THERMODYNAMICS
AND
THERMO CHEMISTRY

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THEORY

1. THERMODYNAMICS

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

2. THERMODYNAMICS TERMINOLOGY

2.1 System

The part of the Universe under observation is called system.

2.2 Surrounding

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

System + Surrounding = Universe

2.3 Types of system

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

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

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

3. STATE OF A SYSTEM

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

4. PROPERTIES OF SYSTEM

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

4.1 Extensive Properties

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

4.2 Intensive Properties

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

5. STATE AND PATH FUNCTIONS

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

6. THERMODYNAMIC EQUILIBRIUM

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

6.1 Mechanical Equilibrium

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

6.2 Thermal Equilibrium

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

6.3 Chemical Equilibrium

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

7. INTERNAL ENERGY

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

8. MODES OF ENERGY TRANSFER

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

8.1 Heat

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

8.2 Work

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

9. FIRST LAW OF THERMODYNAMICS

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

$\Delta U = q + w$

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

10. REVERSIBILITY

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

10.1 Quasi Static State

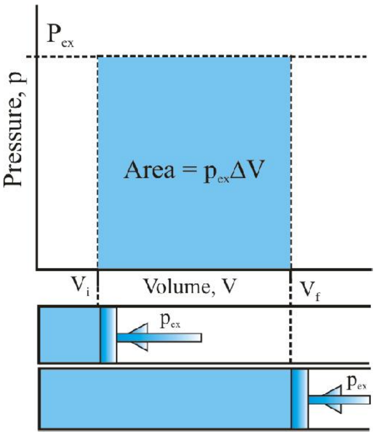
A quasi static state means that the system seems to be static at all intervals of time but actually is not. The motion is so slow that it is almost impossible to detect the motion and the system seems to be in equilibrium with the surroundings at all instants of time.

11. EXPANSION WORK

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

Always remember, be it expansion or compression we always take the external pressure as the driving force. For a reversible process, $P_{ex} \approx P_{GAS}$ and $w = -\int P_{GAS} dV$.

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



NOTE

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

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

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

12. CYCLIC PROCESS

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

13. ENTHALPY (H)

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

14. HEAT CAPACITY (C)

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

$C = q/\Delta T$.

14.1 Molar Heat Capacity

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

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

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

$C_p = q_p/n\Delta T$.

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

$C_V = q_V/n\Delta T$.

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

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

15. TYPES OF THERMODYNAMIC PROCESSES

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

15.1 Isothermal Process

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

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

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

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

15.2 Adiabatic Process

These processes are the ones in which the heat exchanged with the surroundings is zero. Such processes are defined by the equation

$TV^{\gamma-1}$ = constant, $T^{\gamma}P^{1-\gamma}$ = constant, PV^{γ} = constant.

$q = 0 \quad \Rightarrow \quad w = \Delta U$

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

$\Delta H = nC_P\Delta T$

15.3 Isochoric Process

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

$w = 0$

$\Delta U = nC_V\Delta T = q_V \qquad \Delta H = nC_P\Delta T$

15.4 Isobaric Process

These are the processes in which the pressure remains constant.

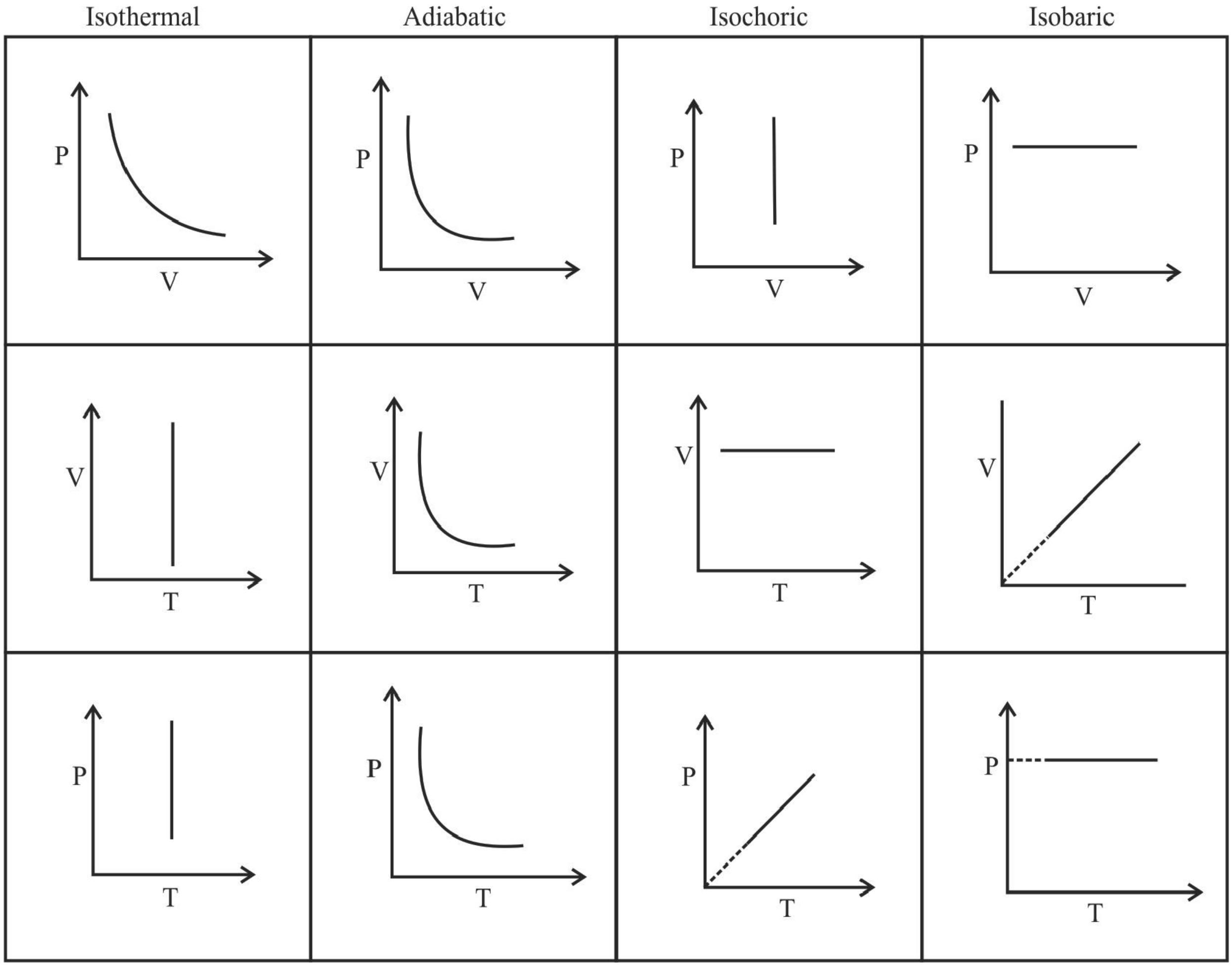
$w = -P\Delta V = -nR\Delta T$

$\Delta U = nC_V\Delta T$

$\Delta H = nC_P\Delta T$

NOTE

All these processes are happening on a system containing an ideal gas therefore we can apply $PV = nRT$ at any stage that we find suitable.



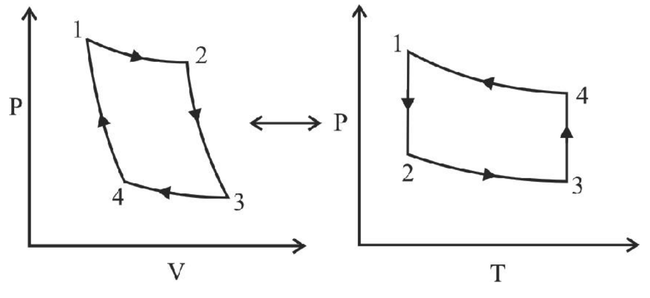
NOTE

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

16. GRAPH TRANSFORMATION

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

1. Identify the type of curve given, whether it is P-V, V-T or P-T graph.
2. Then, Identify every step of the process
3. Then one by one convert every step into the required graph bearing in mind critical points like, an expansion process will remain an expansion process and so on.
4. A cyclic process should remain cyclic whichever graph we make.



Note : From the given P–V graph.

Process 1→2 is isothermal expansion; 2→3 adiabatic expansion; 3→4 isothermal compression & 4→1 adiabatic compression.

17. IRREVERSIBLE PROCESS

For an irreversible process the work done is given by $W = -\int P_{EXT}dV$. We cannot take the external pressure to be equal to the pressure of the gas in these processes.

18. FREE EXPANSION

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

19. POLYTROPIC PROCESS

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

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

20. NEED FOR SECOND LAW

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

21. TYPES OF PROCESSES

21.1 Spontaneous processes

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

21.2 Non-Spontaneous processes

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

22. CONCEPT OF ENTROPY

- Matter has a natural tendency to get disordered or randomised
- Energy has a tendency to become disordered or dispersed.

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

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

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

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

(for a sponataneous change)

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

22.1 Entropy changes in a Thermodynamic Process

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

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

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

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

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

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

22.2 Important points to Remember

1. Entropy of a system remains constant in a reversible adiabatic process. Therefore, it is also known as **"isentropic process".**
2. Entropy of an ideal gas will always increase in isothermal expansion.
3. In a reversible adiabatic process the entropy of both system and surroundings remains the same and there is no overall change in entropy as well.

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

4. In a reversible isothermal expansion the entropy of surroundings will always decrease to balance the increase in system's entropy to make the overall entropy constant.
5. In free expansion the entropy of the system always increases and that of surrounding remains constant. Free expansion is both isothermal and adiabatic and is irreversible.

23. GIBB'S FREE ENERGY

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

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

24. THERMOCHEMICAL EQUATION

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

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

24.1 Endothermic Reactions

Are those chemical reactions which absorb energy.

(ΔH = positive)

24.2 Exothermic Reactions

Are those chemical reactions which release energy.

(ΔH = negative)

For a chemical reaction, $\Delta H_{REACTION} = H_{PRODUCTS} - H_{REACTANTS}$

The change in enthalpy during a chemical reaction occurs due to breaking and making of bonds.

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

25. ENTHALPY OF REACTIONS

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

25.1 Enthalpy of Formation ΔH_f^0

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

ΔH_f^0 (O_2, g) = 0
ΔH_f^0 (C, graphite) = 0
ΔH_f^0 (Br_2, l) = 0
ΔH_f^0 (S, Rhombic) = 0
ΔH_f^0 (P, white) = 0
ΔH_f^0 (H^+, aq) = 0

25.2 Enthalpy of Combustion

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

$$\mathbf{CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g) \quad \Delta H = -890 \text{ kJ/mol}}$$

25.3 Enthalpy of Solution

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

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

$$\mathbf{\Delta H^0_{Sol} = -91.211 \text{ kJ/mol}}$$

25.4 Enthalpy of Hydration

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

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

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

25.5 Enthalpy of Neutralization

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

$$\mathbf{H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)}$$

$$\mathbf{\Delta H_R = -57.3 \text{ kJ/mol}}$$

26. HESS LAW OF CONSTANT HEAT SUMMATION

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

27. BORN HABER CYCLE

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

28. BOND DISSOCIATION ENTHALPY

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

29. HEAT OF ATOMIZATION

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

30. RESONANCE ENERGY

Many compounds exhibit resonance. Due to resonance they exist in a structure which is different from the expected one and more stable.

Resonance energy = ΔH^0_f(actual) – ΔH^0_f(calculated)

SOLVED EXAMPLE

Example : 1

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

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

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

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

$w = -5\text{ kJ}$

$\therefore$ According to first law of thermodynamics, $\Delta U = q + w = 15 + (-5) = \mathbf{10\ kJ}$

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

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

$q = -5\text{ kJ}$

$\therefore$ According to first law of thermodynamics, $\Delta U = q + w = -15 + (+5) = \mathbf{-10\ kJ}$

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

Example : 2

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

Sol. For isothermal reversible expansion of an ideal gas, $w = -2.303\ nRT \log \frac{V_2}{V_1}$ Putting $n = 0.75$ mol, $V_1 = 15$ L, $V_2 = 25$ L, $T = 27 + 273 = 300$ K and $R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$, we get

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

(–ve sign represents work of expansion)

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

$\therefore \Delta U = q + w$ gives $q = -w = \mathbf{+955.5\ J.}$

Example : 3

Carbon monoxide is allowed to expand isothermally and reversibly from 10 m³ to 20 m³ at 300 K and work obtained is 4.754 kJ. Calculate the number of moles of carbon monoxide.

Sol. $w = -2.303\ n RT \log \frac{V_2}{V_1}$

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

This given n = **2.75 moles.**

Example : 4

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

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

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

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

$$w_{\text{exp}} = -P\Delta V = -1 \times 241.3\text{ L atm} = -241.3 \times 101.3\text{ J}$$

$$= \mathbf{-24443.7\ J.}$$

Example : 5

Two moles of an ideal gas initially at 27°C and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas is 10 atm. Calculate q, w and ΔU for the process.

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

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

$$300\text{ K} \times \log \frac{1}{10} = \mathbf{11488\ J}$$

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

Further, $\Delta U = q + w \therefore \mathbf{q = -w = -11488\ J.}$

Example : 6

10g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10L to 5L. Calculate q, W, ΔU and ΔH for this process. $R = 2.0\text{ cal K}^{-1}\text{ mol}^{-1}$. $\log_{10} 2 = 0.30$ Atomic wt. of Ar = 40

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

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

W = 103.991 cal

$\Delta U = 0$; $\Delta H = 0$ (Constant temperature)

$\because q = \Delta U - W \quad \therefore q = -W =$ **– 103.991 cal**

Example : 7

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

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

Given, $\Delta V = (6 - 2) = 4$ litre; $P = 1$ atm

$\therefore W = -1 \times 4$ litre-atm $= -4 \times 1.01325 \times 10^2$ J

$= 405.3$ J

Now from first law of thermodynamics

$q = \Delta U - W$

$800 = \Delta U + 405.3 \quad \therefore \Delta U =$ **394.7 Joule**

Example : 8

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

Sol. For an isothermal irreversible expansion :

$\Delta U = \Delta H = 0$

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

V_2 and V_1 can be calculated from ideal gas equation.

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

$V_2 = nRT/P_2 = 124.7\ m^3$

Therefore, $w = -100 \times (124.5 - 24.9)$

= – 9980 J

q = + 9980 J

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

$\Delta U = \Delta H = 0$ (temperature is constant)

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

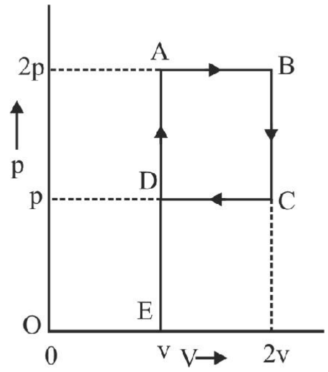
$= -5 \times 8.314 \times 300 \times ln\,5$

= – 20071.3 J

q = + 20071.3 J

Example : 9

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



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

Sol. **State A to State B** (Isobaric expansion)

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

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

State B to State C (Isochoric process)

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

$\therefore W_2 = 0\ (\because \Delta V = 0)$

State C to State D (Isobaric compression)

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

$\therefore W_3 = -p\,(v - 2v) = pv$

State D to State A (Isochoric process)

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

$\therefore W_4 = 0\ (\because \Delta V = 0)$

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

or $W = -2pv + 0 + pv + 0 = \mathbf{-pv}$ (= area ABCD)

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

$\therefore\ q = -w \Rightarrow \mathbf{q = +pv}$

where q is the heat absorbed in the cylic process.

Example : 10

Two mole of a perfect gas undergo the following processes:

(a) a reversible isobaric expansion from (1.0 atm, 20.0L) to (1.0 atm, 40.0L).

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

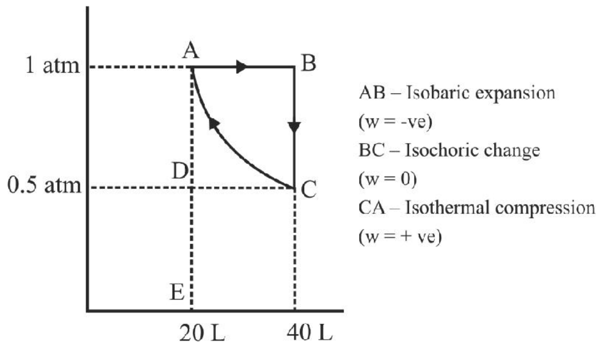
(c) a reversible isothermal compression from (0.5 atm, 40.0L) to (1.0 atm, 20.0L).

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

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

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

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



Now, total work $W = W_{A\to B} + W_{B\to C} + W_{C\to A}$

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

$= -1(40 - 20) = -20\text{L atm}$

$= -20 \times 1.01325 \times 10^2\ \text{J}$

$= -2026.5\ \text{J}$

$W_{BC} = O$ (Isochoric)

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

n = 2 mol.

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

PV = nRT

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

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

$= 1404.07\ \text{J}$

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

$\mathbf{= -622.43\ J}$

For cyclic process : $\mathbf{\Delta U = 0}$

$\Rightarrow\quad q = -w$

$\mathbf{q = +622.43\ J}$

Example : 11

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

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

(ii) One mole of a gas is allowed to expand from a volume of 1 litre to a volume of 5 litres against the constant external pressure of 1 atm (1 litres atm = 101.3 J) Calculate the internal energy change (ΔU) in each case if the process were carried out adiabatically.

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

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

For adiabatic process, $q = 0\ \therefore\ \mathbf{\Delta U} = q + w = 0 + 0 = \mathbf{0.}$

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

$P = 1\ \text{atm}\ \therefore\ w = -P\Delta V$

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

$= -4 \times 101.3\ \text{J} = \mathbf{-405.2\ J}$ (1 L – atm = 101.3J)

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

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

Example : 12

5.6 dm³ of an unknown gas at S.T.P. required 52.25 J of heat to raise its temperature by 10°C at constant volume. Calculate C_v, C_p and γ of the gas

Sol. The 22.4 dm³ of a gas at S.T.P. = 1 mol

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

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

∴ For 1° rise, 1 mol of the gas at constant volume will

$$\text{require heat} = \frac{52.25}{10 \times 0.25} = 20.9$$

$\therefore$ **$C_v = 20.9\ \text{J K}^{-1}\ \text{mol}^{-1}$**

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

$$\therefore \qquad \gamma = \frac{C_p}{C_v} = \frac{29.214}{20.9} = \mathbf{1.4}$$

Example : 13

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

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

(ii) the entropy change in the surroundings

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

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

Sol. $T_{system} = 130^\circ\text{C} = 130 + 273\ \text{K} = 403\ \text{K}$, $T_{surr} = 32^\circ\text{C} = 32 + 273\ \text{K} = 305\ \text{K}$ $q_{system} = -340\ \text{J}$, $q_{surr} = +340\ \text{J}$

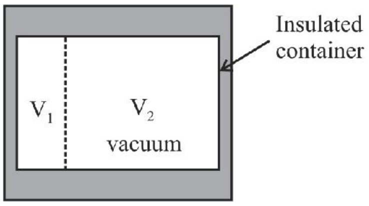
$$\text{(i) } \Delta S_{system} = \frac{q_{system}}{T_{system}} = \frac{-340\,\text{J}}{403\,\text{K}} = \mathbf{-0.84\,JK^{-1}}$$

$$\text{(ii) } \Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{+340\,\text{J}}{305\,\text{K}} = \mathbf{+1.11\ J\,K^{-1}}$$

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

Example : 14

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



Sol. This is a process of adiabatic free expansion of an ideal gas. The internal energy does not change thus the temperature also stays the same, i.e., the final temperature is still T.

$$\Delta S_{system} = nR \ln \frac{V_1 + V_2}{V_1} > 0 \quad \because\ V_1 + V_2 > V_1$$

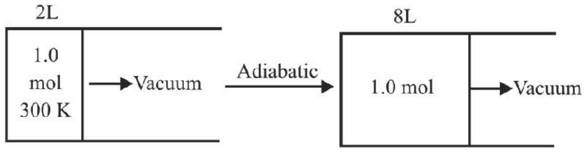
$$\Delta S_{surr} = 0 \quad \because\ q_{surr.} = 0$$

$$\Rightarrow\ \mathbf{\Delta S_{univ} > 0}$$

Example : 15

1.0 mol of an ideal gas, initially present in a 2.00 L insulated cylinder at 300 K is allowed to expand against vacuum to 8.00 L. Determine W, ΔE, ΔH, ΔS_{univ} and ΔG.

Sol.



$$W = -p_{ext}\,\Delta V = 0,\ q = 0, \quad \Rightarrow \Delta E = 0 = \Delta H$$

$$\Rightarrow \qquad T_f = 300\ \text{K}$$

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

$$\Delta S_{surr} = 0 \qquad \because\ q_{sys} = q_{surr} = 0$$

$$\Rightarrow \Delta S_{univ} = 11.52\ \text{JK}^{-1}$$

$$\Rightarrow \Delta G = -T\Delta S_{univ} = -300 \times 11.52 = \mathbf{-3456\ J/mol.}$$

Example : 16

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

Sol. The reaction is:

$$C_6H_6(\ell)+7\frac{1}{2}O_2(g)\longrightarrow 6CO_2(g)+3H_2O(\ell)$$

In this reaction, O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$$\therefore \quad \Delta n_g = n_p - n_r = 6-7\frac{1}{2} = -1\frac{1}{2} = -\frac{3}{2}$$

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

$T = 25^\circ C = 298 K$

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

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

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

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

Example : 17

Calculate the amount of heat evolved when

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Hence, heat evolved = 57.1 × 0.08 = **4.568 kJ**

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

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

Assuming density of solution = 1g/mL

So mass of solution = 700g

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

$$Q = m\times C\times \Delta T \quad \therefore\ \Delta T = \frac{Q}{m\times C} = \frac{2284}{700\times 4.18} = \mathbf{0.78^\circ C}$$

In case (ii), heat produced = 4.568 kJ = 4568 J

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

$$\therefore \quad \Delta T = \frac{Q}{m\times C} = \frac{4568}{600\times 4.18} = \mathbf{1.82^\circ C}$$

Example : 18

Calculate the enthalpy change accompanying the transformation of C (graphite) to C(diamond). Given that the enthalpies of combustion of graphite and diamond are 393.5 and 395.4 kJ mol^{-1} respectively.

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

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

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

We aim at $C(\text{graphite}) \longrightarrow C(\text{diamond}), \Delta_{\text{trans}} H^{\circ} = ?$

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

$$C(\text{graphite} - C(\text{diamond}) \longrightarrow 0;$$

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

or $C(\text{graphite}) \longrightarrow (\text{diamond})\ ;\ \Delta_{\text{trans}} H = +1.9 \text{ kJ}$

Example : 19

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

Sol. We are given

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

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

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

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

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

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

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

Example : 20

Calculate the enthalpy of formation of methane, given that the enthalpies of combustion of methane, graphite and hydrogen are 890.2 kJ, 393.4 kJ and 285.7 kJ mol^{-1} respectively.

Sol. Remember : Enthalpy of combustion is always negative.

We are given :

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

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

(iii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,\ \Delta H = -285.7 \text{ kJ mol}^{-1}$

We aim at : $C + 2H_2 \longrightarrow CH_4, \Delta H = ?$

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

$$C + 2H_2 \longrightarrow CH_4,$$

$$\Delta H = -393.4 + 2(-285.7)$$

$$-(-890.2) \text{ kJ mol}^{-1} = -74.6 \text{ kJ mol}^{-1}$$

Hence, the heat of formation of methane is :

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

Example : 21

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

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

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

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

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

(v) $KCl\,(s) + aq \longrightarrow KCl\,(aq)$, $\Delta H = +18.4$ kJ mol^{-1}

Sol. We aim at : $K(s) + \frac{1}{2}Cl_2\,(g) \longrightarrow KCl(s),\ \Delta_f H = ?$

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

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

$$K\,(s) + \frac{1}{2}Cl_2\,(g) + H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow KCl(s) +$$

$$HCl\,(aq) + KOH\,(aq) - KCl\,(aq)$$

$$\Delta H = -487.4 + (-164.4) - (18.4) = -670.2 \text{ kJ mol}^{-1} \ldots \text{(vii)}$$

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

$$K(s) + \frac{1}{2}Cl_2\,(g) \longrightarrow KCl(s);$$

$\Delta_f H = -670.2 + 57.3 - (-286.2) = \mathbf{-441.3\ kJ}$

Example : 22

The combustion of 1 mole of benzene takes place at 298 K and 1 atm. After combustion, CO_2 (g) and H_2O (*l*) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\circ$ of benzene. Standard enthalpies of formation of CO_2 (g) and H_2O (*l*) are – 393.5 kJ mol^{-1} and –285.83 kJ mol^{-1} respectively.

Sol. Aim : $6\,C\,(s) + 3\,H_2\,(g) \longrightarrow C_6H_6\,(\ell), \Delta H = ?$

Given :

(i) $C_6H_6\,(l) + \frac{15}{2}\,O_2\,(g) \longrightarrow 6\,CO_2\,(g) + 3\,H_2O\,(l), \Delta H$

$= -3267.0\ kJ\ mol^{-1}$

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

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

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

$$6C\,(s) + 3H_2\,(g) \longrightarrow C_6H_6\,(l);$$

$$\Delta H = 6\,(-393.5) + 3\,(-285.83) - (-3267.0)$$

$$= -2361 - 857.49 + 3267.0 = 48.51\ kJ\ mol^{-1}$$

Thus, the enthalpy of formation of benzene is $\mathbf{\Delta_f H = -48.51\ kJ\ mol^{-1}}$

Example : 23

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

Sol. We are given :

(i) $C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g),\ \Delta H_1^\circ = -393.5\ kJ\ mol^{-1}$

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

(iii) $2C\,(s) + 2H_2\,(g) \longrightarrow C_2H_4(g),\ \Delta H_3^\circ = +52.3\ kJ\ mol^{-1}$

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

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

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

Example : 24

Given the following thermochemical equations:

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

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

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

Sol. We aim at

S (rhombic) → S (monoclinic), ΔH = ?

Equation (i) → Equation (ii) gives

$S(rhombic) - S(monoclinic) \longrightarrow 0,$

$\Delta H = 297.5 - (-300.0) = 2.5\ kJ\ mol^{-1}$

or $S(rhombic) \longrightarrow S(monoclinic), \mathbf{\Delta H = +2.5\ kJ\ mol^{-1}}$

Thus, for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur, 2.5 kJ mol^{-1} of heat is absorbed.

Example : 25

Enthalpy of solution (ΔH) for $BaCl_2.2H_2O$ and $BaCl_2$ are 8.8 and –20.6 kJ mol^{-1} respectively. Calculate the heat of hydration of $BaCl_2$ to $BaCl_2.2H_2O$.

Sol. We are given

(i) $BaCl_2.2H_2O(s) + aq \longrightarrow BaCl_2(aq), \Delta_{sol}\ \Delta H_1^\circ = 8.8 kJ mol^{-1}$

(ii) $BaCl_2\,(s) + aq \longrightarrow BaCl_2(aq), \Delta_{sol}\ \Delta H_2^\circ = -20.6\ kJ\ mol^{-1}$

We aim at

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

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

Example : 26

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

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

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

(iii) $C_2H_6(g)+3\frac{1}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l), \Delta H$

$=-1560.6\,kJ\,mol^{-1}$

We aim at: $C_2H_4+H_2(g)\longrightarrow C_2H_6(g), \Delta H=?$

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

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

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

Example : 27

The thermite reaction used for welding of metals involves the reaction

$2\,Al(s)+Fe_2O_3(s)\longrightarrow Al_2O_3(s)+2Fe(s)$

What is ΔH° at 25°C for this reaction ? Given that the standard heats of formation of Al_2O_3 and Fe_2O_3 are – 1675.7 kJ and –828.4 kJ mol^{-1} respectively.

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

$\Delta_r H$ = Sum of $\Delta_f H^\circ$ of products – Sum of $\Delta_f H^\circ$ of reactants

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

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

Example : 28

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

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

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

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

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

Sol. (a) From the given equation.

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

∴ 445.15 kJ of heat is produced from **8 g of CH_4**

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

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

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

= 44.8 litres at STP

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

Example : 29

From the thermochemical equation,

$$C_6H_6(\ell)+7\frac{1}{2}O_2(g)\longrightarrow 3H_2O(\ell)+6CO_2(g),$$

$\Delta_c H=-3264.64$ kJ mol^{-1},

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

Sol. From the given equation,

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

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

Example : 30

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

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

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

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(1);$$

$$\Delta H=-285.9\text{ kJ mol}^{-1}$$

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

(b) Determine ΔH for the reaction :

$Al_2O_3(s)\longrightarrow 2Al(s)+1\frac{1}{2}O_2(g)$.

Sol. (a) From the first given equation, 2 moles of Al (i.e., 2 × 27 g = 54 g) on combustion give heat = 1667.8 kJ

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

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

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

Thus, **H_2 is a better rocket fuel.**

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

$$Al_2O_3(s) \longrightarrow 2Al(s) + 1\frac{1}{2}O_2(g); \Delta H = +1667.8 \text{ kJ mol}^{-1}$$

Thus, for the reaction given in part (b) of the problem, **$\Delta H = +1667.8$ kJ mol^{-1}**

Example : 31

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

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

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

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

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

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

i.e., Enthalpy of fusion (Δ_{fus} H) **= + 19072 joules/mole**

Example : 32

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

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

$= -2840$ kJ mol^{-1}

What is the energy requirement for production of 0.36 g of glucose by the reverse reaction ?

Sol. The given equation is :

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

$$\Delta_r H = -2840 \text{ kJ mol}^{-1}$$

Writing the reverse reaction, we have

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

$$\Delta_r H = +2840 \text{ kJ mol}^{-1}$$

Thus, for production of 1 mole of $C_6H_{12}O_6$ (= 72 + 12 + 96 = 180 g), heat required (absorbed) = 2840 kJ.

$\therefore$ For production of 0.36 g of glucose, heat absorbed

$= \frac{2840}{180} \times 0.36 = \mathbf{5.68\ kJ}$

Example : 33

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

Sol. Here, we are given

$$C(s) + 2H_2(g) \longrightarrow CH_4(g), \Delta_r H^\circ = -74.8 \text{ kJ}$$

$$\Delta H = e_{sub(C)} + 2e_{H-H} - 4e_{C-H}$$

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

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

Example : 34

Calculate the enthalpy change for the reaction

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

Given that the bond enthalpies of H–H, Br–Br, H–Br are 435, 192 and 364 kJ mol^{-1} respectively.

Sol. $\Delta_r H = \Sigma$ B.E. (Reactants) – Σ B.E. (Products)

= [B.E. (H_2) + B.E. (Br_2)] – 2 B.E. (HBr) =

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

Example : 35

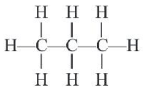
Propane has the structure $H_3C–CH_2–CH_3$. Calculate the change in enthalpy for the reaction:

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

Given that average bond enthalpies are:

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

Sol.



$$\mathrm{H_3C{-}CH_2{-}CH_3} + 5\ O = O \rightarrow 3\ O = C = O + 4\ H - O - H$$

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

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

$$= \mathbf{– 1662\ kJ\ mol^{-1}}$$

Example : 36

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

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

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

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

Example : 37

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

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

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

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

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

Example : 38

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

Sol. Since the given process is in equilibrium, $\Delta G = 0$

Putting this value in the relationship, $\Delta G = \Delta H – T\Delta S$, we get

$$0 = \Delta H – T\Delta S \text{ or } T\Delta S = \Delta H \text{ or } \Delta S = \frac{\Delta H}{T}$$

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

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

Example : 39

$A + B \longrightarrow C + D$; $\Delta H = – 10{,}000\ J\ mol^{-1}$,

$\Delta S = – 33.3\ J\ mol^{-1}\ K^{-1}$

(i) At what temperature the reaction will occur spontaneously from left to right ?

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

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

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

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

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

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

Example : 40

Calculate the standard free energy change for the reaction,

$4NH_3\,(g) + 5O_2\,(g) \longrightarrow 4NO\,(g) + 6H_2O\,(l)$

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

Sol. Here, we are given

$$\Delta_f G^o\,(NH_3) = -16.8 \text{ kJ mol}^{-1}$$

$$\Delta_f G^o\,(NO) = +86.7 \text{ kJ mol}^{-1}$$

$$\Delta_f G^o\,(H_2O) = -237.2 \text{ kJ mol}^{-1}$$

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

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

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

Example : 41

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

$4\,Fe\,(s) + 3\,O_2\,(g) \longrightarrow 2\,Fe_2O_3\,(s), \Delta H^o = -1648$ kJ mol^{-1}

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

Sol. $\Delta_r S^o = \Sigma\, S^o$(Products) – $\Sigma\, S^o$(Reactants) =

$$2\,S^o(Fe_2O_3) - [4\,S^o\,(Fe) + 3\,S^o\,(O_2)]$$

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

$$-549.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

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

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

$= -1648000 + 163721$ J K^{-1} mol^{-1} =

$$\mathbf{-1484279\ J\ K^{-1}\ mol^{-1}}$$

As ΔG^o is –ve, the reaction is spontaneous.

Example : 42

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

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

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

(iii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(\ell); \Delta_f\ H^o = $ **– 286 kJ mol^{-1}.**

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

$$\Delta_f\ H^o = ?$$

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

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

Example : 43

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

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

(ii) $H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O(\ell),$

$\Delta_r\ H^o = -285.8$ kJ mol^{-1}

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

$\Delta_r\ H^o = -890.3$ kJ mol^{-1}

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

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

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

or $C(s) + 2H_2(g) \longrightarrow CH_4(g); \Delta_f H^o = -74.8\ \text{kJ mol}^{-1}$

Hence, enthalpy of formation of methane is :

$$\mathbf{\Delta_f H^o = -74.8\ kJ\ mol^{-1}}$$

Example : 44

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

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

(ii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow (g);\ \Delta_r H^o = -283.0\ \text{kJ mol}^{-1}$

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

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

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

$$\Delta_r H^o = -393.5 - (-283.0) = -110.5\ \text{kJ mol}^{-1}$$

or $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta_r H^o = -110.5\ \text{kJ.}$

$\therefore$ Heat of formation of CO is : $\mathbf{\Delta_f H^o = -110.5\ kJ\ mol^{-1}}$

Example : 45

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

Sol. The given reaction is :

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

Hence, $\Delta G^o = 3 \times G_f^0(Na_2O) - G_f^0(Al_2O_3)$

(G^o for Na and $Al = 0$)

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

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

Example : 46

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

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

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

$$\Delta n = 6 - \frac{15}{2} = -\frac{3}{2}$$

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

Now, $\Delta H = \Delta U + \Delta nRT$

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

$\mathbf{\Delta H = -3273.735\ kJ}$

Example : 47

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

Sol. We have to find ΔH for

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

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

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

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2;\ \Delta H = -1108.76\ \text{kJ}$ .... (3)

Multiply Eq. (2) by 2 and add in Eq. (1)

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

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

$C + 2S \rightarrow CS_2;$ $\Delta H = +128.02\ \text{kJ}$

$\mathbf{\Delta H_f\ of\ CS_2 = +128.02\ kJ}$

Example : 48

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

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

$-1100 = 275 + 6(80) - 6e_{S-F}$

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

Example : 49

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

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

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

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

(iii) $H_2(g) + 1/2\,O_2(g) \rightarrow H_2O\,(l)$ $\Delta_r H_3 = -286$ kJ mol^{-1}

Sol. AIM : $12C(s) + 11\,H_2(g) \rightarrow C_{12}H_{22}O_{11}(s)$ $\Delta H = ?$

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

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

$= -2218$ kJ/mol

Example : 50

The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25ºC are – 156 and + 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25ºC is – 119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene.

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

ΔH_f() – ΔH_f()

$= -156 - (+49)$ kJ

$= -205$ kJ.

Given, that,

 $+ H_2 \rightarrow$  $\Delta\,;H = -119$ kJ

Theoretical enthalpy of formation of 3 double bonds in benzene ring

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

$\therefore$ resonance energy of benzene $= -357 - (-205)$ kJ

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

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

State Function

1. Which of the following is not a state function ?

(a) Heat (b) Internal energy

(c) Enthalpy (d) Entropy

2. Which of the following quantities is not a state function ?

(a) Temperature (b) Entropy

(c) Enthalpy (d) Work

Extensive/Intensive

3. Which of the following is not an intensive property ?

(a) Entropy (b) Pressure

(c) Temperature (d) Molar volume

4. Which of the following is a state function and also an extensive property?

(a) Internal energy (b) Pressure

(c) Molar heat capacity (d) Temperature

System

5. Warming ammonium chloride with sodium hydroxide in a test tube is an example of :

(a) Closed system (b) Isolated system

(c) Open system (d) None of these

6. A tighly closed thermoflask contains some ice cubes. This constitutes

(a) closed system (b) open system

(c) isolated system

(d) Non-thermodynamic system

Internal Energy

7. A sample of gas changes from p_1, V_1 and T_1 to p_2, V_2 and T_2 by one path and then back to p_1, V_1 and T_1, ΔU for the process is :

(a) Infinite (b) > 0

(c) < 0 (d) equal to 0

8. Which of the following changes would definitely increase the internal energy of a system?

(a) The system gains heat and performs work.

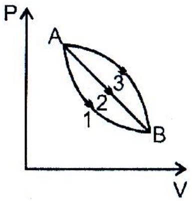
(b) The system gains heat and has work performed on it.

(c) The system loses heat and performs work.

(d) The system loses heat and has work performed on it.

PV-Work

9. A given mass of gas expands from the state A to the state B by three paths 1, 2 and 3 as shown in the figure. If w_1, w_2 and w_3 respectively be the magnitudes work done by the gas along three paths then :

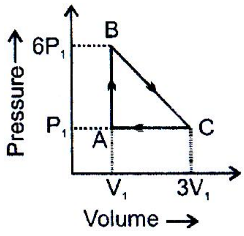


(a) $w_1 > w_2 > w_3$ (b) $w_1 < w_2 < w_3$

(c) $w_1 = w_2 = w_3$ (d) $w_2 < w_3 < w_1$

10. An ideal gas is taken around the cycle ABCA as shown in P-V diagram

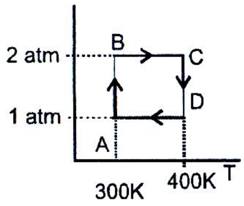
The net work done by the gas during the cycle is equal to :



(a) $12\,P_1V_1$ (b) $6P_1V_1$

(c) $5P_1V_1$ (d) P_1V_1

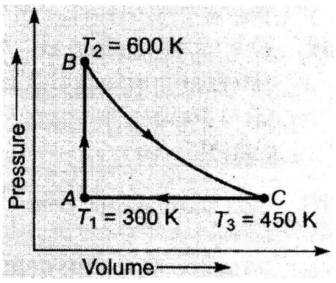
11. Two moles of Helium gas undergo a reversible cyclic process as shown in figure. Assuming gas to be ideal. What is the work for the process C to D ?



(a) $-800\,R\ell n2$ (b) zero

(c) $+200\,R\ell n2$ (d) $-600\,R\ell n2$

12. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in figure, the amount of heat added in the process AB and heat removed in the process CA are:



(a) $q_{AB} = 450$ R and $q_{CA} = -450$ R

(b) $q_{AB} = 450$ R and $q_{CA} = -225$ R

(c) $q_{AB} = 450$ R and $q_{CA} = -375$ R

(d) $q_{AB} = 375$ R and $q_{CA} = -450$ R

First Law

13. A system absorb 10 kJ of heat at constant volume and its temperature rises from 27°C to 37°C. The value of ΔU is

(a) 100 kJ (b) 10 kJ

(c) 0 (d) 1 kJ

14. An ideal gas receives 10 J of heat in a reversible isothermal expansion. Then the work done by the gas :

(a) would be more than 10 J

(b) 10 J

(c) would be less than 10 J

(d) cannot be determined

15. As per the First Law of thermodynamics, which of the following statement would be apropriate :

(a) Energy of the system remains constant

(b) Energy of the surroundings remains constant

(c) Entropy of the universe remains constant

(d) Energy of the universe remains constant

16. What is the change in internal energy when a gas contracts from 377 mL to 177 mL under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat?

(a) 40.52 J (b) –83.48 J

(c) –248 J (d) None of these

17. A sample of liquid in a thermally insulated container (a calorimeter) is stirred for 2 hr. by a mechanical linkage to a motor in the surrounding, for this process;

(a) $w < 0; q = 0; \Delta U = 0$ (b) $w > 0; q > 0; \Delta U > 0$

(c) $w < 0; q > 0; \Delta U = 0$ (d) $w > 0; q = 0; \Delta U > 0$

18. For a particular process $q = -10$ kJ and w=25 kJ. Which of the following statements is true?

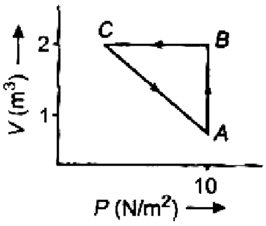
(a) Heat flows from the surroundings to the system.

(b) The system does work on the surroundings.

(c) $\Delta E = -35$ kJ

(d) None of the above is true

19. An ide al gas is taken through the cycle $A \to B \to C \to A$ as shown in fig. If the net heat supplied to the gas in cycle is 5 J, the work done by the gas in the process $C \to A$.



(a) –5 J (b) –10 J

(c) –15 J (d) –20 J

20. In a system where $\Delta E = -51.0$ kJ, a piston expanded against a p_{ext} of 1.2 atm giving a change in volume of 32.0 L. What was the change in heat of this system?

(a) –36 kJ (b) –13 kJ

(c) –47 kJ (d) 24 kJ

Isothermal Process

21. In an isothermal expansion of an ideal gas

(a) $q = 0$ (b) $\Delta V = 0$

(c) $\Delta U = 0$ (d) $w = 0$

22. The maximum work obtained by an isothermal reversible expansion of 1 mole of an ideal gas at 27°C from 2.24 to 22.4 L is (R = 2 cal)

(a) – 1381.8 cal (b) – 600 cal

(c) –138.18 cal (d) – 690.9 cal

23. 2 mole of an ideal gas at 27°C expands isothermally and reversibly from a volume of 4 litres to 40 litre. The work done (in kJ) is:

(a) w = –28.72 kJ (b) w = –11.488 kJ

(c) w = –5.736 kJ (d) w = –4.988 kJ

24. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. w_{irr} at 300 K is:

(a) –15.921kJ (b) –11.224 kJ

(c) –110.83 kJ (d) None of these

25. 10 mole of ideal gas expand isothermally and reversibly from a pressure of 10 atm to 1 atm at 300 K. What is the largest mass which can lifted through a height of 100 meter?

(a) 31842 kg (b) 58.55 kg

(c) 342.58 kg (d) None of these

Processes

26. Which of the following statement is true?

(a) A thermodynamic process is defined by initial and final states.

(b) $\Delta E=0$ for a reversible phase change at constant T and P.

(c) q must be zero for an isothermal process.

(d) A reversible adiabatic process is also isentropic.

27. In the thermodynamic sense of the word, an irreversible process

(a) does the same work (but of opposite sign) as a reversible process

(b) violates the 1st law of thermodynamics, unlike a reversible process

(c) involves non-ideal gases (as opposed to ideal gases in a reversible process)

(d) exchanges the same amount of heat (but of opposite sign) as a reversible process.

28. The temperature of the system decreases in an

(a) Isothermal compression (b) Isothermal expansion

(c) Adiabatic compression (d) Adiabtic expansion

First Law

29. For a chemical reaction at constant P and V, ΔH is equal to

(a) ΔU (b) zero

(c) $\Delta U + P\Delta V$ (d) p/T

Adiabatic Process

30. In an adiabatic expansion of an ideal gas

(a) $\Delta T = 0$ (b) $w = 0$

(c) $q = 0$ (d) $\Delta U = 0$

31. 1 mole of NH_3 gas at 27°C is expanded in reversible adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done by the gas respectively are :

(a) 150 K, 900 cal (b) 150 K, 400 cal

(c) 250 K, 1000 cal (d) 200 K, 800 cal

32. During the adiabatic expansion of an ideal gas against atmospheric pressure, the internal energy will

(a) Increase (b) decrease

(c) stay the same (d) Impossible to say

33. One mole of an ideal gas expands reversibly and adiabatically from a temperature of 27°C. If the work done during the process is 3 kJ, then final temperature of the gas is:($C_V = 20$ J/K)

(a) 100 K (b) 150 K

(c) 195 K (d) 255 K

Heat Capacities

34. 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 J K^{-1} mol^{-1}

35. Ice–Water mass ratio is maintained as 1 : 1 in a given system containing water in equilibrium with ice at constant pressure. If C_P (ice) = C_P (water) = 4.18 J mol^{-1} K^{-1} molar heat capacity of such a system is

(a) Zero (b) Infinity

(c) 4.182 JK^{-1} mol^{-1} (d) 75.48 JK^{-1} mol^{-1}

2nd Law

36. The statement "A heat engine always loses some of its heat energy to the surroundings." is an example of which of the following laws?

(a) The Law of Corresponding States

(b) The Zeroth Law of Thermodynamics

(c) The First Law of Thermodynamics

(d) The Second Law of Thermodynamics

37. Heat cannot by self flow from a body at lower temperature to a body at higher temperature a statement of consequence of:

(a) 1st law of thermodynamics

(b) 2nd law of thermodynamics

(c) conservation of momentum

(d) conservation of mass

38. When steam condenses to water at 90°C, the entropy of the system decreases. What must be true if the second law of thermodynamics is to be satisfied?

(a) Entropy of the universe also decreases.

(b) Entropy of the surroundings also decreases.

(c) Entropy of the surroundings increases to same extent to which entropy of the system decreases.

(d) Increase in entropy in the surroundings is greater than decrease in entropy of the system.

Entropy

39. The entropy of the universe

(a) tends towards a maximum

(b) tends towards a minimum

(c) tends to be zero (d) remains constant

40. Which of the following has highest entropy ?

(a) Mercury (b) Hydrogen

(c) Water (d) Graphite

41. Which of the following processes is not accompanied by increase of entropy ?

(a) dissolution of NH_4Cl in water

(b) burning of rocket fuel

(c) sublimation of dry ice

(d) condensing steam

42. For a reversible process at equilibrium, the change in entropy may be expressed as :

(a) $\Delta S = Tq_{rev}$ (b) $\Delta S = \frac{q_{rev}}{T}$

(c) $\Delta S = -\frac{\Delta H}{T}$ (d) $\Delta S = \Delta G$

43. Entropy is a measure of

(a) disorder (b) internal energy

(c) efficiency

(d) useful work done by the system

44. When a solid is converted directly into gaseous state, the process is called sublimation. The entropy change during the process is :

(a) zero (b) negative

(c) positive (d) may be negative or zero

45. The enthalpy of vaporisation of a substance is 8400 J mol^{-1} and its boiling point is –173ºC. The entropy change for vaporisation is :

(a) 84 J mol^{-1} K^{-1} (b) 21 J mol^{-1} K^{-1}

(c) 49 J mol^{-1} K^{-1} (d) 12 J mol^{-1} K^{-1}

46. The enthalpy of vaporisation of a compound AB at its boiling point (127°C) is 6.4 kJ mol^{-1}. Its entropy of vaporisation is :

(a) 2.56 kJ mol^{-1} (b) 16 J mol^{-1}

(c) 16×10^{-3} J mol^{-1} (d) 1.6×10^{3} kJ mol^{-1}

47. The entropy change for the conversion of 1 mol of α–tin (at 13°C, 1 atm) to 1 mol of β–tin (13°C, 1 atm), if enthalpy of transition is 2.095 kJ mol^{-1} is :

(a) 7.32 J mol^{-1} K^{-1} (b) 14.62 J K^{-1} mol^{-1}

(c) 56.3 J mol^{-1} K^{-1} (d) 0

48. The following data is known about the melting of a compound AB. $\Delta H = 9.2$ kJ mol^{-1}. $\Delta S = 0.008$ kJ K^{-1} mol^{-1}. Its melting point is :

(a) 736 K (b) 1050 K

(c) 1150 K (d) 1150°C

49. When two mole of an ideal gas $\left(C_{p,m.} = \frac{5}{2}R\right)$ heated from 300 K to 600 K constant pressure. The change in entropy of gas (ΔS) is :

(a) $\frac{3}{2}R\,\ell n\,2$ (b) $-\frac{3}{2}R\,\ell n\,2$

(c) $5\,R\,\ell n\,2$ (d) $\frac{5}{2}R\,\ell n\,2$

50. In the above question calculate ΔS_{gas} if process is carried out at constant volume :

(a) $5\,R\,\ell n\,2$ (b) $\frac{3}{2}R\,\ell n\,2$

(c) $3\,R\,\ell n\,2$ (d) $-3\,R\,\ell n\,2$

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

(a) $\frac{3}{2}R\,\ell n\left(\frac{300}{200}\right)$ (b) $\frac{5}{2}R\,\ell n\left(\frac{573}{273}\right)$

(c) $3R\,\ell n\left(\frac{573}{473}\right)$ (d) $\frac{3}{2}R\,\ell n\left(\frac{573}{473}\right)$

52. If one mole of an ideal gas $\left(C_{p.m.} = \frac{5}{2}R\right)$ is expanded isothermally at 300 K until it's volume is tripled, then change in entropy of gas is :

(a) zero (b) infinity

(c) $\frac{5}{2}R\,\ell n\,3$ (d) $R\,\ell n\,3$

53. When one mole of an ideal gas is compressed to half of its initial volume and simultaneously heated to twice its initial temperature, the change in entropy of gas (ΔS) is :

(a) $C_{p,m} \ln 2$ (b) $C_{v,m} \ln 2$

(c) $R \ln 2$ (d) $(C_{v,m} - R) \ln 2$

54. Two mole of a monoatomic ideal gas is expanded irreversibly and isothermally at T Kelvin until its volume is doubled and q joules heat is absorbed from surrounding. ΔS_{total} (J/K) (system + surrounding) is :

(a) zero (b) $2R\ln 2 - q/T$

(c) $3R\ln 2 - q/T$ (d) $-2R\ln 2 + q/T$

55. One mole of an ideal diatomic gas (C_v = 5 cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. The entropy change of the process can be expressed as (R = 2 calories/mol/K)

(a) $3\ell n\dfrac{298}{373} + 2\,\ell n 10$ (b) $5\ell n\dfrac{373}{298} + 2\,\ell n 10$

(c) $7\ell n\dfrac{373}{298} + 2\,\ell n\dfrac{1}{10}$ (d) $5\ell n\dfrac{373}{298} + 2\,\ell n\dfrac{1}{10}$

Gibbs Energy

56. Which of the following conditions is not favourable for the feasibility of a process ?

(a) $\Delta H = -ve$, $T\Delta S = -ve$ and $T\Delta S < \Delta H$

(b) $\Delta H = +ve$, $T\Delta S = +ve$ and $T\Delta S > \Delta H$

(c) $\Delta H = -ve$, $T\Delta S = +ve$ and $\Delta H > T\Delta S$

(d) $\Delta H = +ve$, $T\Delta S = +ve$ and $\Delta H > T\Delta S$

57. In which of the following cases, the reaction is spontaneous at all temperatures ?

(a) $\Delta H > 0, \Delta S > 0$ (b) $\Delta H < 0, \Delta S > 0$

(c) $\Delta H < 0, \Delta S < 0$ (d) $\Delta H > 0, \Delta S < 0$

58. For an endothermic reaction, ΔS is positive. The reaction is :

(a) feasible when $T\Delta S > \Delta H$

(b) feasible when $\Delta H > T\Delta S$

(c) feasible at all temperatures

(d) not feasible at all

59. When potassium chloride is dissolved in water

(a) Entropy increases (b) Entropy decreases

(c) Entropy increases and then decreases

(d) Free energy increases

60. Which of the following is true for the reaction ?

$H_2O(\ell) \rightleftharpoons H_2O(g)$ at 100°C and 1 atm pressure

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

(c) $\Delta H = \Delta U$ (d) $\Delta H = 0$

61. For a reaction to be spontaneous at all temperatures

(a) ΔG and ΔH should be negative

(b) $\Delta H = \Delta G = 0$

(c) ΔG and ΔH should be positive

(d) $\Delta H < \Delta G$

62. For isothermal expansion in case of an ideal gas :

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

(c) $\Delta G = -T.\Delta S$ (d) None of these

63. A reaction has $\Delta H = -33$ kJ and $\Delta S = +58$ J/K. This reaction would be :

(a) spontaneous below a certain temperature

(b) non-spontaneous at all temperature

(c) spontaneous above a certain temperature

(d) spontaneous at all temperature

Relation b/w ΔH & ΔE

64. For the reaction :

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

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

(c) $\Delta H = \Delta U$ (d) $\Delta H = 0$

65. For which of the following reactions, ΔH is greater than ΔU ?

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

(b) $CH_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

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

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

66. For the reaction,

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

(a) $\Delta H = \Delta U$ (b) $\Delta H > \Delta U$

(c) $\Delta H < \Delta U$ (d) None of these

67. $(\Delta U - \Delta H)$ for the formation of NH_3 from N_2 and H_2 is :

(a) –2 RT (b) 2 RT

(c) RT (d) $\frac{1}{2}$ RT

68. The difference between heats of reaction at constant pressure and constant volume for the reaction.

$2C_2H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C is

(a) –7.43 kJ (b) +3.72 kJ

(c) –3.72 kJ (d) 7.43 kJ

69. For the reaction :

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(\ell)$

at 298 K, $\Delta U = -1415$ kJ.

If $R = 0.0084$ kJ K^{-1}, then ΔH is equal to

(a) –1400 kJ (b) –1410 kJ

(c) –1420 kJ (d) –1430 kJ

70. The difference between ΔH and ΔE on a molar basis for the combustion of methane gas at 300K (kelvin) would be :

(a) zero (b) –RT

(c) –2RT (d) –3RT

71. Consider the reaction at 300 K

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g); \quad \Delta H° = -185$ kJ

If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl. What is $\Delta U°$ for this reaction ?

(a) 0 (b) –185 kJ

(c) 370 kJ (d) –370 kJ

ΔH Reaction

72. The enthalpies of formation of N_2O and NO at 298 K are 82 and 90 kJ mol^{-1}. The enthalpy of the reaction :

$N_2O(g) + ½O_2(g) \longrightarrow 2NO(g)$

(a) –8 kJ (b) 98 kJ

(c) –74 kJ (d) 8 kJ

73. The enthalpies of solution of anhydrous $CuSO_4$ and $CuSO_4.5H_2O$ are –15.89 and 2.80 k cal mol^{-1} respectively. The enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$ is :

(a) –18.69 kcal (b) 13.09 kcal

(c) –13.09 kcal (d) 18.69 kcal

74. Calculate the heat required to make 6.4 Kg CaC_2 from CaO(s) and C(s) from the reaction :

$CaO(s) + 3\,C(s) \longrightarrow CaC_2(s) + CO(g)$ given that

$\Delta_f H^{\circ}(CaO) = -151.6$ kcal, $\Delta_f H^{\circ}(CaC_2) = -14.2$kcal.

$\Delta_f H^{\circ}(CO) = -26.4$ kcal.

(a) 5624 kcal (b) 1.11×10^4 kcal

(c) 86.24×10^3 (d) 1100 kcal

75. Given :

$H_2(g) + ½O_2(g) = H_2O(g) + q_1$

$H_2(g) + ½O_2(g) = H_2O\,(l) + q_2$

The enthalpy of vaporisation of water is equal to

(a) $q_1 + q_2$ (b) $q_1 - q_2$

(c) $q_2 - q_1$ (d) q_1q_2

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

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

The enthalpy change for the reaction :

$CH_3COOH \longrightarrow CH_3COO^- + H^+$ is

(a) x + y (b) x – y

(c) y – x (d) x – y/2

77. The enthalpies of elements in their standard states are taken as zero. Hence the enthalpy of formation of a compound

(a) should always be negative

(b) should always be positive

(c) will be equal to twice the energy of combination

(d) may be positive or negative

78. Which of the following reactions represents enthalpy of formation of AgCl ?

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

(b) $AgCl(s) \longrightarrow Ag(s) + \frac{1}{2}Cl_2(g)$

(c) $Ag(s) + AuCl(s) \longrightarrow AgCl(s) + Au(s)$

(d) $Ag(s) + \frac{1}{2}Cl_2(g) \longrightarrow AgCl(s)$.

79. Which of the following equations represents standard heat of formation of methane ?

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

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

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

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

80. For the reaction,

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \quad \Delta H = 571.6\ KJ$$

$\Delta_f H^0$ of water is :

(a) 285.8 kJ (b) –285.8 kJ

(c) 1143.2 kJ (d) –1143.2 kJ

81. ΔH for the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad \Delta H = -98.3\ kJ$$

If the enthalpy of formation of $SO_3(g)$ is –395.4 kJ then the enthalpy of formation of $SO_2(g)$ is :

(a) –297.1 kJ (b) 493.7 kJ

(c) –493.7 kJ (d) 297.1 kJ

82. The standard heat of formation at 101.3 kNm^{-2} and 298 K is arbitrarily taken to be zero for :

(a) gaseous bromine atoms

(b) gaseous bromine molecules

(c) liquid bromine

(d) solid bromine.

83. The enthalpy of formation of two compounds A and B are –84 kJ and –156 kJ respectively. Which one of the following statements is correct ?

(a) A and B are endothermic compounds

(b) A is more stable than B

(c) A is less stable than B

(d) Both A and B are unstable

84. When 0.5 g of sulphur is burnt to SO_2 4.6 kJ of heat is liberated. What is the enthalpy of formation of sulphur dioxide ?

(a) –147.2 kJ (b) +147.2 kJ

(c) +294.4 kJ (d) –294.4 kJ

ΔH reaction & formation

85. The heat of formation of $Fe_2O_3(s)$ is –824.2 kJ mol^{-1}. ΔH for the reaction.

$$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g) \text{ is :}$$

(a) –412.1 kJ (b) –1648.4 kJ

(c) –3296.8 kJ (d) 1648.4 kJ

86. The ΔH^0 for the reaction,

$$4S(s) + 6O_2(g) \longrightarrow 4\,SO_3(g)$$

is –1583.2 kJ. Standard enthalpy of formation of sulphur trioxide is :

(a) –3166.4 kJ (b) 3166.4 kJ

(c) –395.8 kJ (d) 395.8 kJ

87. Calculate the heat of formation of $PCl_5(s)$ from the following data :

$$2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l) \qquad \Delta H = -151.8\ kcal$$

$$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s) \qquad \Delta H = -32.8\ kcal$$

(a) –108.7 kcal (b) 108.7 kcal

(c) –184.6 kcal (d) 184.6 kcal

88. If $S + O_2 \longrightarrow SO_2 \qquad \Delta H = -298.2\ kJ$

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 \qquad \Delta H = -98.2\ kJ$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \quad \Delta H = -130.2\ kJ$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H = -287.3\ kJ$$

the enthalpy of formation of H_2SO_4 at 298 K will be

(a) –433.7 kJ (b) –650.3 kJ

(c) +320.5 kJ (d) –813.9 kJ

ΔH formation & Combustion

89. The enthalpies of combustion of carbon and carbon monoxide are –393.5 and –283.0 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide is :

(a) –676.5 kJ (b) 110.5 kJ

(c) –110.5 kJ (d) 676.5 kJ

90. On combustion, carbon forms two oxides CO and CO_2. Heat of formation of CO_2 is –393.5 kJ and that of CO is –110.5 kJ. Heat of combustion of CO is :

(a) –393.5 kJ (b) –504.0 kJ

(c) –283.0 kJ (d) 2830.0 kJ

ΔH dissolution

91. Which of the following compounds will absorb maximum quantity of heat when dissolved in the same amount of water. The enthalpies of solution of these compounds at 25°C in kJ/mole are given in brackets ?

(a) P ($\Delta H = -32.6$ kJ mol^{-1}) (b) Q ($\Delta H = -17.3$ kJ mol^{-1})

(c) R ($\Delta H = +2.56$ kJ mol^{-1}) (d) S ($\Delta H = +25.6$ kJ mol^{-1})

92. Which of the following salts will have maximum cooling effect when 0.5 mole of the salt is dissolved in same amount of water. Integral heat of solution at 298 K is given for each salt ?

(a) KNO_3 ($\Delta H = 35.4$ kJ mol^{-1})

(b) NaCl ($\Delta H = 5.35$ kJ mol^{-1})

(c) HBr ($\Delta H = -83.3$ kJ mol^{-1})

(d) KOH ($\Delta H = -55.6$ kJ mol^{-1})

ΔH neutralisation

93. Which of the following pairs has heat of neutralisation equal to –57.1 kJ ?

(a) HNO_3,KOH (b) HCl, NH_4OH

(c) H_2SO_4,NH_4OH (d) CH_3COOH,NaOH

94. Which of the following neutralisation reactions is most exothermic ?

(a) HCl and NaOH

(b) HCN and NaOH

(c) HCl and NH_4OH

(d) CH_3COOH and NH_4OH

95. The enthalpy of neutralisation of HCl by NaOH is –57.1 kJ and that of HCN by NaOH is –12.1 kJ mol^{-1}. The enthalpy of ionization of HCN is :

(a) –69.2 kJ (b) –45.0 kJ

(c) 69.2 kJ (d) 45.0 kJ

96. The enthalpy of neutralisation of NH_4OH and HCl is :

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

(c) > 57.1 kJ mol^{-1} (d) zero

97. The heat of neutralisation of NaOH and HCl is 57.3 kJ mol^{-1}. The amount of heat liberated when 0.25 mol of H_2SO_4 reacts with 1 mole of NaOH is

(a) 57.3 kJ (b) 14.325 kJ

(c) 28.65 kJ (d) 114.6 kJ

98. The heat of neutralisation of strong base and strong acid is 57.0 kJ. The heat released when 0.5 mol of HNO_3 is added to 0.2 mol of NaOH solution is :

(a) 57.0 kJ (b) 11.40 kJ

(c) 28.5 kJ (d) 34.9 kJ

99. In which of the following neutralisation reaction, the heat of neutralisation will be highest ?

(a) NH_4OH and H_2SO_4 (b) HCl and NaOH

(c) CH_3COOH and KOH (d) CH_3COOH and NH_4OH

100. The enthalpies of neutralization of a weak base AOH and a strong base BOH by HCl are –12250 cal/mol and –13000 cal/mol respectively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was –12500 cal/mol. In what ratio is the acid distribution between AOH and BOH?

(a) 2:1 (b) 2:3

(c) 1:2 (d) None of these

101. In what proportion 1 M NaOH and 0.5 H_2SO_4 are mixed so as to release maximum amount of energy and to form 100 mL solution ?

(a) 33 and 67 (b) 67 and 33

(c) 40 and 60 (d) 50 and 50

ΔH of Physical Transition

102. The enthalpy change for the reaction,

$H_2O(s) \longrightarrow H_2O(\ell)$ is called

(a) Enthalpy of formation

(b) Enthalpy of fusion

(c) Enthalpy of vaporisation

(d) Enthalpy of transition

103. The enthalpies of combustion of rhombic sulphur and monoclinic sulphur are –295.1 and –296.4 kJ mol^{-1} respectively. The enthalpy of allotropic transformation of monoclinic to rhombic sulphur is :

(a) 1.3 kJ

(b) –1.3 kJ

(c) –591.5 kJ

(d) 0

Enthalpy (Reaction Based)

104. In an endothermic reaction

(a) ΔH is negative

(b) Heat is given to the surroundings

(c) Enthalpy of the reactants is less than that of the products

(d) ΔE is negative

105. Which of the following enthalpies is always negative ?

(a) Enthalpy of solution

(b) Enthalpy of combustion

(c) Enthalpy of sublimation

(d) Enthalpy of formation

106. In the reaction :

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

$$\Delta H = 2.8 \text{ kJ}$$

then ΔH represents

(a) heat of formation

(b) heat of reaction

(c) heat of solution

(c) heat of combustion

107. Calculate the entropy change (J/mol K) of the given reaction. The molar entropies [J/K–mol] are given in brackets after each substance.

$$2\,PbS(s)\,[91.2] + 3O_2(g)[205.1] \longrightarrow$$

$$2PbO(s)\,[66.5] + 2SO_2(g)[248.2]$$

(a) –113.5

(b) –168.3

(c) +72.5

(d) –149.2

108. For the process : $CO_2(s) \longrightarrow CO_2(g)$

(a) Both ΔH and ΔS are +ve

(b) ΔH is –ve, ΔS is +ve

(c) ΔH is +ve, ΔS is –ve

(d) Both ΔH and ΔS are –ve.

109. Given $\Delta_r S^o = -266$ and listed [S^o_m values] calculate S^o for $Fe_3O_4(s)$:

$$4Fe_3O_4(s)[.......] + O_2(g)[205] \rightarrow 6Fe_2O_3(S)[87]$$

(a) +111.1

(b) +122.4

(c) +145.75

(d) 248.25

Gibss Energy (Reaction Based)

110. For the reaction at 300 K

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

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

$(R \approx 2 \text{ cal mol}^{-1} K^{-1})$

ΔG is :

(a) –600 cal

(b) –3600 cal

(c) 2400 cal

(d) 3000 cal

Bond Energy

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

(a) +431.3 kJ

(b) 236.9 kJ

(c) –431.3 kJ

(d) 339.1 kJ

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

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

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

the bond enthalpy of the O–H bond is :

(a) 498 kJ mol^{-1}

(b) 463 kJ mol^{-1}

(c) 428 kJ mol^{-1}

(d) 70 kJ mol^{-1}

113. Calculate the heat of the reaction

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

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

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

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

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

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

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

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

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

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

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

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

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

$N\equiv N$ = 941 kJ mol^{-1}, N–H = 398 kJ mol^{-1}

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

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

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

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

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

Born Haber

118. Using the following energy values, determine the lattice energy of KF(s):

Property	**Energy (kJ mol^{-1})**
$\Delta H_{atomization}$ of K(s)	90
$\Delta H_{atomization}$ of F_2(s)	158
ΔH_f of KF(s)	–567
IE of K(s)	419
EA of F(g)	328

(a) 51 kJ (b) + 827 kJ

(c) + 1145 kJ (d) + 1483 kJ

119. The lattice enthalpy and hydration enthalpy of four compounds are given below:

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

The pair of compounds which is soluble in water is

(a) P and Q (b) Q and R

(c) R and S (d) P and R

Hess' Law

120. An imaginary reaction $X \rightarrow Y$ takes place in three steps

$X \rightarrow A, \Delta H=-q_1; B \rightarrow A, \Delta H=-q_2, B \rightarrow Y, \Delta H=-q_3$

If Hess' law is applicable, then the heat of the reaction $(X \rightarrow Y)$ is:

(a) $q_1-q_2+q_3$ (b) $q_2-q_3-q_1$

(c) $q_1-q_2-q_3$ (d) $q_3-q_2-q_1$

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTION

1. A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water, then **(2002)**

	ΔH	ΔS
(a)	+ ve	+ ve
(b)	– ve	– ve
(c)	– ve	+ ve
(d)	+ ve	– ve

2. 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 **(2002)**

(a) First law of thermodynamics

(b) Second law of thermodynamics

(c) Joules equivalent law

(d) None of the above

3. Heat required to raise the temperature of 1 mole of a substance by 1° is called **(2002)**

(a) specific heat
(b) molar heat capacity
(c) water equivalent
(d) specific gravity

4. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **(2003)**

(a) $\Delta G = RT \ln K_c$
(b) $-\Delta G = RT \ln K_c$
(c) $\Delta G^o = RT \ln K_c$
(d) $-\Delta G^o = RT \ln K_c$

5. 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

(a) + 250 kJ
(b) – 250 kJ
(c) + 125 kJ
(d) – 125 kJ

6. The internal energy change when a system goes from state A to B is 40 kJ/mol. 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 ? **(2003)**

(a) 40 kJ
(b) > 40 kJ
(c) < 40 kJ
(d) zero

7. The enthalpy change for a reaction does not depend upon the **(2003)**

(a) physical state of reactants and products

(b) use of different reactants for the same product

(c) nature of intermediate reaction steps

(d) difference in initial or final temperatures of involved substances

8. 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 is **(2004)**

(a) 110.5 kJ
(b) 676.5 kJ
(c) – 676.5 kJ
(d) – 110.5 kJ

9. An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is **(2004)**

(a) – 900 J
(b) – 900 kJ
(c) 270 kJ
(d) 900 kJ

10. For a spontaneous reaction the ΔG, equilibrium constant (K) and E^o_{cell} will be respectively **(2005)**

(a) –ve, >1, –ve
(b) –ve, <1, –ve
(c) +ve, >1, –ve
(d) –ve, >1, + ve

11. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be **(2005)**

(a) 400 kJ mol^{-1}
(b) 300 kJ mol^{-1}
(c) 200 kJ mol^{-1}
(d) None of these

12. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔE are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **(2005)**

(a) $\Delta H > \Delta E$
(b) $\Delta H < \Delta E$
(c) $\Delta H = \Delta E$
(d) $\Delta H = 0$

13. The standard enthalpy of formation (ΔH^o_f) at 298 K 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 **(2006)**

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon

(b) latent heat of vaporisation of methane

(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen

(d) the dissociation energy of hydrogen molecule, H_2

14. The enthalpy changes for the following processes are listed below :

$Cl_2(g) = 2Cl(g)$, 242.3 kJ mol^{-1}

$I_2(g) = 2I(g)$, 151.0 kJ mol^{-1}

$ICl(g) = I(g) + Cl(g)$, 211.3 kJ mol^{-1}

$I_2(s) = I_2(g)$, 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation of $ICl(g)$ is **(2006)**

(a) – 14.6 kJ mol^{-1} (b) – 16.8 kJ mol^{-1}

(c) + 16.8 kJ mol^{-1} (d) + 244.8 kJ mol^{-1}

15. $(\Delta H - \Delta E)$ for the formation of carbon monoxide (CO) from its elements at 298 K is (R=8.314 JK^{-1} mol^{-1}) **(2006)**

(a) – 1238.78 J mol^{-1} (b) 1238.78 J mol^{-1}

(c) – 2477.57 J mol^{-1} (d) 2477.57 J mol^{-1}

16. 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 ? **(2006)**

(a) $(T_f)_{irrev} > (T_f)_{rev}$

(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(c) $(T_f)_{rev} = (T_f)_{irrev}$

(d) $T_f = T_i$ for both reversible and irreversible processes

17. In conversion of limestone to lime,

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

the values of ΔH^o and ΔS^o are + 179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH^o and ΔS^o do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is **(2007)**

(a) 1008 K (b) 1200 K

(c) 845 K (d) 1118 K

18. Identify the correct statement regarding a spontaneous process. **(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

19. Assuming that water vapour is an ideal gas, the internal energy change (ΔE) when 1 mole of water is vaporised at 1 bar pressure and 100°C, (Given : molar enthalpy of vaporisation of water at 1 bar and 373 K = 41 KJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1}) will be **(2007)**

(a) 4.100 kJ mol^{-1} (b) 3.7904 kJ mol^{-1}

(c) 37.904 kJ mol^{-1} (d) 41.00 kJ mol^{-1}

20. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectivley. For the reaction,

$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3, \Delta H = -30$ kJ, to be at equilibrium, the temperature will be **(2008)**

(a) 1250 (b) 500 K

(c) 750 K (d) 1000 K

21. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below :

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^0} Cl(g) \xrightarrow{\Delta_{EA}H^0}$$

$$Cl^-(g) \xrightarrow{\Delta hydH^0} Cl^-(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq)$ will be (using the data, $\Delta_{diss}H^0_{Cl_2} = 240$ kJ mol^{-1} $\Delta_{EA}H^0_{Cl} = -349$kJ mol^{-1}, $\Delta_{hyd}H^0_{Cl} = -381$ kJ mol^{-1}) **(2008)**

(a) + 152 kJ mol^{-1} (b) – 610 kJ mol^{-1}

(c) – 850 kJ mol^{-1} (d) + 120 kJ mol^{-1}

22. On the basis of the following thermochemical data [ΔfG^o $H^+(aq) = 0$]

$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq); \Delta H = 57.32$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$

$\Delta H = -286.02$ kJ

The value of enthalpy of formation of OH^- ion at 25°C is

(a) – 22.88 kJ (b) – 228.88 kJ

(c) + 228.88 kJ (c) – 343.52 kJ

23. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is $CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$. At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are – 166.2, –237.2 and –394.4 kJ mol^{-1} respectively. If standard enthalpy of combustion of methanol is – 726 kJ mol^{-1}, efficiency of the fuel cell will be **(2009)**

(a) 80% (b) 87%

(c) 90% (d) 97%

24. 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 **(2010)**

(a) $T_e > T$ (b) $T > T_e$
(c) T_e is 5 times T (d) $T = T_e$

25. 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 **(2010)**

(a) – 964 kJ mol^{-1} (b) + 352 kJ mol^{-1}
(c) + 1056 kJ mol^{-1} (d) – 1102 kJ mol^{-1}

26. Consider the reaction

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g), \Delta_r H = -111$ kJ. If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be

(Given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1}) **(2011)**

(a) – 165 kJ (b) + 54 kJ
(c) +219 kJ (d) – 219 kJ

27. The value of enthalpy change (ΔH) for the reaction

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$,

at 27°C is – 1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be **(2011)**

(a) – 1371.5 kJ (b) – 1369.0 kJ
(c) – 1364.0 kJ (d) – 1361.5 kJ

28. In view of the signs of $\Delta_r G^\circ$ for the following reactions

$PbO_2 + Pb \rightarrow 2PbO, \quad \Delta_r G^\circ < 0$,

$SnO_2 + Sn \rightarrow 2\,SnO, \quad \Delta_r G^\circ > 0$

Which oxidation states are more characteristic for lead and tin ? **(2011)**

(a) For lead + 4, For tin + 2 (b) For lead + 2, for tin + 2
(c) For lead + 4, for tin + 4 (d) For lead +2, for tin + 4

29. 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 **(2011)**

(a) 38.3 J $mol^{-1}K^{-1}$ (b) 35.8 J $mol^{-1}K^{-1}$
(c) 32.3 J $mol^{-1}K^{-1}$ (d) 42.3J $mol^{-1}K^{-1}$

30. For complete combustion of ethanol,

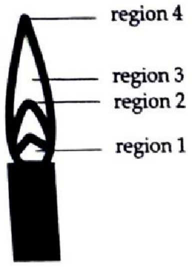
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$,

the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the Enthalpy of combustion, $\Delta_C H$, for the reaction will be :

(R = 8.314 kJ mol^{-1}) **(2014)**

(a) –1361.95 kJ mol^{-1} (b) –1460.50 kJ mol^{-1}
(c) – 1350.50 kJ mol^{-1} (d) – 1366.95 kJ mol^{-1}

31. The hottest region of Bunsen flame shown in the figure below is: **(2016)**



(a) region 2 (b) region 3
(c) region 4 (d) region 1

32. ΔU is equal to : **(2017)**

(a) Isobaric work (b) Adiabatic work
(c) Isothermal work (d) Isochoric work

33. Given

$C_{(graphite)} + O_2(g) \rightarrow CO_2(g)$;

$\Delta_r H^\circ = -393.5$ kJ mol–1

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(1)$;

$\Delta_r H^\circ = -285.8$ kJ mol^{-1}

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$;

$\Delta_r H^\circ = +890.3$ kJ mol^{-1}

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

$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$ will be : **(2017)**

(a) + 144.0 kJ mol^{-1} (b) –74.8 kJ mol^{-1}
(c) –144.0 kJ mol^{-1} (d) +74.8 kJ mol^{-1}

34. The combustion of benzene (I) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25°C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be:

(R = 8.314 JK^{-1} mol^{-1}) **(2018)**

(a) – 3267.6 (b) 4152.6
(c) –452.46 (d) 3260

JEE MAINS ONLINE QUESTION

Online 2014 SET (1)

1. 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:

Online 2014 SET (1)

(a) – 1102 kJ mol^{-1} (b) – 964 kJ mol^{-1}

(c) + 352 kJ mol^{-1} (d) + 1056 kJ mol^{-1}

2. The molar heat capacity (C_p) of CD_2O is 10 cals at 1000 K. The change in entropy associated with cooling of 32 g of CD_2O vapour from 1000 K to 100 K at constant pressure will be: **Online 2014 SET (2)**

(D = deuterium, at. Mass = 2 u)

(a) 2.303 cal deg^{-1} (b) 23.03 cal deg^{-1}

(c) –23.03 cal deg^{-1} (d) –2.303 cal deg^{-1}

3. The entropy (S^o) of the following substances are:

CH_4 (g) 186.2 J K^{-1} mol^{-1}

O_2 (g) 205.0 J K^{-1} mol^{-1}

CO_2 (g) 213.6 J K^{-1} mol^{-1}

H_2O (*l*) 69.9 J K^{-1} mol^{-1}

The entropy change (ΔS^o) for the reaction

$CH_4(g) + 2O_2(g)$ '! $CO_2(g) + 2H_2O$ (*l*) is:

Online 2014 SET (3)

(a) –37.6 J K^{-1} mol^{-1}

(b) –312.5 J K^{-1} mol^{-1}

(c) –242.8 J K^{-1} mol^{-1}

(d) –108.1 J K^{-1} mol^{-1}

4. The standard enthalpy of formation ($\Delta_f H^o 298$) for methane, CH_4 is –74.9 kJ mol^{-1}. In order to calculate the average energy given out in the formation of a C – H bond from this it is necessary to know which one of the following?

Online 2014 SET (3)

(a) The dissociation energy of H_2 and enthalpy of sublimation of carbon (graphite)

(b) the dissociation energy of the hydrogen molecule, H_2.

(c) the first four ionisation energies of carbon and electron affinity of hydrogen.

(d) the first four ionisation energies of carbon.

5. The ΔH and ΔS for a reaction at one atmospheric pressure are +30.558 kJ and 0.066 kJk^{-1} respectively. The temperature at which the free energy change will be zero and below of this temperature the nature of reaction would be

Online 2015 SET (1)

(a) 483 K, spontaneous

(b) 443 K, spontaneous

(c) 463 K, spontaneous

(d) 463 K, non-spontaneous

6. A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature. Identify the correct statement about the reaction among the following : **Online 2016 SET (1)**

(a) Both “H and “S are negative.

(b) Both “H and “S are positive.

(c) “H is positive while “S is negative.

(d) “H is negative while “S is positive

7. For the reaction, $A(g) + B(g) \rightarrow C(g) + D(g)$, ΔH° and ΔS° are respectively, –29.8 kJ mol^{-1} and –0.100 kJ K^{-1} mol^{-1} at 298 K. The equilibrium constant for the reaction at 298 K is : **Online 2016 SET (1)**

(a) 1.0×10^{-10} (b) 1.0×10^{10}

(c) 10 (d) 1

8. If 100 mole of H_2O_2 decompose at 1 bar and 300 K, the work done (kJ) by one mole of $O_2(g)$ as it expands against 1 bar pressure is :

$$2H_2O_2(l) \rightleftharpoons 2H_2O(l) + O_2(g)$$

$(R = 8.3\ JK^{-1}mol^{-1})$ **Online 2016 SET (2)**

(a) 62.25 (b) 124.50

(c) 249.00 (d) 498.00

9. For a reaction, A(g) '! A(*l*); “H = “ 3RT. The correct statement for the reaction is : **Online 2017 SET (1)**

(a) “H = “U `” O (b) “H = “U = O

(c) |”H| < |”U| (d) |ΔH| > |ΔU|

10. What is the value of change in internal energy at 1 atm in the process?

$$H_2O(\ell, 323\,K) \longrightarrow H_2O(g, 423\,K)$$

Given :

$C_{v,m}(H_2O, \ell) = 75.0\ JK^{-1}mol^{-1}$;

$C_{p,m}(H_2O, g) = 33.314\ JK^{-1}mol^{-1}$;

ΔH_{vap} at 373 K = 40.7 kJ/mol **Online 2017 SET (1)**

(a) 42.91 kJ/mol (b) 43086 kJ/mol

(c) 42.6 kJ/mol (d) 49.6 kJ/mol

11. An ideal gas undergoes isothermal expansion at constant pressure. During the process : **Online 2017 SET (2)**

(a) enthalpy increases but entropy decreases.

(b) enthalpy remains constant but entropy increases.

(c) enthalpy decreases but entropy increases.

(d) Both enthalpy and entropy remain constant.

12. A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5J and 8J, respectively. Now gas is brought back to A by another process during which 3J of heat is evolved. In this reverse process of B to A : **Online 2017 SET (2)**

(a) 10J of the work will be done by the gas.

(b) 6J of the work will be done by the gas.

(c) 10J of the work will be done by the surrounding on gas.

(d) 6J of the work will be done by the surrounding on gas.

13. For which of the following reactions, ΔH is equal to ΔU? **Online 2018 SET (1)**

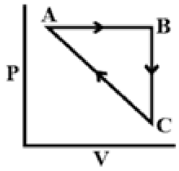
(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(b) $2HI(g) \rightarrow H_2(g) + I_2(g)$

(c) $2NO_2(g) \rightarrow N_2O_4(g)$

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

14. An ideal gas undergoes a cyclic process as shown in Figure.



$\Delta U_{BC} = -5kJ\ mol^{-1}$, $q_{AB} = 2kJ\ mol^{-1}$

$W_{AB} = -5\ kJ\ mol^{-1}$, $W_{CA} = 3\ kJ\ mol^{-1}$

Heat absorbed by the system during process CA is : **Online 2018 SET (1)**

(a) -5 kJ mol^{-1} (b) +5 kJ mol^{-1}

(c) 18 kJ mol^{-1} (d) -18 kJ mol^{-1}

15. $\Delta_f G^0$ at 500 K for substance 'S' in liquid state and gaseous state are +100.7 kcal mol^{-1} and +103 kcal mol^{-1}, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to :

(R = 2 cal K^{-1} mol^{-1}) **Online 2018 SET (2)**

(a) 0.1 atm (b) 1 atm

(c) 10 atm (d) 100 atm

16. Given

(i) $2Fe_2O_3(s) \rightarrow 4Fe(s) + 3O_2(g);\ \Delta_r G^0$

$= +\ 1487.0\ kJ\ mol^{-1}$

(ii) $2CO(g) + O_2(g)\ \ 2CO_2(g)\ ;\ = -514.4\ kJ\ mo\ l^{-1}$

Free energy change, for the reaction $2Fe_2O_3(s) + 6CO(g)$ $4Fe(s) + 6CO_2(g)$ will be : **(Online 2018 SET (2)**

(a) -112.4 kJ mol^{-1} (b) -56.2 kJ mol^{-1}

(c) -168.2 kJ mol^{-1} (d) -208.0 kJ mol^{-1}

17. For which of the following processes, ΔS is negative ? **(Online 2018 SET 3)**

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

(b) N_2(g, 1 atm) N_2(g, 5 atm)

(c) C(diamond) C(graphite)

(d) N_2(g, 273 K) N_2(g, 300 K)

18. At 320 K, a gas A_2 is 20 percent dissociated to A(g). The standard free energy change at 320 K and 1 atm in J mol^{-1} is approximately :

(R=8.314 $JK^{”1}$ $mol^{”1}$; ln 2=0.693; ln 3=1.098)

(Online 2018 SET 3)

(a) 4763 (b) 2068

(c) 1844 (d) 4281

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. All questions marked **"S"** are single choice questions
2. All questions marked **"M"** are multiple choice questions
3. All questions marked **"C"** are comprehension based questions
4. All questions marked **"A"** are assertion–reason type questions
   (A) If both assertion and reason are correct and reason is the correct explanation of assertion.
   (B) If both assertion and reason are true but reason is not the correct explanation of assertion.
   (C) If assertion is true but reason is false.
   (D) If reason is true but assertion is false.
5. All questions marked **"X"** are matrix–match type questions
6. All questions marked **"I"** are integer type questions

Extensive/Intensive

1. (A) **Assertion :** The extensive properties of a single pure substance will not only depend upon the number of moles of the substance present but also on any two of the three variables.

Reason : Any extensive property if expressed as per mole or per gram becomes an intensive property.

(a) A (b) B

(c) C (d) D

Internal Energy

2. (S) An ideal gas at constant temperature and pressure expands, then its

(a) Internal energy remains same

(b) Internal energy decreases

(c) Internal energy increases

(d) Entropy first increases and then decreases

3. (S) The internal energy of a substance

(a) Increases with increase in temperature

(b) Decreases with increase in temperature

(c) Can be calculated by the relation $E = mc^2$

(d) Remains unaffected with change in temperature

4. (A) **Assertion :** There is no change in internal energy for an ideal gas at constant temperature.

Reason : Internal energy of an ideal gas is a function of temperature only.

(a) A (b) B

(c) C (d) D

First Law

5. (S) Consider an ideal gas. When $dW = 0$ and $dq < 0$,

(a) the temperature will decrease

(b) the volume will increase

(c) the pressure will remain constant

(d) the temperature will increase

Isothermal Process

6. (S) When heat is supplied to an ideal gas in an isothermal process, the

(a) gas will do positive work

(b) gas will do negative work

(c) kinetic energy of the gas will increase

(d) gas will not obey the law of conservation of energy

Adiabatic Process

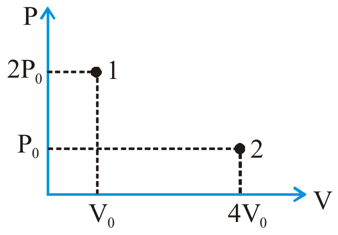
7. (S) The magnitudes of enthalpy changes for irreversible adiabatic expansion of a gas from 1L to 2L is ΔH_1 and for reversible adiabatic expansion for the same expansion is ΔH_2. Then

(a) $\Delta H_1 > \Delta H_2$ (b) $\Delta H_1 < \Delta H_2$

(c) $\Delta H_1 = \Delta H_2$, enthalpy being a state function

(d) $\Delta H_1 = \Delta E_1$ & $\Delta H_2 = \Delta E_2$ where ΔE_1 & ΔE_2 are magnitudes of change in internal energy of gas in these expansions respectively.

8. (S) A liquid which is confined inside an adiabatic piston is suddenly taken from state 1 to state 2 by a single stage process. If the piston comes to rest at point 2 as shown. Then the enthalpy change for the process will be :



(a) $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$ (b) $\Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$

(c) $\Delta H = -P_0 V_0$ (d) None of these

9. (S) A gas expands adiabatically at constant pressure such that $T \propto V^{-1/2}$. The value of γ ($C_{p,m}/C_{v,m}$) of the gas will be :

(a) 1.30 (b) 1.50

(c) 1.70 (d) 2

10. (S) 1 mole of an ideal gas A ($C_{v,m}$ = 3 R) and 2 mole of an ideal gas B $\left(C_{v,m} = \frac{3}{2}R\right)$ are taken in a container and expanded reversible and adiabatically from 1 litre to 4 litre starting from initial temperature of 320 K. ΔE or ΔU for the process is :

(a) –240 R (b) 240 R

(c) 480 R (d) –960 R

11. (S) 0.5 mole each of two ideal gases A $\left(C_{v,m} = \frac{5}{2}R\right)$ and B ($C_{v,m}$ = 3R) are taken in a container and expanded reversibly and adiabatically, during this process temperature of gaseous mixture decreased from 350 K and 250 K. Find ΔH (in cal/mol) for the process :

(a) –100 R (b) –137.5 R

(c) –375 R (d) None of these

Processes

12. (A) **Assertion :** A reversible process produces more work than the same process if it is carried out irreversibly for the same increase in volume.

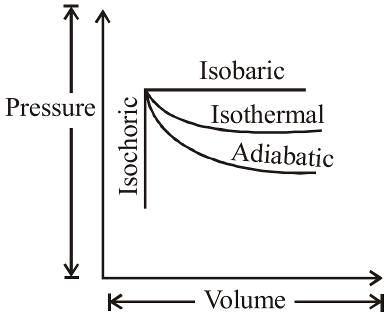
Reason : A reversible process is exothermic while irreversible process is endothermic

(a) A (b) B

(c) C (d) D

COMPREHENSION

Observe the following graphic representation of four basic thermodynamic processes.



13. (C) Which of the following is true for isochoric process ?

(a) $\Delta V = 0$ (b) $\Delta U = q + P\Delta V$ (c) $\Delta U = q_v$

(d) All of these

14. (C) Which of the following is not true for isothermal process ?

(a) $w_{exp} = -2.303\ nRT \log \frac{V_2}{V_1}$

(b) $w_{exp} = -2.303\ nRT \log \frac{P_1}{P_2}$

(c) $\Delta T = 0$ (d) $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

15. (C) If the ratio $\frac{C_P}{C_V} = 1.30$, the atomicity of gas is

(a) 1 (b) 2

(c) 3 (d) 4

16. (S) 2 mole of an ideal monoatomic gas undergoes a reversible process for which $PV^2 = C$. The gas is expnaded from initial volume of 1 L to final volume of 3L starting from initial temperature of 300 K. Find ΔH for the process:

(a) –600R (b) –1000R

(c) –3000R (d) None of these

Heat Capacity

17. (S) A certain gas in expanded from (lL, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If the initial temperature of gas is 300 K and heat capacity for the process is 50 J/°C, the enthalpy change during the process is : (Use : 1L atm $\approx$ 100 J)

(a) 15 kJ (b) 15.7 kJ

(c) 14.3 kJ (d) 14.7 kJ

18. (S) The molar heat capacities at constant pressure (assumed constant with respect to temperature) for A, B and C are in ratio of 3 : 1.5 : 2.0. The enthalpy change for the exothermic $A + 2B \rightarrow 3C$ at 300 K and 310 K is ΔH_{300} and ΔH_{310} (magnitudes) respectively then :

(a) $\Delta H_{300} > \Delta H_{310}$ (b) $\Delta H_{300} < \Delta H_{310}$

(c) $\Delta H_{300} = \Delta H_{310}$

(d) if $T_2 > T_1$ then $\Delta H_{310} > \Delta H_{300}$ and if $T_2 < T_1$ then $\Delta H_{310} < \Delta H_{300}$

COMPREHENSION

Molar heat capacity is heat required to raise the temperature of one mole of material by one degree, since heat is not a state function, the amount of heat required to produce a given change in its state depends on the path followed.

C_P = Specific heat × Molecular weight. It is measured at constant pressure.

C_V - Specific heat × Molecular weight. It is measured at constant volume.

19. (C) Which of the following is correct ?

(a) $C_P - C_V = R$ (b) $\frac{C_P}{C_V} = \gamma$

(c) $C_P > C_V$ (d) All of these

20. (C) C_P for monoatomic gas is

(a) 5/2 R (b) 3/2 R

(c) 7/2 R (d) R

21. (C) The specific heat of a gas at constant volume is 0.075 cal/g. Predict the atomicity of the gas. Molar mass of gas is 40 g mol^{-1}.

(a) 1 (b) 2

(c) 3 (d) None of these

22. (S) 10 mole of an ideal gas is heated at constant pressure of one atmosphere from 27°C to 127°C. If $C_{v,m} = 21.686 + 10^{-3}$ T, then ΔH for the process is :

(a) 3000 J (b) 3350 J

(c) 3700 J (d) 30350

Entropy (Reaction based)

23. (S) For an ideal gas undergoing adiabatic expansion in vaccum,

(a) $\Delta U = 0$ (b) $q = 0$

(c) $W = 0$ (d) all the above are true

24. (S) What is the change in molar entropy of helium in the following process ?

1 He (298 K, 1 bar) $\rightarrow$ 1 He (100 K, 10 bar)

(a) 41.8 J K^{-1} mol^{-1} (b) 4.18 J K^{-1} mol^{-1}

(c) – 41.8 J K^{-1} mol^{-1} (d) – 4.18 J K^{-1} mol^{-1}

25. (S) $\Delta S = \frac{\Delta H}{T}$ holds good for

(a) an adiabatic process

(b) an isothermal reversible-phase change

(c) a process at constant pressure

(d) a process under any condition

26. (S) $\Delta_r H^0$ for solid-to-liquid transition for proteins A and B are 2.73 kcal mol^{-1} and 3.03 kcal mol^{-1}. The two melting points are 0°C and 30°C respectively. The entropy changes ΔS_A and ΔS_B at two transition temperatures are related as :

(a) $\Delta S_A = \Delta S_B$ (b) $\Delta S_A < \Delta S_B$

(c) $\Delta S_B > \Delta S_A$ (d) $\Delta S_B = \frac{303 \Delta S_A}{273}$

27. (A) **Assertion :** Entropy change in reversible adiabatic expansion of an ideal gas is zero.

Reason : The increase in entropy due to volume increase just componsate the decrease in entropy due to fall in temperature.

(a) A (b) B

(c) C (d) D

Relation b/w ΔH & ΔE

28. (S) For the real gases reaction

$$2CO\,(g) + O_2(g) \longrightarrow 2CO_2\,(g)$$

$$\Delta H = -560\text{ kJ.}$$

In 10 litre rigid vessel at 500 K the initial pressure is 70 bar and after the reaction it becomes 40 bar. The change in internal energy is :

(a) –557 kJ (b) –530 kJ

(c) –563 kJ (d) None of these

29. (A) **Assertion :** When internal energy of reactants becomes greater than that of products the energy is given out to the surrounding.

Reason : All exothermic reactions take place at constant temperature, ΔE will be positive.

(a) A (b) B

(c) C (d) D

30. (S) At 5×10^5 bar pressure, density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature 'T'. Find the value of ΔU–ΔH for the conversion of 1 mole of graphite to 1 mole of diamond at temperature 'T':

(a) 100 kJ/mol (b) 50 kJ/mol

(c) – 100 kJ/mol (d) None of these

ΔH formation

31. (S) The enthalpy of formation of NH_3(g) at constant pressure and 350^0C temperature is –50.0 kJ mol^{-1}. What will be the enthalpy of formation of NH_3(g) at constant volume at the same temperature ?

(a) – 50.0 kJ mol^{-1} (b) – 45 kJ mol^{-1}

(c) – 60.4kJ mol^{-1} (d) – 54 kJ mol^{-1}

ΔH reaction & formation

32. (S) $Mg(s) + 2HCl(aq.) \rightarrow MgCl_2(aq) + H_2(g);$

$$\Delta_r H^0 = -467\text{ kJ/mol}$$

$MgO\,(s) + 2HCl\,(aq) \rightarrow MgCl_2\,(aq) + H_2O\,(l)\,;$

$$\Delta_r H^0 = -151\text{ kJ/mol}$$

According to the information, and given the fact that for water, $\Delta_f H^0 = -\,286$ kJ/mol, what is the $\Delta_f H^0$ for MgO(s) ?

(a) – 904 kJ/mol (b) – 602 kJ/mol

(c) – 334 kJ/mol (d) – 30 kJ/mol

ΔH combustion

33. (S) The enthalpy of reaction $CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH\,(l)$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively then which of the following relations is correct?

(a) $x > y$ (b) $x < y$

(c) $x = y$ (d) $x \geq y$

34. (S) For the allotropic change represented by the equation

C (diamond) → (graphite) the enthalpy change is $\Delta H = -\,1.89$ kJ

If 6g of diamond and 6 g of graphite are separately burnt to yield carbon dioxide, the heat, liberated in the first case is

(a) less than in the second case by 1.89 kJ

(b) more than in the second case by 1.89 kJ

(c) less than in the second case by 11.34 kJ

(d) more than in the second case by 0.945 kJ

35. (S) The enthalpy of combustion for octane (a major component of gasoline) is – 47.8 kJ/g. How much energy is released by burning 1.0 L of octane (density 0.740 g/mL) ?

(a) – 35400 kJ (b) – 64600 kJ

(c) – 47800 kJ (d) – 57200 kJ

ΔH formation & combustion

36. (S) Standard molar enthalpy of formation of CO_2 is equal to

(a) zero

(b) the standard molar enthalpy of combustion of gaseous carbon

(c) the sum of standard enthalpies of formation of CO and O_2

(d) the standard molar enthalpy of combustion of carbon (graphite)

37. (S) Given that $\Delta H_f^0 (CO_2, g)$

$= -393.509\ \text{kJ mol}^{-1},\ \Delta H_f^0 (H_2O, l)$

$= -285.830\ \text{kJ mol}^{-1},\ \Delta H_f^0 (C_2H_5OH, l)$

$= -277.800\ \text{kJ mol}^{-1}$.

Calculate the ΔH° (combustion) of liquid ethanol. The following is the required reaction.

$C_2H_5OH (l) + 3O_2 (g) \rightarrow 2CO_2 (g) + 3H_2O (l)$

(a) $-1366.82\ \text{kJ mol}^{-1}$ (b) $-278.82\ \text{kJ mol}^{-1}$

(c) $-2264.66\ \text{kJ mol}^{-1}$ (d) $-1155.78\ \text{kJ mol}^{-1}$

ΔH neutralisation

38. (S) The enthalpy of neutralization of a strong acid by a strong base is $-57.32\ \text{kJ mol}^{-1}$. The enthalpy of formation of water is $-285.84\ \text{kJ mol}^{-1}$. The enthalpy of formation of the hydroxyl ion is

(a) $+228.52\ \text{kJ mol}^{-1}$ (b) $-114.26\ \text{kJ mol}^{-1}$

(c) $-228.52\ \text{kJ mol}^{-1}$ (d) $+114.26\ \text{kJ mol}^{-1}$

39. (S) Heat of neutralisation of NaOH and HCl is –57.46 kJ/equivalent. The heat of ionisation of water will be :

(a) –57.46 kJ/mol (b) 57.46 kJ/mol

(c) – 114.92 kJ/mol (d) 114.92 kJ/mol

40. (S) In which case of mixing of a strong acid and strong base, each of 1N concentration, temperature increase is the highest ?

(a) 20 ml acid and 30 ml alkali

(b) 10 ml acid and 40 ml alkali

(c) 25 ml acid and 25 ml alkali

(d) 35 ml acid and 15 ml alkali

41. (S) Heat of neutralization of a strong dibasic acid in dilute solution by NaOH is nearly

(a) – 27.4 kcal/eq (b) 13.7 kcal/mol

(c) – 13.7 kcal/eq (d) – 13.7 kcal/mol

42. (S) Heat released in neutralization of strong acid and strong base is 13.4 kcal/mol. The heat released on neutralization of NaOH with HCN is 2.9 kcal/mol, then ΔH° of ionization of HCN in water is

(a) 10.5 kcal (b) 16.3 kcal

(c) 9.5 kcal (d) 11.5 kcal

43. (A) **Assertion :** Heat of neutralization of HF is more than that of HC*l* by NaOH.

Reason : HC*l* is stronger acid than HF.

(a) A (b) B

(c) C (d) D

44. (A) **Assertion :** Enthalpy of neutralization of CH_3COOH by NaOH is less than that of HCl by NaOH.

Reason : Enthalpy of neutralization of CH_3COOH is less because of the absorption of heat in the ionization process.

(a) A (b) B

(c) C (d) D

ΔH of Physical Transition

45. (S) Calculate the enthalpy change when 1.0 g of water is frozen at 0^0C ($\Delta H_f^0 = 1.435\ \text{kcal mol}^{-1}$) ?

(a) $-1.435\ \text{cal g}^{-1}$ (b) $-80.0\ \text{cal g}^{-1}$

(c) $80.0\ \text{cal g}^{-1}$ (d) $-55.6\ \text{cal g}^{-1}$

46. (S) The mathematical expression for the standard enthalpy of sublimation is given by

(a) ΔH° (sublimation) = ΔH° (fusion) – $2\Delta H^\circ$ (vaporization)

(b) ΔH° (sublimation) = ΔH° (fusion) – ΔH° (vaporization)

(c) ΔH° (sublimation) = ΔH° (fusion) + ΔH° (vaporization)

(d) ΔH° (sublimation) = ΔH° (combustion) + ΔH° (dissociation)

Entropy (Rx Based)

47. (S) Given are the following entropy values at 298 K and 1 atm:

$H_2 (g) = 130.6\ \text{J K}^{-1}\ \text{mol}^{-1};\ Cl_2 (g) = 223.0\ \text{J K}^{-1}\ \text{mol}^{-1};$

$HCl (g) = 186.7\ \text{J K}^{-1}\ \text{mol}^{-1}$

The entropy change for the reaction

$H_2 (g) + Cl_2 (g) \rightarrow 2HCl (g)$ would be

(a) $+540.3\ \text{J K}^{-1}\ \text{mol}^{-1}$ (b) $+727\ \text{J K}^{-1}\ \text{mol}^{-1}$

(c) $-166.9\ \text{J K}^{-1}\ \text{mol}^{-1}$ (d) $+19.8\ \text{J K}^{-1}\ \text{mol}^{-1}$

COMPREHENSION

Standard Gibb's energy of reaction ($\Delta_r G^o$) at a certain temperature can be computed as $\Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$ and the change in the value of $\Delta_r H^o$ and $\Delta_r S^o$ for a reaction with temperature can be computed as follow:

$$\Delta_r H^o_{T_2} - \Delta_r H^o_{T_1} = \Delta_r C^o_p (T_2 - T_1)$$

$$\Delta_r S^o_{T_2} - \Delta_r S^o_{T_1} = \Delta_r C^o_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$$

and by $\Delta_r G^o = -RT \ln K_{eq}$.

Consider the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Given: $\Delta_f H^o(CH_3OH, g) = -201$ kJ/mol; $\Delta_f H^o(CO, g) = -144$ kJ/mol

$S^o(CH_3OH, g) = 240$ J/K-mol; $S^o(H_2, g) = 29\ JK^{-1}mol^{-1}$

$S^o(CO, g) = 198$ J/mol-K; $C^o_{p,m}(H_2) = 28.8$ J/mol-K

$C^o_{p,m}(CO) = 29.4$ J/mol-K; $C^o_{p,m}(CH_3OH) = 44$ J/mol-K

and $\ln\left(\frac{320}{300}\right) = 0.06$, all data at 300 K

48. (C) $\Delta_r S^o$ at 300 K for the reaction is :

(a) 152.6 J/K-mol (b) 181.6 J/K-mol
(c) –16 J/K-mol (d) None of these

49. (C) $\Delta_r H^o$ at 300 K for the reaction is :

(a) –87 kJ/mol (b) 87 kJ/mol
(c) –315 kJ/mol (d) –288 kJ/mol

50. (C) $\Delta_r S^o$ at 320 K is:

(a) 155.18 J/mol-K (b) 150.02 J/mol-K
(c) 172 J/mol-K (d) None of these

Gibb's Energy (Rx Based)

51. (S) The free-energy change for the conversion of maleate into fumarate is 3.0 kJ. In metabolism, this reaction is coupled with the conversion fumarate to asparate, which is exergonic by 15.5 kJ. Calculate ΔG^0 for the overall reaction.

(a) – 185. kJ (b) + 18.5 KJ
(c) – 12.5 kJ (d) – 25.0 kJ

52. (S) The ΔG for the following reactions at 800^{0}C are given as

$S_2(s) + 2O_2(g) \rightarrow 2SO_2(g)$; ΔG = – 544 kJ

$2Zn(s) + S_2(s) \rightarrow 2ZnS(s)$; ΔG = – 293 kJ

$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$; ΔG = – 480 kJ

The ΔG for the reaction

$2ZnS + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$ will be

(a) – 357 kJ (b) – 731 kJ
(c) – 773 kJ (d) – 229 kJ

53. (S) Consider the reaction below at 298 K :

	C (graphite) +	2H$_2$ (g) →	CH$_4$ (g)
$\Delta_f H^o$ (kJ/mol)			– 74.9
S^0_m (J/K/mol)	+ 5.6	+ 130.7	+ 186.3

Which statement below is correct ?

(a) $\Delta_r G^0$ is – 50.8 kJ and the reaction is driven by enthalpy only.

(b) $\Delta_r G^0$ is – 50.8 kJ and the reaction is driven by entropy only.

(c) $\Delta_r G^0$ is + 50.8 kJ and the reaction is driven by both enthalpy and entropy.

(d) $\Delta_r G^0$ is – 50.8 kJ and the reaction is driven by both enthalpy and entropy.

54. (S)

Given	$\Delta_f H^0$ (KJ/mol)	S^0_m (J/K/mol)
$CCl_4(l)$	– 135.4	215.4
$CCl_4(g)$	– 103.0	308.7

What is the boiling point of carbon tetrachloride ?

(a) 8.25ºC (b) 74.3ºC
(c) 92.3ºC (d) 45.8ºC

55. (S) Calculate $\Delta_f G^o$ for (NH_4Cl, s) at 310 K.

Given : $\Delta_f H^o$ $(NH_4Cl, s) = -314.5$ kJ/mol; $\Delta_r C_p = 0$

$S^o_{N_2(g)} = 192\ JK^{-1}\ mol^{-1}$; $S^o_{H_2(g)} = 130.5 JK^{-1}\ mol^{-1}$

$S^o_{Cl_2(g)} = 233\ JK^{-1}\ mol^{-1}$ $S^o_{NH_4Cl(s)} = 99.5\ JK^{-1}\ mol^{-1}$

(All data given at 300K)

(a) – 198.56 kJ/mol (b) –426.7 KJ/mol

(c) –202.3 KJ/mol (d) None of these

Bond Energy

56. (S) The bond energy of H_2 is 104.3 kcal/mol. It means that

(a) 104.3 kcal heat is needed to break one bond to form two atoms

(b) 104.3 kcal is required to break 6.02×10^{23} molecules into atoms of hydrogen

(c) 104.3 kcal is required to break 3.015×10^{23} hydrogen molecules to 6.02×10^{23} hydrogen atoms

(d) none of these

57. (S) Energy required to dissociate 4g of gaseous hydrogen into free gaseous atoms is 208 kcal at 25°C. The bond energy of H — H bond will be

(a) 104 kcal (b) 10.4 kcal

(c) 1040 kcal (d) 1.04 kcal

58. (S) Determine C–C and C–H bond enthalpy (in kJ/mol)

Given: $\Delta_f H^o (C_2H_6, g) = -85$ kJ/mol

$\Delta_f H^o (C_3H_8, g) = -104$ kJ/mol

$\Delta_{sub} H^o (C, s) = 718$ kJ/mol B.E.(H – H) = 436 kJ/mol

(a) 414, 345 (b) 345, 414

(c) 287, 404.5 (d) None of these

59. (S) What is the bond enthalpy of Xe–F bond?

$$XeF_4 \rightarrow Xe^+(g) + F^-(g) + F_2(g) + F(g);$$
$$\Delta_r H = 292\ kcal/mol$$

Given: Ionization energy of Xe=279 kcal/mol

B.E. (F–F) = 38 kcal/mol, Electron affinity of F=85 kcal/mol

(a) 24 kcal/mol (b) 34 kcal/mol

(c) 8.5 kcal/mol (d) None of these

Lattice Energy

60. (S) The lattice energy of solid NaCl is 180 kcal per mol. The dissolution of the solid in water in the form of ions is endothermic to the extent of 1 kcal per mol. If the solvation energies of Na^+ and Cl^- ions are in the ratio 6 : 5, what is the enthalpy of hydration of sodium ion ?

(a) – 85.6 kcal/mol (b) – 97.5 kcal/mol

(c) 82.6 kcal/mol (d) + 100 kcal/mol

61. (A) **Assertion :** When a salt dissolves in water, the temperature of solution decreases.

Reason : Energy equal to lattice energy is required to ionize the salt in solution.

(a) A (b) B

(c) C (d) D

Resonance Energy

62. (S) If enthalpy of hydrogenation of $C_6H_6(l)$ into $C_6H_{12}(l)$ is –205 kJ and resonance energy of $C_6H_6(l)$ is –152 kJ/mol then enthalpy of hydrogenation of  is

Assume ΔH_{vap} of $C_6H_6(l)$, $C_6H_8(l)$, $C_6H_{12}(l)$ all are equal:

(a) – 535.5 kJ/mol (b) – 238 kJ/mol

(c) – 357 kJ/mol (d) – 119 kJ/mol

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

1. The difference between heats of reaction at constant pressure and constant volume for the reaction

$2C_6H_6(l) + 15O_2 \rightarrow 12CO_2(g) + 6H_2O(l)$

at 25° C in kJ is **(1991)**

(a) – 7.43
(b) + 3.72
(c) – 3.72
(d) + 7.43

2. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be **(1992)**

(a) less than ΔH
(b) zero
(c) more than ΔH
(d) equal to ΔH

3. The ΔH^o_f for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, – 110.5 and – 241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ mol^{-1}) for the reaction

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is. **(2000)**

(a) 524.1
(b) + 41.2
(c) – 262.5
(d) – 41.2

4. In thermodynamics, a process is called reversible when **(2001)**

(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

5. Which of the following statements is false ? **(2001)**

(a) Work is a state function
(b) Temperature is a state function
(c) Change in the state is completely defined when the initial and final states are specified
(d) Work appears at the boundary of the system

6. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) $\rightarrow$ (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta E = 30.0$ L-atm. The change in enthalpy (ΔH) of the process in L-atm is **(2002)**

(a) 40.0
(b) 42.10
(c) 44.0
(d) not defined, because pressure is not constant

7. Which of the following reactions defines ΔH^o_f ? **(2003)**

(a) $C_{(diamond)} + O_2(g) \rightarrow CO_2(g)$
(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$
(c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(d) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

8. Spontaneous adsorption of a gas on solid surface is an exothermic process because **(2004)**

(a) ΔH increases for system
(b) ΔS increases for gas
(c) ΔS decreases for gas
(d) ΔG increases for gas

9. $\Delta H_{vap} = 30$ kJ/mol and $\Delta S_{vap} = 75$ Jmol^{-1}K^{-1}. Find temperature of vapour, at one atmosphere. **(2004)**

(a) 400 K
(b) 350 K
(c) 298 K
(d) 250 K

10. 2 moles of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change ? **(2004)**

(a) 4.98 kJ
(b) 11.47 kJ
(c) – 11.47 kJ
(d) 0 kJ

11. When one mole of monoatomic ideal gas at TK undergoes adiabatic change under a constant external pressure of 1 atm changes volume from 1 L to 2 L. The final temperature in kelvin would be **(2005)**

(a) $\frac{T}{2^{2/3}}$
(b) $T + \frac{2}{3 \times 0.0821}$
(c) T
(d) $T - \frac{2}{3 \times 0.0821}$

12. A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas ? **(2006)**

(a) $\frac{4R}{2}$
(b) $\frac{3R}{2}$
(c) $\frac{5R}{2}$
(d) 0

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

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given $\Delta S_{(A\to C)} = 50$ eu

$\Delta S_{(C\to D)} = 30$ eu

$\Delta S_{(D\to B)} = 20$ eu

where eu is entropy unit, then $\Delta S_{(A\to B)}$ is **(2006)**

(a) + 100 eu (b) + 60 eu

(c) – 100 eu (d) – 60 eu

14. For the process $H_2O\,(l)$ (1 bar, 273 K) → $H_2O(g)$ (1 bar, 373 K), the correct set of themodynamic parameters is **(2007)**

(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = –ve$

(c) $\Delta G = +\,ve, \Delta S = 0$ (d) $\Delta G = –\,ve, \Delta S = +ve$

15. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

(Given : $\Delta_r H^o_{298K} = –54.07\ kJ\ mol^{-1}$,

$\Delta_r S^o_{298\,K} = 10\ JK^{-1}\ mol^{-1}$ and $R = 8.314\ JK–1\ mol^{-1}$;

$2.303 \times 8.314 \times 298 = 5705$ **(2010)**

(a) 5 (b) 10

(c) 95 (d) 100

16. One mode of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is (1L atm = 101.3 J) **(2016)**

(a) 5.763 (b) 1.013

(c) –1.013 (d) –5.763

17. For the pocess

$$H_2O(\ell) \to H_2O(g)$$

at T = 100°C and 1 atmosphere pressure, the correct choice is **(2014)**

(A) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$

(B) $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$

(C) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$

(D) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

18. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are

$\Delta_f G^o$ [C(graphite)] = 0 kJ mol^{-1}

$\Delta_f G^o$ [C(diamond)] = 2.9 kJ mol^{-1}

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by $2 \times 10^{-6}\ m^3\ mol^{-1}$. If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information : $1\ J = 1\ kg\ m^2 s^{-2}$,

$1\ Pa = 1\ kg\ m^{-1}\ s^{-2}$; $1\ bar = 10^5\ Pa$] **(2017)**

(a) 58001 bar (b) 1450 bar

(c) 14501 bar (d) 29001 bar

Objective Questions (One or more than one correct option)

19. Identify the intensive quantities from the following **(1993)**

(a) enthalpy (b) temperature

(c) volume (d) refractive index

20. The following is (are) endothermic reaction (s) **(1999)**

(a) combustion of methane

(b) decomposition of water

(c) dehydrogenation of ethane to ethylene

(d) conversion of graphite to diamond

21. Among the following, the state function(s) is (are) **(2009)**

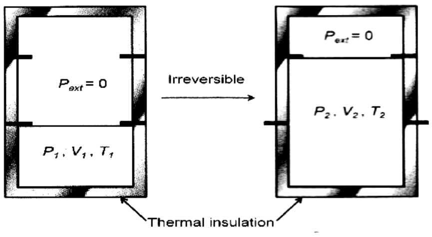
(a) internal energy

(b) irreversible expansion work

(c) reversible expansion work

(d) molar enthalpy

22. 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, **(2014)**



(a) $q = 0$ (b) $T_2 = T_1$

(c) $P_2V_2 = P_1V_1$ (d) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

23. An ideal gas is expanded from (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are) **(2017)**

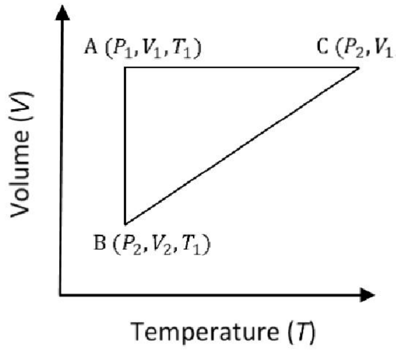
(a) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly from V_1 to V_2 under isothermal conditions.

(b) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 \neq T_2$.

(c) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

(d) The work done on the gas is maximum when it is compressed irrversibly from (p_2, V_2) to (p_1, V_1) against constant pressure p_1.

24. A reversible cyclic process for an ideal gas is shown below, Here, P, V, and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.



The correct option(s) is (are) **(2018)**

(a) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$

(b) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(c) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{BC} = \Delta H_{AC}$

(d) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

Assertion Reason

(A) If both ASSERTION and REASON are true and reason is the correct explanation of the assertion.

(B) If both ASSERTION and REASON are true but reason is not the correct explanation of the assertion.

(C) If ASSERTION is true but REASON is false.

(D) If both ASSERTION and REASON are false.

25. **Assertion :** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Reason : The volume occupied by the molecules of an ideal gas is zero.

(a) A (b) B

(c) C (d) D

26. **Assertion :** For every chemical reaction at equilibrium standard Gibbs' energy of reaction is zero.

Reason : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs' energy. **(2008)**

(a) A (b) B

(c) C (d) D

27. **Assertion :** There is a natural asymmetry between converting work to heat and converting heat to work.

Reason : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. **(2008)**

(a) A (b) B

(c) C (d) D

Fill in the Blanks

28. The total energy of one mole of an ideal monatomic gas at 27ºC is .... cal. **(1984)**

29. $C_p - C_V$ for an ideal gas is .... **(1984)**

30. A system is said to be .... if it can neither exchange matter nor energy with the surroundings. **(1993)**

31. The heat content of the products is more than that of the reactants in an .... reaction. **(1993)**

32. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is .... **(1997)**

33. Enthalpy is an .... property. **(1997)**

True/False

34. First law of thermodynamics is not adequate in predicting the direction of a process. **(1982)**

35. Heat capacity of a diatomic gas is higher than that of a monatomic gas. **(1985)**

Subjective Questions

36. The enthalpy for the following reactions (ΔH°) at 25ºC are given below

(i) $\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$ $\Delta H^\circ = -10.06$ kcal

(ii) $H_2(g) \rightarrow 2H(g)$ $\Delta H^\circ = 104.18$ kcal

(iii) $O_2(g) \rightarrow 2O(g)$ $\Delta H^\circ = 118.32$ kcal

Calculate the O — H bond energy in the hydroxyl radical. **(1981)**

37. The standard heats of formation of $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and HCl(g) at 298 K are –25.5, –57.8, – 94.1 and –22.1 kcal/mol respectively. Calculate ΔH^o (298 K) for the reaction

$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$ **(1982)**

38. The molar heats of combustion of $C_2H_2(g)$, C (graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal respectively. Calculate the standard heat of formation of $C_2H_2(g)$. **(1983)**

39. Following statement is true only under some specific conditions. Write the conditions for that in not more than two sentences

"The heat energy q, absorbed by a gas is ΔH." **(1984)**

40. Given the following standard heats of reactions

(i) heat of formation of water = – 68.3 kcal

(ii) heat of combustion of acetylene = – 310.6 kcal

(iii) heat of combustion of ethylene = – 337.2 kcal

Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25° C). **(1984)**

41. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal/mol respectively. Calculate the enthalpy of formation of HCl gas. **(1985)**

42. The standard molar heat of formation of ethane, carbon dioxide and liquid water are –21.1, –94.1, and –68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

43. An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows :

$$H_f(Al_2O_3) = -399 \text{ kcal/mol}$$

$$H_f(Fe_2O_3) = -199 \text{ kcal/mol}$$

Density of Fe_2O_3 = 5.2 g/cc,

Density of Al = 2.7 g/cc **(1989)**

44. An athlete is given 100g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 percent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water the would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol.

(1989)

45. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, – 3800 and –3920 kJ/mol respectively. Calculate the heat of hydrogenation of cyclohexene. **(1989)**

46. Using the data (all values are in kilocalories per mol at 25°C) given below, calculate the bond energy of C—C and C—H bonds.

$C(s) \longrightarrow C(g),\quad \Delta H = 172$

$H_2(g) \longrightarrow 2H(g),\quad \Delta H = 104$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l),\quad \Delta H = -68.0$

$C(s) + O_2(g) \longrightarrow CO_2(g),\quad \Delta H = -94.0$

Heat of combustion of $C_2H_6 = -372.0$

Heat of combustion of $C_3H_8 = -530.0$ **(1990)**

47. A gas mixture of 3.67L of ethylene and methane on complete combustion at 25°C produces 6.11L of CO_2. Find out the amount of heat evolved on burning 1L of the gas mixture. The heat of combustion of ethylene and methane are – 1423 and –891 kJ mol^{-1} at 25°C. **(1991)**

48. Determine the enthalpy of the reaction,

$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, at 25°C, using the given heat of combustion values under standard conditions.

Compound :	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C(graphite)
ΔH^o (kJ/mol) :	–285.8	–890.0	–1560.0	–393.0

The standard heat of formation of $C_3H_8(g)$ is –103 kJ/mol.

(1992)

49. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion etc., are the same for both fuels and that the gases behave ideally. Heats of combustions :

$CH_4 = -809$ kJ/mol, $C_4H_{10} = -2878$ kJ/mol **(1993)**

50. The polymerization of ethylene to linear polyethylene is represented by the reaction,

$$n\,[CH_2 = CH_2] \longrightarrow -\!\![CH_2 - CH_2]\!\!-_n$$

where, n has large integral value. Given that the average enthalpies of bond dissociation for C═C and C—C at 298 K are + 590 and +311 kJ/mol respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K. **(1994)**

51. The standard enthalpies of formation of cyclohexane (*l*) and benzene (*l*) at 25ºC are –156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (*l*) at 25ºC is –119 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene. **(1996)**

52. Compute the heat of formation of liquid methyl alcohol in kJ mol^{-1}, using the following data. Heat of vaporization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states : H = 218 kJ/mol, C = 715 kJ/mol, O = 249 kJ/mol.

Average bond energies :

C—H = 415 kJ/mol
C—O = 356 kJ/mol
O—H = 463 kJ/mol **(1997)**

53. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_2(g), H_2O (*l*) and propane (g) are –393.5, –285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerization of cyclopropane to propene is –33.0 kJ mol^{-1}. **(1998)**

54. Estimate the average S–F bond energy in SF_6. The values of standard enthalpy of formation of SF_6(g), S(g) and F(g) are :

– 1100, 275 and 80 kJ mol^{-1} respectively. **(1999)**

55. A sample of argon gas at 1 atm pressure and 27ºC expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process C_{V_m} for argon is 12.49 JK^{-1} mol^{-1}. **(2000)**

56. Show that the reaction,

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ at 300 K, is spontaneous and exothermic, when the standard entropy change is –0.094 kJ mol^{-1} K^{-1}. The standard Gibbs' free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1}, respectively. **(2000)**

57. Diborane is a potential rocket fuel which undergoes combustion according to the reaction

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane. **(2000)**

$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s),\quad \Delta H = -1273 \text{ kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l),\quad \Delta H = -286 \text{ kJ mol}^{-1}$

$H_2O(l) \longrightarrow H_2O(g),\quad \Delta H = 44 \text{ kJ mol}^{-1}$

$2B\,(s) + 3H_2\,(g) \longrightarrow B_2H_6\,(g),\quad \Delta H = 36 \text{ kJ mol}^{-1}$

58. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175ºC, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175ºC. Calculate ΔGº for the following equilibria.

$B \rightleftharpoons A,\quad \Delta G_1^o = ?$

$B \rightleftharpoons C,\quad \Delta G_2^o = ?$

From the calculated value of ΔG_1^o and ΔG_2^o indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C) **(2001)**

59. Two moles of a perfect gas undergo the following processes :

(a) a reversible isobaric expansion from (1.0 atm, 20.0L) to (1.0 atm, 40.0 L)

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

(c) a reversible isothermal compression from (0.5 atm, 40.0L) to (1.0 atm, 20.0 L)

(i) Sketch with labels each of the processes on the same p-V diagram.

(ii) Calculate the total work (W) and the total heat change (Q) involved in the above processes.

(iii) What will be the values of ΔU, ΔH and ΔS for the overall process ? **(2002)**

60. C_V value of He is always $\frac{3R}{2}$ but C_V value of H_2 is $\frac{3R}{2}$ at low temperature and $\frac{5R}{2}$ at moderate temperature and more than $\frac{5R}{2}$ at higher temperature. Explain in two or three lines. **(2003)**

61. 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the ΔH and ΔU. **(2004)**

62. For the reaction, $2CO + O_2 \rightarrow 2CO_2$; $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K.

(1 L-atm = 0.1 kJ) **(2006)**

63. In a constant volume calorimeter, 3.5g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increases 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 **(2009)**

64. The surface of copper gets tarnished by the formation of copper oxide. N_2 gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N_2 gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below : **(2018)**

$$2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$$

p_{H_2} is the minimum partial pressure of H_2 (in bar) needed to prevent the oxidation at 1250 K. The value of $\ln(p_{H_2})$ is ....

(Given : total pressure = 1 bar, R (universal gas constant) = 8J K^{-1} mol^{-1}, ln (10) = 2.3. Cu(s) and $Cu_2O(s)$ are mutually immiscible.

At 1250 K : $2Cu(s) + \frac{1}{2} O_2(g) \rightarrow Cu_2O(s)$;

$\Delta G^{-} = -78{,}000$ J mol^{-1}

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$; $\Delta G^{-} = -1{,}78{,}000$ J mol^{-1};

G is the Gibbs energy

ANSWER KEY

EXERCISE - 1 : (Basic Objective Questions)

1. (a) **2.** (d) **3.** (a) **4.** (a) **5.** (c) **6.** (c) **7.** (d) **8.** (b) **9.** (b) **10.** (c)

11. (a) **12.** (c) **13.** (b) **14.** (b) **15.** (d) **16.** (b) **17.** (d) **18.** (d) **19.** (a) **20.** (c)

21. (c) **22.** (a) **23.** (b) **24.** (b) **25.** (b) **26.** (d) **27.** (c) **28.** (d) **29.** (a) **30.** (c)

31. (a) **32.** (b) **33.** (b) **34.** (b) **35.** (b) **36.** (d) **37.** (b) **38.** (d) **39.** (a) **40.** (b)

41. (d) **42.** (b) **43.** (a) **44.** (c) **45.** (a) **46.** (b) **47.** (a) **48.** (c) **49.** (c) **50.** (c)

51. (c) **52.** (d) **53.** (d) **54.** (b) **55** (b) **56.** (d) **57.** (b) **58.** (a) **59.** (a) **60.** (b)

61. (a) **62.** (c) **63.** (d) **64.** (c) **65.** (c) **66.** (b) **67.** (c) **68.** (a) **69.** (c) **70.** (c)

71. (d) **72.** (b) **73.** (a) **74.** (b) **75.** (c) **76.** (c) **77.** (d) **78.** (d) **79.** (b) **80.** (b)

81. (a) **82.** (c) **83.** (c) **84.** (d) **85.** (d) **86.** (c) **87.** (a) **88.** (d) **89.** (c) **90.** (c)

91. (d) **92.** (a) **93.** (a) **94.** (a) **95.** (d) **96.** (b) **97.** (c) **98.** (b) **99.** (b) **100.** (a)

101. (d) **102.** (b) **103.** (b) **104.** (c) **105.** (b) **106.** (b) **107.** (b) **108.** (a) **109.** (c) **110.** (a)

111. (a) **112.** (b) **113.** (a) **114.** (a) **115.** (d) **116.** (b) **117.** (d) **118.** (b) **119.** (d) **120.** (b)

EXERCISE - 2 : (Previous year JEE MAINS Questions)

1. (a) **2.** (c) **3.** (b) **4.** (d) **5.** (d) **6.** (d) **7.** (c) **8.** (d) **9.** (a) **10.** (d)

11. (d) **12.** (b) **13.** (a) **14.** (c) **15.** (b) **16.** (a) **17.** (d) **18.** (a) **19.** (c) **20.** (c)

21. (b) **22.** (b) **23.** (d) **24.** (b) **25.** (b) **26.** (d) **27.** (c) **28.** (d) **29.** (a) **30.** (d)

31. (a) **32.** (b) **33.** (b) **34.** (a)

JEE Mains Online

1. (c) **2.** (b) **3.** (c) **4.** (a) **5.** (d) **6.** (b) **7.** (d) **8.** (b) **9.** (d) **10.** (c)

11. (b) **12.** (d) **13.** (b) **14.** (b) **15.** (a) **16.** (b) **17.** (b) **18.** (a)

EXERCISE - 3 : (Advanced Objective Questions)

1. (b) **2.** (a) **3.** (a) **4.** (a) **5.** (a) **6.** (a) **7.** (b) **8.** (c) **9.** (b) **10.** (d)

11. (c) **12.** (c) **13.** (d) **14.** (d) **15.** (c) **16.** (b) **17.** (b) **18.** (c) **20.** (d) **20.** (a)

21. (a) **22.** (d) **23.** (d) **24.** (c) **25.** (b) **26.** (a) **27.** (a) **28.** (b) **29.** (c) **30.** (a)

31. (b) **32.** (b) **33.** (a) **34.** (d) **35.** (a) **36.** (d) **37.** (a) **38.** (c) **39.** (b) **40.** (c)

41. (c) **42.** (a) **43.** (b) **44.** (a) **45.** (b) **46.** (c) **47.** (d) **48.** (c) **49.** (a) **50.** (d)

51. (c) **52.** (b) **53.** (a) **54.** (b) **55.** (a) **56.** (b) **57.** (a) **58.** (b) **59.** (b) **60.** (b)

61. (d) **62.** (d)

EXERCISE - 4 : (Previous year JEE ADVANCED Questions)

1. (a) **2.** (c) **3.** (b) **4.** (c) **5.** (a) **6.** (c) **7.** (b) **8.** (c) **9.** (a) **10.** (d)

11. (d) **12.** (a) **13.** (a) **14.** (a) **15.** (b) **16.** (c) **17.** (b) **18.** (c) **19.** (b, d) **20.** (b, c, d)

21. (a, c, d) **22.** (a,b,c) **23.** (a,b,d) **24.** (b,c) **25.** (b) **26.** (d) **27.** (b) **28.** 900 **29.** R **30.** isolated

31. exothermic reaction **32.** zero **33.** extensive **34.** True **35.** True **36.** 121.31 kcal

37. –41.4 kcal **38.** 54.2 kcal **40.** –41.7 kcal **41.** – 22 kcal/mol **42.** –372 kcal/mol

43. 3.94 kcal/cc **44.** 17.72 mole **45.** –121 kJ/mol **46.** C–H = 99 kcal, C–C = 82 kcal

47. 49.82 kJ **48.** – 55 kJ **49.** 5.46 x L/h **50.** –32 kJ/mol **51.** – 152 kJ/mol

52. –266 kJ/mol **53.** –2091.32 kJ **54.** 309.16 kJ/mol **55.** –116.4 J **56.** –285.4 kJ < 0

57. – 2035 kJ **58.** 12.3 kJ **61.** 9900 bar mL, 100 bar mL **62.** – 557 kJ

63. 9 kJ **64.** –14.6

Dream on !!