

THERMODYNAMICS

INTRODUCTION

In thermodynamics we study the energy changes that accompany physical and chemical process. Usually these energy changes involve heat-hence the “thermo-” part of the term. Thermochemistry is concerned with how we observe, measure, and predict energy changes for both physical changes and chemical reactions.

THERMODYNAMICS

BASIC TERMS

* **System and surroundings:** The part of the universe chosen for thermodynamic study of called system. It is separated from the rest of the universe by a real or imaginary boundary.

The remaining portion of the universe, excluding the system is called **surroundings**.

* **Type of Systems**

(a) **Isolated System :** A system that cannot exchange mass and/or energy from the surroundings. For example, ice, milk or any other liquid kept in a thermos flask.

(b) **Closed system :** It exchanges only energy from the surroundings. For example, (i) water in closed bottle (boundaries of closed system act as conductor of heat), (ii) heating of CaCO_3 in sealed tube, etc.

(c) **Open system :** It exchanges energy and mass from the surroundings. For example, trees in forest, tea in an open cup, etc.

(d) **Macro System :** A very large number of molecules/atoms are present in this system. Properties of a macro system are called macro properties. For example, pressure, temperature, density, composition, viscosity, surface tension, colour, refractive index, etc.

(e) **State of system :** The system in which the values of macro properties are definite. It is said to be in definite state. Thus, the state of system is determined by its macro properties.

(f) **State Functions :** The properties of a system which depend only on initial and final states, and do not depend on its path. For example, free energy, enthalpy, internal energy, etc.

(g) **Extensive Property :** The property which depends on the amount of substance present in the system. For example, mass volume, heat capacity, entropy, enthalpy, free energy internal energy, etc.

(h) **Intensive Property :** These do not depend on the amount of substance present in the system. For example, temperature, density, viscosity, melting point, boiling point, surface tension, refractive index. etc.

THERMODYNAMIC EQUILIBRIUM

When macro properties of a system do not change with time, the system is said to be in equilibrium.

- (a) **Mechanical Equilibrium :** When no work is done by one part of the system on its other part, it is said to be in a state of mechanical equilibrium. Pressure remains constant throughout the system.
- (b) **Thermal Equilibrium :** Temperature remains constant throughout the system. No transfer of heat takes place from one part of the system to the other.
- (c) **Chemical Equilibrium :** In this, composition of the system remains constant and definite.

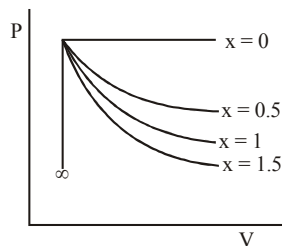
THERMODYNAMIC PROCESS

The process by which a system gets changed from one state to the other state. Macro properties get changed in this process. These are of the following types.

- (a) **Isothermal Process :**
 - * Process in which temp. of the system remains constant.
 - * In this process, the boundaries of the system are mobile.
 - * The change in temperature, $dT = 0$.
- (b) **Adiabatic Process :**
 - * In a closed system, heat is not exchanged by the surroundings, i.e. the system is in isolated state.
 - * In this process, temperature can increase and can decrease also.
 - * Change in heat $(dQ) = 0$
- (c) **Isobaric Process :**
 - * This process takes place at constant pressure.
 - * Change in pressure $(dp) = 0$.
 - * For example, vaporisation of water, heating of water up to its boiling point at same atmospheric pressure.
- (d) **Isochoric Process :**
 - * The process which takes place at constant volume.
 - * Change in volume, $(dV) = 0$.
- (e) **Cyclic Process :**
 - * The process in which a system proceeds via many intermediate steps and returns to the initial state.
 - * Change in internal energy $(dE) = 0$,
Change in enthalpy $(dH) = 0$
- (f) **Reversible Process :**
 - * This process is slow and unreal. Its direction can be changed at any step. By this, the maximum work done by the system can be obtained.
- (g) **Irreversible Process :**
 - * This process is fast. All the natural processes are of this type. In this, the work done is less than that in the reversible process. $W_{\text{Irreversible}} < W_{\text{Reversible}}$

(h) **Polytropic process:** For polytropic process, value of exponential constant are different for various process

- $PV^x = \text{constant}$
- $x = 0$, Isobaric process
- $x = 1$, Isothermal process
- $x = \gamma$, Adiabatic process
- $x = \infty$, Isochoric process



FIRST LAW OF THERMODYNAMICS

- * Energy can neither be produced nor destroyed, it can only be changed from one form to the other i.e., total energy of an isolated system remains constant.
- * Total energy of universe remains constant. Whenever some amount of any form of energy disappears, the same amount of energy of other form is produced.

INTERNAL ENERGY

The fixed amount of energy contained in a substance.
Quantitative Property – Internal energy depends on chemical nature, pressure, temperature and volume of the substance.

State Functions – Internal energy depends on the physical state of the system.

Internal energy is the total of all types of energy e.g., potential energy, kinetic energy, vibrational energy, rotational energy, etc. Absolute value of internal energy cannot be determined. Only change in internal energy (ΔE or ΔU) can be determined.

$\Delta E = \text{Energy in final state} - \text{Energy in initial state.}$

$\Delta E = E_2 - E_1$

$\Delta E = \text{Energy of the products} - \text{Energy of reactants}$

Internal energy is an extensive property. In most stable form, internal energy of the system is regarded as zero. Internal energy of one mole of a monoatomic gas at T

Kelvin is $\frac{3}{2} RT$.

$\Delta E = -ve$ in exothermic reactions

$\Delta E = +ve$ in endothermic reactions

Note : According to Law of equipartition of energy,

- (i) Each translation and rotational degree of freedom in a molecule contributes $\frac{1}{2}RT$ to the thermal energy of one mole of a gas, and
- (ii) Each vibrational degree of freedom in a molecule contributes RT to the thermal energy of one mole of a gas.

HEAT

The energy exchanged between a system and the surroundings when their temperatures are different is commonly known as heat. It flows from higher temperature to lower temperature.

Note : Heat is a path function.

Sign conventions of heat :

- (i) Energy entering the system (or absorbed by the system) is positive.

- (ii) Any energy leaving the system (or given off by the system) is negative.

Total heat capacity : Heat required to raise the temperature of system by 1°C under the given process.

$C_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} \text{ J}/^\circ\text{C} ; q = \int C_T dT$

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

$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT} \text{ J mole}^{-1}\text{K}^{-1} ; q = \int n C dT = nC\Delta T$

Note :

- * C is intensive path function.
- * C_p and C_v are intensive but not a path function.
- * $C_p - C_v = R$
- * For isothermal process, $C = \pm \infty$
- For isobaric process, $C = C_p$
- For isochoric process, $C = C_v$
- For adiabatic process, $C = 0$

WORK

All kinds of PV work is expressed as : $W = -P\Delta V$
 The above expression satisfy the sign conventions.
 For expansion ΔV or $(V_2 - V_1)$ +ve and $W = -ve$
 For compression ΔV or $(V_2 - V_1) = -ve$ and $W = +ve$

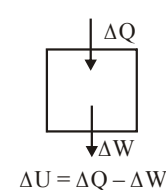
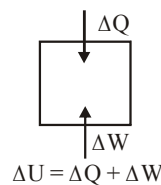
Note :

- * Work done by the system on the surroundings
(-w) = negative
- * Work done on the system by the surroundings
(+w) = positive
- * The sign convention is different from physics, but the meaning always comes out to be same only in equation we have to use a different sign convention for work.
So, if in any problem, $w = -10 \text{ J}$

It means system has done work of 10 joule on surroundings.

In chemistry

In physics



MATHEMATICAL FORM OF FIRST LAW

Energy absorbed by a system

$\Delta E \text{ (or } \Delta U) = q + W$

For isothermal process (PV = constant) :

$\Delta E = 0$ as temperature is constant

$\therefore 0 = q + W$ or $q = -W$

* Max. work done in expansion of n moles of an ideal gas.

$W_{\text{max}} = -2.303 nRT \log \frac{V_2}{V_1}$

where, $V_1 = \text{Initial volume of the gas}$
 $V_2 = \text{Final volume of the gas}$

For isochoric process (V = constant) :

W = 0 (System does not do any work)

$\Delta E = q + 0$ heat given to system at constant volume changes internal energy.

For adiabatic process (PV $^\gamma$ = constant) :

q = 0 ; $\Delta E = 0 + W$ or $\Delta E = W$ work done on system change internal energy

When a gas expands against a constant pressure, P, then

(a) $\Delta V (\Delta V = V_2 - V_1)$

$\Delta E = q - P\Delta V$. Then,

W = litre atmosphere [1 litre atmosphere = 101.3 Joule]

(b) If a gas expands in vacuum, the work done, W = 0, because P = 0.

(c) Reversible adiabatic :

$$w = -\int P_{\text{ext}} dV = -\int \frac{K}{V^\gamma} dV = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

Note :

- * If the external pressure is constant in isothermal process, process is irreversible.
- * Whenever work is done on the gas then it will be minimum in case of reversible process.
- * For irreversible adiabatic process equations PV $^\gamma$ or TV $^{\gamma-1}$ = constant are not applicable.
- * Single stage adiabatic expansion means irreversible process.
- * Infinite stage adiabatic expansion means reversible process.

Example 1 :

Find the work done in each case :

- (a) When one mole of ideal gas in 10 litre container at 1 atm, is allowed to enter a vacuumed bulb of capacity 100litre.
- (b) When 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

Sol. (a) W = -P ΔV

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.

(b) W = -P ΔV = -1 (5 - 1) = -4 litre-atm.

Example 2 :

The pressure of a fluid is a linear function of a volume (P = a + bV) and the internal energy of the fluid is U = 34 + 3PV (S.I. units). Find a, b, w, ΔE and q for change in state from (100 Pa, 3m 3) to (400 Pa, 6m 3)

Sol. $w = -\int_{V_1}^{V_2} P dV$ (100 = a + 3b; 400 = a + 6b; a = -200 & b = 100)

$$w = -\int_{V_1}^{V_2} (a + bV) dV = -\left\{ [aV] + \left[\frac{bV^2}{2} \right] \right\}_{V_1}^{V_2}$$

$$= -[-600 + 13.5 \times 100] = -750$$

$$\Delta U = 6300$$

Example 3 :

One mole of an ideal gas is expanded isothermally at 300K from 10 atm to 1 atm. Calculate q, w, ΔU & ΔH under the following conditions:

- (i) Expansion is carried out reversibly
- (ii) Expansion is carried out irreversibly

Sol. Isothermal process

(i) For ideal gas, $\Delta U = 0$; $\Delta H = 0$

q = -w

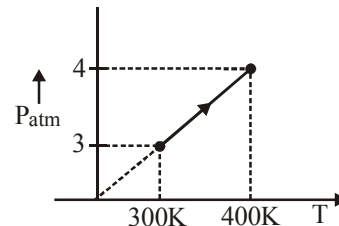
$$w_{\text{rev}} = -nRT \ln \frac{P_1}{P_f} = -1 \times R \times 300 \ln \frac{10}{1} = -690.9 R$$

$$(ii) w_{\text{irrev}} = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

$$= -1 \times 1 \times R \times 300 \left[\frac{1}{1} - \frac{1}{10} \right] = -270 R$$

Example 4 :

For 1 mole of monoatomic gas. Calculate w, ΔU , ΔH , q.



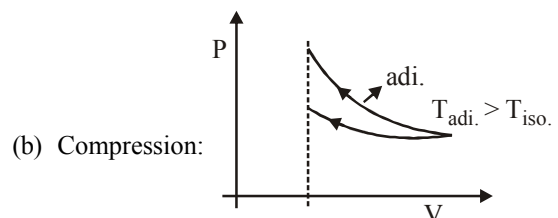
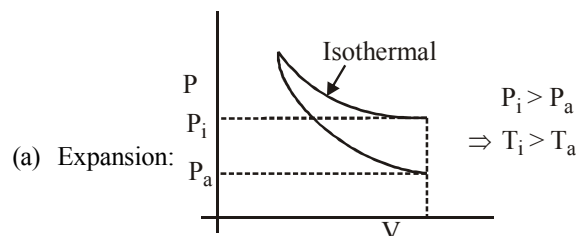
Sol. Isochoric process, w = 0

$$q = dU = CV (T_2 - T_1) = \frac{3}{2} \times (400 - 300) = 150 R$$

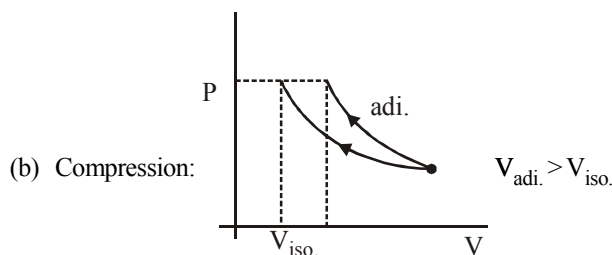
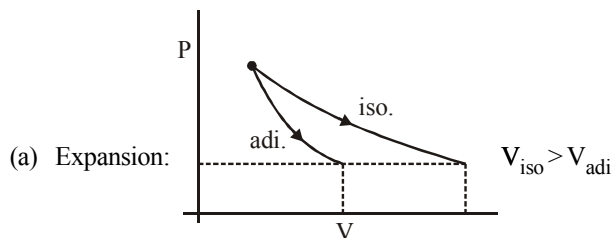
$$\Delta H = C_p \Delta T = \frac{5}{2} R (400 - 300) = 250 R$$

COMPARISON B/W ISOTHERMAL & ADIABATIC PROCESS

Case-I : For same final volume



Case-II : For same final pressure



HEAT CONTENT OR ENTHALPY, H

$$H = E + PV \quad ; \quad P = \text{External pressure}$$

At constant temperature and pressure

$$\Delta H = \Delta E + P\Delta V \quad ; \quad \Delta E = \text{Change in internal energy}$$

$$P\Delta V = \Delta W = \text{Work done}$$

Most of the chemical reactions occur at constant pressure (1 atmospheric) and in an open vessel .

When $\Delta V = 0$, $\Delta H = \Delta E$

$\Delta H = -ve$, (reaction is exothermic)

$\Delta H = +ve$, (reaction is endothermic)

Enthalpy of a system depends on physical state (solid, liquid and gas).

H is a state function. Therefore, it depends only on initial and final states. Absolute value of enthalpy cannot be determined

$$\text{Enthalpy of monoatomic gas} = \frac{5}{2} RT \text{ per mole.}$$

Change in enthalpy of the products and reactants at 298 K and 1 atmospheric pressure is called standard molar enthalpy change.

Relationship between ΔH and ΔE (or ΔU)

At constant pressure

$$\Delta H = \Delta E + P\Delta V, \text{ According to first law of thermodynamics}$$

$$\Delta E = Q + W \quad ; \quad W = -P\Delta V$$

$$\Delta E = Q - P\Delta V$$

$$\Delta H = Q - P\Delta V + P\Delta V \quad ; \quad \Delta H = Q$$

For liquids and solids

$$\Delta V = 0 \quad W = 0 \quad ; \quad \Delta H = \Delta E$$

For gaseous state

$$PV = nRT \quad P\Delta V = \Delta nRT$$

$$\Delta H = \Delta E + (\Delta n)RT$$

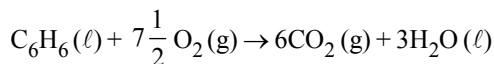
$$(a) \Delta n = 0 \quad \Delta H = \Delta E$$

$$(b) \Delta n = -ve \quad \Delta H < \Delta E$$

$$(c) \Delta n = +ve \quad \Delta H > \Delta E$$

Example 5 :

For the combustion of 1 mole of liquid benzene at 25°C, the heat of reaction at constant pressure is given by



$$\Delta H = -780980 \text{ cal.}$$

What would be the heat of reaction at constant volume ?

Sol. We have, $\Delta H = \Delta E + \Delta n_g RT$

$$\text{Here, } \Delta n_g = 6 - 7.5 = -1.5$$

$$\text{Thus, } \Delta E = \Delta H + \Delta n_g RT$$

$$= -780980 - (-1.5) \times 2 \times 298 = -780090 \text{ calories}$$

Example 6 :

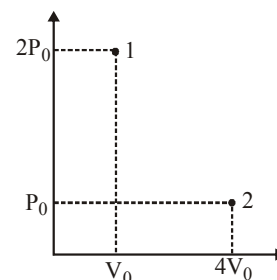
A liquid confined inside an adiabatic container is suddenly taken from state 1 to state 2 by a single process as shown, then ΔH is –

$$(A) \Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$$

$$(B) \Delta H = -P_0 V_0$$

$$(C) \Delta H = -3P_0 V_0$$

$$(D) \Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$$



Sol. (B), $Q = 0$

$$\Delta U = Q + w = w$$

$$w = -P_0(4V_0 - V_0) = -3P_0V_0$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

$$= -3P_0V_0 + (4P_0V_0 - 2P_0V_0)$$

$$= -3P_0V_0 + 2P_0V_0 = -P_0V_0$$

TRY IT YOURSELF-1

Q.1 Which of the following is intensive property?

- (A) Temperature (B) Heat
(C) Mass (D) Volume

Q.2 Calculate work done during evaporation of 1 mole of water at 373 K temperature and at atmospheric pressure.

Q.3 8g of helium gas expands isothermally and reversibly from a volume of 10 litre to 20 litre at constant temperature of 300K. Calculate work done during the expansion. [log 2 = 0.3010]

Q.4 A gas absorbs 2000 J of heat and expands against an internal pressure of 2 atm from a volume of 0.1 L to 10L. What is the change in internal energy (1 L atm = 101.3 J)?

Q.5 The enthalpy of bond dissociation of CH₄ at constant pressure is 400 kcal at 25°C, then calculate bond dissociation enthalpy at constant volume.

Q.6 When an ideal gas undergoes adiabatic expansion, it gets cooled. This is because –

- (A) It is an exothermic process
(B) It is an endothermic process
(C) Internal energy of the system decreases
(D) Ideal gas becomes a real gas

- Q.7** 1g graphite is combusted at constant atmospheric pressure at 300 K. During the combustion temperature rises from 300K to 310 K. If the heat capacity of the container and its content is 22 kJ/K then calculate enthalpy of reaction. $C(s) + O_2 \rightarrow 2CO_2(g)$
- Q.8** An ideal gas is allowed to expand from 5L to 15L once rapidly and once very slowly. The magnitude of work done in two processes are W_1 & W_2 , they are related as
 (A) $W_1 = W_2$ (B) $W_1 > W_2$
 (C) $W_1 < W_2$ (D) Data is insufficient
- Q.9** The heat of formation of methane at 298 K at constant pressure is -17.89 kcal. Calculate its heat of formation at constant volume.
- Q.10** A cylinder of LPG contains 14 kg of isobutane. If a normal family requires 20,000 kJ of heat per day, how long will the cylinder last? The enthalpy of combustion of isobutane is -2660 kJ mol $^{-1}$. If the combustion efficiency is decreased to 60 percent, how long will it last now?
- Q.11** One mole of a real gas is subjected to a process from (2 bar, 30 lit, 300 K) to (2 bar, 40 lit, 500 K).
 Given : $C_v = 25$ J/mol/K, $C_p = 40$ J/mol/K
 Calculate ΔU .
 (A) 5000 J (B) 6000 J
 (C) 8000 J (D) 10000 J
- Q.12** The temperature of a definite amount of an ideal monoatomic gas becomes four times in reversible process for which heat exchange is zero. Which of the following is correct relation between the final and initial parameters of gas?
 (A) $V_f = 8V_i$ (B) $P_f = 32 P_i$
 (C) $V_f = 16 V_i$ (D) $P_f = (1/16) P_i$
- Q.13** What is the change in internal energy when a gas contracts from 377ml to 177ml under a constant pressure of 1520torr, while at the same time being cooled by removing 124 J heat? [Take (1 L atm) = 100 J]
 (A) -24 J (B) -84 J
 (C) -164 J (D) -248 J
- Q.14** Molar heat capacity of water in equilibrium with ice at constant pressure is –
 (A) zero (B) ∞
 (C) 40.45 kJ K $^{-1}$ mol $^{-1}$ (D) 75.48 JK $^{-1}$ mol $^{-1}$

ANSWERS

- (1) (A) (2) -3.10 kJ (3) -3.46 kJ
 (4) -5.74 J (5) 398.2 kcal (6) (C)
 (7) -2640 kJ (8) (C) (9) -17.293 kcal
 (10) 32.1 days, 19.26 days. (11) (B)
 (12) (B) (13) (B) (14) (B)

SECOND LAW OF THERMODYNAMICS

Entropy of an isolated system increases and becomes stationary on reaching maximum i.e., stability is maximum at the state of maximum entropy.

Clausius statement : Transfer of heat from a cold body to a hot body is not possible without doing some work.
 Spontaneously, heat cannot flow from cold regions to hot

regions without external work being performed on the system, which is evident from ordinary experience of refrigeration, for example. In a refrigerator, heat flows from cold to hot, but only when forced by an external agent, a compressor.

Kelvin statement : “No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.”

This means it is impossible to extract energy by heat from a high-temperature energy source and then convert all of the energy into work. At least some of the energy must be passed on to heat a low temperature energy sink. Thus, a heat engine with 100% efficiency is thermodynamically impossible.

ENTROPY, S

It is a thermodynamic property and is a measure of disorderliness or randomness of a system, i.e., greater the disorder in a system, higher is the entropy of that system.

Solid < Liquid < Gas

Entropy is a state function. It does not depend on path.

$$\Delta S = S_2 - S_1 = \frac{q(\text{reversible})}{T}$$

q = amount of heat (At temperature T) absorbed by the system in a reversible way.

Some important points related to entropy :

- Entropy change, $\Delta S = S(\text{Final state}) - S(\text{Initial state})$
- $\Delta S =$ Increase in entropy of positive system.
- $\Delta S =$ Decrease in entropy of negative system.
- When a solute gets dissolved in the solvent, the entropy increases.
- When the number of gaseous products increases in a chemical reaction, the entropy also increases. For example.
 $(NH_4)_2S(s) \longrightarrow 2NH_3(g) + H_2S(g)$
- $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ Entropy is decreasing.
- For a reaction, change in entropy
 $\Delta S =$ Total of entropies of the products
 $-$ Total of entropies of the reactants.
- Unit of entropy is joule kelvin $^{-1}$ mole $^{-1}$.
- At equilibrium, $\Delta S = 0$
- Entropy change in an isothermic reversible expansion of a

gas. $\Delta S = 2.303 nR \log \frac{V_2}{V_1}$

V_2 and V_1 are final and initial volumes of the gas.

Spontaneous Processes :

This type of physical and chemical change occurs of its own under specific circumstances or on proper initiation.
 Examples–

- Flow of liquids from higher to lower level.
- Flow of gases from higher pressure to lower pressure.
- Conduction of heat from hot body to the colder body
- Flow of electric current from higher potential to lower potential.

- (5) Dissolution of sugar in water.
- (6) All naturally occurring processes.
- (7) Burning of coal and other fuels.

Some important points related to spontaneous changes ;

1. These changes occur only in single direction. They do not occur in opposite direction by themselves. For example, water does not flow itself from lower to upper level.
2. Work can be done by a spontaneous change. For example, motion of a piston by expansion of gas, rotation of a wheel when water falls on it from some height, etc.
3. For a spontaneous change for an isolated system.
 $\Delta S = \text{Positive}$
4. When it not an isolated system
 $\Delta S_{\text{(total)}} = \Delta S_{\text{(system)}} + \Delta S_{\text{(surrounding)}} > 0$
5. Change in entropy of a system

$$\Delta S_{\text{(system)}} = \frac{q(\text{Reversible})}{T}$$

$$\Delta S_{\text{(Surroundings)}} = \frac{q(\text{Reversible})}{T}$$

For a reversible process

$$\begin{aligned} \Delta S_{\text{(System)}} + \Delta S_{\text{(Surroundings)}} \\ = \frac{q(\text{Reversible})}{T} + \frac{q(\text{Reversible})}{T} = 0 \end{aligned}$$

For nonreversible process

$$\Delta S_{\text{(Total)}} = \frac{q(\text{Reversible})}{T} - \frac{q(\text{Reversible})}{T} > 0$$

6. **Adiabatic expansion :** In adiabatic systems. $q = 0$ at each step. Therefore, $\Delta S = 0$. Thus. reversible adiabatic processes are called isentropic.
7. **Phase Transition :** In phase transition process

$$\Delta S = S_2 - S_1 = \frac{q(\text{Reversible})}{T} = \frac{\Delta H}{T}$$

$$\Delta S(\text{Fusion}) = \frac{\Delta H(\text{Fusion})}{T}$$

(Latent heat of fusion of solid)

T = Melting point of solid in kelvin

$$\Delta S(\text{Vaporisation}) = \frac{\Delta H(\text{Vapourisation})}{T}$$

where, $\Delta H(\text{Vaporisation}) = \text{Latent heat of vaporisation}$
 T = Boiling point

It is difficult to find out the value of $\Delta S(\text{Surroundings})$. Therefore, there is no proper evidence in favour of entropic spontaneous change. Gibbs suggested the free energy step which is related only to the system. This is convenient.

Example 7 :

One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Find the values of ΔS_{sys} , ΔS_{surr} & ΔS_{total} under the following conditions.

- (i) Expansion is carried out reversibly
- (ii) Expansion is carried out irreversibly

(iii) Expansion is free.

Sol. (i) $\Delta S_{\text{sys}} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0 + R \ln 10 = R \ln 10$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = -R \ln 10 ; \Delta S_{\text{total}} = 0$$

(ii) $\Delta S_{\text{sys}} = R \ln 10 ; \Delta S_{\text{surr.}} = \frac{-q_{\text{irr}}}{T}$

$$\Delta U = 0 = q + w ; q_{\text{irr}} = P_{\text{ext}} (v_2 - v_1)$$

$$q_{\text{irr}} = P_{\text{ext}} \left[\frac{RT}{P_2} - \frac{RT}{P_1} \right] = RT \left[\frac{1}{1} - \frac{1}{10} \right]$$

$$= RT \times \frac{9}{10} = \frac{9}{10} \times R \times 300 = 270 R$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = \frac{-9R}{10}$$

$$\Rightarrow \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = R \ln 10 - \frac{9R}{10}$$

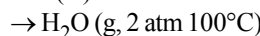
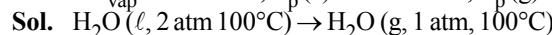
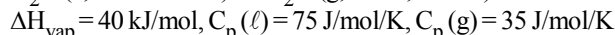
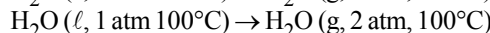
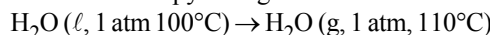
(iii) Free expansion, $\Delta T = 0, w = 0, q = 0$

$$\Delta S_{\text{sys}} = R \ln 10$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0 ; \Delta S_{\text{total}} = R \ln 10$$

Example 8 :

Calculate entropy change



(C)

$$\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40.000}{373}, \Delta S_{B \rightarrow C} = nR \ln \frac{P_2}{P_1} = 1 \times R \ln \frac{1}{2}$$

Example 9 :

1 kg stone at 27°C falls 100m into a lake whose temperature is 27°C. Find the entropy change of (a) the stone (b) the lake (c) the universe when

- (i) stone is lowered reversibly
- (ii) stone is dropped freely.

Compare the loss of available energy in two cases.

Sol. (i) If the stone is lowered reversibly no amount of heat will be produced. Also since term of stone remains the same.

$$\Delta S_{\text{stone}} = 0$$

$$q_{\text{rev}} = 0 \Rightarrow \Delta S_{\text{lake}} = 0$$

$$\text{and } \Delta S_{\text{total}} = \Delta S_{\text{universe}} = \Delta S_{\text{lake}} + \Delta S_{\text{stone}} = 0$$

(ii) If the stone is lowered irreversibly, the potential energy will be entirely lose in form of heat energy

$$q_{\text{actual}} = q_{\text{irr}} = mgh$$

$$\Delta S_{\text{stone}} = 0$$

$$\Delta S_{\text{lake}} = -\frac{q_{\text{irr}}}{T} = -\left(\frac{-1 \times 9.8 \times 1000}{300}\right) = \frac{900}{300} \text{ J/K}$$

$$= 3.26 \text{ J/K}$$

$$\Delta S_{\text{total}} = 3.26 \text{ J/K}$$

Loss of available energy in first process = 0

Loss of available energy in second process = 980 Joules

FREE ENERGY (G)

The available amount of energy during the process in the system which can be changed into maximum useful work, is called free energy of the system.

Thus, free energy change in the system (ΔG), is the measure of the capability of doing useful work by the system

$$G = H - TS \quad [\text{Gibbs-Helmholtz equation}]$$

$$H = E - PV; \quad \Delta G = \Delta H - T\Delta S$$

If $\Delta G = \text{Negative}$, then the reaction is spontaneous in forward direction

$$\Delta G = 0, \text{ at equilibrium}$$

$\Delta G = \text{Positive}$, then the reaction is nonspontaneous in backward direction.

Variation of Gibb's function (G) with temperature and pressure:

$$G = H - TS = U + PV - TS$$

$$dG = dU + PdV - TdS + VdP - SdT$$

$$dG = VdP - SdT$$

(i) At constant temperature, $dT = 0$

For every substance

$$dG = V dP \text{ or } \left(\frac{\partial G}{\partial P}\right)_T = V$$

(a) For an ideal gas, at constant temperature

$$dT = 0 \text{ and } V = \frac{nRT}{P}$$

$$\text{So, } dG = \frac{nRT}{P} dp = nRT \ln \frac{p_2}{p_1}$$

(b) For solids/liquids, at constant temperature

$dT = 0$ and V is almost constant change in pressure

So, $dG = v dp$ [$v = \text{constant}$]

$$\Delta G = v (p_2 - p_1)$$

At constant pressure, $dP = 0$

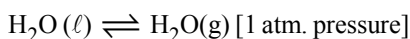
For any substance, $dG = -S dT$

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

If in a question, given that $S = f(T)$, by integrating ΔG can be calculate.

Example 10 :

For the vaporisation of water :



Given : $\Delta S = 120 \text{ JK}^{-1}$ and $\Delta H = +45.0 \text{ kJ}$.

Evaluate the temperature at which liquid water and water vapours are in equilibrium at 1 atm. pressure –

Sol. We know that : At equilibrium $\Delta G = 0$

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

$$\therefore \Delta S = \frac{\Delta H}{T}; \quad T = \frac{\Delta H}{\Delta S} = \frac{45.0 \times 10^3 \text{ J}}{120 \text{ JK}^{-1}} = 375 \text{ K}$$

Example 11 :

For a certain reaction the change in enthalpy and change in entropy are $40.63 \text{ kJ mol}^{-1}$ and 100 JK^{-1} . What is the value of ΔG at 27°C and indicate whether the reaction is possible or not ?

Sol. We know that : $\Delta G = \Delta H - T\Delta S$

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

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

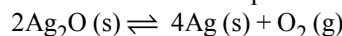
$$\Delta S = 100 \text{ JK}^{-1}$$

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

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

Example 12 :

If $\text{Ag}_2\text{O}(\text{s})$ is exposed to atmosphere having pressure 1 atm and temperature 27°C . Under these conditions comment whether it will dissociate spontaneously or not.



Given:	ΔH_f° (kJ/mol)	ΔS° (J/Kmol) at 27°C
Ag (s)	0	42.0
Ag_2O (s)	-30	121.0
O_2 (g)	0	204.0

(Air consist of 20% O_2 by volume)

Take : $R = 8.3 \text{ JK}^{-1}\text{mol}^{-1}$

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

$$\Delta H^\circ = \Delta H_f^\circ (\text{product}) - \Delta H_f^\circ (\text{reactants}) = 2 \times 30 = 60 \text{ kJ}$$

$$\Delta S^\circ = 204 + 4(42) - 2(121) = +130$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 60000 - 300 \times 130$$

$$\Delta G^\circ = 21000 \text{ J} = -RT \ln K$$

$$\log K = -\left(\frac{21000}{300 \times 8.3 \times 2.3}\right); \quad K_p = 2.15 \times 10^{-4} \text{ atm}$$

The dissociation of Ag_2O is nonspontaneous at 27°C

THIRD LAW OF THERMODYNAMICS

Entropy \propto Temperature

According to Nernst, entropy of an ideal crystalline substance is zero at absolute temperature

Absolute entropy of a pure substance can be calculated at different temperatures by this law. For this, the value of C_p (Heat capacity) is necessary.

Limitations of third Law

1. Entropy of glass-like substances is more than zero at 0 K.
2. Entropy of the solids, which are mixture of isotopes, is not zero at 0 K, e.g., $\text{Cl}_{2(\text{s})}$
3. There is no ideal order in the crystals of NO, H_2O , CO, N_2O at 0 K. Therefore their entropy is not zero at 0K.

TRY IT YOURSELF-2

- Q.1** The enthalpy change for the transition of liquid water to steam ΔH_{vap} is 40.8 kJ mol^{-1} at 373 K . Calculate the entropy change associated with vaporisation.
- Q.2** Enthalpy and entropy changes of a reversible reaction are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. Predict the feasibility of the reaction at 27°C .
- Q.3** The spontaneous nature of a reaction is impossible if –
 (A) $\Delta H = +ve, \Delta S = +ve$ (B) $\Delta H = -ve, \Delta S = -ve$
 (C) $\Delta H = -ve, \Delta S = +ve$ (D) $\Delta H = +ve, \Delta S = -ve$
- Q.4** ΔG° of reversible reaction at its equilibrium is –
 (A) Positive (B) Negative
 (C) Always zero (D) may be (A) or (B)
- Q.5** Out of boiling point (I), entropy (II), pH (III) and density (IV), Intensive properties are –
 (A) I, II (B) I, II, III
 (C) I, III, IV (D) All of these
- Q.6** The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm, is –
 (A) 1.385 cal/K (B) -1.2 cal/K
 (C) 1.2 cal/K (D) 2.77 cal/K
- Q.7** Standard entropy of X_2, Y_2 and XY_3 are $60, 40$ & $50 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively. For the reaction

$$\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3; \Delta H = -30 \text{ kJ}$$
 to be at equilibrium, the temperature will be –
 (A) 1250 K (B) 500 K
 (C) 750 K (D) 1000 K
- Q.8** For the reaction takes place at certain temperature $\text{NH}_4\text{HS (s)} \rightleftharpoons \text{NH}_3 \text{ (g)} + \text{H}_2\text{S (g)}$, if equilibrium pressure is X bar, then $\Delta_r G^\circ$ would be –
 (A) $-2RT \ln X$ (B) $-RT \ln (X - \ln 2)$
 (C) $-2RT (\ln X - \ln 2)$ (D) None of these

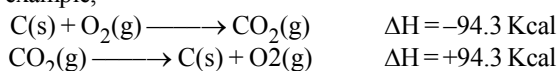
ANSWERS

- (1) $109.4 \text{ J mol}^{-1} \text{ K}^{-1}$ (2) backward direction.
 (3) (D) (4) (D) (5) (C)
 (6) (D) (7) (C) (8) (C)

THERMOCHEMISTRY

LAVOISIER AND LAPLACE'S LAW

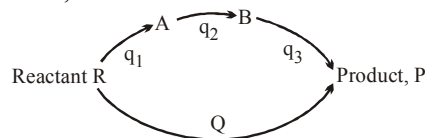
This law is based on the first law of thermodynamics. The heat released in the preparation of a compound from its constituent elements, is same as the amount of heat required to decompose that compound into its elements. For example,



HESS'S LAW OF CONSTANT HEAT SUMMATION

When a chemical reaction gets completed directly in one step or indirectly in two or more steps, the total energy change in the reaction remains same. i.e., the change does not depend on the path of a chemical reaction.

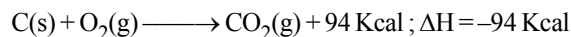
Reactant ,



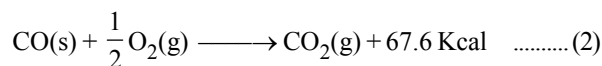
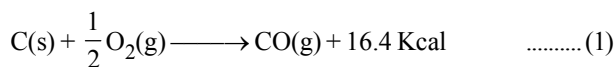
$$Q = q_1 + q_2 + q_3$$

Example – Combustion of carbon

Method 1 :



Method 2 :



On summing up equations (1) and (2),
 $\Delta H = -94 \text{ Kcal}$

Applications – Determination of heat of formation, heat of combustion, heat of transition, heat of reaction and bond energy.

HEAT OF REACTION

According to stoichiometry of balanced equation of a reaction change in total heat on complete reaction of the reactants at constant temperature and pressure (or constant volume) is called heat of reaction of that reaction.

- (a) At constant pressure
 $q_{(p)} = \Delta H = H_p(\text{Product}) - H_R(\text{Reactant})$
- (b) At constant volume
 $q_{(v)} = \Delta E = E_p(\text{Product}) - E_R(\text{Reactant})$

Standard Heat of Reaction : Change in total heat (ΔH) at 25°C and 1 atmospheric pressure is called standard heat of reaction. Heat of reaction measured by Bomb calorimeter is ΔE .

Relation between QP and QV

$$\begin{aligned} \Delta H &= \Delta E + P\Delta V \\ q_{(p)} &= \Delta H \\ q_{(p)} &= q_{(v)} + P\Delta V; \quad q_{(v)} = \Delta E \\ PV &= nRT \\ P\Delta V &= \Delta nRT \end{aligned}$$

$$q_{(p)} = q_{(v)} + \Delta nRT$$

$$\begin{aligned} q_{(p)} \text{ and } q_{(v)} &\text{ have same unit} \\ R &= 1.987 \text{ cal kelvin}^{-1} \text{ mol}^{-1} \\ R &= 8.314 \text{ joule kelvin}^{-1} \text{ mol}^{-1} \end{aligned}$$

When $\Delta n = 0$

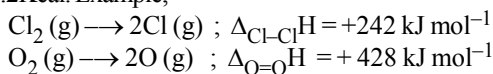
$$\begin{aligned} q_{(p)} &= q_{(v)} \\ \text{C(s)} + \text{O}_2\text{(g)} &\rightarrow \text{CO}_2\text{(g)} \\ \Delta n &= 0 \end{aligned}$$

Here, solids are not taken into consideration. For solids, liquids and solutions (all reactants and product)

$$q_{(p)} = q_{(v)} \quad ; \quad \Delta H = \Delta E$$

Example – Esterification, neutralisation

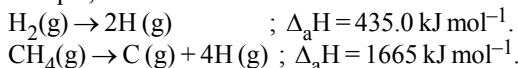
Bond energy values of same type of bonds in the same compound are different. Therefore, average of bond energy values is taken into consideration. For example in CH_4 . C–H bond energy values are different. H–H bond energy 104.2 Kcal. Example,



5. Enthalpy of atomisation :

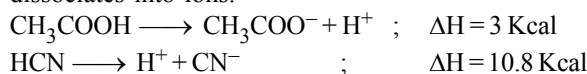
It is the enthalpy change when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition.

For example,



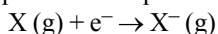
6. Enthalpy of ionisation :

It is defined as the amount of heat absorbed when 1 mole of an electrolyte completely dissociates into ions.



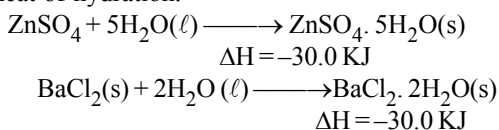
7. Electron gain enthalpy :

It is the enthalpy change when an electron is added to a neutral gaseous atom to convert it into a negative ion under conditions of constant temperature and pressure.



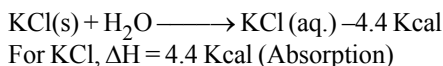
8. Enthalpy of Hydration :

Heat released on complete hydration of one mole an anhydrous substance is called heat of hydration.



9. Enthalpy of Solution

One mole of a substance is dissolved in so much amount of water that no change take place in heat on greater dilution. In this process, change in total heat is called heat of solution.



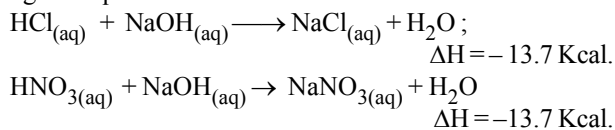
Heat is liberated for MgSO_4 .

Integral Heat of Solution : Heat change on dissolving one mole of a substance in definite amount of solvent is called integral heat of solution.

Heat of Dilution : Difference of two integral heats is called heat of dilution.

10. Enthalpy of Neutralisation

It is defined as the change in heat enthalpy when one gram equivalent of an acid is completely neutralised by 1 gram equivalent of a base in dilute solutions.



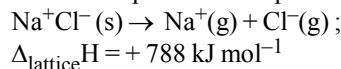
Thus it is clear that heat of formation is -13.7 K cal but in case when 1 gm equivalent each of weak acid and strong base or a strong acid and weak base or weak acid and weak base are allowed to react, the apparent value of heat of neutralization is lesser than 13.7 K Cal

Example

$\text{HCl}(\text{aq}) + \text{NH}_4\text{OH}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq}) + \text{H}_2\text{O}; \Delta\text{H} = -12.3 \text{ K Cal}$
The reason for the lower value of enthalpy of neutralisation is that the part of heat energy evolved is utilised in the complete ionisation of a weak acid (or) a weak base (or) both. Hence, the net heat of neutralisation is less than 13.7 kcal . In the above reaction, heat energy of ionisation of $\text{NH}_4\text{OH} = 1.4 \text{ kcal}$.

11. Lattice Enthalpy ($\Delta_{\text{lattice}}\text{H}$) :

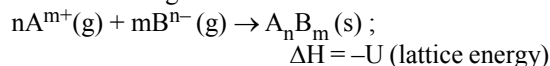
The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state under conditions of constant temperature and pressure.



Lattice enthalpy can also be defined for the reverse process. In that case the value of $\Delta\text{H}_{\text{LE}}$ will be negative.

12. Born-Haber Cycle For NaCl :

This cycle is based on thermochemical changes taking place in the formation of a lattice. This cycle can be used to determine lattice energy which cannot be directly measured. It is defined as that energy released when one mole of the ionic compound (lattice) is formed from its isolated ions in the gaseous state under standard condition.



Formation of $\text{NaCl}(\text{s})$ lattice involves thus,

$$S + I + \frac{\epsilon_{\text{Cl-Cl}}}{2} - E - U = q$$

hence, U can be calculated.

Here, S = enthalpy of sublimation of $\text{Na}(\text{s}) = \Delta\text{H}_{\text{sublimation}}$

I = ionisation energy of $\text{Na}(\text{g}) = \Delta\text{H}_{\text{ionization}}$

ϵ = bond energy of Cl_2

U = lattice energy

q = enthalpy of formation of $\text{NaCl}(\text{s}) = \Delta\text{H}_{\text{formation}}$

If lattice is $\text{MgX}_2(\text{s})$ then

$$S + (I_1 + I_2) + \epsilon - 2E - U = q$$

where, $(I_1 + I_2)$ = total ionisation energy to form $\text{Mg}^{2+}(\text{g})$.

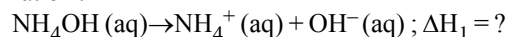
Example 15 :

Enthalpy of neutralization of HCl by NaOH is -57.1 kJ/mol and by NH_4OH is -51.1 kJ/mol . Calculate the enthalpy of dissociation of NH_4OH .

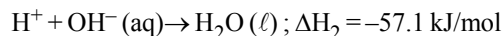
Sol. Given that, $\text{H}^+(\text{aq}) + \text{NH}_4\text{OH}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\ell)$
; $\Delta\text{H} = -51.1 \text{ kJ/mol}$.

We may consider neutralization in two steps :

(i) Ionization :



(ii) Neutralization :



Thus, $\Delta\text{H} = \Delta\text{H}_1 + \Delta\text{H}_2$

Therefore, $\Delta\text{H}_1 = \Delta\text{H} - \Delta\text{H}_2$

$$= -51.1 \text{ kJ/mol} + 57.1 \text{ kJ/mol} = 6.0 \text{ kJ/mol}$$

Example 16 :

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



Given : $\Delta H_f(\text{HCl, g}) = -92 \text{ kJ mol}^{-1}$ and

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

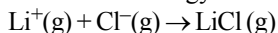
Sol. For the reaction, $\text{HCl (g)} + \text{aq} \rightarrow \text{H}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$

We have, $\Delta H^\circ = \Delta_f H^\circ(\text{Cl}^-, \text{aq}) - \Delta_f H^\circ(\text{HCl, g})$

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

Example 17 :

Calculate lattice energy for the change,



Given that $\Delta H_{\text{sublimation}}$ of Li = $160.67 \text{ kJ mol}^{-1}$,

$\Delta H_{\text{Dissociation}}$ of $\text{Cl}_2 = 244.34 \text{ kJ mol}^{-1}$,

$\Delta H_{\text{ionisation}}$ of Li (g) = $520.07 \text{ kJ mol}^{-1}$,

$\Delta H_{E.A.}$ of Cl (g) = $-365.26 \text{ kJ mol}^{-1}$,

ΔH_f of LiCl (s) = $-401.66 \text{ kJ mol}^{-1}$.

Sol. Considering the different changes that occur in the formation of solid lithium chloride based on data given the lattice energy of the above can be constituted as :

$$\Delta H_f^0 = \Delta H_{\text{subl.}} + \Delta H_{\text{I.E.}} + \frac{1}{2} \Delta H_{\text{diss}} + \Delta H_{E.A.} + \Delta H_{\text{lattice}}$$

$$\text{or } \Delta H_{\text{lattice}} = \Delta H_f^0 - \Delta H_{\text{subl.}} - \Delta H_{\text{I.E.}} - \frac{1}{2} \Delta H_{\text{diss}} - \Delta H_{E.A.}$$

$$= -839.31 \text{ kJ mol}^{-1}$$

RESONANCE ENERGY

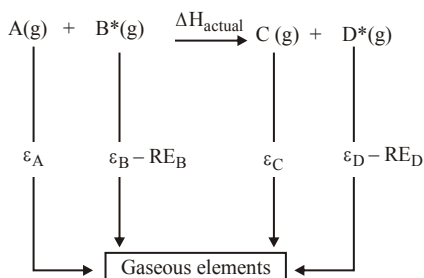
When two or more double bond are in conjugation, there is possibility of delocalization of electron through conjugation. The phenomenon is called resonance. Due to resonance the molecule gain stability. The actual structure of molecule is average of many possible canonical structure. Resonance energy is difference in energy of most stable canonical structure and energy of actual molecule. Whenever there is possibility of resonance in molecule, the molecule become more stable and breaking become difficult.

Calculation of resonance energy using bond energy:

Resonance energy can be calculated using the formula $\Delta H(\text{Actual}) - \Delta H(\text{theoretical}) = \text{resonance energy of products} - \text{Resonance energy of reactants}$

Consider a reaction : $\text{A (g)} + \text{B}^* \text{(g)} \rightarrow \text{C (g)} + \text{D}^* \text{(g)}$

where (*) showing that molecules exhibit phenomena of resonance.



Actual energy required to break a bond is equal to

$$\epsilon_{\text{actual}} = \epsilon_{\text{theoretical}} - \text{resonance energy}$$

$$\Delta H_{\text{actual}} = \epsilon_A + \epsilon_B - R.E_B - \{\epsilon_C + \epsilon_D - R.E_D\}$$

$$\Delta H_{\text{actual}} = (\epsilon_A + \epsilon_B - \epsilon_C - \epsilon_D) + R.E_B - R.E_D$$

$$\Delta H_{\text{actual}} - \Delta H_{\text{theoretical}} = R.E_{\text{products}} - R.E_{\text{reactants}}$$

Note: The value of resonance energy may be positive or negative, but assign it's sign on the basis that resonance always increases the stability and decreases the energy of molecule. Due to resonance in a molecule, bond breaking become difficult hence actual energy required to break a bond = theoretical bond energy – resonance energy.

Example 18 :

Calculate resonance energy of $\text{C}_6\text{H}_6 \text{(g)}$.

Given : $\Delta H_f[\text{C}_6\text{H}_6 \text{(g)}] = -360 \text{ kJ mol}^{-1}$

$\Delta H_{\text{sub}}[\text{C (graphite)}] = 716 \text{ kJ mol}^{-1}$

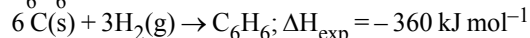
$B.E_{\text{H-H}} = 437 \text{ kJ mol}^{-1}$

$B.E_{\text{C=C}} = 620 \text{ kJ mol}^{-1}$

$B.E_{\text{C-C}} = 340 \text{ kJ mol}^{-1}$

$B.E_{\text{C-H}} = 490 \text{ kJ mol}^{-1}$

Sol. For C_6H_6



$$\therefore \Delta H_{\text{cal}} = -[3(\text{C-C}) + 3(\text{C=C}) + 6(\text{C-H})]$$

$$+ [6\text{C}_{\text{s} \rightarrow \text{g}} + 3(\text{H-H})]$$

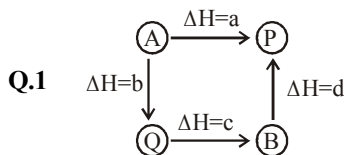
$$= -[3 \times 340 + 3 \times 620 + 6 \times 490] + [6 \times 716 + 3 \times 437]$$

$$= -5820 + 5607 = -213 \text{ kJ mol}^{-1}$$

$$\therefore \text{Resonance energy} = \text{Exp. } \Delta H_f - \text{Calculated } \Delta H_f$$

$$= -360 - (-213) = -360 + 213 = -147 \text{ kJ mol}^{-1}$$

TRY IT YOURSELF-3



On the basis of Hess's law of constant heat summation, choose the correct relation –

(A) $b = a - d + c$ (B) $c = a - b + d$

(C) $d = a + b + c$ (D) $a - c = b + d$

Q.2 The heat of neutralisation of four acids P, Q, R, S are $-13.7, -9.4, -11.2$ and -12.4 kcal , respectively when they are neutralised by a common base. The acidic character obeys the order –

(A) $P > Q > R > S$ (B) $P > S > R > Q$

(C) $S > R > Q > P$ (D) $S > Q > R > P$

Q.3 The heats of combustion of yellow phosphorus and red phosphorus are -9.19 KJ and -8.78 KJ respectively, then find heat of transition of yellow phosphorus to red phosphorus.

Q.4 For the reaction,
 $\text{N}_2\text{H}_4 \text{(g)} \rightarrow \text{N}_2\text{H}_2 \text{(g)} + \text{H}_2 \text{(g)}; \Delta_f H^\circ = 109 \text{ kJ/mol}$
Calculate the bond enthalpy of $\text{N}=\text{N}$.

Given : $BE(\text{N-N}) = 163 \text{ kJ/mol}$, $BE(\text{N-H}) = 391 \text{ kJ/mol}$,
 $BE(\text{H-H}) = 436 \text{ kJ/mol}$.

Q.5 A 500g sample of water is reacted with an equimolar amount of CaO (both at an initial temp. at 25°C). What is the final temperature of the product?

[Assume that the product absorbs all of the heat released in the reaction]. Heat produced per mole of Ca(OH)₂ is 65.2kJ and specific heat Ca(OH)₂ is 1.2 J/g°C.

- (A) ≈ 735°C (B) ≈ 760°C
(C) ≈ 746°C (D) ≈ 789°C

Q.6 ΔH_f^o of water is -285 kJ mol⁻¹. If enthalpy of neutralisation of monoacid strong base is -57.3 kJ mol⁻¹, ΔH_f^o of OH⁻ ion will be -

- (A) -228.5 kJ mol⁻¹ (B) 228.5 kJ mol⁻¹
(C) 114.25 kJ mol⁻¹ (D) -114.25 kJ mol⁻¹

Q.7 If x₁, x₂ and x₃ are enthalpies of H-H, O=O and O-H bonds respectively, and x₄ is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen -

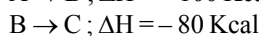
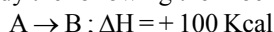
(A) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$ (B) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$

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

Q.8 The standard enthalpy of atomisation of PCl₃(g) is 195 Kcal/mol. What will be the standard enthalpy of atomisation of PCl₅(g), if the bond dissociation energies of axial P-Cl bonds in PCl₅(g) are 10% lesser and the bond dissociation energies of equatorial P-Cl bonds in PCl₅(g) are 10% higher than the bond dissociation energies of P-Cl bonds in PCl₃(g).

- (A) 195 Kcal/mol (B) 325 Kcal/mol
(C) 331.5 Kcal/mol (D) 318.5 Kcal/mol

Q.9 Study the following thermochemical equations:



The correct order of enthalpies of formation of A, B and C is

- (A) A < B < C (B) A < C < B
(C) C < A < B (D) B < C < A

ANSWERS

- (1) (D) (2) (B) (3) -1.13 KJ
(4) 400 kJ/mole (5) (B) (6) (A)
(7) (B) (8) (C) (9) (B)

CALORIMETRY

* A calorimeter is a device used to measure heat of reaction. In order to measure heats of reactions, we often enclose reactants in a calorimeter, initiate the reaction, and measure the temperature difference before and after the reaction. The temperature difference enables us to evaluate the heat released in the reaction.

Two basic types of calorimetry are discussed:

- (a) measurement based on constant volume.
(b) measurements based on constant pressure.

(i) Bomb calorimeter (ΔU measurement) :

A bomb calorimeter measures the heat evolved under constant volume, q_v,

$$q_v = C \Delta T, \text{ where } \Delta T \text{ is the temperature increase.}$$

The q_v so measured is also called the change in internal energy, ΔE. $\Delta E = q_v = C \times \Delta T$

Example 19 :

A calorimeter with heat capacity equivalent to having 13.3 moles of water is used to measure the heat of combustion from 0.303 g of sugar (C₁₂H₂₂O₁₁). The temperature increase was found to be 5.0 K. Calculate the heat released, the amount of heat released by 1.0 g, and 1.0 mole of sugar.

Sol. Heat released, q_v, $q_v = 13.3 \times 75.2 \times 5.0 \text{ K} = 5000 \text{ J}$

The amount of heat released by 1.0 g would be,

$$5000 \text{ J} / 0.303 \text{ g} = 16.5 \text{ kJ/g}$$

Since the molecular weight of sugar is 342 g/mol, the amount of heat released by 1.0 mole would be

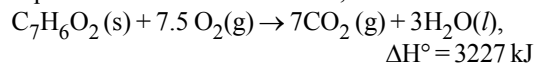
$$16.5 \times 342 = 56431 \text{ kJ/mol.}$$

(ii) ΔH measurement: Measurement of heat change at constant pressure (generally at atmospheric pressure) can be done in a Calorimeter. In this case, the Calorimeter is left open to atmosphere. The heat capacity of the calorimeter can also be determined by burning an exactly known amount of a standard substance, whose enthalpy of combustion has been determined. Benzoic acid, C₇H₆O₂, is one such standard.

Example 20 :

When 0.1025 g of benzoic acid was burnt in a bomb calorimeter the temperature of the calorimeter increased by 2.165°C. For benzoic acid ΔH^o_{comb} = -3227 kJ mol⁻¹. Calculate the heat capacity of the calorimeter.

Sol. The equation for the combustion is,



Since 7.5 moles of O₂ gas is needed, and 7 moles of CO₂ is produced, some pressure-volume work done, to the calorimeter:

$$PV = \Delta n_g RT, \text{ where } \Delta n = (7 - 7.5) = -0.5 \text{ mol}$$

$$\Delta E = \Delta H - \Delta n_g RT = -3227 - (-0.5 \times 8.314 \times 298)$$

$$= -3226 \text{ kJ/mol (a small correction)}$$

The amount of heat produced by 0.1025 g benzoic acid is $q = 0.1025 / 122.13 \times 3226 = 2.680 \text{ kJ}$

Thus, the heat capacity is

$$C = q_v / \Delta T = 2.680 / 2.165 = 1.238 \text{ kJ/K.}$$

After the heat capacity is determined, the calorimeter is ready to be used to measure the enthalpy of combustion of other substances.

IMPORTANT POINTS

- * One calorie is the amount of energy required to raise the temperature of 1g water by 1°C from 14.5°C to 15.5°C is : 1 calorie = 4.18 Joule.
- * For Cyclic Process : Change in internal energy (dE) = 0, Change in enthalpy (dH) = 0

- * Irreversible isothermal expansion of ideal gas
 $W = -P_{\text{ex}} \times \Delta V$
- * Work done in irreversible process is less than reversible process $W_{\text{Irreversible}} < W_{\text{Reversible}}$
- * Reversible isothermal process

$$W = -2.303 nRT \log \frac{V_2}{V_1} \quad \text{or} \quad W = -2.303 nRT \log \frac{P_1}{P_2}$$

- * Enthalpy $H = E + PV$
- * Enthalpy change, $\Delta H = \Delta E + P\Delta V$
- * An endothermic reaction which may be non-spontaneous at low temperature may become spontaneous at high temperature whereas an exothermic reaction which may be non-spontaneous at high temperature may become spontaneous at low temperature.
- * For hydrated salts like $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ etc. or for salts which do not form hydrates (like NaCl , KCl etc), the process of dissolution is endothermic.
- * According to first law of thermodynamics (law of conservation of energy), $\Delta E = q + w$ or $q = \Delta E - w$.
- * ΔH is negative for exothermic reaction while it is positive for endothermic reactions.
- * Heat of formation of $\text{H}_2\text{O}(\ell)$ ($\Delta H_f^\circ = -285 \text{ kJ mol}^{-1}$) is greater than that of $\text{H}_2\text{O}(\text{g})$ ($\Delta H_f^\circ = -248.8 \text{ kJ mol}^{-1}$) because the former includes heat of condensation of water vapour.
- * $q_p = q_v + P\Delta V = q_v + \Delta n_g RT$ where $\Delta n_g = (n_p - n_r)_{\text{gaseous}}$. Thus $q_p = q_v$ when
 - the reaction is carried out in a closed vessel.
 - The reaction does not involve any gaseous reactant or product.
 - $\Delta n_g = \text{i.e. } n_p(\text{g}) = n_r(\text{g})$
- * Standard enthalpy changes are measured at 298 K and 1 atmospheric pressure.
- * $\Delta H_{\text{reaction}}^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$
- * Entropy change in an isothermic reversible expansion of a

$$\text{gas.} \quad \Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

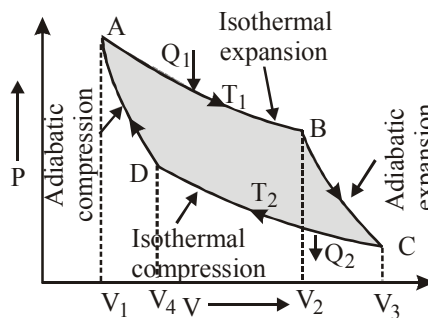
V_2 & V_1 are final and initial volumes of the gas.

Gibb's free energy change

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

ΔH	ΔS	ΔG	Properties of reaction
-	+	Always Negative	Reaction is spontaneous at all temperature
+	-	Always positive	Reaction is nonspontaneous at all temperature
-	-	Negative at low temperature but positive at high temperature	Spontaneous at low temp. & non spontaneous at high temperature
+	+	Positive at low temperature but negative at high temperature	Nonspontaneous at low temp. & spontaneous at high temperature

Carnot cycle



Process	Temperature	Volume	Heat	Type change
A to B	T_1 constant	$V_2 > V_1$	$+Q_1$	Isothermal expansion
B to C	$T_2 < T_1$	$V_3 > V_2$	0	Adiabatic expansion Temp. falls
C to D	T_2 constant	$V_4 < V_3$	$-Q_2$	Isothermal compression
D to A	$T_2 < T_1$	$V_1 < V_4$	0	Adiabatic compression Temp. increases

ADDITIONAL EXAMPLES

Example 1:

The work of expansion for a system is 500 cal. The heat given to the system is 80 cal. Find the change in internal energy in the process.

Sol. $\Delta E = q + w$; $80 + (-500) = -420 \text{ cal.}$

Example 2:

1 mole of a real gas is subjected to a process from (2 bar, 40 lit, 300 K) to (4 bar, 30 lit, 400 K). If change in internal energy is 20 kJ then calculate enthalpy change for the process.

Sol. $\Delta H = \Delta U + \Delta(PV)$

$$\Delta(PV) = P_2 V_2 - P_1 V_1 = 4 \times 30 - 2 \times 40 = 40 \text{ (l-bar)} = 4 \text{ kJ}$$

$$\Delta H = 20 + 4 = 24$$

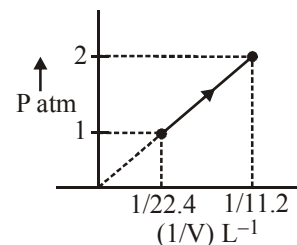
Example 3:

Calculate work done for an ideal gas ($\ln 2 = 0.7$)

Sol. $w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}$

$$= -P_1 V_1 \ln \frac{V_2}{V_1} = -22.4 \ln \frac{1}{2}$$

$$= 22.4 \times 0.7 = 15.68 \text{ L atm.}$$



Example 4 :

For a reaction at 25°C, enthalpy change ΔH and entropy change ΔS are -11.7×10^3 and 10^5 Joule per mole K^{-1} , respectively, the which of the following statements is true?
 (A) Spontaneous reaction (B) Nonspontaneous reaction
 (C) Can be 1 as well as 2 (D) At equilibrium

Sol. (B). $\Delta G = \Delta H - T\Delta S$; $\Delta H = -11.7 \times 10^3 \text{ J mol}^{-1}$
 $\Delta S = -105 \text{ J mol}^{-1} \text{ K}^{-1}$; $T = (25 + 273) = 298 \text{ K}$
 $\Delta G = (-11.7 \times 10^3) - 298 \times (-10^5) = +19.59 \text{ KJ mol}^{-1}$
 Therefore, ΔG is positive Reaction is not spontaneous.

Example 5 :

Calculate entropy change in each step for an ideal gas (monoatomic)

State (A) \longrightarrow State (B) \longrightarrow State (D)
 (1 atm, 22.4 l, 273K) (1 atm, 33.6 l, 409.5 K) (2 atm, 33.6 l, 819 K)

Sol. $\Delta S_{A-B} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = nC_p \ln \frac{409.5}{273} = C_p \ln \frac{3}{2}$

$\Delta S_{AC} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_v \ln \frac{546}{273} = C_v \ln 2$

Example 6 :

For the reaction : $N_2 + 2O_2 \rightarrow 2NO_2$; Given : at 1 atm, 300K

$S_{N_2} = 180 \text{ J/mol/K}$ $C_p(N_2) = 30 \text{ J/mol/K}$
 $S_{O_2} = 220 \text{ J/mol/K}$ $C_p(O_2) = 30 \text{ J/mol/K}$
 $S_{NO_2} = 240 \text{ J/mol/K}$ $C_p(NO_2) = 40 \text{ J/mol/K}$
 Calculate (i) $\Delta S_{300K, 1atm}$ (ii) $\Delta S_{400K, 1atm}$

Sol. (i) $(\Delta S_r)_{300} = 2S_{NO_2} - 2S_{O_2} - S_{N_2}$
 $= 2 \times 240 - 2 \times 220 - 180 = -140 \text{ J mol}^{-1} \text{ K}^{-1}$
 $(\Delta C_p)_r = 2C_p(NO_2) - 2C_p(O_2) - C_p(N_2)$
 $= 2 \times 40 - 2 \times 30 - 30 = -10 \text{ J mol}^{-1} \text{ K}^{-1}$

(ii) $(\Delta S_r)_{400} = (\Delta S_r)_{300} + (\Delta C_p)_r \ln \frac{T_2}{T_1} = -140 - 10 \ln \frac{4}{3}$
 $= -142.88 \text{ J mol}^{-1} \text{ K}^{-1}$

Example 7 :

γ for NH_3 including contribution from vibrational degree's of freedom is -

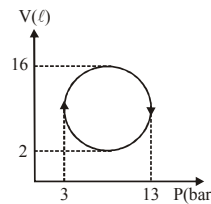
- (A) 4/3 (B) 10/9
 (C) 7/6 (D) 13/12

Sol. (B). $C_v = \frac{n_{tr}}{2} R + \frac{n_{rot}}{2} R + n_{vib} = \frac{3}{2} R + \frac{3}{2} R + 6R = 9R$

$C_p = 9R + R = 10R$; $\gamma = \frac{C_p}{C_v} = \frac{10}{9}$

Example 8

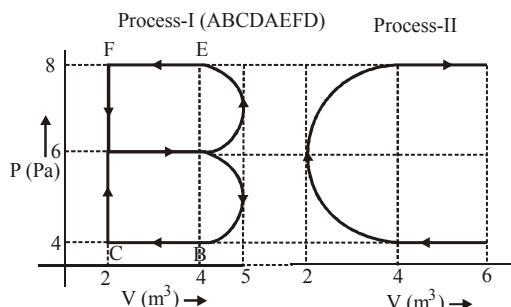
Work done (in kJ) by the gas in the following cyclic process is -
 (A) -11 (B) -11000
 (C) 11 (D) 11000



Sol. (A). $|w| = \pi ab = \frac{22}{7} \times 7 \times 5$
 $= 110 \text{ bar lit.} = 11000 \text{ J} = 11 \text{ kJ}$
 Final answer = -11

Example 9 :

Calculate difference in work done in process-I to process-II, (Given: $\pi = 3$)

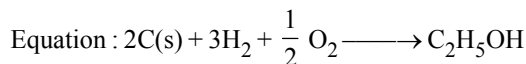
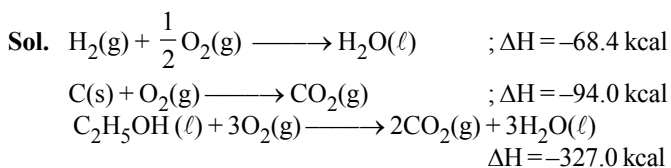


Sol. Process-I : $w_{ABCDAEFD} = w_{ABCDA} + w_{AE} + w_{EF} + w_{FD}$
 $= -\left(2 \times 2 + \frac{3 \times 1 \times 1}{2}\right) + \frac{3 \times 1 \times 1}{2} + 8 \times 2 + 0$
 $= -5.5 + \frac{3}{2} + 16 = 12$

Process-II : $w = \left(\frac{3 \times 2 \times 2}{2} + 4 \times 2\right) = -(6 + 8) = -14$
 Difference in work done = $12 - (-14) = 26$

Example 10 :

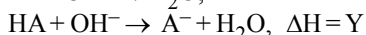
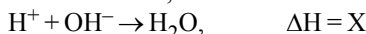
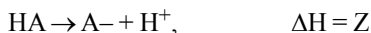
Enthalpy of carbon, hydrogen and ethyl alcohol on combustion at 25°C are -94.0, -68.4 and -327.0 kcal per mole, then find the formation enthalpy of ethyl alcohol.



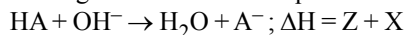
Multiplying eq. 1 by 3 and eq. 2 by 2 and eq 3 by -1, adding all the three would give enthalpy of formation of ethyl alcohol. $(3 \times -68.4) + (2 \times -94) - (-327) = -66.2 \text{ Kcal}$

Example 11 :

From the following thermochemical equations, find out the heat of ionisation Z for a weak acid HA-



Sol. Adding first and second equations :



Clearly: $Z + X = Y \quad \therefore Z = [Y - X]$

Example 12 :

What is true for the reaction : $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

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

(2) $\Delta H > \Delta E$

(3) $\Delta H < \Delta E$

(4) None of these

Sol. (2). $\Delta H = \Delta E + \Delta n RT$; $\Delta n = 2 - 1 = 1 \quad \therefore \Delta H > \Delta E$

Example 13 :

The gaseous endothermic reaction $\text{P} + \text{Q} \rightarrow 2\text{R} + 3\text{S}$ at 27°C takes place spontaneously, because -

(A) $\Delta H < 0; \Delta S < 0$

(B) $\Delta H > 0; \Delta S > 0$

(C) $\Delta H < 0; \Delta S > 0$

(D) $\Delta H > 0; \Delta S < 0$

Sol. (B). For an endothermic reaction, $\Delta H = +ve$
[less molecules \rightarrow more molecules], $\Delta S = +ve$
 $\therefore T\Delta S > \Delta H$, and $\Delta G = -ve$
Hence, the reaction occurs spontaneously.

Example 14 :

The heat capacity of a bomb calorimeter is $500 \text{ J}^\circ\text{C}$. In an experiment, in the combustion of 0.1 gm . methane, the temperature rise was by 2.0°C . What is the value of ΔE per mole?

Sol. For 2.0°C : Heat change = $2 \times 500 \text{ J} = 1000 \text{ J}$
 \therefore For the combustion of 0.1 gm methane = 1000 J
 \therefore For the combustion of 16 gm methane

$$= \frac{1000}{0.1} \times 16 = 160000 \text{ J} = 160 \text{ kJ/mole}$$

(Heat of combustion is negative)

Example 15 :

The bond dissociation energies of methane and ethane are $360 \text{ kcal mol}^{-1}$ and $620 \text{ kcal mol}^{-1}$ respectively. Find the C-C bond energy in kcal mol^{-1} .

Sol. Methane contains four C-H bonds. Ethane contains six C-H bonds and one C-C bond.

\therefore Energy of four C-H bonds = 360 kcal

\therefore Energy of six C-H bonds = $\frac{360}{4} \times 6 = 540 \text{ kcal}$

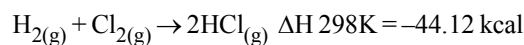
For ethane

energy of six C-H bonds and one C-C bond = 620 kcal .

\therefore Energy of C-C bond = $620 - 540 \text{ kcal} = 80 \text{ kcal}$

Example 16 :

For the reaction :

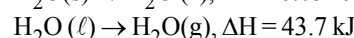
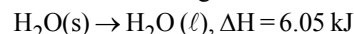


At 298 K , find the enthalpy of formation of HCl.

Sol. Enthalpy of HCl will be half of -44.12 kcal . So its value is -22.06 kcal .

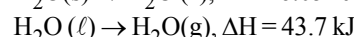
Example 17 :

Consider the following data

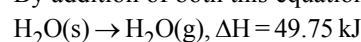


At 273 K , find the sublimation energy of $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g})$.

Sol. $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\ell), \Delta H = 6.05 \text{ kJ}$



By addition of both this equation



Example 18 :

The heat of formation of ICl $\Delta H(\text{ICl}) = 4.2 \text{ kcal mol}^{-1}$, $\Delta H(\text{Cl}) = 29.0 \text{ kcal mol}^{-1}$, $\Delta H(\text{I}) = 25.5 \text{ kcal mol}^{-1}$. What will be the bond energy of ICl ?

Sol. $\Delta H = \Sigma \text{Bond energy (Reactants)}$
 $\quad \quad \quad - \Sigma \text{Bond energy (Products)}$
 $4.2 = 29.0 + 25.5 - \text{Bond energy (I-Cl)}$
 $\text{Bond energy I-Cl} = 29.0 + 25.5 - 4.2 = 50.3 \text{ kcal}$

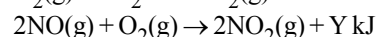
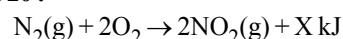
Example 19 :

For a spontaneous process the values of free energy and entropy change are respectively -

- (A) Positive and negative (B) Negative and positive
(C) Positive and positive (D) Negative and negative

Sol. (B). In a spontaneous process, entropy increases and free energy decreases.

Example 20 :



What is the heat of formation (ΔH_f) of NO -

(A) $(2X - 2Y)$

(B) $X - Y$

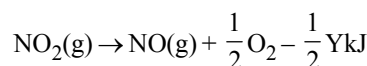
(C) $\frac{1}{2}(Y - X)$

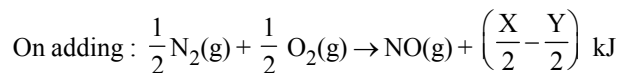
(D) $\frac{1}{2}(X - Y)$

Sol. (C). Dividing eqn. (1) by (2) :



On reversing eqn. [2] and dividing by 2





$\therefore (\Delta H_f)$ heat of formation = $\left(\frac{Y-X}{2}\right) \text{kJ}$

Example 21 :

If $\Delta H_{\text{vaporisation}}$ of $(\text{C}_2\text{H}_5)_2\text{O} (l)$ is 350 J/g at its boiling point 300 K, then molar entropy change for condensation process is –

- (A) 86.33 J/mol.K
- (B) –86.33 J/mol.K
- (C) –1.16 J/mol.K
- (D) 1.16

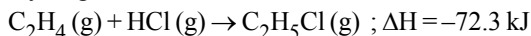
Sol. (B). $\Delta H_{\text{vaporisation}} = 350 \times 74 \text{ J/mol}$

$$\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vaporisation}}}{T_{\text{boiling point}}} = \frac{-350 \times 74}{300} \text{ J/mol.K}$$

$$= -86.33 \text{ J/mol.K}$$

Example 22 :

Ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$), is prepared by reaction of ethylene with hydrogen chloride :



What is the value of ΔE (in kJ), if 98g of ethylene and 109.5g of HCl are allowed to react at 300 K.

- (A) –64.81
- (B) –190.71
- (C) –209.71
- (D) –224.38

Sol. (C). No. of mole of $\text{C}_2\text{H}_4 = \frac{98}{28} = 3.5$,

No. of mole of HCl (Limiting reagent) = $\frac{109.5}{36.5} = 3$

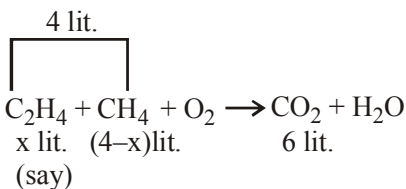
$\Delta H = \Delta E + \Delta n_g RT$;

$-72.3 = \Delta E + (-1 \times 8.314 \times 300) / 1000$; $\Delta E = -69.80$;

For three mole $\Delta E = -69.80 \times 3 = -209.41 \text{ kJ/mol}$

Example 23:

A gas mixture of 4 litres of ethylene and methane on the complete combustion at 25°C produces 6 litres of CO_2 . Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are : –1464 and –976 kJ mol^{-1} at 25°C.



Sol.

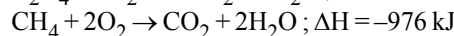
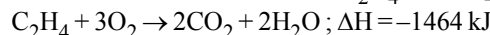
or x moles (4 – x) moles 6 moles

Applying POAC for C atoms,

$2 \times x + 1 \times (4 - x) = 1 \times 6$; $x = 2 \text{ lit.}$

Thus, the volue of $\text{C}_2\text{H}_4 = 2 \text{ lit.}$ and volume of $\text{CH}_4 = 2 \text{ lit.}$
 \therefore Volume of C_2H_4 in a 1 litre mixture = $2/4 = 0.5 \text{ lit.}$
 and Volume of CH_4 in a 1 litre mixture = $1 - 0.5 = 0.5 \text{ lit.}$

Now, thermochemical reactions for C_2H_4 and CH_4 are



As ΔH values given are at 25°C, let us first calculate the volume occupied by one mole of any gas at 25°C (at pressure 1 atm).

Volume per mole at 25°C = $\frac{298}{273} \times 22.4 = 24.4 \text{ lit.}$

Thus, heat evolved in the combustion of 0.665 lit. of C_2H_4

$= -\frac{1464}{24.4} \times 0.5 = -30 \text{ kJ}$

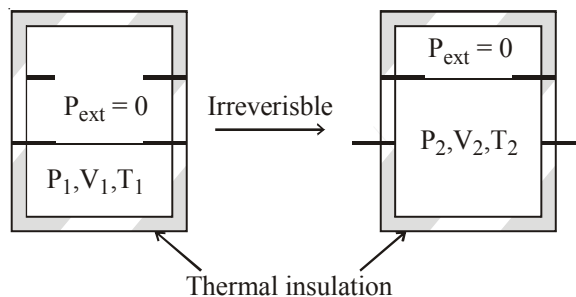
and heat evolved in the combustion of 0.335 lit. of CH_4

$= \frac{976}{24.4} \times 0.5 = -20 \text{ kJ}$

\therefore Total heat evolved in the combustion of 1 litre of the mixture = $-30 + (-20) = -50 \text{ kJ}$

Example 24:

An ideal gas in a thermally insulated vessel at internal pressure = P_1 , volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are P_2 , V_2 and T_2 , respectively. For this expansion,



- (A) $q = 0$
- (B) $T_2 = T_1$
- (C) $P_2 V_2 = P_1 V_1$
- (D) $P_2 V_2^\gamma = P_1 V_1^\gamma$

Sol. (ABC). Work against zero external pressure is zero $q = 0$ due to insulated boundary

So, $q = 0$

$\Delta U = 0$; $\Delta T = 0$ $\therefore T_2 = T_1$ and $P_2 V_2 = P_1 V_1$

Example 25:

For the process : $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{g})$ at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is –

- (A) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$
- (B) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$
- (C) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$
- (D) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$

Sol. (B). Given conditions are boiling conditions for water due to which $\Delta S_{\text{total}} = 0$

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

For process, $\Delta S_{\text{system}} > 0$; $\Delta S_{\text{surroundings}} < 0$

Example 26:

One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.

State 1 (8.0 bar, 4.0 litre, 300 K)

State 2 (2.0 bar, 16 litre, 300 K)

State 3 (1.0 bar, 32 litre, 300 K)

Total heat absorbed by the gas in the process is –

- (A) 116 J
- (B) 40 J
- (C) 4000 J
- (D) None of these

Sol. (C). $W = -P_{\text{ext}} [V_2 - V_1]$

$$W_1 = -2 [16 - 4] \times 100 = -2400 \text{ J}$$

$$W_2 = -[32 - 16] \times 100 = -1600 \text{ J}$$

$$\text{-----}$$

$$-4000 \text{ J}$$

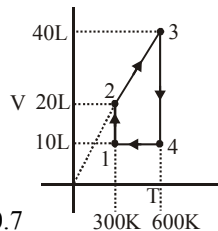
$$q = -W = 4000 \text{ J}$$

Example 27:

What is the net work done (in calories) by 1 mole of monoatomic ideal gas in a process described by 1, 2, 3, 4 in given V-T graph.

Use : $R = 2 \text{ cal/mole K}$, $\ln 2 = 0.7$

- (A) – 600 cal
- (B) – 660 cal
- (C) + 660 cal
- (D) + 600 cal



Sol. (B). $w_{12} = -nRT \ln (v_2/v_1) = -420 \text{ cal}$
 $w_{23} = -P\Delta V = -nR\Delta T = -600 \text{ cal}$
 $w_{34} = -1 \times 2 \times 600 \times \ln 2 = -840 \text{ cal}$
 $w = 660 \text{ cal}$ (i.e., work is done on the gas)
 Work done by the gas = – 660 cal

Example 28:

Match the thermodynamic processes given under Column I with the expressions given under Column II.

Column I

Column II

- | | |
|--|---------------------------------|
| (1) Freezing of water at 273 K and 1 atm | (P) $q = 0$ |
| (2) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions | (Q) $w = 0$ |
| (3) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container | (R) $\Delta S_{\text{sys}} < 0$ |
| (4) Reversible heating of $\text{H}_2(\text{g})$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm. | (S) $\Delta U = 0$ |
| | (T) $\Delta G = 0$ |
- (A) 1-R,T ; 2-P,Q,S ; 3-P,Q,S ; 4-P,Q,S,T
 (B) 1-R,S ; 2-P,T,S ; 3-P,Q,S ; 4-P,Q,S,T
 (C) 1-R,T ; 2-P,Q,S ; 3-P,S,T ; 4-P,S,T
 (D) 1-P,Q ; 2-P,Q,S ; 3-S,T ; 4-S,T

Sol. (A). (1) $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{s})$ at 273 K. & 1 atm
 $\Delta H = -ve = q$; $\Delta S_{\text{sys}} < 0$, $\Delta G = 0$.

$w \neq 0$ (as water expands on freezing), $\Delta U \neq 0$

- (2) Free expansion of ideal gas, $q = 0$; $w = 0$; $\Delta U = 0$
 $\Delta S_{\text{sys}} > 0$; $\Delta G < 0$
- (3) Mixing of equal volume of ideal gases at constant pressure & temp in an isolated container
 $q = 0$, $w = 0$, $\Delta U = 0$, $\Delta S_{\text{sys}} > 0$, $\Delta G < 0$
- (4) $\text{H}_2(\text{g})$ 300 K $\xrightarrow[\text{Heating, 1atm}]{\text{Reversible}}$ 600 K $\xrightarrow[\text{Cooling, 1atm}]{\text{Reversible}}$ 300 K.
 $q = 0$, $w = 0$, $\Delta U = 0$, $\Delta G = 0$, $\Delta S_{\text{sys}} = 0$

QUESTION BANK

CHAPTER 6 : THERMODYNAMICS

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART 1 : THERMODYNAMIC TERMS

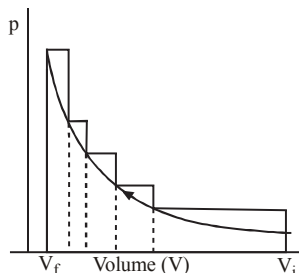
- Q.1** The universe is equal to –
 (A) system (B) surrounding
 (C) system + surrounding (D) None of the above
- Q.2** Select the correct match.
 (A) $q = +ve$ means heat is transferred from the system to the surroundings.
 (B) $q = -ve$ means heat is transferred from the surroundings to the system.
 (C) $q = +ve$ means heat is transferred from the surroundings to the system.
 (D) All of the above
- Q.3** On what factor(s) does the internal energy of the system depend?
 (A) Matter enters or leaves the system.
 (B) Work is done on or by the system.
 (C) Heat passes into or out of the system.
 (D) All of the above
- Q.4** The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. Which of the following variables are called state variable?
 (A) p, V (B) V, T
 (C) p, T (D) p, V, T
- Q.5** A system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surrounding through its boundary. This process is called as
 (A) isothermal process (B) adiabatic process
 (C) isochoric process (D) isobaric process
- Q.6** For the process to occur under adiabatic conditions, the correct condition is:
 (A) $\Delta T = 0$ (B) $\Delta p = 0$
 (C) $q = 0$ (D) $w = 0$
- Q.7** Which of the following statements is correct?
 (A) The presence of reacting species in a covered beaker is an example of open system.
 (B) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
 (C) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
 (D) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.
- Q.8** $\Delta E = q + W$ is mathematical expression for
 (A) first law of thermodynamics
 (B) second law of thermodynamics
 (C) third law of thermodynamics
 (D) zeroth law of thermodynamics.
- Q.9** The __ (i) __ of a system can be changed by transfer of heat from the surrounding to the system or vice-versa without expenditure of __ (ii) __.
 Correct words for (i) and (ii) are –
 (A) (i) enthalpy ; (ii) work
 (B) (i) internal energy ; (ii) heat
 (C) (i) enthalpy ; (ii) heat
 (D) (i) internal energy ; (ii) work
- Q.10** A thermodynamic state function is a quantity
 (A) used to determine heat changes
 (B) whose value is independent of path
 (C) used to determine pressure volume work
 (D) whose value depends on temperature only.
- Q.11** In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.
 (A) $q = 0, \Delta T \neq 0, W = 0$ (B) $q \neq 0, \Delta T = 0, W = 0$
 (C) $q = 0, \Delta T = 0, W = 0$ (D) $q = 0, \Delta T < 0, W \neq 0$
- Q.12** Thermodynamics mainly deals with
 (a) interrelation of various forms of energy and their transformation from one form to another.
 (b) energy changes in the processes which depend only on initial and final states of the microscopic systems containing a few molecules.
 (c) how and at what rate these energy transformations are carried out.
 (d) the system in equilibrium state or moving from one equilibrium state to another equilibrium state.
 Choose the correct option –
 (A) a & b (B) b & c
 (C) b & d (D) a & d
- Q.13** Which of the following statement is incorrect?
 (A) The system is defined as physical boundaries like beaker or test tube or the system may simply be defined by a set of cartesian coordinates specifying a particular volume in space.
 (B) The wall that separates the system from the surrounding is called boundary.
 (C) Boundary is designed to allow us to control and keep the track of all the movements of matter and energy in or out of the system.
 (D) System is not separated from the surrounding by some sort of wall which may be real or imaginary.
- Q.14** Thermodynamics is not concerned about –
 (A) energy changes involved in a chemical reaction.
 (B) the extent to which a chemical reaction proceeds.
 (C) the rate at which a reaction proceeds.
 (D) the feasibility of a chemical reaction.

- Q.15** The state of a gas can be described by quoting the relationship between –
 (A) pressure, volume, temperature
 (B) temperature, amount, pressure
 (C) amount, volume, temperature
 (D) pressure, volume, temperature, amount
- Q.16** Which of the following statements/expressions is/are correct?
 (A) $\Delta U = W_{\text{adiabatic}}$
 (B) $W_{\text{ad}} = +ve$, when work is done on the system
 (C) $W_{\text{ad}} = -ve$, when work is done by the system
 (D) All of the above
- Q.17** In thermodynamics, _____ is the sum of all energy of the system, i.e., chemical, electrical, mechanical etc. Fill the blank with an appropriate word.
 (A) external energy (B) reversible energy
 (C) internal energy (D) irreversible energy

PART 2: APPLICATIONS

- Q.18** When heat is absorbed by the system at constant pressure then –
 (A) $\Delta H = qV$ (B) $\Delta E = q_p$
 (C) $\Delta H = q_p$ (D) $\Delta E = qV$
- Q.19** Consider the following reaction:

$$\text{CO (g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$$
 How are ΔE and ΔH related for the reaction?
 (A) $\Delta H = \Delta E - 0.5 RT$ (B) $\Delta H = \Delta E - RT$
 (C) $\Delta H = \Delta E + 0.5 RT$ (D) $\Delta H = \Delta E - 1.5 RT$
- Q.20** In thermodynamics, which one of the following properties is not an intensive property?
 (A) Pressure (B) Temperature
 (C) Volume (D) Density
- Q.21** Select the correct statement about the graph.



- (A) It is an irreversible compression.
 (B) Pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f
 (C) Both (A) and (B)
 (D) None of the above
- Q.22** Which of the following relationships is not correct for the relation between ΔH and ΔU ?
 (A) When $\Delta n_g = 0$ then $\Delta H = \Delta U$
 (B) When $\Delta n_g > 0$ then $\Delta H > \Delta U$
 (C) When $\Delta n_g < 0$ then $\Delta H < \Delta U$
 (D) When $\Delta n_g RT = 0$ then $\Delta H > \Delta U$

- Q.23** Which of the following statement (s) is/are correct?
 (A) $q = \text{coefficient} \times \Delta T$, the magnitude of the coefficient depends on the size, composition and nature of the system.
 (B) $q = C \Delta T$, The coefficient C is called the heat capacity
 (C) Water has a larger heat capacity
 (D) All of the above
- Q.24** In an adiabatic expansion of ideal gas
 (A) $W = -\Delta E$ (B) $W = \Delta E$
 (C) $\Delta E = 0$ (D) $W = 0$
- Q.25** In the equation, $\Delta U = q_p - p\Delta V$. Select the correct match.
 (A) $q_p \rightarrow$ heat absorbed by the system,
 $-p\Delta V \rightarrow$ expansion work done by the system
 (B) $q_p \rightarrow$ heat absorbed by the system,
 $-p\Delta V \rightarrow$ expansion work done on the system
 (C) $q_p \rightarrow$ heat absorbed on the system,
 $-p\Delta V \rightarrow$ expansion work done by the system
 (D) $q_p \rightarrow$ heat absorbed on the system,
 $-p\Delta V \rightarrow$ expansion work done on the system
- Q.26** A system changes from state X to Y with a change in internal energy measuring to 25 kJ mol^{-1} , by a reversible path and returns from Y to X by an irreversible path. What will be the net change in internal energy?
 (A) 25 kJ (B) $> 25 \text{ kJ}$
 (C) $< 25 \text{ kJ}$ (D) zero
- Q.27** The enthalpy change of a reaction does not depend upon
 (A) state of reactants and products
 (B) nature of reactants and products
 (C) different intermediate reaction
 (D) initial and final enthalpy change of a reaction.
- Q.28** According to the first law of thermodynamics, $\Delta U = q + W$. In special cases the statement can be expressed in different ways. Which of the following is not a correct expression?
 (A) At constant temperature: $q = -W$
 (B) When no work is done: $\Delta U = q$
 (C) In gaseous system: $\Delta U = q + P \Delta V$
 (D) When work is done by the system: $\Delta U = q + W$
- Q.29** Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres. How much work is done in the expansion?
 (A) 10 J (B) 8 J
 (C) 18 J (D) 0 J
- Q.30** For the given equation, $\Delta H = \Delta U + \Delta n_g RT$ which of the following expression is correct for the above equation?
 (A) $\Delta n_g =$ number of moles of gaseous reactants
 $-$ number of moles of gaseous products
 (B) $p\Delta V = \Delta n_g RT$
 (C) $p\Delta V \neq \Delta n_g RT$
 (D) All of the above

- Q.31** A process is called reversible when
 (A) surrounding and system change are same
 (B) there is no boundary between system and surrounding
 (C) surrounding is always in equilibrium with system
 (D) system changes into surroundings spontaneously.
- Q.32** What will be the change in internal energy when 12 kJ of work is done on the system and 2 kJ of heat is given by the system?
 (A) +10 kJ (B) -10 kJ
 (C) +5 kJ (D) -5 kJ

PART 3 : MEASUREMENT OF ΔU AND ΔH : CALORIMETRY

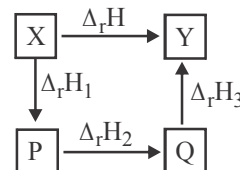
- Q.33** Which of the following condition(s) is/are applied for the measurement of ΔU ?
 (A) Constant volume q_v (B) Constant pressure q_p
 (C) Either (A) or (B) (D) None of the above
- Q.34** Select the correct statement for the bomb calorimeter.
 (A) Temperature change of the calorimeter produced by the completed reaction is then converted to q_v by the known heat capacity of the calorimeter.
 (B) No work is done as the reaction is carried out at constant volume in the bomb calorimeter
 (C) Both (A) and (B)
 (D) None of the above

PART 4 : ENTHALPY CHANGE, $\Delta_r H$ OF A REACTION – REACTION ENTHALPY

- Q.35** Which of the following does not represent enthalpy change during phase transformation?
 (A) Standard enthalpy of fusion
 (B) Standard enthalpy of vaporisation
 (C) Standard enthalpy of sublimation
 (D) Standard enthalpy of formation
- Q.36** For the given reaction,
 $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$
 Select the correct option for $\Delta_r H$.
 (A) $[\text{H}_m(\text{CO}_2, \text{g}) + 2\text{H}_m(\text{O}_2, \text{g}) - [2\text{H}_m(\text{H}_2\text{O}, \ell) + \text{H}_m(\text{CH}_4, \text{g})]]$
 (B) $[\text{H}_m(\text{O}_2, \text{g}) + \text{H}_m(\text{CH}_4, \text{g}) - [\text{H}_m(\text{CO}_2, \text{g}) + 2\text{H}_m(\text{H}_2\text{O}, \ell)]]$
 (C) $[\text{H}_m(\text{CO}_2, \text{g}) + 2\text{H}_m(\text{H}_2\text{O}, \ell) - [\text{H}_m(\text{CH}_4, \text{g}) + 2\text{H}_m(\text{O}_2, \text{g})]]$
 (D) $[\text{H}_m(\text{CO}_2, \text{g}) + \text{H}_m(\text{H}_2\text{O}, \ell) - [\text{H}_m(\text{CH}_4, \text{g}) + 2\text{H}_m(\text{O}_2, \text{g})]]$
- Q.37** The statement “The change of enthalpy of a chemical reaction is same whether the reaction takes place in one or several steps” is
 (A) Le Chatelier's law

- (B) van't Hoff's law
 (C) first law of thermodynamics
 (D) Hess's law.

- Q.38** On the basis of thermochemical equations (a), (b) and (c), find out which of the algebraic relationships given in options (A) to (D) is correct.
 (a) $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_r H = x \text{ kJ mol}^{-1}$
 (b) $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}); \Delta_r H = y \text{ kJ mol}^{-1}$
 (c) $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_r H = z \text{ kJ mol}^{-1}$
 (A) $z = x + y$ (B) $x = y - z$
 (C) $x = y + z$ (D) $y = 2z - x$
- Q.39** The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation is called –
 (A) standard molar enthalpy of condensation.
 (B) standard molar enthalpy of formation.
 (C) molar enthalpy of condensation.
 (D) molar enthalpy of formation.
- Q.40** Hess's law is applicable for the determination of heat of
 (A) transition (B) formation
 (C) reaction (D) all of these
- Q.41** The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of .
 (A) sublimation (B) vaporisation
 (C) formation (D) fusion
- Q.42** Which of the following reactions will have the value of enthalpy of neutralisation as $-57.1 \text{ kJ mol}^{-1}$
 (A) $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$
 (B) $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
 (C) $\text{HCl} + \text{NH}_4\text{OH} \rightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}$
 (D) $\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOONa} + \text{H}_2\text{O}$
- Q.43** Which of the following statement is incorrect?
 (A) The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.
 (B) The standard state of a substance at a specified temperature is its pure form at 1 bar
 (C) The standard state of solid iron at 298 K is pure iron at 1 bar.
 (D) Standard conditions are denoted by adding the superscript to the symbol ΔH . e.g., $-\Delta H^\ominus$
- Q.44** Which thermochemical process is shown by the following figure?



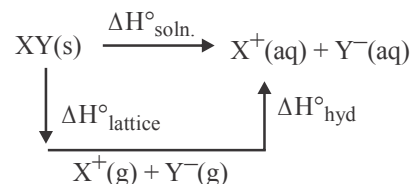
- (A) Standard enthalpy of a reaction
 (B) Born – Haber cycle of lattice enthalpy
 (C) Hess's law of constant heat summation
 (D) Standard enthalpy of a solution.

- Q.45** Which of the following statement(s) is/are correct?
 (A) Unit of $\Delta_f H^\ominus$ is kJ mol^{-1}
 (B) Enthalpy is an intensive quantity
 (C) When a chemical equation is reversed the value of $\Delta_f H^\ominus$ remain same in sign
 (D) All of the above
- Q.46** Which of the following expressions is correct to calculate enthalpy of a reaction?
 (A) $\Delta H_{\text{reaction}} = \sum \Delta_f H_{\text{reactants}} - \sum \Delta_f H_{\text{products}}$
 (B) $\Delta H_{\text{reaction}} = \sum \text{B.E.}_{\text{products}} - \sum \text{B.E.}_{\text{reactants}}$
 (C) $\Delta H_{\text{reaction}} = \sum \text{B.E.}_{\text{reactants}} - \sum \text{B.E.}_{\text{products}}$
 (D) $\Delta H_{\text{reaction}} = \Delta H_1 \times \Delta H_2 \times \Delta H_3 \dots$

PART 5: ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

- Q.47** Lattice enthalpies are determined by
 (A) Born-Haber cycle (B) Hess's law
 (C) lattice cycle (D) None of the above
- Q.48** Dissociation of water takes place in two steps:
 $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}; \Delta H = +497.8 \text{ kJ}$
 $\text{OH} \rightarrow \text{H} + \text{O}; \Delta H = 428.5 \text{ kJ}$
 What is the bond energy of O – H bond?
 (A) 463.15 kJ mol^{-1} (B) 428.5 kJ mol^{-1}
 (C) 69.3 kJ mol^{-1} (D) 926.3 kJ mol^{-1}
- Q.49** What is the enthalpy change for the given reaction, if enthalpies of formation of Al_2O_3 and Fe_2O_3 are $-1670 \text{ kJ mol}^{-1}$ and -834 kJ mol^{-1} respectively?
 $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
 (A) -836 kJ mol^{-1} (B) $+836 \text{ kJ mol}^{-1}$
 (C) -424 kJ mol^{-1} (D) $+424 \text{ kJ mol}^{-1}$
- Q.50** In the given reaction, $\text{Na(s)} \rightarrow \text{Na(g)}$
 The enthalpy of atomisation is same as the
 (A) enthalpy of dissociation
 (B) enthalpy of sublimation
 (C) enthalpy of association
 (D) enthalpy of vaporisation
- Q.51** Formation of ammonia is shown by the reaction,
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}); \Delta_f H^\ominus = -91.8 \text{ kJ mol}^{-1}$
 What will be the enthalpy of reaction for decomposition of NH_3 according to the reaction?
 $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}); \Delta_f H^\ominus = ?$
 (A) $-91.8 \text{ kJ mol}^{-1}$ (B) $+91.8 \text{ kJ mol}^{-1}$
 (C) $-45.9 \text{ kJ mol}^{-1}$ (D) $+45.9 \text{ kJ mol}^{-1}$
- Q.52** In the given reaction, $\text{Na}^+\text{Cl}^-(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$
 Identify the enthalpy involved in the given reaction
 (A) Enthalpy of hydration (B) Lattice enthalpy
 (C) Enthalpy of solution (D) Enthalpy of dissociation
- Q.53** How much heat is evolved if 3.2 g of methane is burnt and if the heat of combustion of methane is -880 kJ mol^{-1} ?
 (A) 88 kJ (B) 264 kJ
 (C) 176 kJ (D) 440 kJ

- Q.54** Study the figure given below and mark the correct expression.

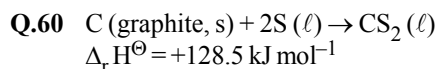


The enthalpy of solution of XY(s) , $\Delta H^\ominus_{\text{soln}}$ in water can be determined by

- (A) $\Delta H^\ominus_{\text{lattice}} = \Delta H^\ominus_{\text{hyd}} + \Delta H^\ominus_{\text{soln}}$
 (B) $\Delta H^\ominus_{\text{hyd}} = \Delta H^\ominus_{\text{lattice}} + \Delta H^\ominus_{\text{soln}}$
 (C) $\Delta H^\ominus_{\text{soln}} = \Delta H^\ominus_{\text{lattice}} + \Delta H^\ominus_{\text{hyd}}$
 (D) $\Delta H^\ominus_{\text{soln}} = \Delta H^\ominus_{\text{lattice}} \times \Delta H^\ominus_{\text{hyd}}$
- Q.55** Enthalpy change when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase. It is called as
 (A) bond association enthalpy
 (B) bond dissociation enthalpy
 (C) mean bond dissociation enthalpy
 (D) mean bond association enthalpy
- Q.56** Which of the following is not a correct statement about enthalpy of solution?
 (A) For most ionic compounds, $\Delta H^\ominus_{\text{soln}}$ is positive and the dissociation process is endothermic.
 (B) Solubility of most salts increases with increase in temperature.
 (C) If the lattice enthalpy is very high, the dissolution of compound becomes very easy.
 (D) Enthalpy of solution is determined by the selective values of the lattice enthalpy and hydration enthalpy.
- Q.57** Which is the correct order of bond energy of single, double and triple bonds between carbon atoms?
 (A) $\text{C}-\text{C} > \text{C}=\text{C} > \text{C}\equiv\text{C}$ (B) $\text{C}=\text{C} > \text{C}\equiv\text{C} > \text{C}-\text{C}$
 (C) $\text{C}\equiv\text{C} > \text{C}-\text{C} > \text{C}=\text{C}$ (D) $\text{C}\equiv\text{C} > \text{C}=\text{C} > \text{C}-\text{C}$

PART 6: SPONTANEITY

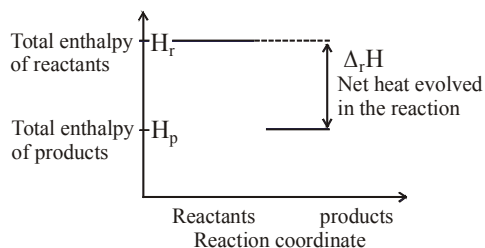
- Q.58** The first law of the thermodynamics tells
 (A) about the relationship between the heat absorbed.
 (B) about the work performed on or by a system
 (C) that no restrictions are applied on the direction of heat flow
 (D) All of the above
- Q.59** Which of the following processes is a non-spontaneous process?
 (A) Dissolution of salt or sugar in water
 (B) Mixing of different gases through diffusion
 (C) Precipitation of copper when zinc rod is dipped in aqueous solution of copper sulphate.
 (D) Flow of heat from a cold body to a hot body in contact.



The above reaction is

- (A) exothermic and spontaneous.
 (B) exothermic and non-spontaneous.
 (C) endothermic and spontaneous.
 (D) endothermic and non-spontaneous.

Q.61 The given enthalpy diagram represents which of the following reactions?



- (A) Enthalpy diagram for endothermic reaction
 (B) Enthalpy diagram for exothermic reaction
 (C) Enthalpy diagram for reversible reaction
 (D) Enthalpy diagram for non-spontaneous reaction.

Q.62 If a reaction has a positive enthalpy change and positive entropy change it can be spontaneous when $T \Delta S$ is large enough to outweigh ΔH . Select the way(s) in which the above statement can happen.

- (A) The positive entropy change of the system can be small in which case T must be large.
 (B) The positive entropy change of the system can be large in which case T may be small.
 (C) Both (A) and (B)
 (D) None of the above

Q.63 Which of the following statements regarding Gibbs energy change is correct?

- (A) If ΔG is negative (< 0), the process is non spontaneous.
 (B) If ΔG is positive (> 0), the process is spontaneous.
 (C) If ΔG is negative (< 0), the process is spontaneous.
 (D) If ΔG is positive (> 0), the process is in equilibrium.

Q.64 I. Gas expanding to fill the available volume.

II. Burning carbon with dioxygen gives carbon dioxide.

III. Gas in a container will contract into one corner.

Which of the following statement is an example of the spontaneous reaction?

- (A) I, II (B) II, III
 (C) III, I (D) I, II, III

Q.65 Read the statements regarding spontaneity of a process and mark the appropriate choice.

- (i) When enthalpy factor is absent then randomness factor decides spontaneity of a process.
 (ii) When randomness factor is absent then enthalpy factor decides spontaneity of a process.

(iii) When both the factors take place simultaneously, the magnitude of both of factors decide spontaneity of a process.

- (A) Statements (i) and (ii) are correct and (iii) is incorrect,
 (B) Statement (iii) is correct, (i) and (ii) are incorrect.
 (C) Statements (i), (ii) and (iii) are correct
 (D) Statements (i), (ii) and (iii) are incorrect

Q.66 Which of the following reactions will have the value of ΔS with a negative sign?

- (A) $H_2O(\ell) \rightarrow H_2O(g)$
 (B) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
 (C) $Cl_2(g) \rightarrow 2Cl(g)$
 (D) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Q.67 Which of the following statement is false regarding entropy?

- (A) The greater the disorder in an isolated system, the lower is the entropy.
 (B) The entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the product)
 (C) Decrease of regularity in structure would mean increase in entropy.
 (D) The gaseous state is the state of highest entropy

Q.68 For a reaction to be spontaneous at any temperature, the conditions are

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

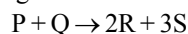
Q.69 The entropy of crystalline substances at absolute zero going by the third law of thermodynamics should be taken

- (A) 100
 (B) 50
 (C) Zero
 (D) Different for different substances

Q.70 Choose the correct statement –

- (A) When a liquid crystallizes into a solid entropy decreases
 (B) When temperature of a crystalline solid is raised from 0 K to 115 K entropy increases
 (C) In reaction, $H_2(g) \rightarrow 2H(g)$, entropy increases.
 (D) All of these

Q.71 The gaseous endothermic reaction



at 27°C takes place spontaneously, because -

- (A) $\Delta H < 0; \Delta S < 0$ (B) $\Delta H > 0; \Delta S > 0$
 (C) $\Delta H < 0; \Delta S > 0$ (D) $\Delta H > 0; \Delta S < 0$

PART 7: GIBBS ENERGY CHANGE AND EQUILIBRIUM

- Q.72** At equilibrium
 (A) $\Delta_r G > 0$ (B) $\Delta_r G < 0$
 (C) $\Delta_r G \geq 0$ (D) $\Delta_r G = 0$
- Q.73** Match the following parameters with description for spontaneity and choose the correct codes given below.

	Δ Parameters			Description
	$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	
a.	+	-	+	1. Non-spontaneous at high temperature
b.	-	-	+ at high T	2. Spontaneous at all temperatures
c.	-	+	-	3. Non-spontaneous at all temperatures

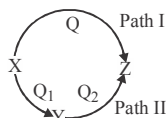
Codes :

- (A) a-1, b-3, c-2 (B) a-3, b-2, c-1
 (C) a-1, b-2, c-3 (D) a-3, b-1, c-2
- Q.74** $\Delta_r G^\ominus =$
 (A) $-2.303 RT \log K$ (B) $+2.303 RT \log K$
 (C) $\Delta_r H^\ominus - T \Delta_r S^\ominus$ (D) Both (A) and (C)
- Q.75** Choose the correct statement –
 (A) For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and positive value of equilibrium constant will be much smaller than 1.
 (B) In case of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too value of equilibrium constant will be much larger than 1.
 (C) For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and negative.
 (D) Both (A) and (B)

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

- Q.1** What is the true regarding complete combustion of gaseous isobutane -
 (A) $\Delta H = \Delta E$ (B) $\Delta H > \Delta E$
 (C) $\Delta H = \Delta E = 0$ (D) $\Delta H < \Delta E$
- Q.2** Bond energies of H-H and Cl-Cl are 430 kJ mol^{-1} and 242 kJ mol^{-1} respectively. ΔH_f for HCl is 91 kJ mol^{-1} . What will be the bond energy of H-Cl?
 (A) 672 kJ (B) 182 kJ
 (C) 245 kJ (D) 88 kJ
- Q.3** A reaction proceeds through two paths I and II to convert X \rightarrow Z.



What is the correct relationship between Q, Q₁ and Q₂?

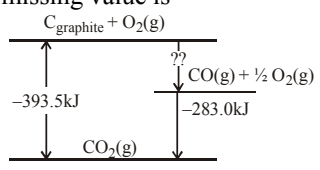
- (A) $Q = Q_1 \times Q_2$ (B) $Q = Q_1 + Q_2$
 (C) $Q = Q_2 - Q_1$ (D) $Q = Q_1 / Q_2$
- Q.4** Enthalpy of sublimation of a substance is equal to
 (A) enthalpy of fusion + enthalpy of vapourisation
 (B) enthalpy of fusion
 (C) enthalpy of vapourisation
 (D) twice the enthalpy of vapourisation
- Q.5** The gaseous endothermic reaction : $P + Q \rightarrow 3R$ at 327°C takes place spontaneously, because-
 (A) $\Delta H < 0; \Delta S < 0$ (B) $\Delta H > 0; \Delta S > 0$
 (C) $\Delta H < 0; \Delta S > 0$ (D) $\Delta H > 0; \Delta S < 0$
- Q.6** A system does 100J work on surroundings by absorbing 150J of heat. Calculate the change in internal energy-
 (A) 100 J (B) 50 J
 (C) 25 J (D) 150 J
- Q.7** A gas absorbs 200J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 litre to

1.0 litre, Calculate the change in internal energy-

- (A) 124 J (B) 224 J
 (C) 114 J (D) 154 J
- Q.8** Heat of reaction for
 $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\ell)$
 at constant pressure is -651 Kcal at 17°C . Calculate the heat of reaction at constant volume at 17°C -
 (A) -554.5 Kcal (B) -654.5 Kcal
 (C) -354.5 Kcal (D) -154.5 Kcal
- Q.9** What is true for the reaction :
 $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (A) $\Delta H = \Delta E$ (B) $\Delta H > \Delta E$
 (C) $\Delta H < \Delta E$ (D) None of these
- Q.10** How much heat is produced when 4.50g methane gas is burnt in a constant pressure system.
 Given : $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$; $\Delta H = -802 \text{ KJ}$
 (A) 225.6 KJ (B) 125.6 KJ
 (C) 175.6 KJ (D) 325.6 KJ
- Q.11** The value for ΔU for the reversible isothermal evaporation of 90 g water at 100°C will be (ΔH_{evap} of water = 40.8 kJ mol^{-1} , $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
 (A) 4800 kJ (B) 188.494 kJ
 (C) 40.8 kJ (D) 125.03 kJ
- Q.12** Two moles of an ideal gas placed in a vessel at two atm pressure expand into vacuum. The work done is –
 (A) 2J (B) 4J
 (C) ∞ (D) Zero
- Q.13** For the isothermal expansion of an ideal gas
 (A) E and H increases
 (B) E increases but H decreases
 (C) H increases but E decreases
 (D) E and H are unaltered
- Q.14** In thermodynamics which one of the following is not an intensive property
 (A) Pressure (B) Density
 (C) Volume (D) Temperature

- Q.15** At constant T and P, choose the correct statements
- $$\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$$
- (A) ΔH is independent of the physical state of the reactants of that compound
 (B) $\Delta H > \Delta E$
 (C) $\Delta H < \Delta E$
 (D) $\Delta H = \Delta E$
- Q.16** The work done by a system is 8 joule, when 40 joule heat is supplied to it. Increase in internal energy of system
 (A) 25 J (B) 30 J
 (C) 32 J (D) 28 J
- Q.17** When enthalpy and entropy change for a chemical reaction are -2.5×10^3 cal and 7.4 cal deg^{-1} respectively. The reaction at 298K is
 (A) Spontaneous (B) Reversible
 (C) Irreversible (D) Non-spontaneous
- Q.18** The heat of formations of CO (g) and CO_2 (g) are -26.4 kcal and -94.0 kcal respectively. The heat of combustion of carbon monoxide will be
 (A) $+26.4$ kcal (B) -67.6 kcal
 (C) -120.6 kcal (D) $+52.8$ kcal
- Q.19** In the combustion of 2.0gm of methane 25kcal heat is liberated, heat of combustion of methane would be
 (A) 100kcal (B) 200 kcal
 (C) 300 kcal (D) 400 kcal
- Q.20** The enthalpy of combustion of $\text{C}_6\text{H}_6(\ell)$ is -3250 kJ. When 0.39 g of benzene is burnt excess of oxygen in an open vessel, the amount of heat evolved is
 (A) 16.25 J (B) 16.25 kJ
 (C) 32.5 J (D) 32.5 kJ
- Q.21** Heats of combustion (ΔH°) for C(s), H_2 (g) and CH_4 (g) are -94 , -68 and -213 kcal/mol respectively. The value of ΔH° for the reaction,

$$\text{C(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)}$$
 (A) -85 kcal (B) -111 kcal
 (C) -17 kcal (D) -170 kcal
- Q.22** In the following process,

$$\text{H}_2\text{(g)} \rightarrow 2\text{H(g)}, \Delta_{\text{H-H}} H^\ominus = 435.0 \text{ kJ mol}^{-1}$$
 The enthalpy change involved in this process is the –
 (A) bond dissociation enthalpy of H-H bond
 (B) bond association enthalpy of H-H bond
 (C) mean bond dissociation enthalpy of H-H bond
 (D) mean bond association enthalpy of H-H bond
- Q.23** The essential condition for the feasibility of a reaction is
 (A) The reaction should be exothermic.
 (B) The entropy of products must be larger than that of reactants.
 (C) The reaction is to be accompanied with free energy decrease.
 (D) The reaction has to possess high activation energy.
- Q.24** A schematic representation of enthalpy changes for the reaction, $\text{C}_{\text{(graphite)}} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$ is given below. The missing value is
- 
- (A) $+10.5$ kJ (B) -11.05 kJ
 (C) -110.5 kJ (D) -10.5 J
- Q.25** The standard enthalpy of formation ($\Delta_f H^\circ$) 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 –
 (A) latent heat of vapourization of methane
 (B) the first four ionization energies of carbon and electron gain enthalpy of hydrogen
 (C) the dissociation energy of hydrogen molecule H_2
 (D) The dissociation energy of H_2 and enthalpy of sublimation of carbon
- Q.26** The enthalpy of vaporization of benzene is $+35.3$ kJ/mol at its boiling point of 80°C . The entropy change in the transition of vapour to liquid at its boiling point is – [in $\text{J mol}^{-1} \text{K}^{-1}$]
 (A) $+100$ (B) -100
 (C) -342 (D) $+342$
- Q.27** The process is spontaneous at the given temperature, if
 (A) ΔH is +ve and ΔS is –ve
 (B) ΔH is –ve and ΔS is +ve
 (C) ΔH is +ve and ΔS is +ve
 (D) ΔH is +ve and ΔS is equal to zero
- Q.28** What is the work done when 1 mole of a gas expands isothermally from 25 L to 250 L at a constant pressure of 1 atm and a temperature of 300 K?
 (A) -3542 J (B) -5744 J
 (C) -2657 J (D) -4890 J
- Q.29** The heat of combustion of ethane and benzene is -1560 and -3268 kJ mol^{-1} respectively. Which of two has higher efficiency as fuel per gram and the amount of heat produced per gram?
 (A) Benzene, 41.9 kJ g^{-1} (B) Ethane, 52 kJ g^{-1}
 (C) Benzene, 78 kJ g^{-1} (D) Ethane, 30 kJ g^{-1}
- Q.30** 200 joules of heat was supplied to a system at constant volume. It resulted in the increase in temperature of the system from 298 to 323 K. What is the change in internal energy of the system?
 (A) 400 J (B) 200 J
 (C) 50 J (D) 150 J
- Q.31** What will be the heat of reaction for the following reaction? Will the reaction be exothermic or endothermic?

$$\text{Fe}_2\text{O}_3\text{(s)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{Fe(s)} + 3\text{H}_2\text{O}(\ell)$$

$$\Delta_f H^\circ (\text{H}_2\text{O}, \ell) = -285.83 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{Fe}_2\text{O}_3, \text{s}) = -824.2 \text{ kJ mol}^{-1}$$

- (A) $-824.2 \text{ kJ mol}^{-1}$, exothermic
 (B) $+33.3 \text{ kJ mol}^{-1}$, endothermic
 (C) $-33.3 \text{ kJ mol}^{-1}$, exothermic
 (D) $+824.2 \text{ kJ mol}^{-1}$, endothermic
- Q.32** A system absorbs 50 kJ heat and does 20 kJ of work. What is the net change in the internal energy of the system?
 (A) Increase by 30 kJ (B) Decrease by 30 kJ
 (C) Increase by 70 kJ (D) Decrease by 70 kJ
- Q.33** For the reaction: $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}$;
 $\Delta H = -44 \text{ kcal}$. What is the enthalpy of decomposition of HCl?
 (A) $+44 \text{ kcal/mol}$ (B) -44 kcal/mol
 (C) -22 kcal/mol (D) $+22 \text{ kcal/mol}$
- Q.34** Match the following Column I with Column II and choose the correct codes given below.
- | Column I | Column II |
|---|-----------------------------------|
| a. $P_{\text{ext}} = 0$ | 1. Free expansion of an ideal gas |
| b. $q = P_{\text{ext}}(V_f - V_i)$ | 2. Adiabatic change |
| c. $q = 2.303 nRT \times \log(V_f/V_i)$ | 3. Isothermal reversible change |
| d. $\Delta U = W_{\text{adi}}$ | 4. Isothermal irreversible change |
- Codes
 (A) a-1, b-4, c-3, d-2 (B) a-1, b-3, c-3, d-4
 (C) a-1, b-3, c-4, d-2 (D) a-1, b-3, c-2, d-4
- Q.35** The work done during the expansion of a gas from 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is ($1 \text{ L atm} = 101.32 \text{ J}$)
 (A) -6 J (B) -608 J
 (C) $+304 \text{ J}$ (D) -304 J
- Q.36** Two reactions are given below:
 $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H = -393.7 \text{ kJ}$
 $\text{C}(\text{diamond}) \rightarrow \text{C}(\text{graphite}); \Delta H = -2.1 \text{ kJ}$
 What quantity of diamond will give 800 kJ of heat on burning?
 (A) 24.25 g (B) 15.24g
 (C) 2 g (D) 12.12 g
- Q.37** ΔH for the reaction, $\text{OF}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{HF}$
 (B.E. of O-F, O-H, H-F and O=O are 44, 111, 135 and 119 kcal mol⁻¹ respectively)
 (A) -222 kcal (B) -88 kcal
 (C) -111 kcal (D) -79 kcal
- Q.38** Match the column I with column II and mark the appropriate choice.
- | Column I | Column II |
|---|---------------------------------------|
| (a) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}$ | (i) $\Delta_{\text{sol}}H^\circ$ |
| (b) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$ | (ii) $\Delta_{\text{lattice}}H^\circ$ |
| (c) $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$ | (iii) $\Delta_{\text{c}}H^\circ$ |
| (d) $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ | (iv) $\Delta_{\text{bond}}H^\circ$ |
- (A) (a)–(iv), (b)–(iii), (c)–(i), (d)–(ii)
 (B) (a)–(ii), (b)–(i), (c)–(iv), (d)–(iii)
 (C) (a)–(i), (b)–(ii), (c)–(iii), (d)–(iv)
 (D) (a)–(iii), (b)–(iv), (c)–(ii), (d)–(i)
- Q.39** In the reaction : $\text{S} + \frac{3}{2} \text{O}_2 \rightarrow \text{SO}_3 + 2x \text{ kcal}$ and
 $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 + y \text{ kcal}$,
 heat of formation of SO_2 is
 (A) $(x+y)$ (B) $(x-y)$
 (C) $(2x+y)$ (D) $(2x-y)$

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE: The answer to each question is a NUMERICAL VALUE.

Q.1 The standard enthalpy of formation for glucose is $126.82 \times 10^4 \text{ J mol}^{-1}$, given the heat of combustion of one mole of glucose to form carbon dioxide and water at 298K is -2821.8 kJ . The standard heats of formation of carbon dioxide and water are -393.51 kJ/mol and -285.83 kJ/mol . Find the value of A.

Q.2 A cylinder contains 45L of an ideal gas at a pressure of 140atm. If the gas expands at a constant temperature against an opposing pressure of 1.00 atm, work done is $-6.32 \times 10^4 \text{ J}$. Find the value of A.

Q.3 The vapour pressure of water at 15°C is $1.67 \times 10^{-4} \text{ atm}$. Find the value of A.

Q.4 For a reaction $\text{M}_2\text{O}(\text{s}) \longrightarrow 2\text{M}(\text{s}) + \frac{1}{2}\text{O}_2$; $\Delta H = 30 \text{ kJ mol}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at (1 atm). Temperature upto which the reaction would not be spontaneous is $\frac{30 \times 10^3}{A} \text{ K}$. Find the value of A.

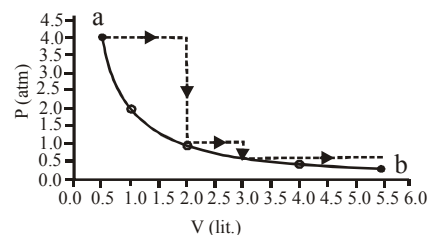
Q.5 The direct conversion of A to B is difficult, hence it is carried out by the following shown path :



$\Delta S (\text{A} \rightarrow \text{C}) = 50$; $\Delta S (\text{C} \rightarrow \text{D}) = 30$; $\Delta S (\text{B} \rightarrow \text{D}) = 20$
The entropy change for process $\text{A} \rightarrow \text{B}$ is $10x$. Find the value of x.

Q.6 In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1} , the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

Q.7 One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d , then the integer closest to the ratio w_d/w_s is



Q.8 One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) \longrightarrow (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0 \text{ L atm}$. The change in enthalpy (ΔH) of the process in L atm is :

Q.9 $\Delta H_{\text{vap}} = 30 \text{ kJ/mole}$ and $\Delta S_{\text{vap}} = 75 \text{ J mol}^{-1} \text{ K}^{-1}$.
Find temperature (in K) of vapour, at one atmosphere.

Q.10 The dissociation energy of CH_4 and C_2H_6 are respectively 360 and 620 Kcal/mole. The bond energy (in Kcal/mole) of C – C is-

EXERCISE - 4 [PREVIOUS YEARS AIEEE / JEE MAIN QUESTIONS]

- Q.1** Heat required to raise the temperature of 1 mole of a substance by 1°C is called – [AIEEE-2002]
 (A) specific heat (B) molar heat capacity
 (C) water equivalent (D) specific gravity
- Q.2** A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water, then [AIEEE-2002]
 (A) ΔH : +ve, ΔS : +ve (B) ΔH : -ve, ΔS : -ve
 (C) ΔH : -ve, ΔS : +ve (D) ΔH : +ve, ΔS : -ve
- Q.3** A heat engine absorbs heat q_1 from a source at temperature T_1 and heat q_2 from a source at temperature T_2 . Work done is found to be $J (q_1 + q_2)$. This is in accordance with – [AIEEE-2002]
 (A) first law of thermodynamics (B) second law of thermodynamics
 (C) Joules equivalent law (D) None of the above
- Q.4** In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done the change in Gibbs free energy (dG) and change in entropy (dS) satisfy the criteria - [AIEEE-2003]
 (A) $(dS)_{V,E} = 0, (dG)_{T,P} = 0$ (B) $(dS)_{V,E} = 0, (dG)_{T,P} > 0$
 (C) $(dS)_{V,E} < 0, (dG)_{T,P} < 0$ (D) $(dS)_{V,E} > 0, (dG)_{T,P} < 0$
- Q.5** The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy – [AIEEE-2003]
 (A) < 40 kJ (B) Zero
 (C) 40 kJ (D) > 40 kJ
- Q.6** If at 298 K the bond energies of C-H, C-C, C=C and H-H bonds are respectively 414, 347, 615 and 435 kJ mol⁻¹, the value of enthalpy change for the reaction ; $H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$ at 298 K will be – [AIEEE-2003]
 (A) +125 kJ (B) -125 kJ
 (C) +250 kJ (D) -250 kJ
- Q.7** The enthalpy change for a reaction does not depend upon [AIEEE-2003]
 (A) The nature of intermediate reaction steps
 (B) The differences in initial or final temperatures of involved substances
 (C) The physical states of reactants and products
 (D) Use of different reactants for the same product
- Q.8** The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_C is [AIEEE-2003]
 (A) $\Delta G^\circ = RT \ln K_C$ (B) $-\Delta G^\circ = RT \ln K_C$
 (C) $\Delta G = RT \ln K_C$ (D) $-\Delta G = RT \ln K_C$
- Q.9** The enthalpies of combustion of carbon and carbon monoxide are - 393.5 and - 283 kJ mol⁻¹ respectively. The enthalpy of formation of carbon monoxide per mole [AIEEE-2004]
 (A) 110.5 kJ (B) 676.5 kJ
 (C) -676.5 kJ (D) -110.5 kJ
- Q.10** An ideal gas expands in volume from $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work done is - [AIEEE-2004]
 (A) -900 J (B) -900 kJ
 (C) 2710 kJ (D) 900 kJ
- Q.11** For a spontaneous reaction the ΔG , equilibrium constant (K) and E°_{cell} will be respectively – [AIEEE-2005]
 (A) +ve, > 1, -ve (B) -ve, > 1, +ve
 (C) -ve, > 1, -ve (D) -ve, < 1, -ve
- Q.12** Consider the reaction : $N_2 + 3 H_2 \longrightarrow 2 NH_3$ 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 ? [AIEEE-2005]
 (A) $\Delta H = \Delta U$ (B) $\Delta H = 0$
 (C) $\Delta H > \Delta U$ (D) $\Delta H < \Delta U$
- Q.13** If the bond dissociation energies of XY, X₂ and Y₂ (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and $\Delta_f H$ for the formation of XY is -200 kJ mol⁻¹. The bond dissociation energy of X₂ will be - [AIEEE-2005]
 (A) 200 kJ mol⁻¹ (B) 100 kJ mol⁻¹
 (C) 800 kJ mol⁻¹ (D) 300 kJ mol⁻¹
- Q.14** An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct – [AIEEE 2006]
 (A) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process.
 (B) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
 (C) $T_f = T_i$ for both reversible and irreversible processes
 (D) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
- Q.15** The standard enthalpy of formation ($\Delta_f H^\circ$) at 298 K for methane, CH₄(g), is -74.8 kJ mol⁻¹. The additional information required to determine the average energy for C-H bond formation would be - [AIEEE 2006]
 (A) latent heat of vapourization of methane.
 (B) the first four ionization energies of carbon and electron gain enthalpy of hydrogen.
 (C) the dissociation energy of hydrogen molecule H₂.
 (D) The dissociation energy of H₂ and enthalpy of sublimation of carbon
- Q.16** ($\Delta H - \Delta U$) for the formation of carbon monoxide (CO) from its elements at 298 K is -(R = 8.314 J K⁻¹ mol⁻¹) [AIEEE 2006]
 (A) 1238.78 J mol⁻¹ (B) -2477.57 J mol⁻¹
 (C) 2477.57 J mol⁻¹ (D) -1238.78 J mol⁻¹
- Q.17** In conversion of lime-stone to lime, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ the values of ΔH° and ΔS° are + 179.1 kJ mol⁻¹ and 160.2 J/K respectively at 298K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is [AIEEE 2007]
 (A) 1008 K (B) 1200 K
 (C) 845 K (D) 1118 K

- Q.18** 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 $373\text{ K} = 41\text{ kJ mol}^{-1}$ and $R = 8.3\text{ J mol}^{-1}\text{K}^{-1}$ will be) – [AIEEE 2007]
 (A) 4.100 kJ mol^{-1} (B) $3.7904\text{ kJ mol}^{-1}$
 (C) $37.904\text{ kJ mol}^{-1}$ (D) 41.00 kJ mol^{-1}
- Q.19** Identify the correct statement regarding a spontaneous process – [AIEEE 2007]
 (A) For a spontaneous process in an isolated system, the change in entropy is positive.
 (B) Endothermic processes are never spontaneous.
 (C) Exothermic processes are always spontaneous.
 (D) Lowering of energy in the reaction process is the only criterion for spontaneity .
- Q.20** Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below :

$$\frac{1}{2}\text{Cl}_2(\text{g}) \xrightarrow{\frac{1}{2}\Delta_{\text{diss}}H^\ominus} \text{Cl}(\text{g}) \xrightarrow{\Delta_{\text{eg}}H^\ominus} \text{Cl}^-(\text{g}) \xrightarrow{\Delta_{\text{hyd}}H^\ominus} \text{Cl}^-(\text{aq})$$

 The energy involved in the conversion of $\frac{1}{2}\text{Cl}_2(\text{g})$ to $\text{Cl}^-(\text{aq})$
 (Using the data, $\Delta_{\text{diss}}H^\ominus_{\text{Cl}_2} = 240\text{ kJ mol}^{-1}$, $\Delta_{\text{eg}}H^\ominus_{\text{Cl}} = -349\text{ kJ mol}^{-1}$, $\Delta_{\text{hyd}}H^\ominus_{\text{Cl}^-} = -381\text{ kJ mol}^{-1}$) will be [AIEEE 2008]
 (A) -610 kJ mol^{-1} (B) -850 kJ mol^{-1}
 (C) $+120\text{ kJ mol}^{-1}$ (D) $+152\text{ kJ mol}^{-1}$
- Q.21** Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and $50\text{ J K}^{-1}\text{ mol}^{-1}$, respectively. For the reaction,

$$\frac{1}{2}\text{X}_2 + \frac{3}{2}\text{Y}_2 \rightarrow \text{XY}_3 \quad \Delta H = -30\text{ kJ}$$
, to be at equilibrium, the temperature will be [AIEEE 2008]
 (A) 500 K (B) 750 K
 (C) 1000 K (D) 1250 K
- Q.22** On the basis of the following thermochemical data ($\Delta_f G^\ominus_{\text{H}^+(\text{aq})} = 0$)
 $\text{H}_2\text{O}(\ell) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}); \Delta H = 57.32\text{ kJ}$
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell); \Delta H = -286.20\text{ kJ}$
 The value of enthalpy of formation of OH^- ion at 25°C is [AIEEE 2009]
 (A) -228.88 kJ (B) $+228.88\text{ kJ}$
 (C) -343.52 kJ (D) -22.88 kJ
- Q.23** In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$\text{CH}_3\text{OH}(\ell) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$$

 At 298 K standard Gibb's energies of formation for $\text{CH}_3\text{OH}(\ell)$, $\text{H}_2\text{O}(\ell)$ and $\text{CO}_2(\text{g})$ are -166.2 , -237.2 and $-394.4\text{ kJ mol}^{-1}$ respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be - [AIEEE 2009]
 (A) 87% (B) 90%
 (C) 97% (D) 80%
- Q.24** The standard enthalpy 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 -712 kJ mol^{-1} , the average bond enthalpy of N-H bond in NH_3 is - [AIEEE 2010]
 (A) -964 kJ mol^{-1} (B) $+352\text{ kJ mol}^{-1}$
 (C) $+1056\text{ kJ mol}^{-1}$ (D) -1102 kJ mol^{-1}
- Q.25** For a particular reversible reaction at temperature T , ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when - [AIEEE 2010]
 (A) $T_e > T$ (B) $T > T_e$
 (C) T_e is 5 times T (D) $T = T_e$
- Q.26** 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 : [AIEEE 2011]
 (A) $38.3\text{ J mol}^{-1}\text{K}^{-1}$ (B) $35.8\text{ J mol}^{-1}\text{K}^{-1}$
 (C) $32.3\text{ J mol}^{-1}\text{K}^{-1}$ (D) $42.3\text{ J mol}^{-1}\text{K}^{-1}$
- Q.27** The incorrect expression among the following is : [AIEEE 2012]
 (A) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$
 (B) In isothermal process, $w_{\text{reversible}} = -nRT \ln(V_f/V_i)$
 (C) $\ln K = \frac{\Delta H^\ominus - T\Delta S^\ominus}{RT}$ (D) $K = e^{-\Delta G^\ominus/RT}$
- Q.28** 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 – ($R = 8.314\text{ J/mol K}$) ($\ln 7.5 = 2.01$) [JEE MAIN 2013]
 (A) $q = +208\text{ J}$, $w = -208\text{ J}$ (B) $q = -208\text{ J}$, $w = -208\text{ J}$
 (C) $q = -208\text{ J}$, $w = +208\text{ J}$ (D) $q = +208\text{ J}$, $w = +208\text{ J}$
- Q.29** For complete combustion of ethanol,
 $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$, the amount of heat produced as measured in bomb calorimeter, is $1364.47\text{ kJ mol}^{-1}$ at 25°C . Assuming ideality the Enthalpy of combustion, $\Delta_c H$, for the reaction will be: ($R = 8.314\text{ kJ mol}^{-1}$) [JEE MAIN 2014]
 (A) $-1460.50\text{ kJ mol}^{-1}$ (B) $-1350.50\text{ kJ mol}^{-1}$
 (C) $-1366.95\text{ kJ mol}^{-1}$ (D) $-1361.95\text{ kJ mol}^{-1}$
- Q.30** The following reaction is performed at 298 K .
 $2\text{NO}(\text{g}) + \text{O}_2 \rightleftharpoons 2\text{NO}_2(\text{g})$. The standard free energy of formation of $\text{NO}(\text{g})$ is 86.6 kJ/mol at 298 K . What is the standard free energy of formation of $\text{NO}_2(\text{g})$ at 298 K ? ($K_p = 1.6 \times 10^{12}$) [JEE MAIN 2015]
 (A) $86600 + R(298) \ln(1.6 \times 10^{12})$
 (B) $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$
 (C) $0.5 [2 \times 86,600 - R(298) \ln 1.6 \times 10^{12}]$
 (D) $R(298) \ln(1.6 \times 10^{12}) - 86600$

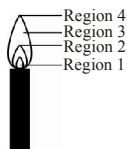
Q.31 The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is :

[JEE MAIN 2016]

- (A) 676.5 (B) -676.5
(C) -110.5 (D) 110.5

Q.32 The hottest region of Bunsen flame shown in the figure:

[JEE MAIN 2016]



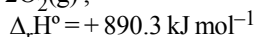
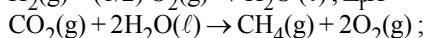
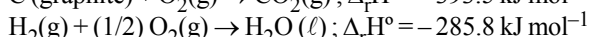
- (A) region 2 (B) region 3
(C) region 4 (D) region 1

Q.33 ΔU is equal to:

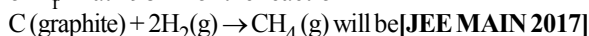
[JEE MAIN 2017]

- (A) Isothermal work (B) Isochoric work
(C) Isobaric work (D) Adiabatic work

Q.34 $\text{C (graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1}$



Based on the above thermochemical equations, the value of $\Delta_f H^\circ$ at 298 K for the reaction



- (A) $-144.0 \text{ kJ mol}^{-1}$ (B) $+74.8 \text{ kJ mol}^{-1}$
(C) $+144.0 \text{ kJ mol}^{-1}$ (D) $-74.8 \text{ kJ mol}^{-1}$

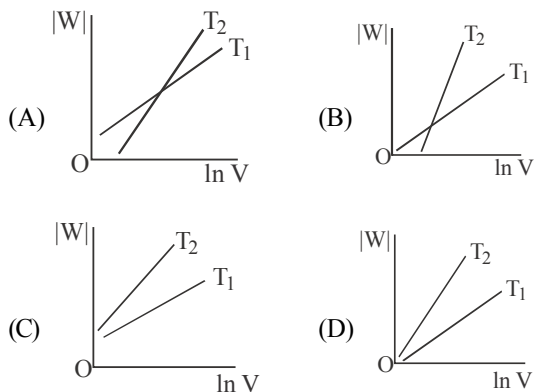
Q.35 The combustion of benzene (ℓ) gives $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$. Given that heat of combustion of benzene at constant volume is $-3263.9 \text{ kJ mol}^{-1}$ at 25°C , heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be :
($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

[JEE MAIN 2018]

- (A) 3260 (B) -3267.6
(C) 4152.6 (D) -452.46

Q.36 Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (W) on the final volume (V) is:

[JEE MAIN 2019 (JAN)]



Q.37 Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ?
(Assume nonexpansion work is zero)

[JEE MAIN 2019 (APRIL)]

- (A) Cyclic process : $q = -w$
(B) Isothermal process : $q = -w$
(C) Adiabatic process : $\Delta U = -w$
(D) Isochoric process : $\Delta U = q$

Q.38 For silver, $C_p (\text{JK}^{-1} \text{mol}^{-1}) = 23 + 0.01T$. If the temperature (T) of 3 moles of silver is raised from 300K to 1000K at 1 atm pressure, the value of ΔH will be close to

[JEE MAIN 2019 (APRIL)]

- (A) 21 kJ (B) 16 kJ
(C) 13 kJ (D) 62 kJ

Q.39 5 moles of an ideal gas at 100K are allowed to undergo reversible compression till its temperature becomes 200K . If $C_{V,m} = 28 \text{ JK}^{-1} \text{mol}^{-1}$, calculate ΔU and ΔpV for this process. ($R = 8.0 \text{ JK}^{-1} \text{mol}^{-1}$)

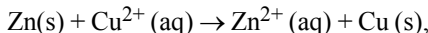
[JEE MAIN 2019 (APRIL)]

- (A) $\Delta U = 14 \text{ kJ}; \Delta (pV) = 4 \text{ kJ}$
(B) $\Delta U = 14 \text{ kJ}; \Delta (pV) = 18 \text{ kJ}$
(C) $\Delta U = 2.8 \text{ kJ}; \Delta (pV) = 0.8 \text{ kJ}$
(D) $\Delta U = 14 \text{ kJ}; \Delta (pV) = 0.8 \text{ kJ}$

Q.40 Among the following, the set of parameters that represents path function, is : [JEE MAIN 2019 (APRIL)]

- (a) $q + w$ (b) q
(c) w (d) $H - TS$
(A) (a) and (d) (B) (b), (c) and (d)
(C) (b) and (c) (D) (a), (b) and (c)

Q.41 The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298K is :



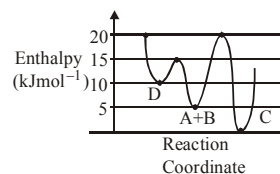
$E^\circ = 2\text{V}$ at 298K (Faraday's constant, $F = 96000 \text{ C mol}^{-1}$)

[JEE MAIN 2019 (APRIL)]

- (A) -384 (B) -192
(C) 192 (D) 384

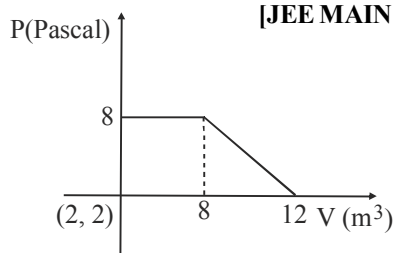
Q.42 Consider the given plot of enthalpy of the following reaction between A and B : $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$
Identify the INCORRECT statement.

[JEE MAIN 2019 (APRIL)]



- (A) C is the thermodynamically stable product.
(B) Formation of A and B from C has highest enthalpy of activation.
(C) D is kinetically stable product.
(D) Activation enthalpy to form C is 5 kJ mol^{-1} less than that to form D.

- Q.43** An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is : **[JEE MAIN 2019 (APRIL)]**
 (A) -9.0 (B) +10.0
 (C) -0.9 (D) -2.0
- Q.44** For the reaction ; $A(\ell) \rightarrow 2B(g)$
 $\Delta U = 2.1 \text{ k cal}$, $\Delta S = 20 \text{ cal/k}$, $T = 300 \text{ K}$.
 Hence ΔG in kcal is _____. **[JEE MAIN 2020 (JAN)]**
- Q.45** The standard heat of formation ($\Delta_f H_{298}^0$) of ethane in (kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are -1560, -393.5 and -286 kJ/mol, respectively is _____. **[JEE MAIN 2020 (JAN)]**
- Q.46** A gas undergoes expansion according to the following graph. Calculate work done by the gas. **[JEE MAIN 2020 (JAN)]**
- Q.47** Temperature of 4 moles of gas increases from 300K to 500 K find ' C_v ' if $\Delta U = 5000 \text{ J}$. **[JEE MAIN 2020 (JAN)]**
- Q.48** If enthalpy of atomisation for $\text{Br}_2(\ell)$ is $x \text{ kJ/mol}$ and bond enthalpy for Br_2 is $y \text{ kJ/mol}$, the relation between them : **[JEE MAIN 2020 (JAN)]**
 (A) is $x = y$ (B) is $x < y$
 (C) does not exist (D) is $x > y$
- Q.49** The first and second ionisation enthalpies of a metal are 496 and 4560 kJ mol^{-1} , respectively. How many moles of HCl and H_2SO_4 , respectively, will be needed to react completely with 1 mole of the metal hydroxide ? **[JEE MAIN 2020 (JAN)]**
 (A) 1 and 0.5 (B) 2 and 0.5
 (C) 1 and 1 (D) 1 and 2



EXERCISE - 5 (PREVIOUS YEARS AIPMT/NEET EXAM QUESTIONS)

Choose one correct response for each question.

- Q.1** The absolute enthalpy of neutralisation of the reaction :
 $\text{MgO(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$
 will be [AIPMT 2005]
 (A) $-57.33 \text{ kJ mol}^{-1}$
 (B) Greater than $-57.33 \text{ kJ mol}^{-1}$
 (C) Less than $-57.33 \text{ kJ mol}^{-1}$
 (D) $57.33 \text{ kJ mol}^{-1}$
- Q.2** A reaction occurs spontaneously if – [AIPMT 2005]
 (A) $T\Delta S < \Delta H$ and both ΔH and ΔS are +ve
 (B) $T\Delta S > \Delta H$ and ΔH is +ve and ΔS is – ve
 (C) $T\Delta S > \Delta H$ and both ΔH and ΔS are +ve
 (D) $T\Delta S = \Delta H$ and both ΔH and ΔS are +ve
- Q.3** Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction [AIPMT 2005]
 (A) Exothermic and increasing disorder
 (B) Exothermic and decreasing disorder
 (C) Endothermic and increasing disorder
 (D) Endothermic and decreasing disorder
- Q.4** The enthalpy of combustion of H_2 , cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241 , -3800 and -3920 kJ per mol respectively. Heat of hydrogenation cyclohexene is – [AIPMT 2006]
 (A) -121 kJ mol^{-1} (B) $+121 \text{ kJ mol}^{-1}$
 (C) $+242 \text{ kJ mol}^{-1}$ (D) -242 kJ mol^{-1}
- Q.5** The enthalpy and entropy change for the reaction
 $\text{Br}_2(\ell) + \text{Cl}_2(\text{g}) \rightarrow 2\text{BrCl}(\text{g})$ are 30 kJ mol^{-1} & $105 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. The temperature at which the reaction will be in equilibrium is – [AIPMT 2006]
 (A) 273K (B) 450K
 (C) 300K (D) 285.7K
- Q.6** Identify the correct statement for change of Gibbs energy for a system (ΔG_{system}) at constant temperature and pressure – [AIPMT 2006]
 (A) If $\Delta G_{\text{system}} = 0$, the system has attained equilibrium
 (B) If $\Delta G_{\text{system}} = 0$, the system is still moving in a particular direction
 (C) If $\Delta G_{\text{system}} < 0$, the process is not spontaneous
 (D) If $\Delta G_{\text{system}} > 0$, the process is not spontaneous
- Q.7** Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$? [AIPMT 2006]
 (A) $\text{C(s)} + 2\text{H}_2\text{O(g)} \rightarrow 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
 (B) $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (C) $2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
 (D) $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr(g)}$
- Q.8** Consider the following reactions – [AIPMT 2007]
 (i) $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) = \text{H}_2\text{O}(\ell)$; $\Delta H = -X_1 \text{ kJ mol}^{-1}$
 (ii) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\ell)$; $\Delta H = -X_2 \text{ kJ mol}^{-1}$
 (iii) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) = \text{CO(g)} + \text{H}_2\text{O}(\ell)$; $\Delta H = -X_3 \text{ kJ mol}^{-1}$
 (iv) $\text{C}_2\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$;
 $\Delta H = +X_4 \text{ kJ mol}^{-1}$
- Enthalpy of formation of $\text{H}_2\text{O}(\ell)$ is
 (A) $+X_3 \text{ kJ mol}^{-1}$ (B) $-X_4 \text{ kJ mol}^{-1}$
 (C) $+X_1 \text{ kJ mol}^{-1}$ (D) $-X_2 \text{ kJ mol}^{-1}$
- Q.9** Given that bond energies of H–H and Cl–Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is -90 kJ mol^{-1} , bond enthalpy of HCl is – [AIPMT 2007]
 (A) 380 kJ mol^{-1} (B) 425 kJ mol^{-1}
 (C) 245 kJ mol^{-1} (D) 290 kJ mol^{-1}
- Q.10** Which of the following are not state functions?
 I. q + w II. q
 III. w IV. H – TS [AIPMT 2008]
 (A) II and III (B) I and IV
 (C) II, III and IV (D) I, II and III
- Q.11** Bond dissociation enthalpy of H_2 , Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is: [AIPMT 2008]
 (A) 245 kJ mol^{-1} (B) 93 kJ mol^{-1}
 (C) -245 kJ mol^{-1} (D) -93 kJ mol^{-1}
- Q.12** For the gas phase reaction,
 $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ [AIPMT 2008]
 which of the following conditions are correct?
 (A) $\Delta H > 0$ and $\Delta S < 0$ (B) $\Delta H = 0$ and $\Delta S < 0$
 (C) $\Delta H > 0$ and $\Delta S > 0$ (D) $\Delta H < 0$ and $\Delta S < 0$
- Q.13** From the following bond energies:
 H–H bond energy: $431.37 \text{ kJ mol}^{-1}$
 C=C bond energy: $606.10 \text{ kJ mol}^{-1}$
 C–C bond energy: $336.49 \text{ kJ mol}^{-1}$
 C–H bond energy: $410.50 \text{ kJ mol}^{-1}$
 Enthalpy for the reaction, [AIPMT 2009]

$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C} = \text{C} + \text{H} - \text{H} \longrightarrow \text{H} - \text{C} - \text{C} - \text{H} \\ | \quad | \quad \quad \quad | \quad | \\ \text{H} \quad \text{H} \quad \quad \quad \text{H} \quad \text{H} \end{array}$$
 will be:
 (A) $-243.6 \text{ kJ mol}^{-1}$ (B) $-120.0 \text{ kJ mol}^{-1}$
 (C) $553.0 \text{ kJ mol}^{-1}$ (D) $1523.6 \text{ kJ mol}^{-1}$
- Q.14** The values of ΔH and ΔS for the reaction,
 $\text{C}(\text{graphite}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ are 170 kJ & 170 JK^{-1} , respectively. This reaction will be spontaneous at [AIPMT 2009]
 (A) 910 K (B) 1110 K
 (C) 510 K (D) 710 K
- Q.15** Standard entropies of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. For the reaction

$$\frac{1}{2}\text{X}_2 + \frac{3}{2}\text{Y}_2 \rightleftharpoons \text{XY}_3$$
; $\Delta H = -30 \text{ kJ}$,
 to be at equilibrium, the temperature should be: [AIPMT (PRE) 2010]
 (A) 750 K (B) 1000 K
 (C) 1250 K (D) 500 K

- Q.16** For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ JK}^{-1} \text{ mol}^{-1}$, respectively. The temperature when Gibb's energy change (ΔG) for this transformation will be zero, is
[AIPMT (MAINS) 2010]
 (A) 273.4 K (B) 393.4 K
 (C) 373.4 K (D) 293.4 K
- Q.17** The following two reactions are known
 $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g}); \Delta H = -26.8 \text{ kJ}$
 $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightarrow \text{Fe}(\text{s}) + \text{CO}_2(\text{g}); \Delta H = -16.5 \text{ kJ}$
[AIPMT (MAINS) 2010]
 The value of ΔH for the following reaction
 $\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \rightarrow 2\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$ is :
 (A) +10.3 kJ (B) -43.3 kJ
 (C) -10.3 kJ (D) +6.2 kJ
- Q.18** Three moles of an ideal gas expanded spontaneously into vacuum. The work done will be :
[AIPMT (MAINS) 2010]
 (A) Infinite (B) 3 Joules
 (C) 9 Joules (D) Zero
- Q.19** Which of the following is correct option for free expansion of an ideal gas under adiabatic condition?
[AIPMT (PRE) 2011]
 (A) $q = 0, \Delta T < 0, w \neq 0$ (B) $q = 0, \Delta T \neq 0, w = 0$
 (C) $q \neq 0, \Delta T = 0, w = 0$ (D) $q = 0, \Delta T = 0, w = 0$
- Q.20** If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C , the entropy change for the process would be -
[AIPMT (PRE) 2011]
 (A) $100 \text{ J mol}^{-1} \text{ K}^{-1}$ (B) $10 \text{ J mol}^{-1} \text{ K}^{-1}$
 (C) $1.0 \text{ J mol}^{-1} \text{ K}^{-1}$ (D) $0.1 \text{ J mol}^{-1} \text{ K}^{-1}$
- Q.21** Enthalpy change for the reaction,
 $4\text{H}(\text{g}) \rightarrow 2\text{H}_2(\text{g})$ is -869.6 kJ . The dissociation energy of H - H bond is -
[AIPMT (PRE) 2011]
 (A) +217.4 kJ (B) -434.8 kJ
 (C) -869.6 kJ (D) +434.8 kJ
- Q.22** Consider the following processes : ΔH (kJ/mol)
 $\frac{1}{2}\text{A} \rightarrow \text{B} \quad +150$
 $3\text{B} \rightarrow 2\text{C} + \text{D} \quad -125$
 $\text{E} + \text{A} \rightarrow 2\text{D} \quad +350$
 For $\text{B} + \text{D} \rightarrow \text{E} + 2\text{C}$, ΔH will be :**[AIPMT (MAINS) 2011]**
 (A) 525 kJ/mol (B) -175 kJ/mol
 (C) -325 kJ/mol (D) 325 kJ/mol
- Q.23** 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 ?
[AIPMT (PRE) 2012]
 (A) $\text{C graphite} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
 (B) $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 (C) $\text{Mg}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO}(\text{s})$
 (D) $\frac{1}{2}\text{C graphite} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \frac{1}{2}\text{CO}_2(\text{g})$
- Q.24** The enthalpy of fusion of water is 1.435 kcal/mol . The molar entropy change for the melting of ice at 0°C is :
[AIPMT (PRE) 2012]
 (A) $10.52 \text{ cal / (mol K)}$ (B) $21.04 \text{ cal / (mol K)}$
 (C) $5.260 \text{ cal / (mol K)}$ (D) $0.526 \text{ cal / (mol K)}$
- Q.25** Standard enthalpy of vapourisation $\Delta_{\text{vap}} H^\circ$ for water at 100°C is $40.66 \text{ kJ mol}^{-1}$. The internal energy of vapourisation of water at 100°C (in kJ mol^{-1}) is :
[AIPMT (PRE) 2012]
 (A) +37.56 (B) -43.76
 (C) +43.76 (D) +40.66
 (Assume water vapour to behave like an ideal gas).
- Q.26** A reaction having equal energies of activation for forward and reverse reactions has -
[NEET 2013]
 (A) $\Delta H = \Delta G = \Delta S = 0$ (B) $\Delta S = 0$
 (C) $\Delta G = 0$ (D) $\Delta H = 0$
- Q.27** For the reaction, $\text{X}_2\text{O}_4(\ell) \rightarrow 2\text{XO}_2(\text{g})$
 $\Delta U = 2.1 \text{ kcal}$, $\Delta S = 20 \text{ cal K}^{-1}$ at 300 K . Hence, ΔG is -
[AIPMT 2014]
 (A) 2.7 kcal (B) -2.7 kcal
 (C) 9.3 kcal (D) -9.3 kcal
- Q.28** Which of the following statements is correct for a reversible process in a state of equilibrium ?
[AIPMT 2015]
 (A) $\Delta G = 2.30 RT \log K$ (B) $\Delta G^\circ = -2.30 RT \log K$
 (C) $\Delta G^\circ = 2.30 RT \log K$ (D) $\Delta G = -2.30 RT \log K$
- Q.29** The heat of combustion of carbon to CO_2 is -393.5 kJ/mol . The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is:
[RE-AIPMT 2015]
 (A) -630 kJ (B) -3.15 kJ
 (C) -315 kJ (D) +315 kJ
- Q.30** The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
[NEET 2016 PHASE-1]
 (A) $\Delta H < 0$ and $\Delta S = 0$ (B) $\Delta H > 0$ and $\Delta S < 0$
 (C) $\Delta H < 0$ and $\Delta S > 0$ (D) $\Delta H < 0$ and $\Delta S < 0$
- Q.31** For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f , the entropy change is given by
[NEET 2016 PHASE-2]
 (A) $\Delta S = nR \ln \left(\frac{p_f}{p_i} \right)$ (B) $\Delta S = nR \ln \left(\frac{p_i}{p_f} \right)$
 (C) $\Delta S = nRT \ln \left(\frac{p_f}{p_i} \right)$ (D) $\Delta S = RT \ln \left(\frac{p_i}{p_f} \right)$
- Q.32** For a given reaction, $\Delta H = 35.5 \text{ kJ mol}^{-1}$ and $\Delta S = 83.6 \text{ JK}^{-1} \text{ mol}^{-1}$. The reaction is spontaneous at :
 (Assume that ΔH and ΔS do not vary with temperature)
[NEET 2017]
 (A) $T > 425 \text{ K}$ (B) All temperatures
 (C) $T > 298 \text{ K}$ (D) $T < 425 \text{ K}$
- Q.33** 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
 (A) -500 J (B) -505 J **[NEET 2017]**
 (C) +505 J (D) 1136.25 J

- Q.34** 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 [NEET 2018]
- (A) 800 kJ mol^{-1} (B) 100 kJ mol^{-1}
 (C) 200 kJ mol^{-1} (D) 400 kJ mol^{-1}
- Q.35** Under isothermal condition, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is [NEET 2019]
- (Given that 1 L bar = 100 J)
 (A) -30 J (B) 5 kJ
 (C) 25 J (D) 30 J
- Q.36** In which case change in entropy is negative? [NEET 2019]
- (A) Evaporation of water.
 (B) Expansion of a gas at constant temperature.
 (C) Sublimation of solid to gas
 (D) $2\text{H (g)} \rightarrow \text{H}_2 \text{ (g)}$

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	C	D	D	B	C	C	A	D	B	C	D	D	C	D	D	C	C	A	C	C	D	D	B	A
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	D	C	D	D	B	C	A	C	C	D	C	D	C	B	D	D	B	C	C	A	C	A	A	A	B
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	B	B	C	C	B	C	D	D	D	C	B	C	C	A	C	B	A	D	C	D	B	D	D	D	D

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	D	C	B	A	B	B	A	B	B	A	B	D	D	C	C	C	A	B	B	B	C	A	C	C	D	B	B	B	B	B
Q	31	32	33	34	35	36	37	38	39																					
A	C	A	D	A	B	A	D	D	D																					

EXERCISE - 3

Q	1	2	3	4	5	6	7	8	9	10
A	4	5	2	70	6	9	2	44	400	80

EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	A	C	D	B	B	A	B	D	A	B	D	A	D	D	A	D	C	A	A	B	A	C	B	B
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	
A	A	C	A	C	C	C	A	D	D	B	B	C	D	A	C	A	D	C	-3	-192.5	48	6.3	D	A	

EXERCISE - 5

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	C	A	A	D	A	D	D	B	A	D	C	B	B	A	C	D	D	D	A	D	B	A	C	A
Q	26	27	28	29	30	31	32	33	34	35	36														
A	D	B	B	C	AC	B	A	B	A	A	D														

THERMODYNAMICS

TRY IT YOURSELF-1

- (1) (A)
 (2) 1 mole = 18g = 18ml, water in liquid form has negligible volume with respect to 1 mole of water vapour.
 Volume of 1 mole water vapour

$$V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 373}{1} = 30.6 \text{ litre}$$

$$W = -P\Delta V = -1 \times 30.6 \times 101.3 = -3099.78 \text{ J}$$

$$W = -3.10 \text{ kJ}$$

- (3) 8g He = 8/4 = 2 mol
 $W = -2.303 nRT \log(V_2/V_1)$
 $= -2.303 \times 2 \times 8.314 \times 300 \log(20/10) \text{ J}$
 $= -3457.97 \text{ J} = -3.46 \text{ kJ}$

- (4) Work done in expansion (W) = $-P\Delta V = -2 \text{ atm}(10 - 0.1)$
 $= 2 \times 9.9 \text{ L atm} = -19.8 \times 101.3 \text{ J} = 2005.74 \text{ J}$
 Heat absorbed (q) = 2000 J

$$\Delta U = q + W = 2000 \text{ J} - 2005.74 \text{ J} = -5.74 \text{ J}$$

- (5) $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{s}) + 4\text{H}(\text{g})$

$$\Delta n_g = 4 - 1 = 3$$

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

$$\Delta E = \Delta H - \Delta n_g RT = 400 - 3 \times 0.002 \times 298 = 398.2 \text{ kcal}$$

- (6) (C)

- (7) $q = C_p \Delta T = 22 \times 10 = 220 \text{ kJ}$

Since the reaction is exothermic therefore, $q = -220 \text{ kJ/g}$
 The given reaction has 1 mole or 12g of C therefore enthalpy of reaction will be

$$\Delta H = q = -220 \times 12 = -2640 \text{ kJ}$$

- (8) (C)

- (9) $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$; $\Delta H = -17.89 \text{ kcal}$

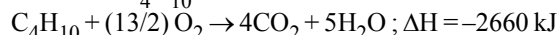
$$\Delta H = \Delta E + \Delta n(\text{g}) RT$$

$$\Delta n(\text{g}) = -1; R = 1.99 \times 10^{-3} \text{ kcal}$$

$$-17.89 = \Delta E - 1 \times 1.99 \times 10^{-3} \times 298$$

$$\Delta E = -17.89 + 0.593 = -17.293 \text{ kcal}$$

- (10) Isobutane C_4H_{10} burns as follows:



58g or $\frac{58}{1000}$ kg of isobutane on combustion produces

2660kJ of heat.

So, 14 kg of isobutane will produce

$$= \frac{2660 \times 1000 \times 14}{58} = 642068.96 \text{ kJ}$$

Energy required per day = 20,000 kJ

$$\text{No. of days cylinder will work} = \frac{642068.96}{20,000} = 32.1 \text{ days}$$

When combustion efficiency decreases to 60%, the days for which the cylinder will work are also reduced to 60%.

$$\text{So, number of days} = \frac{32.1 \times 60}{100} = 19.26 \text{ days}$$

- (11) (B). $\Delta U = q + w = (40 \times 200) + (-2 \times 10 \times 100)$
 $= 6000 \text{ J}$

(12) (B). $\left(\frac{V_1}{V_2}\right) = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} = (3)^{3/2} = 8$

$$\frac{P_1}{P_2} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{1-\gamma}} = (3)^{\frac{5/3}{-2/3}} = (3)^{-5/2} = \frac{1}{32}$$

- (13) (B). $\Delta H = \Delta U + P\Delta V = -124 \text{ J}$

$$\Delta U = -124 + \frac{1520}{760} \text{ atm} \left[\frac{200}{1000}\right] \times 100 = -84 \text{ J}$$

- (14) (B). $C_p = \frac{q}{n\Delta T}$; $\Delta T = 0$; $C_p = \infty$

TRY IT YOURSELF-2

- (1) Entropy change for the phase transition is given by
 $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{g})$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

Here, $\Delta H_{\text{vap}} = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 1000 \text{ J mol}^{-1}$

$$T_b = 273 + 100 = 373 \text{ K}$$

$$\Delta S_{\text{vap}} = \frac{40.8 \times 1000 \text{ J mol}^{-1}}{373 \text{ K}} = 109.4 \text{ J mol}^{-1}\text{K}^{-1}$$

- (2) Given, $\Delta H = 40.63 \text{ kJ} \times 10^3 \text{ J mol}^{-1}$,
 $\Delta S = 108.8 \text{ JK}^{-1} \text{ mol}^{-1}$

$$T = 27^\circ\text{C} = (27 + 273) \text{ K} = 300 \text{ K}$$

Formula to be used $\Delta G = \Delta H - T\Delta S$

Substituting the values,

$$\begin{aligned} \Delta G &= (40.63 \times 10^3 \text{ J mol}^{-1}) - (300 \times 108.8 \text{ J mol}^{-1}) \\ &= (40630 - 32640) \text{ J mol}^{-1} = 7990 \text{ J mol}^{-1} \\ &= 7.99 \text{ kJ mol}^{-1} \end{aligned}$$

i.e., $\Delta G > 0$

\therefore The reaction will not proceed in the forward direction, but will proceed in the backward direction.

- (3) (D)

- (4) (D)

- (5) (C). Boiling point, pH & density are intensive properties. Entropy is an extensive property.

- (6) (D). $\Delta S = nR \ln(V_2/V_1)$

$$V_2 = 40, V_1 = 20$$

$$\Delta S = 2 \times 2 \ln 2 = 4 \ln 2 = 2.77 \text{ cal.}$$

- (7) (C). $\Delta S = -40 \text{ J/K}$

$$\Delta H = T\Delta S$$

$$T = 750 \text{ K}$$

- (8) (C). $\Delta G^\circ = -2.303 RT \log K_{\text{eq}} = -RT \ln K_p$

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{x}{2} \text{ bar} = -RT \ln \left(\frac{x}{2}\right)^2$$

$$= -2RT (\ln x - \ln 2)$$

TRY IT YOURSELF-3

- (1) (D)
 (2) (B)
 (3) (i) $P_4(\text{yellow}) + 5O_2(g) \rightarrow P_4O_{10} + 9.19 \text{ KJ}$
 (ii) $P_4(\text{red}) + 5O_2(g) \rightarrow P_4O_{10} + 8.78 \text{ KJ}$
 Subtracting $P_4(\text{yellow}) - P_4(\text{red}) = 1.13 \text{ KJ}$
 $P_4(\text{yellow}) = P_4(\text{red}) + 1.13 \text{ KJ}$
 So, heat of transition of yellow to red phosphorus is -1.13 KJ

- (4) The equation :
 $\Delta H = 109 = \epsilon_{N-N} + 4 \epsilon_{N-H} - \epsilon_{H-H} - 2 \epsilon_{N-H} - \epsilon_{N=N}$
 $\epsilon_{N=N} = 163 + 2 \times 391 - 436 - 109 = 400 \text{ kJ/mole}$

- (5) (B). No. of moles of H_2O = No. of moles of CaO
 = No. of moles of $Ca(OH)_2$ produced = $500/18$
 $CaO + H_2O \rightarrow Ca(OH)_2$

Total heat released = $\frac{500}{18} \times 62.5 \times 1000J$

Mass of $Ca(OH)_2$ produced = $\frac{500}{18} \times 74 \text{ gm}$

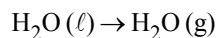
$\therefore \frac{500}{18} \times 74 \times 1.2 \times (T - 25) = \frac{500}{18} \times 65.2 \times 1000$

$88.8(T - 25) = 65200$

$T = 734.23 + 25 = 759.23^\circ\text{C}$

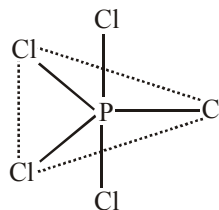
- (6) (A). $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; $\Delta H = -285.8$
 Target reaction $H^+ + OH^- \rightarrow H_2O$; $\Delta H = -57.3$
 $\Delta H = -57.3 = [-285.8 - 0 - x]$
 $x = \Delta H_f^\circ$ of OH^-
 $x = -228.5 \text{ kJ mol}^{-1}$

- (7) (B). $H_2 + \frac{1}{2}O_2 \rightarrow H_2O(\ell)$; $\Delta H = x_1 + \frac{x_2}{2} - 2x_3$



$\Delta H = x_1 + \frac{x_2}{2} - 2x_3 - x_4$

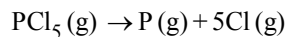
- (8) (C). $PCl_3(g) \rightarrow P(g) + 3Cl(g)$
 $3BE_{P-Cl} = 195 \text{ Kcal/mol}$
 $BE_{P-Cl} = 65 \text{ Kcal/mol}$
 (equatorial)



In PCl_5 , 3P - Cl bonds are equatorial

$BE_{P-Cl}(\text{eq}) = 65 \times 1.1 = 71.5 \text{ kcal}$

$BE_{P-Cl}(\text{axial}) = 65 \times 0.9 = 58.5 \text{ kcal}$



$3BE_{P-Cl} + 3BE_{P-Cl}(\text{axial}) = 3 \times 71.5 + 2 \times 58.5$
 (equatorial) = 331.5 kcal

$\Delta H = 331.5 \text{ Kcal/mol}$

- (9) (B).

CHAPTER-6:
THERMODYNAMICS
EXERCISE-1

- (1) (C). System and the surroundings together constitute the universe.
The universe = the system + the surroundings
- (2) (C). The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.
- (3) (D). Internal energy, U of the system may change when
- heat passes into or out of the system
 - work is done on or by the system
 - matter enters or leaves the system
- (4) (D). The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. Variables like p, V, T are called state variables or state functions.
- (5) (B). A system containing some quantity of water in a thermoflask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and this type of system is called adiabatic system. The manner in which the state of such a system may be changed is called adiabatic process.
- (6) (C). A system is said to be under adiabatic conditions if there is no exchange of heat between the system and its surroundings. Hence, under adiabatic conditions, $q = 0$.
- (7) (C). In a closed system (e.g., the presence of reactants in a closed vessel made of conducting material i.e. copper) there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
- (8) (A). First law of thermodynamics is represented mathematically as $\Delta E = q + W$, where ΔE is change in internal energy, q is heat absorbed and W is work done.
- (9) (D). The internal energy of a system can be changed by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q .
- (10) (B). A thermodynamic state function is a quantity whose value is independent of a path.
Functions like p, V, T etc. depend only on the state of a system and not on the path.
- (11) (C). For free expansion (i.e. in vacuum), $P_{\text{ext}} = 0$.
Thus, $W = -P_{\text{ext}} \Delta V = 0$
For adiabatic change, $q = 0$
 $\therefore \Delta U = q + W = 0$ which is true for isothermal process where T is constant i.e. $\Delta T = 0$.
- (12) (D). Thermodynamics mainly deals with :
- (a) interrelation of various forms of energy and their transformation from one form to another.
 - (d) the system in equilibrium state or moving from one equilibrium state to another equilibrium state.
- (13) (D). The system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary.
- (14) (C). Thermodynamics is not concerned about how and at what rate chemical reactions are carried out, but is based on initial and final states of a system undergoing the change.
- (15) (D). The pressure (P), volume (V), temperature (T), amount (n) etc. are the state variables or state functions.
- (16) (D). The internal energy U is characteristic of the state of a system whereby the adiabatic work, $W_{\text{adiabatic}}$ required to bring about a change of state is equal to the difference between the value of ΔU in one state and that in another state ΔU , i.e.,
$$\Delta U = U_2 - U_1 = W_{\text{adiabatic}}$$

The positive sign expresses that W_{ad} is positive when work is done on the system. If the work is done by the system, W_{ad} will be negative.
- (17) (C). In thermodynamics, internal energy is the sum of all energies of the system, i.e., chemical, electrical, mechanical.
- (18) (C). $\Delta H = q_p \rightarrow$ heat absorbed by the system at constant pressure.
- (19) (A). $\Delta H = \Delta E + \Delta n_g RT$
$$\Delta n_g = 1 - \frac{3}{2} = -\frac{1}{2} \text{ or } -0.5$$

Hence, $\Delta H = \Delta E - 0.5 RT$
- (20) (C). Volume is not an intensive property.
- (21) (C). It is an irreversible compression. The pressure is not constant at every stage of compression, and changes in number of finite steps. Work done on the gas will be summed over all the steps and will be equal to $-\sum p \Delta V$.
- (22) (D). $\Delta H = \Delta U$. When $\Delta n_g RT = 0$
- (23) (D). The increase of temperature is proportional to the heat transferred, $q = \text{coefficient} \times \Delta T$.
The magnitude of the coefficient depends on the size, composition and nature the system. It is also written as $q = C \times \Delta T$. The coefficient C called the heat capacity. When C is large, a given amount heat results in only a small temperature rise. Water has large heat capacity, i.e., a lot of energy is needed to raise temperature.
- (24) (B). Since the system is insulated, heat is not allowed to enter or leave the system.
Thus $q = 0, \Delta E = q + W \Rightarrow \Delta E = W$.
- (25) (A). $\Delta U = q_p - p\Delta V$
 q_p is heat absorbed by the system.
 $-p\Delta V$ represent expansion work done by the system.
- (26) (D). For a cyclic process, net change in internal energy is zero. Change in internal energy does not depend on the path by which final stage is reached.

- (27) (C). Enthalpy change (ΔH) is a state function so it does not depend on the path taken by the reaction. It depends only on the difference of final and initial values of enthalpy change.
- (28) (D). When work is done by the system, $\Delta U = q - W$.
- (29) (D). $q = -W = P_{\text{ex}}(10 - 2) = 0(8) = 0$
For isothermal expansion in vacuum, $p_{\text{ex}} = 0$
- (30) (B). If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products. n_A is the number of moles of gaseous reactants and n_B is the number of moles of of gaseous products at constant pressure and temperature, then $p \Delta V = \Delta n_g RT$
 Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants. Put value of $p \Delta V$ in equation $\Delta H = \Delta U + p \Delta V$
 $\Delta H = \Delta U + \Delta n_g RT$
- (31) (C). A process is called reversible when surrounding is always in equilibrium with system.
- (32) (A). Heat evolved = -2 kJ
Work done on the system = $+12 \text{ kJ}$
 $\Delta U = q + W = -2 + 12 = +10 \text{ kJ}$
- (33) (C). In calorimetry, vessel called calorimeter is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes.
Measurements are made under two different conditions. (i) at constant volume q_v .
(ii) at constant pressure q_p .
- (34) (C). The bomb calorimeter is sealed, its volume does not change, i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to q_v by the known heat capacity of the calorimeter.
- (35) (D). There is no phase change in formation. A new product is formed during the reaction.
- (36) (C). $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$
 $\Delta_f H = \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$
 $= [H_m(\text{CO}_2, \text{g}) + 2H_m(\text{H}_2\text{O}, \ell)] - [H_m(\text{CH}_4, \text{g}) + 2H_m(\text{O}_2, \text{g})]$
 H_m is the molar enthalpy.
- (37) (D). This is the statement of Hess's law of heat summation.
- (38) (C). $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g});$
 $\Delta_f H = x \text{ kJ mol}^{-1}$ (1)
 $\text{C}(\text{graphite}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g});$
 $\Delta_f H = y \text{ kJ mol}^{-1}$ (2)
By subtracting eqn (2) from (1), we get
 $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g});$
 $\Delta_f H = z \text{ kJ mol}^{-1}$ (3)
Thus, $x - y = z$ i.e., $x = y + z$
- (39) (B). The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called standard molar enthalpy of formation. Its symbol is $\Delta_f H^\ominus$.
- (40) (D). According to this law, the total enthalpy change is independent of intermediate steps involved in the change. It depends only on initial and final values of enthalpy change. So it can be used for the calculation of heat of formation, reaction or transition.
- (41) (D). The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion $\Delta_{\text{fus}} H^\ominus$
- (42) (B). Enthalpy of neutralisation is $-57.1 \text{ kJ mol}^{-1}$ for a strong acid and a strong base.
- (43) (C). The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar.

For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar. Standard state of solid iron at 500 K is pure iron at 1 bar. The standard conditions are denoted adding the superscript \ominus to the symbol ΔH e.g., ΔH^\ominus .
- (44) (C). $X \xrightarrow{\Delta H} Y$; $X \xrightarrow{\Delta H_1} P \xrightarrow{\Delta H_2} Q \xrightarrow{\Delta H_3} Y$
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots$
- (45) (A). The unit for $\Delta_f H^\ominus$ is kJ mol^{-1} which means standard molar enthalpy change of reaction. Enthalpy is an extensive quantity. When a chemical equation is reversed, the value of $\Delta_f H^\ominus$ is reversed in sign for example
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}); \Delta_f H^\ominus = -91.8 \text{ kJ mol}^{-1}$
 $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}); \Delta_f H^\ominus = +91.8 \text{ kJ mol}^{-1}$
- (46) (C). $\Delta H_{\text{reaction}} = \sum \text{B.E.}_{\text{reactants}} - \sum \text{B.E.}_{\text{products}}$
- (47) (A). It is impossible to determine lattice enthalpies directly by an experiment. An enthalpy diagram called Born-Haber cycle is used to determine the lattice enthalpies.
- (48) (A). Average of two bond dissociation energies:
 $\frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mol}^{-1}$
- (49) (A). $\Delta H = \sum \Delta H_p - \sum \Delta H_R$
 $= -1670 - (-834) = -836 \text{ kJ mol}^{-1}$
- (50) (B). $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g}); \Delta_a H^\ominus = 108.4 \text{ kJ mol}^{-1}$
The enthalpy of atomisation is same as the enthalpy of sublimation.
- (51) (B). The sign ΔH is reversed.
- (52) (B). Lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociate into its ions in gaseous state.
 $\text{Na}^+\text{Cl}^-(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g});$
 $\Delta_{\text{lattice}} H^\ominus = 788 \text{ kJ mol}^{-1}$.

(53) (C). 16 g CH₄ gives 880 kJ of heat.

$$3.2 \text{ g CH}_4 \text{ will give} = \frac{880}{16} \times 3.2 = 176 \text{ kJ}$$

(54) (C). $\Delta H^\circ_{\text{soln}} = \Delta H^\circ_{\text{lattice}} + \Delta H^\circ_{\text{hyd}}$

(55) (B). The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bond of a gaseous covalent compound is broken to form products in the gas phase.

(56) (C). Dissolution of compound may not take place if lattice enthalpy is very high.

(57) (D). B.E. of triple bond > double bond > single bond.

(58) (D). The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature.

(59) (D). Heat cannot flow from a cold body to a hot body.

(60) (C). $\text{C (graphite, s)} + 2\text{S (l)} \rightarrow \text{CS}_2 \text{ (l)}$

$$\Delta_r H^\ominus = +128.5 \text{ kJ mol}^{-1}$$

The reaction is endothermic and spontaneous.

(61) (B). For an exothermic reaction, $\Delta H_R > \Delta H_P$

(62) (C). If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T \Delta S$ is large enough to outweigh ΔH . This can happen in two ways

- The positive entropy change of the system can be small in which case T must be large.
- The positive entropy change of the system can be large in which case T may be small.

(63) (C). ΔG is negative for a spontaneous process.

(64) (A). Gas expanding to fill the available volume. Burning carbon in dioxygen gives carbon dioxide. These both are the examples of spontaneous process. The heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously.

(65) (C). All the statements regarding spontaneity of a reaction are correct.

(66) (B). $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

$$\Delta n_g = 2 - 3 = -1, \Delta S = -ve$$

(67) (A). The greater the disorder in an isolated system, the higher is the entropy. As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy.

The change in entropy accompanying a chemical reaction may be estimated qualitatively by consideration of the structures of these species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given

substance the crystalline solid state in the state of lowest entropy (most ordered). The gaseous state is the state of highest entropy.

(68) (D). $\Delta G = \Delta H - T\Delta S$

$\Delta G = -ve$ if $\Delta H = -ve$ and ΔS is $+ve$.

(69) (C). It is the third law of thermodynamics.

(70) (D). (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

(ii) At 0 K, the constituent particles are static and entropy is minimum. If temperature is raised to 115K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

(iii) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

(71) (B). For an endothermic reaction, $\Delta H = +ve$

[less molecules \rightarrow more molecules], $\Delta S = +ve$

$\therefore T\Delta S > \Delta H$, and $\Delta G = -ve$

Hence, the reaction occurs spontaneously.

(72) (D). The criterion for equilibrium in the equation

$\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ is $\Delta_r G = 0$

(73) (D).

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

(74) (D). Gibbs energy for a reaction in which all reactants and products are in standard state. $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows :

$$0 = \Delta_r G^\ominus + RT \ln K$$

$$\Delta_r G^\ominus = -RT \ln K$$

$$\Delta_r G^\ominus = -2.303 RT \log K$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus = -RT \ln K$$

(75) (D).

(A) For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and positive value of equilibrium constant will be much smaller than 1.

(B) In case of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too value of equilibrium constant will be much larger than 1.

EXERCISE-2

- (1) (D). $C_4H_{10}(g) + 6.5O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$
 $\Delta n = [4 - 7.5] = -3.5$
 $\Delta H = \Delta E + \Delta n_g RT \quad \therefore \Delta H < \Delta E$
- (2) (C). $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$
 $\Delta H_f(HCl) = 91 \text{ kJ mol}^{-1}$; $H-H = 430 \text{ kJ mol}^{-1}$
 $Cl-Cl = 242 \text{ kJ mol}^{-1}$
 $91 = \frac{1}{2} \times 430 + \frac{1}{2} \times 242 - \text{B.E.}(H-Cl)$
 $91 = 336 - \text{B.E.}(H-Cl)$
 $\text{B.E.}(H-Cl) = 336 - 91 = 245 \text{ kJ}$
- (3) (B). $Q = Q_1 + Q_2$
- (4) (A). Solid $\xrightarrow{\text{Sublimation}}$ Vapour
 This process occurs in two steps,
 Step 1: Solid $\xrightarrow{\text{Fusion}}$ Liquid
 Step 2: Liquid $\xrightarrow{\text{Vaporisation}}$ Vapour
 Thus, Enthalpy of sublimation
 = Enthalpy of fusion + Enthalpy of vaporisation.
- (5) (B). $\Delta G = \Delta H - T\Delta S$
 For an endothermic reaction $\Delta H = +ve$
 [less molecules \rightarrow more molecules], $\Delta S = +ve$
 $\therefore T\Delta S > \Delta H$, and $\Delta G = -ve$
 Hence, the reaction occurs spontaneously.
- (6) (B). $W = -100 \text{ J}$, $q = 150 \text{ J} \quad \therefore q = \Delta E - W$
 $\therefore 150 = \Delta E - (-100) = 150 - 100$
 $\Delta E = 50 \text{ J}$
- (7) (A). $W = -P\Delta V = -1.5(1 - 0.5)$
 $= -0.75 \text{ atm-litre} = -0.75 \times 101 \text{ Joule}$
 $q = 200 \text{ J} \quad \therefore q = \Delta E - W$
 $200 = \Delta E - (-0.75 \times 101)$
 $\Delta E = 124.25 \text{ Joule}$
- (8) (B). $\Delta H = \Delta E + \Delta n RT$
 Given $\Delta H = -651 \times 10^3 \text{ cal}$, $R = 2 \text{ cal}$, $T = 290 \text{ K}$ and
 $\Delta n = 6 + 6 - 6 = 6$
 $\therefore \Delta E = -651 \times 10^3 - 6 \times 2 \times 290$
 $= -654480 \text{ cal} = -654.5 \text{ Kcal}$
- (9) (B). $\Delta H = \Delta E + \Delta n RT$
 $\Delta n = 2 - 1 = 1 \quad \therefore \Delta H > \Delta E$
- (10) (A). Given $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; $\Delta H = -802 \text{ KJ}$
 $\therefore 16 \text{ g } CH_4 \text{ on burning produces heat} = -802 \text{ KJ}$
 $\therefore 4.5 \text{ g } CH_4 \text{ on burning produces heat}$
 $= \frac{-802 \times 4.5}{16} = 225.6 \text{ KJ}$
- (11) (B). ΔH for 18 g water = 40.8 kJ
 For 90 g water = $(40.8/18) \times 90 = 204 \text{ kJ}$
 n for 90 g water = $90/18 = 5$; $\Delta n_g = 5 - 0 = 5$
 $\Delta H = \Delta U + \Delta n_g RT$
 $\Delta U = 204000 - (5 \times 8.314 \times 373)$
 $= 188494 \text{ J or } 188.494 \text{ kJ}$
- (12) (D). As in vacuum, external pressure is zero and as work is done against the external pressure.
 \therefore Work done is zero.
- (13) (D). In isothermal reversible process ideal gas has constant volume and so $\Delta E = 0$ and $\Delta H = \Delta E = 0$.
- (14) (C). Volume is not an intensive property.
- (15) (C). $\Delta n_g = 1 - \frac{3}{2} = \frac{-1}{2}$,
 As Δn_g is negative, thus $\Delta H < \Delta E$.
- (16) (C). $q = 40 \text{ J}$
 $w = -8 \text{ J}$ (work done by the system)
 $\Delta E = q + w = 40 - 8 = 32 \text{ J}$.
- (17) (A). When $\Delta H = -ve$, $\Delta S = +ve$ and $\Delta G = -ve$ then reaction is spontaneous.
- (18) (B). $CO + \frac{1}{2}O_2 \rightarrow CO_2$
 $\Delta H = \Delta H_f^0(CO_2) - \left[\Delta H_f^0(CO) + \frac{1}{2} \Delta H_f^0(O_2) \right]$
 $= -94.0 - (-26.4) = -67.6 \text{ kcal}$.
- (19) (B). $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
 Molecular weight of $CH_4 = 12 + 4 = 16$
 \therefore On the combustion of 2.0 gm of methane = 25.0 kcal
 \therefore On the combustion of
 $16.0 \text{ gm} = \frac{25 \times 16}{2} = 200 \text{ kcal}$.
- (20) (B). Heat evolved during combustion of 0.39g
 $C_6H_6 = \frac{3250 \times 0.39}{78} = 16.25 \text{ kJ}$.
- (21) (C). $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \dots(i)$
 $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -94 \text{ kcal mol}^{-1} \quad \dots(ii)$
 $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O(l) \quad \dots(iii)$
 $\Delta H = -68 \text{ kcal mol}^{-1}$
 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \dots(iv)$
 $\Delta H = -213 \text{ kcal mol}^{-1}$
 To obtain equation (i) operate $-(ii) + 2 \times (iii) - (iv)$.
 $\Delta H = -94 + 2(-68) - (-213) = -17 \text{ kcal}$
- (22) (A). In the given equation
 $H_2(g) \rightarrow 2H(g)$, $\Delta_{H-H} H^\ominus = 435.0 \text{ kJ mol}^{-1}$
 The enthalpy change involved in this process is the bond dissociation enthalpy of H-H bond.
- (23) (C). If $\Delta G = -ve$ reaction is spontaneous.
- (24) (C). (1) $C_{\text{graphite}} + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -393.5 \text{ kJ}$
 (2) $C_{\text{graphite}} + O_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$, $\Delta H = ??$
 (3) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H = -283.0 \text{ kJ}$
 Adding (2) and (3) we get eq. (1)
 $\therefore \Delta H - 283.9 \text{ kJ} = -393.5 \text{ kJ}$; $\Delta H = -110.5 \text{ kJ}$

- (25) (D). ΔH_f° of CH_4 is represent as
 $2\text{H}_2(\text{g}) + \text{C}(\text{g}) \longrightarrow \text{CH}_4(\text{g})$
 In terms of bond energy data
 $\Delta H^\circ_{(\text{r})} = 2 \times \Delta H_{\text{H-H}} + \Delta H_{\text{sub}}(\text{C}) - 4 \Delta H_{\text{C-H}}$
 We require dissociation energy of H_2 and $\Delta_{\text{sub}}\text{H}^\circ$ of carbon.

- (26) (B). $\Delta H = +35.3 \text{ kJ/mol}$
 $T = 80^\circ\text{C} = 80 + 273 = 353 \text{ K}$

$$\Delta S = \frac{\Delta H}{T} = \frac{+35.3}{353} = 0.1 \text{ kJ} = 0.1 \times 10^3 \text{ J/mol/K}$$

Entropy change in the transition of vapour to liquid is negative. $\Delta S = -100$

- (27) (B). $\Delta G = \Delta H - T\Delta S$
 If ΔH is -ve and ΔS is +ve ΔG is always negative. So reaction is spontaneous.

- (28) (B). Work done in reversible isothermal expansion,

$$W = -2.303 \text{ nRT} \log \frac{V_f}{V_i}$$

$$= -2.303 \times 1 \times 8.314 \times 300 \times \log \frac{250}{25}$$

$$= -5744.14 \text{ J}$$

- (29) (B). Heat produced by ethane $\frac{1560}{30} = 52 \text{ kJ g}^{-1}$

$$\text{Heat produced by benzene} \frac{3268}{78} = 41.9 \text{ kJ g}^{-1}$$

- (30) (B). At constant volume, $\Delta V = 0$
 $W = -P \Delta V = 0$; $\Delta E = q = 200 \text{ J}$

- (31) (C). $\Delta_f H^\circ(\text{Fe}(\text{s})) = 0$, $\Delta_f H^\circ(\text{H}_2(\text{g})) = 0$

$$\Delta_r H^\circ = 3(-285.83) - 1(-824.2)$$

$$= -857.5 + 824.2 = -33.3 \text{ kJ mol}^{-1}$$

- (32) (A). $\Delta U = q + (-W) = 50 + (-20) = 30 \text{ kJ}$

- (33) (D). Enthalpy of decomposition of HCl will be
 $44/2 = 22 \text{ kcal/mol}$

- (34) (A). Expansion of a gas in vacuum ($p_{\text{ext}} = 0$) is called free expansion.

For isothermal irreversible change

$$q = -W = p_{\text{ext}}(V_f - V_i)$$

For isothermal reversible change

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

$$= 2.303 \text{ nRT} \log(V_f/V_i)$$

For adiabatic change, $q = 0$, $\Delta U = W_{\text{ad}}$

- (35) (B). Work in expansion = $-P\Delta V$

$$W = -3 \times (6 - 4) = -6 \text{ L atm}$$

$$1 \text{ L atm} = 101.32 \text{ J}$$

$$W = -6 \times 101.32 = -607.92 \text{ J}$$

or $W = -608 \text{ J}$

- (36) (A). $\text{C}_{(\text{diamond})} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

$$= -393.7 + (-2.1) = -395.8 \text{ kJ}$$

12 g diamond gives 395.8 kJ,

800 kJ will be given by

$$\frac{12}{395.8} \times 800 = 24.25 \text{ g}$$

- (37) (D). $\Delta H = \Sigma \text{B.E.}_R - \Sigma \text{B.E.}_P$
 $= (2 \times 44 + 2 \times 111) - (119 + 2 \times 135) = -79 \text{ kcal}$

- (38) (D).

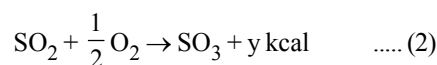
- (a) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}$
 shows combustion reaction.

- (b) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$
 shows bond dissociation.

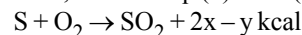
- (c) $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$
 shows dissociation of NaCl.

- (d) $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 shows dissociation of NaCl.

- (39) (D). $\text{S} + (3/2)\text{O}_2 \rightarrow \text{SO}_3 + 2x \text{ kcal} \quad \dots (1)$



Now, subtract eq. (2) from (1), we get,



\therefore Heat of formation of SO_2 is equal to $2x - y \text{ kcal}$.

EXERCISE-3

- (1) 4. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\ell)$
 $\Delta H^\circ_{\text{reaction}} = [6\Delta H_f^\circ[\text{CO}_2] + 6\Delta H_f^\circ[\text{H}_2\text{O}]] - \Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6] + 6\Delta H_f^\circ[\text{O}_2]$
 $-2821.8 = [6 \text{ mol} \times (-393.51 \text{ kJ/mol}) + 6 \text{ mol} \times (-285.83 \text{ kJ/mol})] - [1 \text{ mol} \times \Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6] + 6 \text{ mol} \times (0 \text{ kJ/mol})]$
 $\Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6] = -1268.2 \text{ kJ mol}^{-1}$

- (2) 5. Initial conditions : $V_1 = 45 \text{ L}$, $P_1 = 140 \text{ atm}$
 Final conditions : $V_2 = \text{unknown}$, $P_2 = P_{\text{ext}} = 1.00 \text{ atm}$
 We use Boyle's law to determine the final volume.

Since PV is constant,

$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2} = 6300 \text{ L}$$

$$w = -P_{\text{ext}} \Delta V = -1.00 \text{ atm} (6300 \text{ L} - 45 \text{ L})$$

$$w = -6.26 \times 10^3 \text{ L-atm}$$

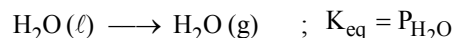
Convert the work to joules

$$w = -6.26 \times 10^3 \text{ L-atm} \times 101 \frac{\text{J}}{\text{L-atm}} = -6.32 \times 10^5 \text{ J}$$

$$= -632 \text{ kJ}$$

The negative sign indicates that the system performs work on the surroundings.

- (3) 2. First, write the equation and expression for the equilibrium constant.



Next determine ΔH° and ΔS° for the process, using the enthalpy and entropy of vapourization. In this case,

$$\Delta G^\circ_{\text{vap}} = +44.01 \text{ kJ mol}^{-1}$$

$$\text{and } \Delta S^\circ_{\text{vap}} = +118.8 \text{ J mol}^{-1} \text{ K}^{-1}.$$

Calculate the standard free energy change :

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

$$\Delta G^\circ = 44010 \text{ J} - 288 \text{ K} \times 118.8 \text{ JK}^{-1} = 9796 \text{ J}$$

Last, calculate the equilibrium constant at the given temperature.

$$K_{\text{eq}} = e^{-\Delta G^\circ/RT}$$

$$\frac{\Delta G^\circ}{RT} = \frac{9796J}{(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298\text{K})} = +4.09$$

$$K_{\text{eq}} = e^{-\Delta G^\circ/RT} = e^{-4.09} = 0.0167$$

$$P_{\text{H}_2\text{O}} = 0.0167 \text{ atm}$$

Notice that the units of pressure are atmospheres.

- (4) 70. Given, for the change

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

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

For a non-spontaneous reaction, $\Delta G = +ve$

$$\text{Since, } \Delta G = \Delta H - T\Delta S$$

$\therefore \Delta H - T\Delta S$ should be $+ve$ or $\Delta H > T\Delta S$

$$\text{or } T < \frac{\Delta H}{\Delta S} < \frac{30 \times 10^3}{70} < 428.57 \text{ K}$$

- (5) 6. $A \rightarrow C$; $\Delta S = 50$

$$C \rightarrow D$$
; $\Delta S = 30$

$$D \rightarrow B$$
; $\Delta S = 20$

$$\text{For } A \rightarrow B: \Delta S = 50 + 30 - 20 = 60 = 10x \Rightarrow x = 6$$

- (6) 9. $n = \frac{3.5}{28}$; $\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45$

$$C_V = 2.5 \text{ kJ k}^{-1} = 2500 \text{ JK}^{-1}$$

$$C_P = C_V + R = 2500 + 8.314 = 2508.314 \text{ JK}^{-1}$$

$$Q_P = C_P \Delta T = 1128.74 \text{ J}$$

$$\Delta H = \frac{Q_P}{n} = \frac{1128.74}{3./28} \Rightarrow 9030 \text{ J mol}^{-1}$$

$$= 9.030 \text{ KJ mol}^{-1} = 9 \text{ KJ mol}^{-1}$$

- (7) 2. $w_d = 4 \times 1.5 + 1 \times 1 + 2.5 \times 2/3 = 8.65$

$$\text{Process is isothermal, } w_s = 2 \times 2.303 \log \frac{5.5}{0.5}$$

$$= 2 \times 2.303 \times \log 11 = 2 \times 2.303 \times 1.0414 = 4.79$$

$$\frac{w_d}{w_s} = \frac{8.65}{4.79} = 1.08 \approx 2$$

- (8) 44. $\Delta H = \Delta U + P_2 V_2 - P_1 V_1$

$$\text{Given, } \Delta U = 30.0 \text{ L atm}$$

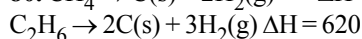
$$P_1 = 2.0 \text{ atm, } V_1 = 3.0 \text{ L, } T_1 = 95 \text{ K}$$

$$P_2 = 4.0 \text{ atm, } V_2 = 5.0 \text{ L, } T_2 = 245 \text{ K}$$

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1 = 30 + (4 \times 5) - (2 \times 3) = 30 + 20 - 6 = 44 \text{ L atm.}$$

- (9) 400. $\Delta S = \frac{\Delta Q_{\text{rev.}}}{T}$ or $75 = \frac{30 \times 10^3}{T}$ or $T = 400 \text{ K}$

- (10) 80. $\text{CH}_4 \rightarrow \text{C(s)} + 2\text{H}_2(\text{g}) \quad \Delta H = 360 \text{ Kcal}$



$$\text{The avg C-H bond energy} = \frac{360}{4} = 90 \text{ Kcal}$$

$$\therefore \text{C-C bond energy} = 620 - 90 \times 6 = 620 - 540 = 80 \text{ Kcal}$$

EXERCISE-4

- (1) (C). The amount of heat required to raise the temperature of one mole of substance through 1°C is called molar heat capacity.

$$C = \frac{q}{T_2 - T_1}$$

- (2) (A). For spontaneity, $\Delta G = -ve$

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

ΔH , for endothermic process $+ve$

At lower temperature, $\Delta S +ve$ hence $\Delta G = +ve$.

But at high temperature $T\Delta S$ will be greater than ΔH , hence $\Delta G = -ve$, spontaneous.

- (3) (C). Joules law suggests

$$J = \frac{\text{Mechanical work done by the system, } W}{\text{Net heat given to the system } Q}$$

$$\text{Hence, } J = \frac{W}{q_1 + q_2}; \text{ Hence, } W = J(q_1 + q_2)$$

is constant with Joules law of equivalence.

- (4) (D). The criteria in term of entropy is $(ds)_{V,E} > 0$ and in terms of free energy is $(dG)_{T,P} < 0$.

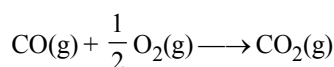
- (5) (B). The net energy change is zero because ΔU is independent of path.

- (6) (B). $\Delta H = 4 \Delta H_{\text{C-H}} + \Delta H_{\text{C=C}} + \Delta H_{\text{H-H}} - \Delta H_{\text{C-C}} - 6 \Delta H_{\text{C-H}}$
 $= \Delta H_{\text{C=C}} + \Delta H_{\text{H-H}} - \Delta H_{\text{C-C}} - 2 \Delta H_{\text{C-H}}$
 $= 615 + 435 - 347 - 2 \times 414 = -125 \text{ kJ}$

- (7) (A). According to Hess's law, ΔH is independent of path.

- (8) (B). $-\Delta G^\circ = RT \ln K_C$.

- (9) (D). Combustion of CO is represented as



$$\Delta H_c(\text{CO}) = \Delta H_f(\text{CO}_2) - \Delta H_f(\text{CO})$$

$$\text{or } \Delta H_f(\text{CO}) = \Delta H_f(\text{CO}_2) - \Delta H_c(\text{CO}) = -393.5 - (-283) = -110.5 \text{ kJ}$$

- (10) (A). $W = P\Delta V$

- (11) (B). For spontaneity of reaction, $E_{\text{cell}} > 0$

$$\Delta G < 0$$

$$K > 1$$

- (12) (D). $\Delta x = 2 - 4 = -2$, thus $\Delta H < \Delta U$.

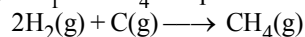
- (13) (A). Bond dissociation energy = 1 : 1 : 0.5
 $\text{XY} : \text{X}_2 : \text{Y}$

$$\Delta H_f \text{ of } \text{XY} = -200 \text{ kJ}$$

So, bond dissociation energy $\text{X}_2 = 200 \text{ kJ/mole}$
 (Due to same ratio $(\text{XY} : \text{X}_2)$)

- (14) (D). Since $W_{\text{irr}} < W_{\text{rev}}$ and the system is isolated, therefore, $T_{\text{f(irr)}} > T_{\text{f(rev)}}$.

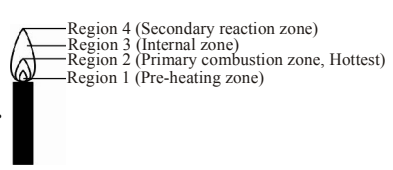
- (15) (D). ΔH_f° of CH_4 is represent as



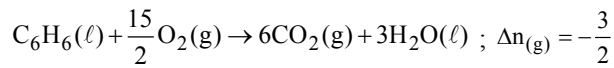
In terms of bond energy data

$$\Delta H_{\text{(r)}}^\circ = 2 \times \Delta H_{\text{H-H}} + \Delta H_{\text{sub}}(\text{C}) - 4 \Delta H_{\text{C-H}}$$

Thus we require dissociation energy of H_2 and $\Delta_{\text{sub}}\text{H}^\circ$ of carbon.

- (16) (A). $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$
 $(\Delta H - \Delta U) = \Delta nRT$
 $= 0.5 \times 0.314 \times 298 = 1238.70 \text{ kJ/mole}$
- (17) (D). $CaCO_3(s) \longrightarrow CaO(l) + CO_2(g)$
 $\Delta G = \Delta H - T\Delta S$ (1)
 Now, ΔH and ΔS both are positive, hence reaction will be spontaneous if $T\Delta S > \Delta H$.
 i.e. $T > \frac{\Delta H}{\Delta S}$ or $T > \frac{179.1 \times 1000}{162.2} \Rightarrow T < 1118 \text{ K}$
- (18) (C). $H_2O(l) \rightleftharpoons H_2O(g)$; $\Delta H = 1$,
 Now, $\Delta H = \Delta E + \Delta nRT$
 $\Delta E = \Delta H - \Delta nRT$
 $= (41 - 1 \times 8.3 \times 373 \times 10^{-3}) \text{ kJ/mol}$
 $= (41 - 3.0959) \text{ kJ/mol} = 37.9 \text{ kJ/mol}$
- (19) (A). For a spontaneous process in an isolated system, the change in entropy is positive.
- (20) (A). For the process $\frac{1}{2}Cl_2(g) \longrightarrow Cl^-(aq)$
 $\Delta H = \frac{1}{2}\Delta H_{\text{diss. of } Cl_2} + \Delta_{\text{eg}}Cl + \Delta_{\text{hyd}}Cl^-$
 $= +\frac{240}{2} - 349 - 381 = -610 \text{ kJ mol}^{-1}$
- (21) (B). From the equation, $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$
 $XY_3 - \frac{1}{2}X_2 - \frac{3}{2}Y_2 = 50 - \left(\frac{1}{2} \times 60\right) - \frac{3}{2} \times 40$
 $= 50 - 30 - 60 = -40$
 $T\Delta S = \Delta H$
 $T = -\frac{30 \times 1000}{-40} = 750 \text{ K}$
- (22) (A). $\Delta_r^0 H = \Delta_f^0 OH - \Delta_f^0 H_2O$
 $57.32 = \Delta_f^0 OH^- + 286.20$
 $\Delta_f^0 OH^- = 57.32 - 286.20 = -228.88 \text{ kJ}$
- (23) (C). Efficiency of fuel cell (η)
 $= \frac{\Delta G^\circ}{\Delta H^\circ} = \frac{-702.6}{-726} \times 100 \cong 97\%$
- (24) (B). Enthalpy of formation of $NH_3 = -46 \text{ kJ/mole}$
 $\therefore N_2 + 3H_2 \longrightarrow 2NH_3$; $\Delta H_f = -2 \times 46 \text{ kJ mol}$
 Bond breaking is endothermic and Bond formation is exothermic
 Assuming 'x' is the bond energy of N-H bond (kJ mol^{-1})
 $\therefore 712 + (3 \times 436) - 6x = -46 \times 2 \therefore x = 352 \text{ kJ/mol}$
- (25) (B). $\Delta G = \Delta H - T\Delta S$
 at equilibrium, $\Delta G = 0$
 for a reaction to be spontaneous ΔG should be negative. $\therefore T > T_e$
- (26) (A). $\Delta S = nR \ln \frac{V_2}{V_1} = 2.303 nR \log \frac{V_2}{V_1}$
 $= 2.303 \times 2 \times 8.314 \log \frac{100}{10} = 38.3 \text{ J mol}^{-1} \text{ K}^{-1}$
- (27) (C). $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 $-RT \ln K = \Delta H^\circ - T\Delta S^\circ$
 $\ln K = -\frac{\Delta H^\circ - T\Delta S^\circ}{RT}$
- (28) (A). The process is isothermal expansion
 Hence, $q = -w$; $\Delta u = 0$
 $q = +208 \text{ J}$
 $w = -208 \text{ J}$ (expansion work)
- (29) (C). $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
 $\Delta E = -1364.47 \text{ kJ/mole}$, $\Delta H = ?$
 $\Delta n_g = -1$
 $\therefore \Delta H = \Delta E + \Delta n_g RT = -1364.47 - \frac{1 \times 8.314 \times 298}{1000}$
 So, $\Delta H = -1366.95 \text{ kJ/mole}$
- (30) (C). $2NO(g) + O_2 \rightleftharpoons 2NO_2(g)$
 $(\Delta G^\circ)_{\text{reaction}} = [(\Delta G^\circ)_{\text{formation}}]_{\text{product}} - [(\Delta G^\circ)_{\text{formation}}]_{\text{reactant}}$
 $\Rightarrow -RT \ln K_p = 2 \times (\Delta G^\circ)_{NO_2} - (\Delta G^\circ)_{NO}$
 $\Rightarrow (\Delta G^\circ)_{NO_2} = 2(\Delta G^\circ)_{NO} - RT \ln K_p$
 $\Rightarrow (\Delta G^\circ)_{NO_2} = \frac{2 \times 86600 - R(298) \ln K_p}{2}$
 $= \frac{2 \times 86600 - R(298) \ln 1.6 \times 10^{12}}{2}$
 $= 0.5 [2 \times 86,600 - R(298) \ln 1.6 \times 10^{12}]$
- (31) (C). $C + O_2 \rightarrow CO_2$... (i)
 $CO + \frac{1}{2}O_2 \rightarrow CO_2$... (ii) } $+ C + \frac{1}{2}O_2 \rightarrow CO$
 $\Rightarrow \Delta_f H_{CO} = (\Delta H_{(i)} - \Delta H_{(ii)}) = -393.5 - (-283.5) = -110.0$
- (32) (A). 
- (33) (D). For adiabatic process : $q = 0$
 So from 1st law $\Delta U = q = w$
 We can write $\Delta U = w$
- (34) (D). $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$; $\Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1}$ (1)
 $H_2(g) + (1/2)O_2(g) \rightarrow H_2O(l)$; $\Delta_f H^\circ = -285.8 \text{ kJ mol}^{-1}$ (2)
 $CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$;
 $\Delta_f H^\circ = +890.3 \text{ kJ mol}^{-1}$ (3)
 $CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$ (4)
 $\Delta_r H_4 = \Delta_f H_1 + 2\Delta_f H_2 + \Delta_f H_3$
 $= -393.5 + (-285.8 \times 2) + 890.3 = -74.8 \text{ kJ/mol}$

(35) (B).



$$\Delta H = \Delta U + \Delta n_{(g)}RT = -3263.9 - \frac{1.5 \times 8.314 \times 298}{1000}$$

$$= -3267.6 \text{ kJ/mol}$$

(36) (B). $W = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{V_b}{V_i}$

$$|W| = nRT \ln \frac{V_b}{V_i} = nRT (\ln V_b - \ln V_i)$$

$$|W| = nRT \ln V_b - nRT \ln V_i$$

$Y = m x - C$. So, slope of curve 2 is more than curve 1.

& intercept of curve 2 is more negative than curve 1.

(37) (C). For cyclic process : $\Delta U = 0 \Rightarrow q = -w$

For isothermal process : $\Delta U = 0 \Rightarrow q = -w$

For adiabatic process : $q = 0 \Rightarrow \Delta U = W$

For isochoric process : $w = 0 \Rightarrow \Delta U = q$

(38) (D). $\Delta H = n \int_{T_1}^{T_2} C_{p,m} dT = 3 \times \int_{300}^{1000} (23 + 0.01T) dT$

$$= 3 \left[23(1000 - 300) + \frac{0.01}{2} (1000^2 - 300^2) \right]$$

$$= 61950 \text{ J} \approx 62 \text{ kJ}$$

(39) (A). $n = 5$; $T_i = 100 \text{ K}$; $T_f = 200 \text{ K}$;

$C_V = 28 \text{ J/mol K}$; Ideal gas

$$\Delta U = nC_V \Delta T$$

$$= 5 \text{ mol} \times 28 \text{ J/mol K} \times (200 - 100) \text{ K} = 14,000 \text{ J} = 14 \text{ kJ}$$

$$\Rightarrow C_p = C_V + R = (28 + 8) \text{ J/mol K} = 36 \text{ J/mol K}$$

$$\Rightarrow \Delta H = nC_p \Delta T = 5 \text{ mol} \times 36 \text{ J/mol K} \times 100 \text{ K} = 18,000 \text{ J} = 18 \text{ kJ}$$

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

$$\Rightarrow \Delta(PV) = \Delta H - \Delta U = (18 - 14) \text{ kJ} = 4 \text{ kJ}$$

(40) (C). (a) $q + w = \Delta U \leftarrow$ definite quantity

(b) $q \rightarrow$ Path function

(c) $w \rightarrow$ Path function

(d) $H - TS = G \rightarrow$ state function

(41) (A). $\Delta G^\circ = -nF E^\circ_{\text{cell}}$

$$= -2 \times 96000 \times 2 = -384000 \text{ J} = -384 \text{ kJ}$$

(42) (D). $A + B \rightarrow C + D$

Activation enthalpy for C = $20 - 5 = 15 \text{ kJ/mol}$

Activation enthalpy for D = $15 - 5 = 10 \text{ kJ/mol}$

(43) (C). $W = -P_{\text{ext}}(V_2 - V_1) = -1 \text{ bar} \times (10 - 1) \text{ lit}$

$$= -9 \text{ bar-lit} = -900 \text{ J} = -0.9 \text{ kJ}$$

(44) **-02.70 kcal**

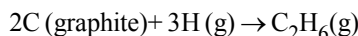
$$\Delta H = \Delta U + \Delta n_{\text{g}}RT$$

$$= 2.1 \times 10^3 + 2(2)(300) = 2100 + 1200 = 3300 \text{ cal}$$

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

$$= 3300 - (300)(20) = 3300 - 6000 = -2700 \text{ cal} = -2.7 \text{ kcal}$$

(45) **-192.5**



$$\begin{aligned} \Delta_f H(C_2H_6) &= 2\Delta H_{\text{comb}}(C_{\text{graphite}}) \\ &\quad + 3\Delta H_{\text{comb}}(H_2) - \Delta H_{\text{comb}}(C_2H_6) \\ &= -(286 \times 2) - (393.5 \times 3) - (-1560) \\ &= -572 - 1180.5 + 1560 = -192.5 \text{ kJ/mole} \end{aligned}$$

(46) **48.00** $|W| = \frac{1}{2}(6+10) \times 6 = 48 \text{ J}$

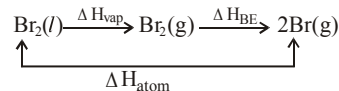
(47) **06.25**

$$\Delta U = nC_V \Delta T$$

$$5000 = 4 \times C_V (500 - 300)$$

$$C_V = 6.25 \text{ JK}^{-1} \text{ mol}^{-1}$$

(48) (D). Enthalpy of atomisation of $Br_2(\ell)$



$$\Delta H_{\text{atom}} = \Delta H_{\text{vap}} + \Delta H_{\text{BE}}$$

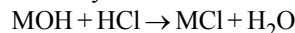
$$x = \Delta H_{\text{vap}} + y. \text{ So, } x > y$$

(49) (A). IE values indicate, that the metal belongs to Ist group

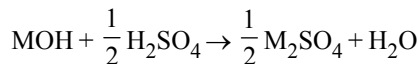
since second IE is very high

(\therefore only one valence electron)

Metal hydroxide will be of type, MOH.



(1mol)(1mol)



(1mol) (1/2 mol)

one mole of HCl required to react with one mole MOH.

1/2 mole of H_2SO_4 required to react with one mole MOH.

EXERCISE-5

(1) (C). As MgO is a oxide of weak base hence some energy is lost to break MgO(s). Hence enthalpy is less than -57.33 kJ/mol

(2) (C). For a spontaneous reaction, ΔG (-ve), which is possible if $\Delta S = +ve$, $\Delta H = +ve$.

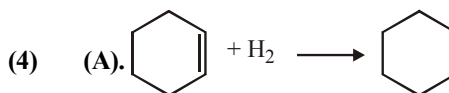
and $T\Delta S > \Delta H$ [$\Delta G = \Delta H - T\Delta S$]

(3) (A). Measure of disorder of a system is nothing but entropy. For a spontaneous reaction, $\Delta G < 0$. As per Gibbs Helmholtz equation, $\Delta G = \Delta H - T\Delta S$

Thus ΔG is -ve only

When $\Delta H = -ve$ (exothermic)

and $\Delta S = +ve$ (increasing disorder)



$$\Delta H = [\Delta H \text{ of combustion of cyclohexane}$$

$$- (\Delta H \text{ of combustion of cyclohexene}$$

$$+ \Delta H \text{ of combustion of } H_2)]$$

$$= -[-3920 - (-3800 - 241)] \text{ kJ}$$

$$= -[-3920 + 4041] \text{ kJ} = -121 \text{ kJ}$$

(5) (D). $\Delta G = \Delta H - T\Delta S$; $\Delta G = 0$

In equilibrium, $0 = \Delta H - T\Delta S$

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{30 \times 1000}{105} = 285.7 \text{ K}$$

(6) (A). If $\Delta G_{\text{system}} = 0$ the system has attained equilibrium

- (7) (D). We know that, $\Delta H = \Delta E + P\Delta V$
In the reactions, $H_2 + Br_2 \longrightarrow 2HBr$ this is no change in volume or $\Delta V = 0$.
So, $\Delta H = \Delta E$ for this reaction.
- (8) (D). This reaction shows the formation of H_2O , and the X_2 represents the enthalpy of formation of H_2O because as the definition suggests that the enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constituent atoms.
- (9) (B). $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$
 $\Delta H_{HCl} = \sum \text{B.E. of reactant} - \sum \text{B.E. of products}$
 $-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - \text{B.E. of HCl}$
 $\therefore \text{B.E. of HCl} = 215 + 120 + 90 = 425 \text{ kJ mol}^{-1}$.
- (10) (A). Heat and work are not state function
- (11) (D). $H_2 + Cl_2 \longrightarrow 2HCl$
$$\Delta H = \frac{[434 + 242] - [2 \times 431]}{2} = \frac{676 - 862}{2}$$
$$= -93 \text{ kJ/mol}$$
- (12) (C). For dissociation reaction enthalpy is positive and since no. of gaseous moles are increasing the entropy also increases, and it is an example of thermal decomposition
- (13) (B). $\Delta H_r = [4 \times BE_{(C-H)} + 1 \times BE_{(C=C)} + 1 \times BE_{(H-H)}] - [6 \times BE_{(C-H)} + 1 \times BE_{(C-C)}]$
 $= [(4 \times 410.5) + 606.1 + 431.3] - [(6 \times 410.5) + 336.49]$
 $= -120.0 \text{ kJ mol}^{-1}$
- (14) (B). $\Delta G = \Delta H - T\Delta S$
 $0 = (170 \times 10^3 \text{ J}) - T(170 \text{ JK}^{-1})$; $T = 1000 \text{ K}$
For spontaneity, ΔG is -ve
Hence T should be $> 1000 \text{ K}$
- (15) (A). For the reaction,
 $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$; $\Delta H = -30 \text{ kJ}$,
$$\Delta S^\circ = S^\circ(XY_3) - \left[\frac{1}{2}S^\circ x_2 + \frac{3}{2}S^\circ y_2 \right]$$
$$= 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right]$$
$$= 50 - [30 + 60] = -40 \text{ kJ}^{-1} \text{ mol}^{-1}$$

We know that, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
At equilibrium, $\Delta G^\circ = 0$; $\Delta H = T\Delta S^\circ$
$$T = \frac{\Delta H}{\Delta S^\circ} = \frac{-30 \times 10^3 \text{ J}}{-40 \text{ JK}^{-1} \text{ mol}^{-1}} = 750 \text{ K}$$
- (16) (C). According to Gibb's equation, .
 $\Delta G = \Delta H - T\Delta S$ when $\Delta G = 0$,
 $\Delta H = T\Delta S$
Given, $\Delta H = 40.63 \text{ kJ mol}^{-1}$
 $= 40.63 \times 10^3 \text{ J mol}^{-1}$
 $\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\therefore T = \frac{\Delta H}{\Delta S} = \frac{40.63 \times 10^3}{108.8} = 373.43 \text{ K}$
- (17) (D). Given
(i) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$;
 $\Delta H = -26.8 \text{ kJ}$
(ii) $FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$; $\Delta H = -16.5 \text{ kJ}$
On multiplying equation (ii) with 2, we get
(iii) $2FeO(s) + 2CO(g) \rightarrow 2Fe(s) + 2CO_2(g)$; $\Delta H = -33 \text{ kJ}$
On subtracting equation (iii) from, (i)
 $Fe_2O_3(s) + CO(g) \rightarrow 2FeO(s) + CO_2(g)$
 $\Delta H = -26.8 - (-33) = +6.2 \text{ kJ}$
- (18) (D). Since the ideal gas expands spontaneously into vacuum, $P_{\text{ext}} = 0$, hence work done is also zero.
- (19) (D). For an ideal gas, for free expansion
 $q = 0$; $\Delta T = 0$ & $w = 0$
- (20) (A). $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{30 \text{ kJ mol}^{-1}}{300 \text{ K}} = 100 \text{ J mol}^{-1} \text{ K}^{-1}$
- (21) (D). Dissociation energy of H - H bond is
 $869.6/2 = 434.8 \text{ kJ}$
- (22) (B). $\frac{1}{2}A \rightarrow B \quad +150 \dots\dots\dots (1)$
 $3B \rightarrow 2C + D \quad -125 \dots\dots\dots (2)$
 $E + A \rightarrow 2D \quad +350 \dots\dots\dots (3)$

 $B + D \rightarrow E + 2C$
 $2 \times \text{eq. (1)} + \text{eq. (2)} - \text{eq. (3)}$,
 $\Delta H = 300 - 125 - 350 = -175 \text{ kJ/mol}$
- (23) (A). In the first reaction
 $C(\text{gr.}) + \frac{1}{2}O_2(\text{g}) \rightarrow CO(\text{g})$; $\Delta S^\circ = +ve$
Therefore, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ that means the value of ΔG decrease on increase temperature.
- (24) (C). $\Delta S = \frac{\Delta H}{T} = \frac{1.435 \times 10^3}{273} = 5.260 \text{ cal/mol-K}$

- (25) (A). $\Delta H = \Delta E + \Delta n(g) RT$
 $40.66 \times 1000 = \Delta E + (1) \times 8.314 \times 373$
 $\Delta E = 37.56 \text{ kJ mol}^{-1}$
- (26) (D). $\Delta H = (Ea)_f - (Ea)_b$
 Given: $(Ea)_f = (Ea)_b \quad \therefore \Delta H = 0$
- (27) (B). $\Delta H = \Delta U + \Delta n_g RT = 3.300 \text{ kcal}$
 $\Delta G = \Delta H - T\Delta S = -2.700 \text{ kcal}$
- (28) (B). $\Delta G^\circ = -2.30 RT \log K$
- (29) (C). Formation of CO_2 from carbon and dioxygen gas can be represented as
 $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$;
 $\Delta_f H = -393.5 \text{ kJ mol}^{-1}$ (1 mole = 44 g)
 Heat released on formation of 44 g CO_2
 $= -393.5 \text{ kJ mol}^{-1}$
 For 35.2 g CO_2 heat released
 $= \frac{-393.5 \text{ kJ mol}^{-1}}{44 \text{ g}} \times 35.2 \text{ g} = -315 \text{ kJ}$
- (30) (AC). $\Delta G = \Delta H - T\Delta S$. For reaction to be spontaneous, ΔG should be -ve
 Note: ΔG can be negative in option (A) also.
- (31) (B). $\Delta S = nR \ln \left(\frac{P_i}{P_f} \right)$
- (32) (A). $\Delta G = \Delta H - T\Delta S$
 For equilibrium $\Delta G = 0$
 $\Delta H = T\Delta S$
 $T_{\text{eq}} = \frac{\Delta H}{\Delta S} = \frac{35.5 \times 1000}{83.6} = 425 \text{ K}$
 Since the reaction is endothermic it will be spontaneous at $T > 425 \text{ K}$.
- (33) (B). Work done in irreversible process
 $W = -P_{\text{ext}} \Delta V = -2.5 [4.5 - 2.5]$
 $= -5 \text{ L atm}$
 $= -5 \times 101.3 \text{ J} = -505 \text{ J}$
 Since system is well insulated $q = 0$
 By FLOT $\Delta E = q + W$
 $\Delta E = W = -505 \text{ J}$
- (34) (A). The reaction for $\Delta_f H^\circ(\text{XY})$
 $\frac{1}{2} \text{X}_2(\text{g}) + \frac{1}{2} \text{Y}_2(\text{g}) \rightarrow \text{XY}(\text{g})$
 Bond energies of X_2 , Y_2 and XY are X , $X/2$, X respectively
 $\Delta H = \left(\frac{X}{2} + \frac{X}{4} \right) - X = -200$
 On solving, we get, $-\frac{X}{2} + \frac{X}{4} = -200$
 $X = 800 \text{ kJ/mole}$
- (35) (A). $W_{\text{irr}} = -P_{\text{ext}} \Delta V$
 $= -2 \text{ bar} \times (0.25 - 0.1) \text{ L}$
 $= -2 \times 0.15 \text{ L-bar} = -0.30 \text{ L-bar}$
 $= -0.30 \times 100 \text{ J} = -30 \text{ J}$
- (36) (D). $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{v})$, $\Delta S > 0$
- Expansion of gas at constant temperature, $\Delta S > 0$
 - Sublimation of solid to gas, $\Delta S > 0$
 - $\text{H}(\text{g}) \rightarrow \text{H}_2(\text{g})$, $\Delta S < 0$ ($\Delta n_g < 0$)