing work.
(1) A (2) B (3) C (4) D

20. ***Assertion :*** Sum of two path functions is always path function.
Reason : Sum of path function depends on path followed.
(1) A (2) B (3) C (4) D

21. ***Assertion :-*** Heat is not a state thermodynamic property.
Reason :- Heat given in a process depends on its type.
(1) A (2) B (3) C (4) D

22. ***Assertion :-*** For ideal gas in a closed container with adiabatic walls, temperature decreases when work is done by the system.
Reason :- Internal energy is used in work done by the system.
(1) A (2) B (3) C (4) D

23. ***Assertion :-*** Adiabatic free expansion of an ideal gas is irreversible.
Reason :- PV = constant for reversible adiabatic expansion.
(1) A (2) B (3) C (4) D

24. ***Assertion :-*** Internal energy at particular temperture does not depend on volume.
Reason :- State function does not depend on volume.
(1) A (2) B (3) C (4) D

25. ***Assertion :-*** Graphite is thermodynamically most stable allotrope of carbon.
Reason :- Standard heat of formation of graphite is +1.9 kJ/mol.
(1) A (2) B (3) C (4) D

26. ***Assertion :*** A gas expands from (P_1, V_1, T_1) to (P_2, V_2, T_2) the work done in 2 steps will be more than, if the process is carried out in single step.
Reason : Work done is path dependent quantity.
(1) A (2) B (3) C (4) D

27. ***Assertion :*** All spontaneous process in nature are irreversible.
Reason : All reversible process are quasistatic.
(1) A (2) B (3) C (4) D

28. ***Assertion :-*** Sum of q and w is different in reversible and irreversible process.
Reason :- Sum of two path function can never state function.
(1) A (2) B (3) C (4) D

29. ***Assertion :*** Internal energy of gas remain constant during adiabatic free expansion.
Reason : Work done is zero and heat exchange is zero.
(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason) — ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	**4**	**1**	**4**	**3**	**2**	**3**	**2**	**4**	**4**	**4**	**4**	**2**	**1**	**4**	**3**
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Ans.	**4**	**4**	**3**	**1**	**4**	**1**	**1**	**3**	**3**	**3**	**1**	**2**	**4**	**1**	