5 Thermodynamics

Thermodynamics describes fundamental principles found in everyday life. Massive structures may appear to be capable of lasting nearly indefinitely, but they are not. During an earthquake, an old building gradually collapses on its own, but it does not rebuild on its own. 2nd law of thermodynamics is a universal law of decay in some ways; the ultimate cause of why everything eventually falls apart and disintegrates over time.

Topic Notes

- ☐ *Thermodynamic Terms and their Applications*
- ☐ *Measurement and Calculation of ΔU and ΔH*
- ☐ *Laws of Thermodynamics, Spontaneity, Gibbs's Energy Change*

THERMODYNAMIC TERMS AND THEIR APPLICATIONS

1

TOPIC 1

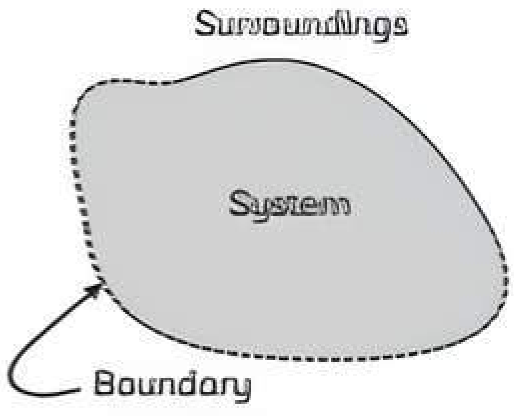
THERMODYNAMIC TERMS

It is a branch of science that deals with the combined effects of heat and works with state changes. The changes and effects of these changes follow certain laws, the laws of thermodynamics. Various chemical reactions release or absorb heat energy, which is then converted into different usable forms by thermodynamic laws. We cannot create or destroy energy. Energy transformation is based on this principle, and its use in different industries is a major application of thermodynamic terms. Chemical reactions also have varying amounts of energy attached to them. Energy flows from one form to another in thermodynamics. Energy and work done are also studied about heat and temperature. The laws of thermodynamics govern the changes in energy that occur during a reaction. This is independent of the reaction rate. When it comes to thermodynamics, we often refer to work, heat, and energy as general terms. Now that we know a bit about these terms, let's make sure we understand them thoroughly. Our focus is on chemical reactions and the energy changes that occur. We need to understand specific thermodynamic terms to do this. Here are some of them:

The System and the Surroundings

The system is defined as the region of a universe where observations can be made, and the rest of the universe is what surrounds it, which is called surroundings. The two components together constitute the universe. However, the changes taking place within the system do not affect the rest of the universe. The surroundings are everything other than the system. In most cases, the region of space surrounding a system is its surroundings.

System+Surrounding=Universe



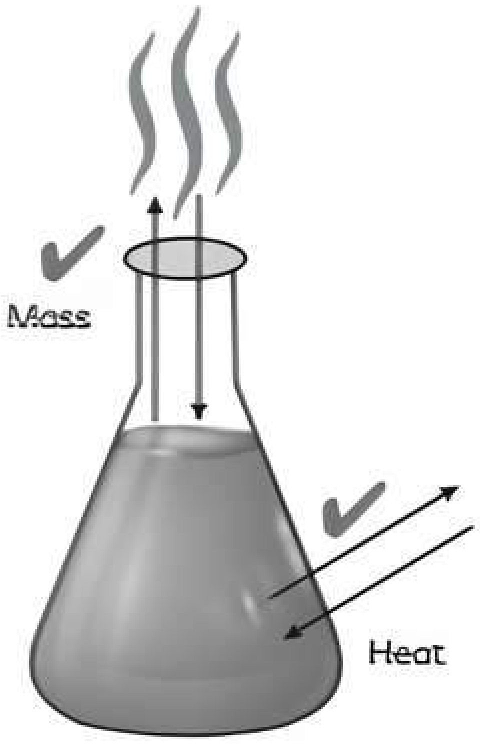
Model of a system

Types of the System

The systems are further divided based on the movement of matter and energy within and outside the system.

Open system

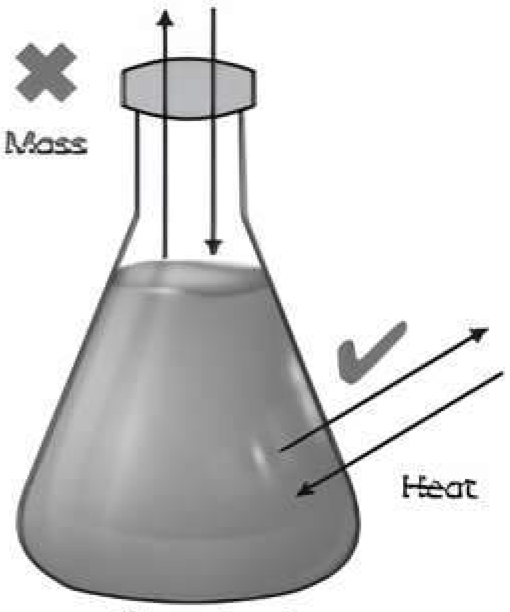
In an open system, energy and matter are exchanged between the system and its surroundings. As an example of an open system, an open beaker contains reactants. Using this example, the boundary refers to the beaker's imaginary surface and reactants.



Open system

Closed system

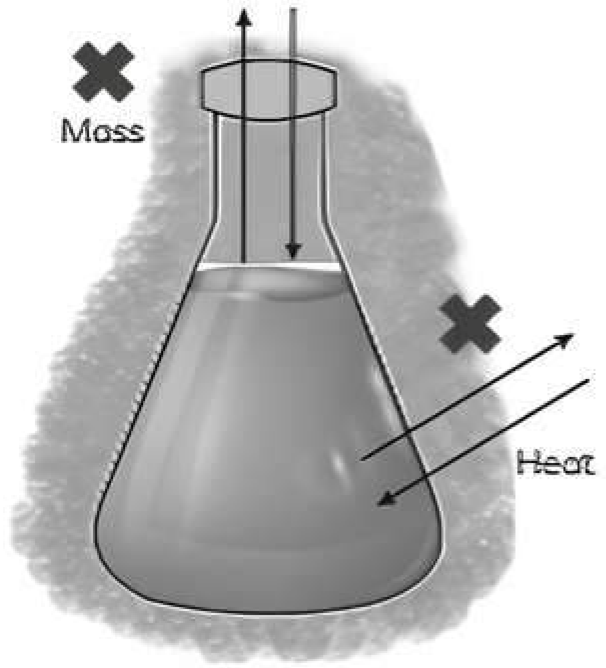
A closed system cannot exchange matter, but it can exchange energy with its surroundings. A secure system includes reaction products in a vessel made of conductors, such as copper or steel.



Closed system

Insulated system

An isolated (insulated) system does not exchange energy or matter with its surroundings—an isolated system of reactants enclosed in a thermos flask or any other closed, insulated vessel.



Insulated system

Thermodynamic properties: The properties that are the characteristics (identifiable and observable) of a system by which it can be specified are called thermodynamic properties. Thermodynamic properties can be divided into:

(1) **Extensive thermodynamic properties:** Extensive properties are those properties which depend on the extent of the system. That means extensive properties are directly related (directly proportional) to the mass. Examples of extensive properties are volume, internal energy, mass, enthalpy, entropy etc.

(2) **Intensive thermodynamic properties:** Intensive properties are those properties of the system which do not depend on the extent of the system. That means intensive properties are not related to the mass. Examples of intensive properties are temperature, pressure, density, etc.

The State of the System

It is essential to describe the system before and after the change. We use state functions or state variables to describe the system's state. In thermodynamics, measurable or macroscopic (bulk) properties define the state of a system. The state of a gas can be expressed using its pressure (p), volume (V), temperature (T), amount (n), etc. The state variables p, V *and* T depend solely on the system's state and not on its achievement.

State functions

A thermodynamic function whose value depends only on the initial and final states of the system, rather than on the path taken is called state function, for example, Internal energy, Enthalpy. In **state function,** the number depends on the nature of the system. The state can never be completely specified but favourably it is not necessary to do that.

Path functions

Functions that depend on the path taken while changing from one state to another are called path functions, *e.g.*, work, and heat. We will now study about some state variables.

The Internal Energy as a State Function

The internal energy U of a system is the sum of the kinetic energy caused by the motion of molecules and the potential energy created by the vibrational motion and electric energy of atoms within molecules. Chemical bonds also contribute to internal energy. There are many ways internal energy can be viewed from a microscopic perspective. This includes any material or repulsion between molecules.

A system's internal energy is a state function and an extensive quantity.

We call it the internal energy of the system which changes when:

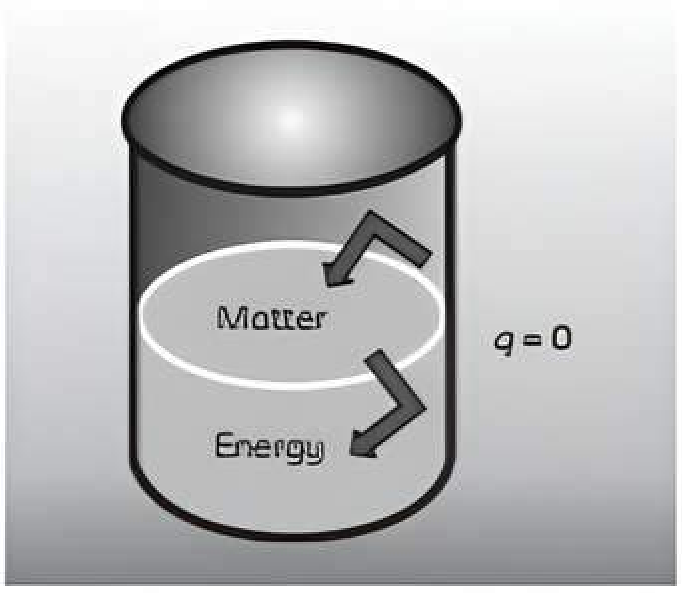
(1) It absorbs or emits heat.

(2) When work is performed on or by the system.

(3) If matter moves in or out of the system.

Work

Consider a thermos flask it would not allow the exchange of heat between the system and surroundings through its boundary. Such a type of system is called **adiabatic**. An adiabatic process is a process where no exchange of heat will happen between the system and the surroundings and the wall separating it is called an adiabatic wall. Work is defined as the amount of energy exchanged between it and its surroundings. Work is entirely governed by external factors such as an external force, pressure or volume, temperature change, etc. According to IUPAC conventions in chemical thermodynamics, the positive sign indicates that the work is positive when work is done on the system, increasing the system's internal energy and if the system does the work, work will be negative because the system's internal energy decreases.



Adiabatic system which does not permit the transfer of heat through its boundary

This experiment was done by J.P. Joule. He showed that the amount of work done produces the same change of state irrespective of the system's path measured by the change in temperature. Consider the system's initial state as A, the temperature of the system as T_A and the internal energy of the system as U_A. The state of the system can be altered in two different ways:

(1) When mechanical work of 1 J is done by rotating paddles to make the water churn. Now, the system moves to the new state B, and its temperature is T_B and internal energy is U_B. The change in internal energy B is $\Delta U = U_B - U_A$.

(2) An equal amount of electrical work done by immersing rod and change in temperature is noted as $T_B - T_A$ same as that of the earlier case.

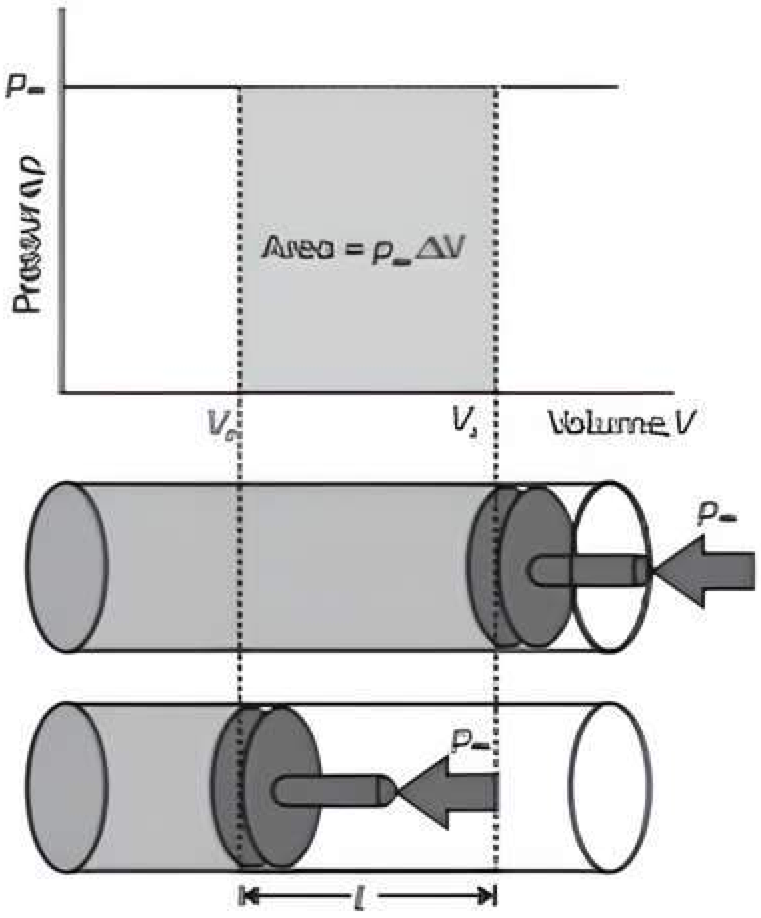
It is concluded that an adiabatic change to bring change in the system is equal to the difference in the value of U in one state and another state.

$$\Delta U = U_2 - U_1 = W_{ad}$$

Mechanical work done by the system

Consider a cylinder containing one mole of an ideal gas fitted with a frictionless piston. The total volume of gas is V_1 and the pressure of the gas inside the cylinder is p.

If external pressure is p_{ex} greater than the inside pressure p of the gas ($p_{ex} > p$) the piston will move inward till both pressures become equal to p_{ex}. Considering this takes place in a single step then the final volume would be V_f. During this process of compression, the distance moved by the piston is l and A is the cross-sectional area of the piston.



The change in volume = $(V_f - V_i)$

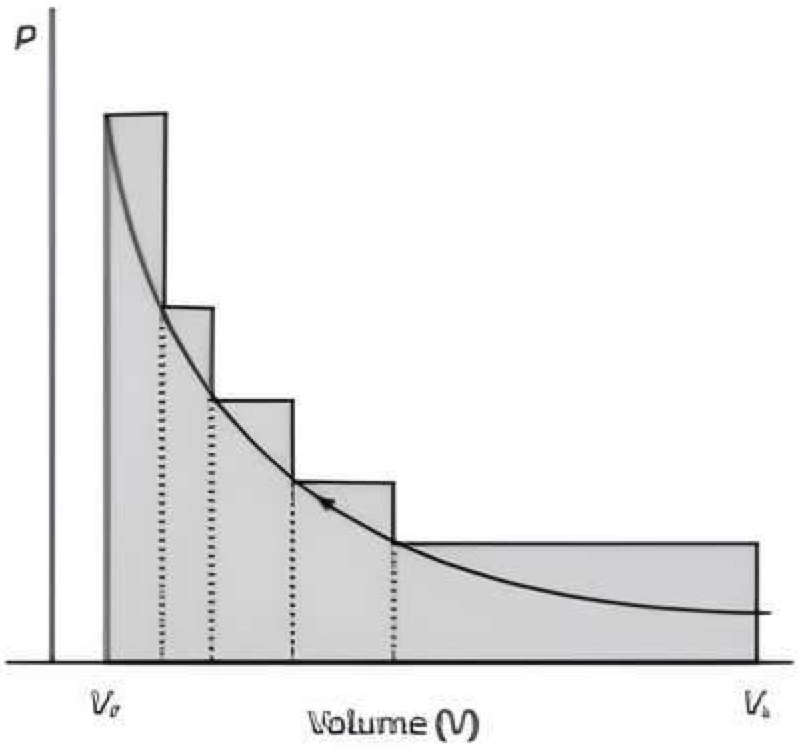
We know that, $\quad$ pressure = $\dfrac{\text{force}}{\text{area}}$

Therefore, force on the piston = $p_{ex}A$

If w is the work done on the system by the movement of the piston then,

$$\begin{aligned} w &= \text{force} \times \text{distance} \\ &= p_{ex}Al \\ &= p_{ex}(-\Delta V) \qquad [\because l \times A = \Delta V] \\ &= -p_{ex}(V_f - V_i) \end{aligned}$$

The negative sign of this expression is to obtain a positive sign for work. It indicates, in case of compression work is done on the system and $(V_f - V_i)$ is negative and multiplied by again negative will give a positive sign for work. If the pressure is changing during the compression process, then all the pressure values are summed up and it is equal to $-\sum p\Delta V$.



p–V plot when pressure is not constant and changes in finite steps during compression from initial volume to the final volume, work done on the gas is represented by the shaded area

If the pressure of the gas is not constant but changes in the process are always infinitesimally then the volume will be decreased by an infinitesimal amount dV. The work done on the gas can be calculated by

$$w = \int_{V_i}^{V_f} p_{ex}\,dv$$

(1) During each stage of the compression process, $p_{ex} = (p_{in} + dp)$

(2) In the case of the expansion process, $p_{ex} = (p_{in} - dp)$. (external pressure less than pressure of the system).

(3) In general, we can write, $p_{ex} = (p_{in} \pm dp)$ these processes are called reversible processes.

Note:

(1) **Sign of w:** When the system's volume increases, w is –ve, and when it decreases, w is +ve.

(2) **Sign of U:** If the system's temperature decreases or the product of pressure and volume (pV) decreases, then U becomes –ve; otherwise, U becomes positive.

Reversible and irreversible process: If a process or change is brought about so that it could be reversed at any time by a tiny change, it is said to be reversible. Reversible processes proceed infinitely slowly by a series of equilibrium states, such that the system and its surroundings are nearly in equilibrium. The term irreversible refers to processes other than reversible processes.

Work done for reversible process with the internal pressure can be written as:

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex}\,dV$$

$$= -\int_{V_i}^{V_f} (p_{in} \pm dp)\,dV$$

Since $dp \times dV$ is very small so we can write

$$w_{rev} = -p_{in}dV$$

Now, as we know from the ideal gas equation $pV = nRT$. For n mole of an ideal gas:

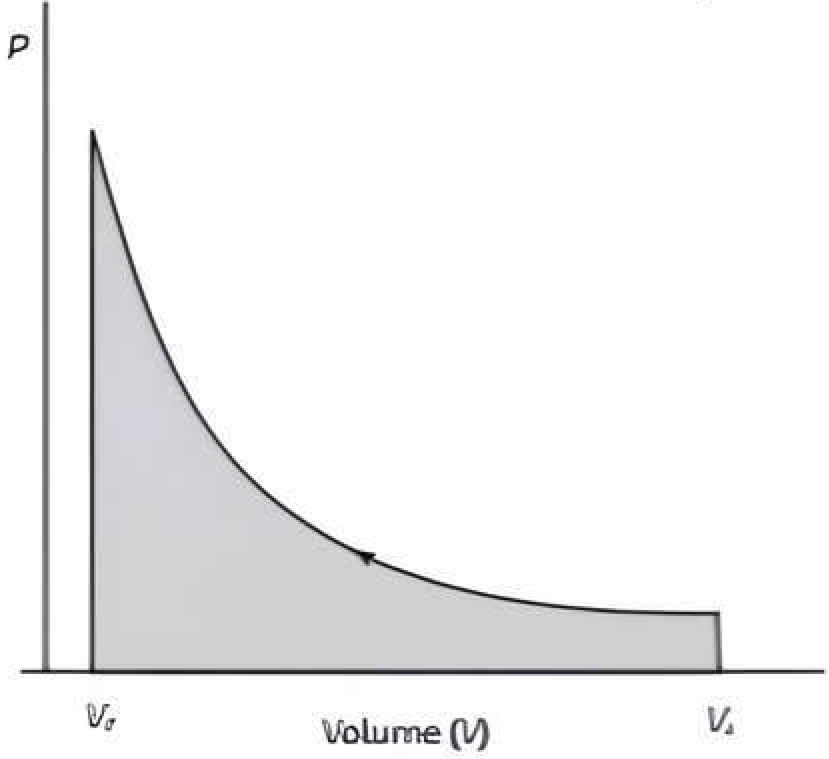
$$P = \frac{nRT}{V}$$

At constant temperature (Isothermal process)

$$w_{rev} = -\int_{V_i}^{V_f} nRT\frac{dV}{V}$$

$$= -nRT\ln\frac{V_f}{V_i}$$

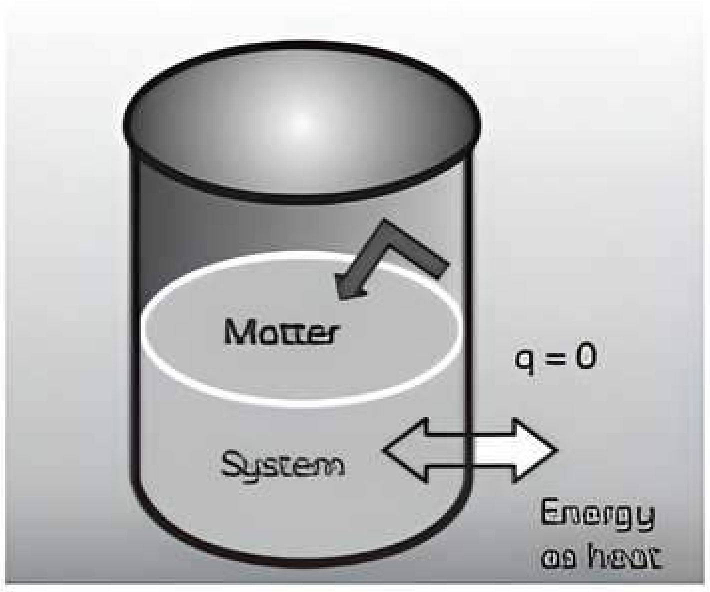
$$= -2.303\,nRT\log\frac{V_f}{V_i}$$



p – V plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from Initial to final volume. Work done on the gas is represented by the shaded area.

Heat

In thermodynamics, heat is defined as the kinetic energy of molecules. Together, heat and thermodynamics provide the basis for process designers and engineers to optimize their processes and harness the energy associated with chemical reactions, from higher to lower temperatures, heat moves.



Surroundings are represented by the shaded area.

Consider a container containing water at temperature T_A having thermally conducting walls made of copper enclosed in a heat reservoir at temperature T_B. The heat energy absorbed by water in terms of temperature difference is $T_B - T_A$. The change in internal energy is $\Delta U = q$ (No work done at constant volume).

We can also change the internal energy without exerting any effort by transferring heat from the surroundings to the system or *vice versa*. According to IUPAC conventions in chemical thermodynamics, heat, *q*, results from energy exchange resulting from temperature differences. Heat is transferred from the surroundings to the system, increasing the system's internal energy; in contrast, heat is transferred from the system to the surroundings, thereby decreasing the system's internal energy.

First Law of Thermodynamics

Let us consider the general case where a state change can be caused by working and transferring heat.

$$\Delta U = q + w$$

For a given change in state, '*q*' and '*w*' can vary depending on how the change is implemented. Nevertheless, it will depend only on the initial and final states. It will not matter how the change is implemented.

$$\Delta U = 0$$

if no energy is transferred as heat or work (isolated system), *i.e.*, if $w = 0$ and $q = 0$. This equation says that an isolated system has constant energy, thus theoretically expressing **the first law of thermodynamics.** It is commonly described as the law of conservation of energy, *i.e.*, energy cannot be created or destroyed.

Note: Thermal properties like energy are very different from mechanical properties like volume. An absolute value can be specified for the volume of a system in a particular state. However, the total value of the internal energy cannot be determined. However, we can only measure changes in the system's internal energy.

Free expansion

Free expansion refers to the expansion of a gas in a vacuum ($p_{ex} = 0$). There is no reversible or irreversible work done during the free expansion of an ideal gas.

Now, as we know that

$$w = -p_{ex}dV$$

Substituting this in the first law thermodynamic equation. We get

$$\Delta U = q - p_{ex}\Delta V$$

The process is carried out at a constant volume ($\Delta V = 0$), then

$\Delta U = q_V$ (Here V represents that heat is supplied at a constant volume).

Isothermal and free expansion of an ideal gas

For isothermal expansion for ideal gas into a vacuum; when T is constant; $w = 0$ since $p_{ex} = 0$. Joule also proved experimentally that $q = 0$, and therefore,

$$\Delta U = 0$$

Now by using the first law of thermodynamic equation $\Delta U = q + w$, we can derive various types of equations for different types of conditions applied as follows:

For irreversible isothermal changes

$$q = -w$$
$$= p_{ex}(V_f - V_i)$$

For an isothermal reversible change

$$q = -w$$
$$= nRT \ln \frac{V_f}{V_i}$$
$$= 2.303\, nRT \log \frac{V_f}{V_i}$$

For adiabatic changes,

$$q = 0, \Delta U = w_{ad}$$

Example 1.1: **In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process? [NCERT]**

Ans. Heat absorbed by the system, $q = 701$ J

Work done by the system $= -394$ J

Change in internal energy $= (\Delta U)$

$= q + w$

$= 701 - 394 = 307$ J.

Example 1.2: **Describe how the internal energy of a system changes when:**

(A) The system absorbs no heat from its surroundings, but it does work. Can you tell what type of wall the system has?

(B) No work is done on the system, but heat is removed and given to the environment. Describe the kind of wall the system has.

(C) In addition, the system performs 'w' amount of work, and amount of heat is supplied. What type of system is it? [NCERT]

Ans. (A) As we know from the first law of thermodynamics, $\Delta U = q + w$ and it is given that there is no absorption of heat from the surroundings means there is no change in the heat, but the work is done, so $w \neq 0$. Hence, the equation becomes $\Delta U = w$. Since the exchange of heat is restricted accordingly, the system is adiabatic $\Delta U = w_{ad}$.

(B) Also, no work is done on the system, so $w = 0$, but the heat loss takes place (the system loses heat), so the first law of thermodynamics becomes $\Delta U = -q$. And the system is showing an exchange of heat but no work, hence the system is thermally conducting walls.

(C) Since the system does the work "$w = -w$" and the heat is given to the system, so "$q = +q$". Hence, the first law of thermodynamics becomes $\Delta U = q - w$. And the system shows both work and exchange of heat therefore, the system is a closed system.

Example 1.3

(A) 2 litres of an ideal gas at a pressure of 10 atm expands isothermally at 25°C into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion?

(B) Consider the same expansion, but this time against a constant external pressure of 1 atm. [NCERT]

Ans. (A) Given,

$$V_i = 2 \text{ L}$$
$$V_f = 10 \text{ L}$$
$$p_{ex} = 10 \text{ atm}$$

We know that, for isothermal compression

$$q = -w$$
$$= p_{ex}(10 - 2)$$
$$= 10(8)$$
$$= 80 \text{ L-atm}$$

Hence, work is done 80 L-atm, and same amount of heat is absorbed.

(B) $p_{ex} = 1$ atm

And we know that $q = -w = p_{ex}\Delta V$

$$= 1\,(8)$$
$$= 8 \text{ L-atm}$$

Example 1.4: Consider the expansion in example 1.3 (A) for 1 mole of an ideal gas conducted reversibly. [NCERT]

Ans. We know

$$q = -w$$

$$= 2.303 nRT \log\frac{V_f}{V_i}$$

$$q = 2.303 \times 1 \times 0.082 \times 298 \times \log\frac{10}{2}$$

$$= 2.303 \times 1 \times 0.082 \times 298 \times \log 5$$

$$= 2.303 \times 1 \times 0.082 \times 298 \times 0.6990$$

$$= 39.33 \text{ litre-atm}$$

Enthalpy

A useful new state function

We know that heat gets absorbed at a constant volume is equal to the change in the internal energy $\Delta U = q_v$, But mostly the chemical reactions are not carried out at this constant volume, but in flasks or test tubes, the atmospheric pressure is constant. So, another system needs to define under these conditions.

The thermodynamic internal energy equation can be written as, $\Delta U = q_p - p\Delta V$ Where q_p is heat absorbed by the system and the $-p\Delta V$ represented work done by expansion of the system.

The initial state of the system is represented by subscript 1 and final state by 2. The equation can be rewritten as

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

On rearranging it, we get

$$q_p = (U_2 + pV_2) - (U_1 + pV_1)$$

The other thermodynamic function can be defined by enthalpy H (Greek word *enthalpie*, to warm or heat content) as:

$$H = U + pV$$

So, equation becomes

$$q_p = H_2 - H_1$$
$$= \Delta H$$

Although q is a path function, H is a state function because it depends on U, p and V which are state functions. Therefore, ΔH is path independent. Hence, q_p is also path independent.

For finite changes at constant pressure, the equation can be written as,

$$\Delta H = \Delta U + p\Delta V_p$$

It is important to note that when heat is absorbed by the system at constant pressure, we measure the changes in the enthalpy of the system.

$\Delta H = q_p$, it is the heat absorbed by the system at constant pressure.

ΔH is negative for an exothermic process (Heat released during the reaction) and ΔH is positive for an endothermic process (Heat absorbed during the reaction from the surroundings).

At constant volume ($\Delta V = 0$), $\Delta U = q_p$ therefore, the equation can be written as,

The difference between $\Delta H = \Delta U = q_p$ is not significant for systems consisting of only solids or liquids. Because they do not suffer any volume changes upon heating. The difference is significant when gases are involved.

Let us assume a reaction where gases are involved in the reaction. V_A is the total volume of the gaseous reactants and V_B is the total volume of the gaseous products. n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant temperature and pressure, then the ideal gas law can be written as

$$pV_A = n_ART \text{ and } pV_B = n_BRT$$

$$\text{Thus, } pV_B - pV_A = n_BRT - n_ART$$

$$pV_B - pV_A = RT(n_B - n_A)$$

$$p\Delta V = \Delta n_g RT$$

The Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ in the equation $\Delta H = \Delta U + p\Delta V$, we get

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

Important

➡ $\Delta H = \Delta U + \Delta n_g RT$

Case 1 $\Delta n_g = 0$, *then* $\Delta H = \Delta U$

Case 2 $\Delta n_g < 0$, *then* $\Delta H < \Delta U$

Case 3 $\Delta n_g > 0$, *then* $\Delta H > \Delta U$

Example 1.5: Case Based:

Enthalpy is a property of a thermodynamic system and is the sum of the system's internal energy and the product of its pressure and volume. It is a state function used in many measurements in chemical, biological, and physical systems at a constant pressure, which is conveniently provided by the large ambient atmosphere. The pressure-volume term expresses the work required to establish the system's physical dimensions. The pressure-volume term is very small for solids and liquids at common conditions and fairly small for gases. Therefore, enthalpy is a stand-in for energy in chemical systems; bonds, lattice, solvation and other "energies" in chemistry are actually enthalpy differences.

(A) What is the enthalpy value for the exothermic process?

(a) Negative value (b) Positive value

(c) Zero (d) Constant value

(B) During the exothermic process, the enthalpy of products will be .... than the enthalpy of reactant.

(a) lower

(b) increases by one unit

(c) decreases infinitely

(d) greater

(C) Explain the term enthalpy.

(D) What are the three conditions for the enthalpy of a reaction?

(E) Change in enthalpy of the system is the heat absorbed at a:

(a) constant pressure

(b) constant volume

(c) constant temperature

(d) none of the above.

Ans. (A) *(a) Negative value*

Explanation: The enthalpy change for an exothermic process is negative because the enthalpy of reactant is greater than the enthalpy of products.

$$\Delta H = -ve \text{ or}$$

$$\Delta H = H_P - H_R$$

$H_P < H_R$ (The reaction is exothermic)

(B) *(a) Lower*

Explanation: The enthalpy change for an exothermic process is negative because the enthalpy of products is lower than the enthalpy of reactants or in other words, the enthalpy of reactants is greater than the enthalpy of products.

(C) The heat content measured at constant temperature and pressure for a system is called as enthalpy of a system. It is the heat energy absorbed or released during the progression of a chemical reaction. It can be calculated by $\Delta H = \Delta E + p\Delta V$.

(D) The three conditions for change in enthalpies are:

(1) $\Delta H = 0$ (The system is in equilibrium)

$\Delta H = H_P - H_R$

$0 = H_P - H_R$

$H_P = H_R$

(2) $\Delta H = +ve$ or $\Delta H > 0$

$\Delta H = H_P - H_R$

$H_P > H_R$ (The reaction is endothermic)

(3) $\Delta H = -ve$ or $\Delta H < 0$

$\Delta H = H_P - H_R$

$H_P < H_R$ (The reaction is exothermic)

(E) *(a) constant pressure*

Explanation: Change in enthalpy of the system is the heat absorbed at a constant pressure i.e.,

$$\Delta H_{sys} = q_p$$

Example 1.6: If water vapour is assumed to be a perfect gas, molar enthalpy changes for vaporisation of 1 mole of water at 1 bar and 100°C is 41 kJmol^{-1}. Calculate the internal energy change when one mole of water is vaporised at 1 bar pressure and 100°C. [NCERT]

Ans. Since we know $H_2O_{(l)} \rightarrow H_2O_{(g)}$

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

or $\Delta U = \Delta H - \Delta n_g RT$

Putting the values we get

$\Delta U = 41.00 \text{ kJmol}^{-1} - 1 \times 8.3 \text{ Jmol}^{-1}\text{K}^{-1} \times 373 \text{ K}$

$= 41.00 \text{ kJmol}^{-1} - 3.096 \text{ kJmol}^{-1}$

$\Delta U = 37.904 \text{ kJmol}^{-1}$

Example 1.7: Case Based:

The state of a system at any given time is referred to as its thermodynamic state. The temperature, pressure, and volume of a gas in a cylinder with a movable piston indicate the state of the system. These are characteristic parameters with definite values at each state that are independent of how the system arrived at that state. In other words, any change in the value of a property is determined solely by the system's initial and final states, rather than by the path the system takes from one state to the next. Such properties are referred to as state functions.

In contrast, the work done by the piston as it moves and the gas expands, as well as the heat absorbed by the gas from its surroundings, is dependent on the precise manner in which the expansion occurs. The behaviour of a complex thermodynamic system, such as the Earth's atmosphere, can be comprehended by first applying the principles of states and properties to its constituent parts—in this case, water, water vapour, and the various gases that comprise the atmosphere. Properties and their interrelationships can be studied as the system changes from state to state by isolating samples of material whose states and properties can be controlled and manipulated.

(A) Which one of the following thermodynamic quantities is not a state function?

(a) Temperature (b) Enthalpy

(c) Pressure (d) Work

(B) A system suffers an increase in internal energy of 80 J and at the same time has 50 J of work done on it. What is the heat change of the system?

(a) + 130 J (b) + 30 J

(c) – 130 J (d) – 30 J

(C) For the reaction $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$:

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

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

(D) Why is internal energy change a state function but work is not?

(E) Assertion (A): Internal energy is a state function.

Reason (R): Temperature is an intensive property.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(d) Work*

Explanation: Thermodynamic functions are those functions whose state affects the system. Thermodynamic state functions are those functions whose values don't depend on the path taken to reach the final state of the system. These functions depend only on the initial and final state of the system.

(B) *(b) + 30 J*

Explanation: Increase in internal energy, $\Delta U = 80$ J

Work done on the system, $w = 50$ J

We have to find the heat change in the system

$$\Delta U = q + w$$
$$80 = q + 50$$
$$80 - 50 = q$$
$$q = 30 \text{ J}$$

(C) *(c)* $\Delta H = \Delta U$

Explanation: Here $\Delta n_g RT = 0$, because reactant and product contain the same number of gaseous molecules. So that

$$\Delta H = \Delta U + \Delta n_g RT$$
$$\therefore \quad \Delta H = \Delta U$$

(D) The change in internal energy in a process is determined by the system's initial and final states. As a result, it is a state function. However, work is dependent on the path taken. As a result, it is not a state function.

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Internal energy is a state function as it is dependent on the initial and final state of a system and not on the path taken. Also, temperature is an intensive property as it is not dependent on the amount of matter taken.

Heat Capacity

Heat capacity is used to measure how much heat is transferred to a system. This heat appears as a rise in the temperature of the system in case of heat absorbed by the system.

The increase in temperature of the system is proportional to the heat transferred.

$$q = \text{Coefficient} \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system. So, we can write the equation as,

$$q = C\Delta T$$

The C is the coefficient and is called the heat capacity. Thus, we can measure the heat supplied by observing the rise in the temperature, provided that the heat capacity of the substance is known. When C is large, the given amount of heat will rise only by a small temperature. Water has a large heat capacity value (More energy is required to raise the temperature).

The heat capacity of the system is the amount of heat required to raise the system's temperature by 1°C or 1K

It can be written mathematically as $C = q / \Delta T$

C is directly proportional to the amount of substance.

The molar heat capacity $C_m = \left(\frac{C}{n}\right)$ is the quantity of heat required to raise the temperature of one mole of the substance by one-degree Celsius (or one Kelvin). Specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one-degree Celsius (or Kelvin). The equation for the heat required to raise the temperature of the sample is calculated by multiplying the value of specific heat capacity c, mass m and temperature change ΔT.

$$q = c \times m \times \Delta T$$
$$= C\Delta T$$

Example 1.8: Determine the amount of heat (kJ) required to raise the temperature of 60g of aluminium from 35 to 55°C. Al has a molar heat capacity of 24 J mol^{-1}K^{-1}. **[NCERT]**

Ans. No of moles of Al (m)

$$= \frac{60}{27}$$
$$= 2.22 \text{ mol}$$

Molar heat capacity (C)

$$= 24 \text{ J mol}^{-1} \text{ K}^{-1}$$

Rise in temperature (T)

$$= 55 - 35$$
$$= 20°\text{C} = 20 \text{ K}$$

Heat evolved (q)

$$= C \times m \times \Delta T$$
$$= (24 \text{ Jmol}^{-1}\text{K}^{-1}) \times (2.22 \text{ mol}) \times (20 \text{ K})$$
$$= 1065.6 \text{ J}$$
$$= 1.067 \text{ kJ}$$

The relationship between C_p and C_V for an ideal gas

At constant volume, the heat capacity is denoted by C_V and at constant pressure by C_P. The relationship between the two can be expressed by

The equation for heat at constant volume is

$$q_V = C_V\Delta T$$
$$= \Delta U$$

and at constant pressure is

$$q_p = C_p\Delta T$$
$$= \Delta H$$

The difference between C_P and C_V can be derived from the ideal gas equation.

For a mole of an ideal gas,

$$\begin{aligned}\Delta H &= \Delta U + \Delta(pV)\\ &= \Delta U + \Delta(RT)\\ &= \Delta U + R\Delta T\end{aligned}$$

On putting the values of ΔH and ΔU we have,

$$\begin{aligned}C_p\Delta T &= C_V\Delta T + R\Delta T\\ C_p &= C_v + R\\ C_p - C_v &= R\end{aligned}$$

Example 1.9: Case Based:

Heat capacity is used to measure how much heat is transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system. The teacher is asking Meena to calculate the heat capacity of the given copper rod. During that experiment, Meena has some doubts. She cleared those questions from Teacher.

(A) The increase in temperature of the system's proportional to the transfer of:

(a) Mass **(b) Heat**

(c) Weight **(d) Flow**

(B) The coefficient of heat capacity is directly proportional to the:

(a) Amount of heat energy.

(b) Amount of substance present.

(c) Amount of reactant.

(d) Amount of product.

(C) Explain the molar heat capacity of the substance.

(D) Derive the relationship between C_p and C_V

(E) Assertion (A): A gas has a specific heat value which is a unique one.

Reason (R): Specific heat is defined as the amount of heat required to raise the temperature of a unit mass of the substance through a unit degree.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. **(A)** *(b) Heat*

Explanation: Heat capacity is used to measure how much heat is transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system. The increase in temperature of the system is proportional to the heat transferred.

$$q = \text{Coefficient} \times T$$

(B) *(b) Amount of substance present.*

Explanation: The molar heat capacity $C_m = \left(\frac{C}{n}\right)$ is the quantity of heat required to raise the temperature of one mole of the substance by one-degree Celsius (or one Kelvin). Specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one-degree Celsius (or Kelvin). The equation for the heat required to raise the temperature of the sample is calculated by multiplying the value of specific heat capacity c, m mass and temperature change ΔT.

$$\begin{aligned}q &= c \times m \times \Delta T\\ &= C\Delta T\end{aligned}$$

(C) The molar heat capacity $C_m = \left(\frac{C}{n}\right)$ is the quantity of heat required to raise the temperature of one mole of the substance by one-degree Celsius (or one Kelvin). Specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one-degree Celsius (or Kelvin).

(D) The difference between C_P and C_V can be derived from the ideal gas equation.

For a mole of an ideal gas,

$$\begin{aligned}\Delta H &= \Delta U + \Delta(pV)\\ &= \Delta U + \Delta(RT)\\ &= \Delta U + R\Delta T\\ \therefore \quad \Delta H &= \Delta U + R\Delta T\end{aligned}$$

On putting the values of ΔH and ΔU, we have

$$\begin{aligned}C_p\Delta T &= C_V\Delta T + R\Delta T\\ C_p &= C_V + R\\ C_p - C_V &= R\end{aligned}$$

(E) *(d) (A) is false but (R) is true.*

Explanation: Gas doesn't have a fixed heat value because when gases are heated small changes in temperature cause a considerable change in both volume and pressure. Due to which the specific heat of gas can have any value between zero and infinite. While the definition of specific heat is the amount of heat required to raise the temperature by unit degree of unit time.

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. In an adiabatic process, no heat transfer occurs between the system and surroundings. Choose the correct option for free expansion of an Ideal gas under the adiabatic condition from the following.

(a) $q = 0, \Delta T = \neq 0, w = 0$

(b) $q \neq 0, \Delta T = 0, w = 0$

(c) $q = 0, \Delta T = 0, w = 0$

(d) $q = 0, \Delta T < 0, w \neq 0$ [NCERT Exemplar]

Ans. *(c)* $q = 0, \Delta T = 0, w = 0$

Explanation: As we know, for free expansion, $w = 0$

And for adiabatic change, $q = 0$

Also, from the first law of thermodynamics, we get $\Delta U = q + w$

By putting all the values, we get, $\Delta U = 0$

And there is no change in internal energy; hence the temperature also remains constant, $\Delta T = 0$.

2. In a reversible process, the system absorbs heat of $q = 600$ kJ while performing work of $w = -250$ kJ on the environment. What is the Increased internal energy of the system?

(a) 850 kJ (b) 600 kJ

(c) 350 kJ (d) 250 kJ

Ans. *(c) 350 kJ*

Explanation: We have $q = 600$ kJ and $w = -250$ kJ

And we know that $\Delta U = q + w$

$$\Delta U = 600 - 250$$
$$\Delta U = 350 \text{ kJ}$$

3. An expansion of a piston against pressure of p_{ex}=1.2 atm produces a volume change of 32.0 L in a system where $U = -51.0$ kJ. Calculate the change in the heat for this system.

(a) – 36 kJ (b) – 13 kJ

(c) – 47 kJ (d) – 24 kJ

Ans. *(c) – 47 kJ*

Explanation: We know $w = -p_{ex}\, dV$

By substituting the values, we get,

$$w = -1.2(32) \times 101.3 \text{ kJ}$$
$$w = -3.89 \text{ kJ}$$

Also, we have $\Delta U = -51.0$ kJ

And we know $U = q + w$

By placing all the values in the above equation, we get, $-51 = q - 3.89$

$\Rightarrow$ $q = -47$ kJ

4. The temperature of a system increases from 27°C to 37°C when it absorbs heat of 10 kJ at constant volume. The value of ΔU is:

(a) 100 kJ (b) 0 kJ

(c) 10 kJ (d) 1 kJ

Ans. *(c) 10 kJ*

Explanation: As we know, at constant volume $w = 0$ ($w = -p_{ex}\, dV$)

Hence, $\Delta U = q_v = 10$ kJ

5. For a particular reaction, the system absorbs 5 kJ of heat and does 3 kJ of work on its surroundings. What is the change in internal energy?

(a) 2.5 kJ (b) 2 kJ

(c) 8 kJ (d) 7 kJ

Ans. *(b) 2 kJ*

Explanation: Given

$q = +5$ kJ (Heat absorbed).

$w = -3$ kJ (Work done on the surroundings)

By the first law of thermodynamics,

$$\Delta U = q + w$$
$$= 5 - 3$$
$$= 2 \text{ kJ}$$

6. A system suffers an increase in internal energy of 80 J and at the same time has 50 J of work done on it. What is the heat change of the system?

(a) +130 J (b) +30 J

(c) –130 J (d) –30 J

Ans. *(b) +30 J*

Explanation: $\Delta q = ?$, $w = +50$J, $\Delta U = 80$J

from the first law of thermodynamics.

$$\Delta U = q + w$$

Therefore, $80 \text{ J} = q + 50$

$$q = 30 \text{ J}$$

$\therefore$ $\Delta q = +30$ J

7. Calculate the work done in the following reaction when one mole of SO_2 is oxidized at constant pressure at 50°C. State whether work is on the system or by the system.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

(a) Work is done on the system.

(b) Work is done by the system.

(c) No work is done.

(d) None of the above.

Ans. *(a) Work is done on the system.*

Explanation: Given: T = 50°C

$$= 50 + 273 = 323\ K$$

$$R = 8.314\ JK^{-1}\ mol^{-1}$$

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Given one mole of sulphur dioxide is used. hence dividing equation by two to get one mole of sulphur dioxide.

$$SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow SO_3$$

$$\Delta n_{(g)} = n_{product(g)} - n_{reactant(g)}$$

$$= (1) - (1 + \frac{1}{2})$$

$$= 1 - \frac{3}{2} = -\frac{1}{2}$$

Work done in a chemical reaction is given by

$$W = -\Delta n_{(g)} RT$$

$$= -\left(-\frac{1}{2}\right) mol \times 8.314\ JK^{-1}\ mol^{-1} \times 323\ K$$

$$= + 1.342\ kJ$$

Positive sign indicates that work is done by the surroundings on the system.

8. **The specific heat capacity at constant pressure is 8 J/kg.K, find the value of heat capacity at constant volume.**

(a) 16.314 J / (kg.K)
(b) 8.314 J / (kg.K)
(c) 8 J / (kg.K)
(d) – 0.314 J / (kg.K)

Ans. *(d) – 0.314 J / (kg.K)*

Explanation:

$$C_p - C_v = R$$

$$C_p = 8\ J/kg.K$$

$$8 - 8.314 = C_v$$

$$0.314 = C_v$$

9. **What will be the work done by 3 moles of an ideal gas when it expands spontaneously in a vacuum?**

(a) Zero
(b) Infinite
(c) 3 Joules
(d) 9 Joules

Ans. *(a) Zero*

Explanation: The work done is the product of pressure and change in volume. $w = p\Delta V$

Since the ideal gas expands spontaneously into vacuum, $p_{ext} = 0$

Hence, work done is also zero.

10. **One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0L, 95K) → (4.0 atm, 5.0 L, 245K) with a change in internal energy, ΔU = 30.0 L-atm. The change in enthalpy of ΔH the process in L-atm is:**

(a) 40.0 **(b) 42.3**
(c) 44.0 **(d) 54.9**

Ans. *(c) 44.0*

Explanation: $p_1 = 2$ atm, $p_2 = 4$ atm

$$V_1 = 3\ L, V_2 = 5\ L$$

$$T_1 = 95\ K, T_2 = 245\ K$$

$$\Delta U = 30\ L\text{-atm}$$

$$\Delta H = \Delta U + (p_2V_2 - p_1V_1)$$

$$\Delta H = 30 + (4 \times 5 - 2 \times 3)$$

$$\Delta H = 30 + 14 = 44\ L\text{-atm}$$

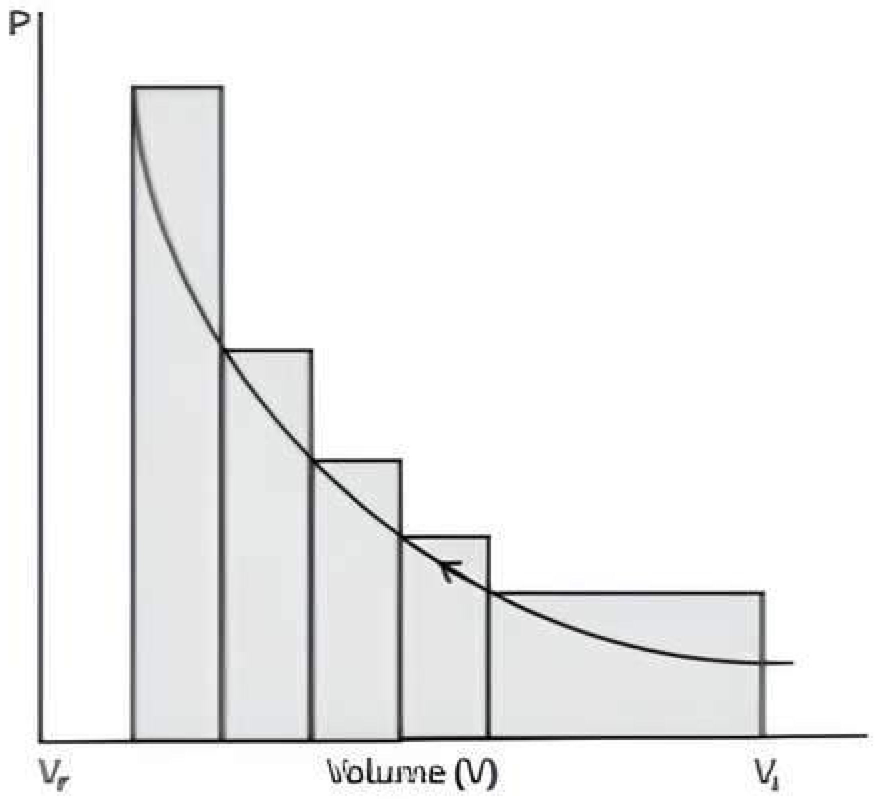
11. **The pressure-volume work for an ideal gas can be calculated by using the expression $w = \int_{V_i}^{V_f} p_{ex} dV$. The work can also be calculated from the pV-plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f. Choose the correct option.**

(a) w (reversible) = w (irreversible)
(b) w (reversible) < w (irreversible)
(c) w (reversible) = w (irreversible)
(d) w (reversible) = w (irreversible) +$p_{ex}\Delta V$

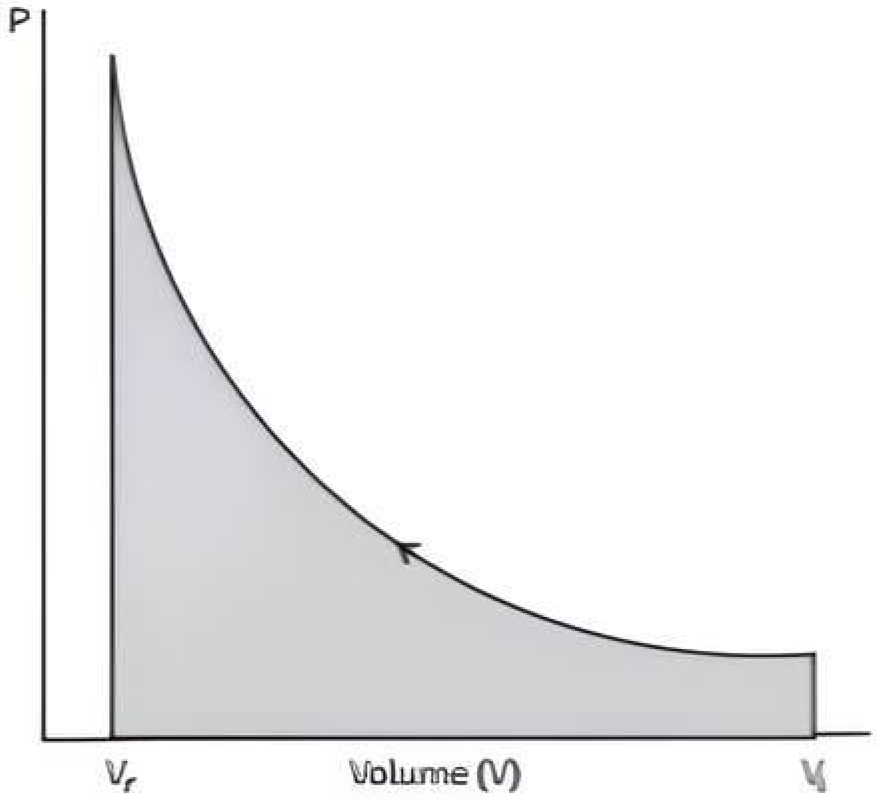
[NCERT Exemplar]

Ans. *(b) w (reversible) < w (irreversible)*

Explanation: The correct option is W (reversible) < W (irreversible). This is because the area under the curve is always more in irreversible compression as can be seen from given figure.



pV-plot when pressure is not constant and changes in finite steps during compresion from initial volume V_i to final volume V_f. Work done on the gas is represented by the shaded area.



pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume V_i to final volume volume V_f. Work done on this gas is represented by the shaded area.

Assertion-Reason (A-R)

In the following question no. (12-14), a statement of assertion followed by a statement or reason is given. choose the correct answer out of the following choices:

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

12. **Assertion (A):** Combustion of all organic compounds is an exothermic reaction.

Reason (R): All elements have zero enthalpies in their standard state.

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: The correct reason is that during combustion all the organic compounds undergo exothermic reaction and enthalpy of all elements in their standard state is zero but combustion reactions are exothermic in nature not just because the enthalpy of all elements in their standard state is zero. So, both statements are correct but reasons is not the correct explanation of assertion.

13. **Assertion (A):** For Isothermal reversible expansion of gas heat is absorbed by the gas.

Reason (R): The sign of 'W' is negative which makes 'Q' overall positive. [Delhi Gov. QB 2022]

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Assertion and reason both are correct statements and reason is correct explanation for assertion.

14. **Assertion (A):** For Adiabatic process, if expansion occurs then the temperature of the system rises.

Reason (R): For Adiabatic process, heat change is zero during the process.

Ans. *(d) (A) is false but (R) is true.*

Explanation: Adiabatic process, implies a process in which no heat exchange takes place between the system and the surroundings, i.e. neither heat is supplied nor heat is loosed. For an adiabatic compression (decreasing the volume of the system, like a piston), the temperature must increase. Likewise, for an expansion (increasing volume), the temperature must decrease.

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

15. *As a matter of definition, a system in physics or chemistry is nothing more than a collection of objects (or smaller systems) whose identities can be determined. In many cases, the word "system" refers to a collection that makes solving a problem more manageable. What surrounds the system is everything else. There are three types of systems : (1) Open system (2) closed system and (3) Isolated system. An open system is one that freely allows both energy and matter to be transferred in and out of a system. For example, boiling water without a lid. Heat escaping into the air. A closed system, on the other hand, does not allow the exchange of matter but allows energy to transfer. Example of a closed system – a pressure cooker. Isolated System : This system is completely sealed. Neither matter nor heat can transfer to or from the surroundings. Example – A thermos flask. The purpose of a thermos flask is to keep your food warm. A thermos flask can be considered as an isolated* *system but only for a short period of time. It prevents both heat and matter from being transferred to the surrounding. It is often more convenient to use an isolated system, where external influences (either cancel each other out or are negligible) can be ignored. Similarly, two balls rolling across a smooth surface to strike each other can be considered an isolated system, while two balls rolling across a gravel path or thick carpet will be affected by friction that originates outside the system and will not be considered an isolated system.*

(A) The humans are which type of system and why? Explain.

(B) The following systems belong to which type of system: Pond and Tea brewed in a kettle.

(C) A person does 10 kJ work on 3 kg of water by stirring using a paddle wheel. While stirring, around 10 kcal of heat is released from water through its container to the surface and surroundings by thermal conduction and radiation. What is the change in internal energy of the system?

Ans. (A) Humans are an example of an open system because we are constantly exchanging matter and energy with our surroundings. If we lift a weight W, simply breathe out and release carbon dioxide into the atmosphere. We take food in and also excrete it out. So, humans are an example of an open system.

(B) Pond-Open system and Tea brewed in a kettle-Closed system.

(C) Work done on the system (By the person while stirring), $w = -10\text{ kJ} = -10000\text{ J}$

Heat flows out of the system

$$q = -10\text{ kcal} = -10 \times 4184\text{ J}$$

$$q = -41840\text{ J}$$

Using the first law of Thermodynamics,

$$\Delta U = q - w$$

$$= -41840\text{ J} - (-10000\text{ J})$$

$$= -41840\text{ J} + 10000\text{ J}$$

$$= 31840$$

Here, the heat lost is more than the work done on the system, so the change in internal energy is negative.

16. *The work performed by a system is transferred by the system to its surroundings, by a mechanism through which the system can spontaneously exert microscopic forces on its surroundings. There are two types of work done:*

*(1) **Work done by the system:** In thermodynamics, work performed by a system is energy transferred by the system to its surroundings, by a mechanism through which the system can spontaneously exert macroscopic forces on its surroundings. In the surroundings, through suitable passive linkages, the work can lift a weight, for example. Energy can also transfer from the surroundings to the system; in a sign convention used in physics, such work has a negative magnitude. Work done by a system is positive.*

*(2) **Work done on the system:** "Work done on a system" is a way of saying that energy has been added to a group of objects which are otherwise treated as being isolated from their surroundings. For example, your system may be a tennis ball. If you pick up the ball and place it on a shelf, you have done work on the system. Your work (requiring energy expended by you) of lifting the ball adds gravitational potential energy to the ball. Work done on a system is negative. It can be found by considering whether system volume expands against a force or system volume contracts under a force.*

(A) The work done by the system is considered as:

(a) negative value (b) positive value

(c) zero (d) infinite

(B) If the external pressure is greater than the pressure inside means what will happen to the piston:

(a) Move upward

(b) Move inward

(c) No changes

(d) Move towards the side

(C) Which one is the correct expression for the compression of gases?

(a) $p_{ex} = (p_{in} \div dp)$ (b) $p_{ex} = (p_{in} \div dp)$

(c) $p_{ex} = (p_{in} \pm dp)$ (b) $p_{ex} = (p_{in} \pm dp)$

(D) The value of work done is negative when:

(a) Volume remains constant

(b) Volume decreases

(c) Volume becomes infinite

(d) Volume increases

(E) Calculate the pressure-volume work done by the system when the gas expands from 2 litres to 3 litres against a constant external pressure of 30 atm.

(a) 30 litres atm (b) – 20 litres atm

(c) – 30 litres atm (d) 20 litres atm

Ans. (A) *(a) negative value*

Explanation: The work done by the system means the system will lose some of its energy to the surroundings. So, the internal energy of the system decreases and the value of work done will be negative.

(B) *(b) Move inward*

Explanation: If the external pressure is greater than the pressure inside the gas then the piston will move inward which is it undergoes compression. Due to the high pressure outside the internal pressure of the gas cannot hold this. So, the external pressure will push the piston inward that is towards the low-pressure region.

(C) *(a)* $p_{ex} = (p_{in} \div dp)$

Explanation: If the pressure of the gas is not constant but changes in the process are always infinitesimally greater than the pressure of a gas at each stage of compression, then the volume will be decreased by an infinitesimal amount of dV. The work done on the gas can be calculated by:

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex} dV$$

During each stage of the compression process, $p_{ex} = (p_{in} \div dp)$

(D) *(d) Volume increases*

Explanation: When the system's volume increases, w is –ve. This is because the work done is negative and the energy is lost by the system. The increase in volume is associated with the expansion of the system which corresponds to work done by the system.

(E) *(c) – 30 litre atm*

Explanation:

$$\begin{aligned} w &= -p_{external} \times \Delta V \\ &= -p_{external} (V_{final} - V_{initial}) \\ &= -(30)(3\ 0\ 2) \\ &= -30 \text{ litre-atm} \end{aligned}$$

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

17. Give the mathematical expression of the first law of thermodynamics.

Ans. The mathematical expression for the first law of thermodynamics is the change in the internal energy is equal to the sum of the heat given to the system and the work done on the system.

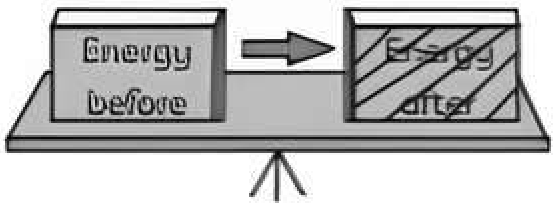
It is given as $\Delta U = q \div w$

18. Identify the state functions and path functions out of the following: enthalpy, entropy, temperature, heat, free energy and work. [NCERT Exemplar]

Ans. State functions: Enthalpy, entropy, temperature and free energy.

Path functions: Heat and work.

19. State the law of thermodynamics, which is depicted in the given picture:



Ans. First law of Thermodynamics says energy can neither be created nor be destroyed, it transfers from one form to another form *i.e.*, conservation of energy.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

20. In a bike showroom, using a vertical clamp of height 3m a KTM bike of mass 166 kg is driven up due to some fault in the engine. Calculate the work done.

Ans. Given : $h = 3$ m, m = 166 kg, $g = 9.8$ ms^{-2}

The work is done against the gravity so,

$$\begin{aligned} w &= mgh \\ &= 166 \times 9.8 \times 3 \\ &= 4880.4 \text{ J} \end{aligned}$$

21. What will be the difference between the enthalpy change and internal energy change at a temperature of 300 K and 1 bar pressure for the reaction?

$$2A_{(g)} \rightarrow 2B_{(g)} \div 2D_{(g)}$$

Ans. We know that the difference between the enthalpy change and internal energy change, *i.e.*, $\Delta H - \Delta U = \Delta n_g RT$;

Where Δn_g = change in the number of moles of gaseous species.

R = Universal gas constant = 8.314 $JK^{-1}\ mol^{-1}$

T = absolute temperature

For this chemical reaction

$$\Delta n_g = (2–4)$$
$$= 2$$
$$T = 300\ K$$
$$\text{So. } \Delta n_g RT = -(2 \times 8.314 \times 300)\ Jmol^{-1}$$
$$= -4988.4\ Jmol^{-1}$$

22. Heat capacity (C_p) is an extensive property but specific heat (c) is an intensive property. What will be the relation between C_p and c for 1 mole of water? [NCERT Exemplar]

Ans. For water. molar heat capacity = 18 × specific heat

$$C_p = 18 \times c$$

But. specific heat

$$c = 4.18\ Jg^{-1}\ K^{-1}$$

Heat capacity.

$$C_p = 18 \times 4.18\ JK^{-1}$$
$$= 75.24\ JK^{-1}$$

23. 0.5 kg of grape juice at 28°C is placed in a refrigerator which can remove heat at an average rate of 35 Js^{-1}. How long will it take to cool the grape juice to 5°C? Specific heat capacity of juice = 4200 $Jkg^{-1}K^{-1}$

Ans. Heat removed by the refrigerator.

$$q = mc\Delta T$$
$$= 0.5 \times 4200 \times (28°C – 5°C)$$
$$= 46200J$$

Now it can remove heat at the rate of 35Js^{-1}. and we need to remove 46200J.

So. time is

$$t = \frac{46200}{35}$$
$$= 1329s$$
$$= 22\ \text{minutes.}$$

24. Calculate the change in internal energy for an isolated system with a constant volume.

Ans. In an isolated system there is no energy transfer as heat or work.

So. $w = 0$ and $q = 0$.

According to the first law of thermodynamics

$$\Delta U = q + w = 0 + 0 = 0$$
$$\Delta U = 0$$

25. The empirical relationship $H = U + pV$ can be used to calculate the difference. For ten moles of an ideal gas, compute the difference between C_p and C_v

Ans. For 1 mole of gas

$$C_p - C_v = R$$

For n moles of gas. the relation is

$$C_p - C_v = nR$$
$$= 10 \times 8.3145J$$
$$= 83.14\ J$$

SHORT ANSWER Type-II Questions (SA-II)

[**3** marks]

26. Expansion of a gas in a vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of an ideal gas expands isothermally into a vacuum until its total volume is 5 litre. [NCERT Exemplar]

Ans. Work done in a vacuum is calculated by:

$$w = -p_{ext}\ (V_f - V_i)$$

p_{ext} = 0. for free expansion (in the vacuum).

Hence. $w = -[0 \times (5 - 1)]$

$$w = 0$$

For an isothermal expansion of ideal gas. no heat will be absorbed or evolved. hence $q = 0$.

According to first law of thermodynamics.

$$q + w = \Delta U$$

As. $w = 0$

and $q = 0$. thus $\Delta U = 0$

So. internal energy ΔU is also zero.

27. Two moles of an ideal gas undergo an isothermal reversible change at a temperature of 25°C from an initial pressure of 10 atm to 5 atm. What is the amount of heat absorbed and the work done during expansion?

Ans. For an isothermal reversible change

$q = -w = nRT \ln (p_i / p_f)$

n = number of moles

R = Universal gas constant = 8.314 $JK^{-1}\ mol^{-1}$

T = Absolute temperature

p_i = Initial pressure

p_f = Final pressure

According to the question.

$$T = (25 + 273)K$$
$$= 298\ K$$
$$p_i = 10\ atm$$
$$p_f = 5\ atm$$

Hence $q = 2 \times 8.314 \times 298 \times \ln\left(\frac{10}{5}\right)$ J

$= 3.43$ kJ

Therefore the work done will be 3.43 kJ.

28. A 2.5 g pentane is burnt in presence of an excess of oxygen in a calorimetric container. The calorimeter temperature rises from 280.5 K to 320 K. If heat capacity of the calorimeter is 9.83 kJ/K, then find the heat transferred to calorimeter.

Ans. Given:

Mass of pentane = 2.5g = 0.0025 kg

$c = 9.83$ kJ/K

Rise in temperature

$$\Delta T = 320 - 280.5 = 39.5 \text{ K}$$

Heat transferred to calorimeter

$$= mc\Delta T$$

$$= 0.0025 \text{ kg} \times 9.83 \text{ kJ/K} \times 39.5\text{K}$$

$$= 0.970 \text{ kJ}$$

29. It has been found that 250.4 J is needed to heat 30 g of propanol from 18°C to 23°C. Calculate: (A) specific heat capacity, and (B) molar heat capacity of propanol.

Ans. (A) Specific heat capacity

$$C = \frac{q}{m\Delta T}$$

$$= \frac{250.4}{30 \times (23 - 18)°C}$$

$$= \frac{250.4}{30 \times 5}$$

$$= 1.669 \text{ J}g^{-1}{}°C^{-1}$$

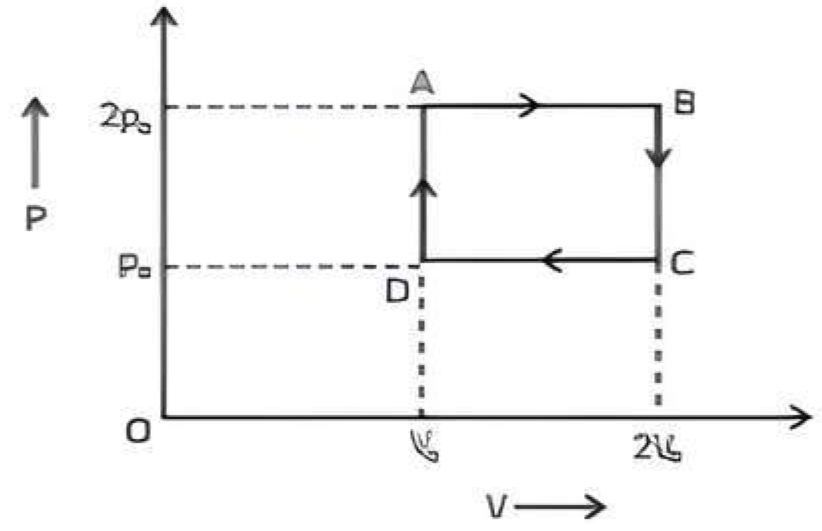
(B) Molar heat capacity

$$C_m = \text{specific heat} \times \text{molar mass}$$

$$C_{m\,(\text{propanol})} = 1.669 \times 60.09$$

$$= 100.29 \text{ Jmol}^{-1}{}°C^{-1}$$

30. An ideal monoatomic gas is taken around the cycle ABCDA as shown in the figure. Calculate the work done during the cycle.



Ans. Net work done during a complete cycle is equal to the area under the cycle.

$$\text{Area} = (2V_0 - V_0)\,(2p_0 - p_0)$$

$$= p_0V_0$$

$$W = -p_0V_0$$

Caution

- *Student must understand that work is negative when work is done by the system i.e. if the cycle is clockwise and positive when work is done on the system i.e. if the cycle is anticlockwise.*

LONG ANSWER Type Questions (LA)

[4 & 5 marks]

31. (A) Derive an expression for an isothermal expansion of an ideal gas during reversible, irreversible and adiabatic processes.

(B) A 0.5 mole of gas at temperature 300 K expands isothermally from an initial volume of 2 L to 6 L then what is the work done by the gas?

Ans. (A) For isothermal expansion for ideal gas expansion into a vacuum when T is constant, $w = 0$ since $p_{ex} = 0$. Joule also proved experimentally that $q = 0$, and therefore $\Delta U = 0$.

Now by using the first law of thermodynamic equation $\Delta U = q + w$, we can derive various types of equations for different types of conditions applied as follows:

For irreversible isothermal changes

$$q = -w$$

$$= p_{ex}(V_f - V_i)$$

For an isothermal reversible change

$$q = -w$$

$$= nRT \ln \frac{V_f}{V_i}$$

$$= 2.303nRT \log \frac{V_f}{V_i}$$

For adiabatic changes,

$$q = 0,\ \Delta U = w_{ad}$$

(B) We know that work done by the gas in an isothermal expansion

$$W = -nRT \ln\left[\frac{V_f}{V_i}\right]$$

$$= -0.5 \times 8.314\ \text{J mol}^{-1}\text{K}^{-1} \times 300\text{K} \ln \frac{6}{2}$$

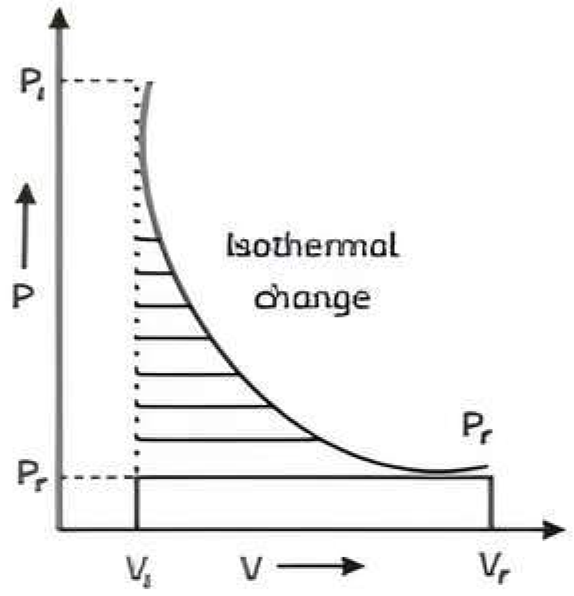
$$W = -1.369\ \text{kJ}$$

Note that work is negative since the work is done by the gas.

32. Graphically show the total work done in an expansion when the state of an ideal gas is changed reversibly and isothermally from (p_i, V_i) to (p_f, V_f). With the help of a pV plot, compare the work done in the above case with that carried out against a constant external pressure p_f. [NCERT Exemplar]

Ans. If a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change, then the process is known as reversible process. A reversible process proceeds infinitely slowly by a series of equilibrium states such that the system and the surroundings are always in near equilibrium with each other.

On plotting pressure versus volume we will get a plot:



The work done in a reversible process to reach isothermally from (p_i, V_i) to (p_f, V_f) is the area under the curve $p_iV_i - p_fV_f$

Where:

V_i → initial volume

V_f → final volume

p_i → initial pressure

p_f → final pressure

Work against constant external pressure p_f is the area under the rectangle AV_iV_fB (shown in yellow colour)

Here we can say that maximum work is obtained when a process is carried out reversibly because it contains maximum area.

Work done in a reversible manner will always be greater than the same work done against a constant pressure i.e., in an irreversible manner.

MEASUREMENT AND CALCULATION OF ΔU AND ΔH

2

TOPIC 1

MEASUREMENT OF ΔU AND ΔH: CALORIMETRY

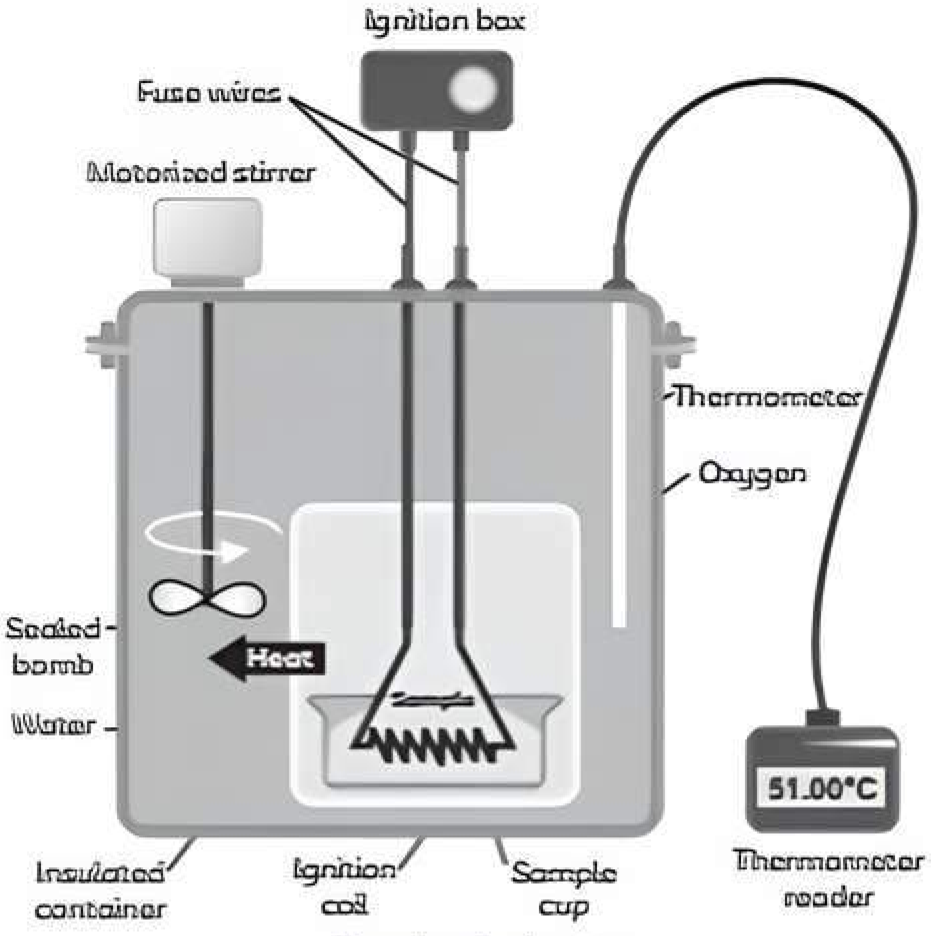
An experimental technique known as calorimetry allows us to measure energy changes associated with chemical or physical processes. The process of calorimetry is carried out in a vessel called a calorimeter, which is immersed in a known volume of a liquid. By measuring temperature changes, it is possible to determine the heat evolved in the process by knowing the heat capacity of the liquid in which the calorimeter is immersed and the heat capacity of the calorimeter. Measurements are taken under two conditions:

(1) q_v at contant volume

(2) q_p at contant pressure

Δ*U* Measurements

For chemical reactions, heat absorbed at constant volume is measured in a bomb calorimeter. In a bomb calorimeter, heat absorbed at constant volume is measured for chemical reactions. A steel vessel (the bomb) is immersed in water.



Bomb calorimeter

The entire apparatus is known as a calorimeter. To ensure that no heat is lost to the environment, the steel vessel is immersed in a water bath. In the steel bomb, a combustible chemical is burned in pure dioxygen. The heat generated by the reaction is transmitted to the water surrounding the bomb, which is monitored for temperature. The volume of the bomb calorimeter does not change because it is sealed, therefore the energy changes associated with reactions are monitored at a constant volume. Under these conditions, no work is done because the reaction is carried out in the bomb calorimeter at a constant volume. Thus,

$$\Delta U = q_v \text{ (constant volume)}$$

Example 2.1: **A bomb calorimeter was used to measure the reaction of cyanamide, $NH_2CN_{(s)}$ with oxygen, and *U* was found to be –742.7 kJ mol^{-1} of cyanamide at 298 K. Calculate the reaction's enthalpy change at 298 K.**

$$NH_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow N_2 + CO_{2(g)} + H_2O_{(l)}$$

[NCERT]

Ans. Given:

$$\Delta U = -742.7 \text{ kJ mol}^{-1}$$

$$\Delta n_g = 2 - \left(\frac{-3}{2}\right) = + \frac{1}{2} \text{ mol}$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{mol}^{-1}$$

$$T = 298 \text{ K}$$

According to the relation,

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

$$\Delta H = (-742.7 \text{ kJ}) + (\frac{1}{2} \text{ mol}) \times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{mol}^{-1}) \times (298 \text{ K})$$

$$= -742.7 \text{ kJ} + 1.239 \text{ kJ}$$

$$= -741.5 \text{ kJ}$$

Δ*H* Measurements

A calorimeter can measure heat change at constant pressure (typically at atmospheric pressure). We are aware that

$$\Delta H = q_p \quad \text{(at constant p)}$$

As a result, the heat absorbed or evolved, *qp* at constant pressure, is also known as the heat of reaction or the enthalpy of reaction, ΔH_r. Heat is produced in an exothermic reaction, and the system loses heat to the surroundings. As a result, q_p will be negative, and ΔH_r will be negative as well. Similarly, heat is absorbed in an endothermic reaction, q_p is positive, and ΔH_r is positive.

TOPIC 2

ENTHALPY CHANGE

The standard enthalpy of formation determined for a wide range of substances is enthalpy change. The reactants undergo chemical changes and combine to form products in any general chemical reaction. The following equation can be used to represent it:

$$\text{Reactants} \rightarrow \text{Products}$$

The change in enthalpy for any such reaction is represented as H_r and is referred to as the reaction enthalpy. Subtracting the sum of the enthalpies of all the reactants from the enthalpies of the products yields the reaction enthalpy.

ΔH_r = Sum of enthalpies of the products – Sum of the enthalpies of the reactants.

$$\Delta H_r = \sum_i a_i H_{products} - \sum_i b_i H_{reactants}$$

The constants a_i and b_i denotes the stoichiometric coefficients of the products and reactants for the balanced chemical reaction under consideration respectively.

Example 2.2: **During the addition of a sodium ion to a chloride ion to form sodium chloride, the enthalpy of ionic sodium is –239.7 kJ/mol, while the enthalpy of chloride ion is –167.4 kJ/mol. The enthalpy of sodium chloride (table salt) is –411 kJ/ mol. Calculate the enthalpy change for the reaction.**

Ans. Reaction can be represented as:

$$Na^{\circ} + Cl^{-} \rightarrow NaCl$$

$$\Delta H_r = \Delta H_{NaCl} - (\Delta H_{Na^{\circ}} + \Delta H_{Cl^{-}})$$

Inserting these values results in:

$$\Delta H = -411\ \text{kJ/mol} - (-239.7\ \text{kJ/mol} - 167.4\ \text{kJ/mol})$$

$$= -411\ \text{kJ/mol} - (-407.1\ \text{kJ/mol})$$

$$= -411\ \text{kJ/mol} + 407.1\ \text{kJ/mol} = -3.9\ \text{kJ/mol}$$

So, the formation of salt releases almost 3.9 kJ of energy per mole.

Standard Enthalpy of Reaction

We already know that the enthalpy of any reaction is affected by physical conditions such as temperature, pressure, and so on. The standard enthalpy of any reaction is calculated when all of the components involved in the reaction, namely the reactants and products, are in their standard form. The enthalpy change that occurs in a system when a matter is transformed by a chemical reaction under standard conditions is thus the standard enthalpy of reaction.

The standard state for any substance at a given temperature is its pure form at a pressure of one bar, according to the convention. For example, liquid ethanol at 298 K and 1 bar of pressure is said to be in its pure state.

Related Theory

It is important to note that the data for a substance's standard state is taken at 298 K.

A reaction's standard enthalpy is denoted as ΔH_r. The heat of the reaction is exactly equal to the enthalpy change of the reacting system at constant pressure.

Enthalpy Changes during Phase Transformation

Enthalpy of fusion

The enthalpy changes when one mole of solid state is converted to a liquid state at its melting point.

It is denoted by $\Delta_{fus}H^{\circ}$

For example, at 273K the enthalpy of fusion of ice is 6.0 kJ mol^{-1}

$$\{ice\}\ H_2O_{(s)} \rightarrow H_2O_{(l)}\ \{water\}$$

Example 2.3: **Calculate the enthalpy change when 1 mole of water at 10.0°C is frozen to ice at –10.0°C. $\Delta_{fus}H$ = – 6.03 kJ mol^{-1} at 0°C; $C_p[H_2O_{(l)}]$ = 75.3 J mol^{-1} K^{-1}; $C_p[H_2O_{(s)}]$ = 36.8 J mol^{-1} K^{-1}.** **[NCERT]**

Ans. The total change in enthalpy is carried out as follows:

ΔH = (1 mole of water at 10°C → 1 mole of water at 0°C) + (1 mole of water at 0°C → 1 mole of ice at –0°C) + (1 mole of ice at –0°C → 1 mole of ice at –10°C)

$$= C_p[H_2O_{(l)}] \times \Delta T + \Delta H_{freezing} + C_p[H_2O_{(s)}] \times \Delta T$$

$$= (75.3\ JK^{-1}\ mol^{-1})(0 - 10\ K) + (-6.03\ kJ\ mol^{-1}) + (36.8\ JK^{-1}) \times (-10\ K)$$

$$= (-753\ J mol^{-1}) - (6.03\ kJ\ mol^{-1}) - (368\ J\ mol^{-1})$$

$$= (-0.753\ kJ\ mol^{-1}) - (6.03\ kJ\ mol^{-1}) - (0.368\ kJ\ mol^{-1})$$

$$= -7.151\ kJ\ mol^{-1}$$

Enthalpy of vapourisation

The enthalpy changes when one mole of the liquid state is converted into a gaseous state at its boiling point.

It is symbolised by $\Delta_{vap}H^{\circ}$.

For example,

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

$$\Delta_{vap}H^{\circ} = 6.0\ kJmol^{-1}$$

Example 2.4: **A swimmer coming out from a pool is covered with a film of water weighing about 18 g. How much heat must supplied to evaporate this water at 298 K? Calculate the internal energy of vaporisation at 100°C.**

$\Delta_{vap}H$ for water at 373 K = 40.66 kJ mol^{-1} **[NCERT]**

Ans. $18g\ H_2O_{(l)} \xrightarrow{\text{vapourisation}} 18g H_2O_{(g)}$

Number of moles in 18g of $H_2O_{(l)}$ is

$$= \frac{18g}{18 g mol^{-1}} = 1 mol$$

As enthalpy of vapourisation is given 40.66 kJ/mol and the swimmer is covered with 1 mol water hence 40.66 kJ energy must be provided to evaporate the water.

$$\Delta_{vap}U = \Delta_{vap}H^{\circ} - p\Delta V$$
$$= \Delta_{vap}H^{\circ} - \Delta n_g RT$$
$$= \Delta_{vap}H^{\circ} - \Delta n_g RT$$
$$= 40.66\ kJmol^{-1} - (1)(8.314 \times 10^{-3}\ kK^{-1}mol^{-1})(373\ K)$$
$$\Delta_{vap}U^{\circ} = 40.66\ kJmol^{-1} - 3.10\ kJmol^{-1}$$
$$= 37.56\ kJmol^{-1}$$

Enthalpy of sublimation

The enthalpy changes when one mole of solid at below its melting point is directly transformed into a gaseous state.

It is represented by $\Delta_{sub}H^{\circ}$

For example.

$$L_{2(s)} \to L_{2(g)}$$

$\Delta_{sub}H = 2$ u cal/g at 200°C

Important

➥ *The Intensity of the change in the enthalpy is determined by the intermolecular interaction strength of the substance.*

Enthalpy of combustion

The enthalpy change when one mole of substance undergoes combustion in the presence of excess air. It is denoted by $\Delta_c H^{\circ}$

For example:

$$CH_{4(g)} + 2O_{2(g)} \to CO_{2(g)} + 2H_2O_{(l)}$$
$$\Delta_c H^{\circ} = -890.3\ kJmol^{-1}$$

The negative sign shows that this reaction is combustion reactions and is always exothermic.

Important

➥ *The standard enthalpy for the formation $\Delta_f H^{\circ}$, of an element in the reference state, i.e., its most stable state of aggregation, is taken to be zero by convention.*

Example 2.6: **What is the change in enthalpy for the following reaction?**

$2Mg + O_2 \to 2MgO$, if

$$\Delta H_f(MgO) = 0\ kJ$$
$$\Delta H_f(O_2) = 0\ kJ$$
$$\Delta H_f(MgO) = -601\ kJ$$

Ans. The change in enthalpy is calculated by:

$$\Delta H_{products} - \Delta H_{reactants}$$

It is important to first balance the reaction before performing calculations. The coefficients are important in determining the change in enthalpy of a reaction.

$$2Mg + O_2 \to 2MgO$$
$$\Delta H_{rxn} = 2(\Delta H_{MgO}) - 2(\Delta H_{Mg}) - \Delta H_{O_2}$$
$$\Delta H_{rxn} = 2(-601\ kJ) - 2(0\ kJ) - 0\ kJ$$
$$\Delta H_{rxn} = -1202\ kJ$$

Standard Enthalpy of Formation

At the standard conditions of temperature, 298 K and 1 atm pressure the enthalpy of formation is the energy involved in change from its constituting elements to one mole of a substance. It is represented by $\Delta_f H^{\circ}$. The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C_{Graphite(s)} + 6H_{2(g)} + 3O_{2(g)} \to C_6H_{12}O_{6(s)}$$
$$\Delta_f H^{\circ} = -1273.3 kJ$$

It is not possible to measure the value of $\Delta_f H^{\circ}$ for glucose, *i.e.*, −1273 kJ/mol, by mixing an approximate amount of graphite, O_2 and H_2 measuring the heat evolved as glucose is produced. Since the reaction does not occur at a measurable rate under any condition.

Example 2.5: Given: $N_{2(g)} + 3H_{2(g)} \to 2NH_{3(g)}$; $\Delta_r H^{\circ} = -92.4\ kJmol^{-1}$. **What is the standard enthalpy of formation of NH$_3$ gas?** [NCERT]

Ans. $\Delta_f H\text{–}NH_{3(g)} = -(92.4)/2 = 46.2\ kJmol^{-1}$

Thermochemical Equations

A thermochemical equation is a balanced chemical equation plus the value of its ΔH_r. In an equation, we specify the physical state (along with the allotropic state) of the substance. For example:

$$C_2H_5OH_{(l)} + 3O_{2(g)} \to 2CO_{2(g)} + 3H_2O_{(l)};$$
$$\Delta H_r^{\circ} = -1367\ kJ\ mol^{-1}$$

The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The fact that the enthalpy change is negative indicates that this is an exothermic reaction.

It is necessary to remember the following thermochemical equation conventions.

(1) In a balanced thermochemical equation, the coefficients refer to the number of moles (never molecules) of reactants and products involved in the reaction.

(2) The number of moles of substances specified by an equation is denoted by the numerical value of ΔH_r°. The units for standard enthalpy change ΔH_r° will be kJ mol^{-1}.

For example. When methane gas is burned. heat is released. causing the reaction to become exothermic. The combustion of 1 mol of methane produces 890.4 kilojoules of heat energy. This data can be displayed as part of the balanced equation.

According to the equation. 1 mol of methane reacts with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water. 890.4 kJ energy is released during the process and is thus written as a reaction product. A thermochemical equation is a chemical equation that includes the reaction's enthalpy change.

Sign conventions for enthalpy.

$\Delta H = -ve$ (For an exothermic reaction)

$\Delta H = +ve$ (For an endothermic reaction)

For example. in the case of methane combustion. the enthalpy change is negative because heat is released by the system. As a result. the system's overall enthalpy decreases. The enthalpy change for a chemical reaction is represented by the heat of reaction. In the preceding example. the heat of reaction is 890.4 kJ. The thermochemical reaction can also be expressed as follows:

$$CH_4 + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$
$$\Delta H = -890.4 \text{ kJ}$$

Hess's Law of Constant Heat Summation

If a reaction occurs in multiple steps. the standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction can be divided at the same temperature.

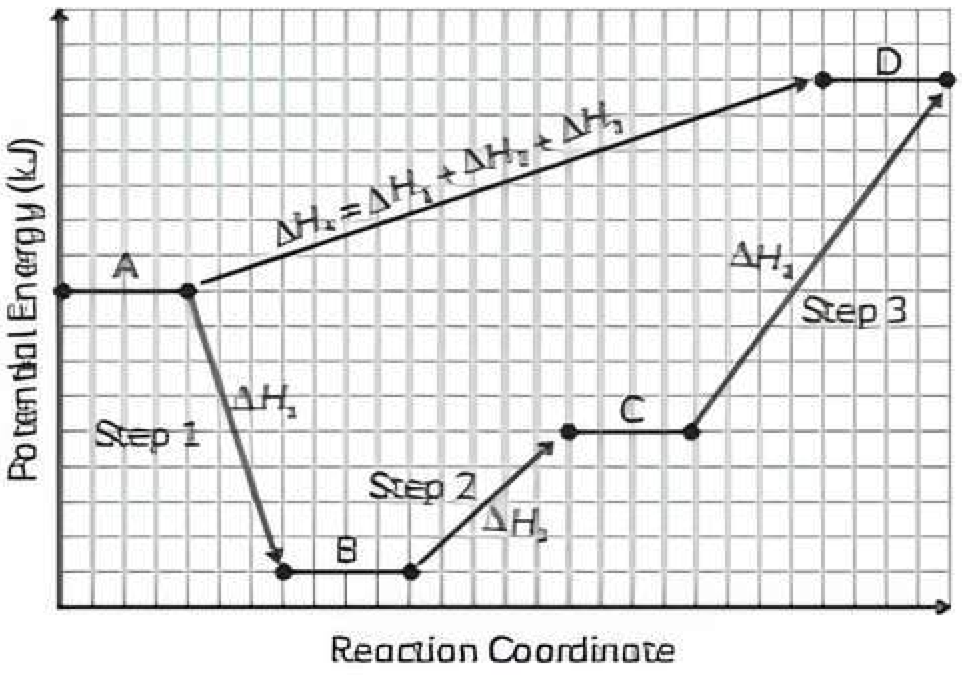
Hess's Law of Constant Heat Summation (or simply Hess's Law) states that the total enthalpy change for a reaction is the sum of all changes. regardless of how many stages or steps are involved.

Related Theory

- *This law demonstrates that enthalpy is a state function.*

Hess's Law is named after Germain Hess. a Russian chemist and doctor. Hess contributed to the early principles of thermochemistry. Because enthalpy is a state function. we can calculate the overall change in enthalpy by simply summing the changes for each step of the way until the product is formed. All steps must take place at the same temperature. and the equations for each step must balance.

In general. if the enthalpy of an overall reaction AD along one route is $\Delta H_4°$ and the enthalpies of reactions leading to the same product. D along another route are $\Delta H_1°$. $\Delta H_2°$. $\Delta H_3°$... then we have $\Delta H_4 = \Delta H_1° + \Delta H_2° + \Delta H_3°$



Step1	A	→	B	ΔH_1
Step2	B	→	C	ΔH_2
Step3	C	→	D	ΔH_3
Net Reaction	A	→	D	ΔH_4

Hess's Law

Applications of Hess's Law

(1) To calculate the enthalpy of formation.

(2) To determine the standard enthalpies of reactions.

Example 2.7: Case Based:

While we are exercising we burn calories. Actually, when we intake food it undergoes an oxidation process and transforms into CO_2 and H_2O. When the energy is changed in the independent pathway. here is what the Hess Law imply. This means that through burning the food equal amount of energy is released. Thus. the carbohydrates split into simple sugar. As we remember that our gym instructor mentions that the higher the oxygen higher the workout. Therefore. do not forget to breathe while exercising.

(A) During the independent chemical reaction which of the following will not change?

(a) Initial condition only

(b) Final condition only

(c) Mid-conditions

(d) The initial and final condition

(B) What are the applications of Hess's Law?

(C) Explain the procedure to calculate the Hess's Law.

(D) Assertion (A): Born-Haber cycle is based on Hess Law.

Reason (R): Lattice enthalpy can be calculated by the Born- Haber cycle.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(d) The initial and final condition*

Explanation: Hess's law state that the overall energy depends upon initial and final conditions.

(B) Applications of Hess's law:

- (1) For calculating the enthalpy of formation.
- (2) To determine the standard enthalpies of reactions.

(C) We can calculate Hess's law in various method:

- (1) By reserving the equation.
- (2) To multiply the equation with a constant.

(D) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Hess's law is the enthalpy change is the same either it takes through one step or more than one step. As per the Born-Haber cycle enthalpy of formation = Σ sublimation energy of the metal atom. ionisation energy which is needed for the metal cation. bond dissociation enthalpy. Hence. it is impossible to determine the lattice enthalpies through the Born-Haber cycle.

Example 2.8: Enthalpy of combustion of carbon to CO_2 is -393.5 kJ mol^{-1}. Calculate the heat released upon the formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Ans: We can represent the formation of carbon dioxide by the equation:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

From the data given. we can say that during the formation of 1 mole of CO_2 releases -393.5 kJ/mol heat.

1 mole CO_2 means 44 g of CO_2 releases -393.5 kJ/mol heat.

1 gram of CO_2 will release $= -393.5/44$ kJ/mol

35.2 g of CO_2 will release $= -393.5/44 \times 35.2$
$= -315$ kJ/mole

Standard Enthalpy of Combustion

The enthalpy change is that one mole of substance undergoes combustion in the presence of excess air. It is also called heat of combustion. Many readily available substances with large enthalpies of combustion are used as fuels. including hydrogen. carbon and hydrocarbons such as methane. propane. and the major components of gasoline.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$
$$\Delta H^\circ_{298} = -1366.8 \text{ kJ}$$

The standard enthalpy of combustion of ethanol. -1366.8 kJ. is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25°C and atmosphere pressure. yielding also at 25°C and atmosphere pressure.

Example 2.9: The combustion of one mole of benzene takes place at 298K 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 the formation of benzene. Standard enthalpies of the formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are -393.5 kJ mol^{-1} and -285.83 kJ mol^{-1} respectively. [NCERT]

Ans. Formation of benzene.

$$6C_{(graphite)} + 3H_{2(g)} \rightarrow C_6H_{6(l)} \quad \text{– (i)}$$
$$\Delta_f H^\circ = ?$$

Enthalpy of combustion for 1mol of benzene.

$$C_6H_{6(l)} + \frac{15}{2}O_2 \rightarrow 6CO_{2(g)} + 3H_2O_{(l)} \quad \text{– (ii)}$$
$$\Delta_c H^\circ = -3267 \text{kJmol}^{-1}$$

Enthalpy of formation for 1mol of $CO_{2(g)}$

$$C_{(graphite)} + O_2 \rightarrow CO_{2(g)} \quad \text{– (iii)}$$
$$\Delta_c H^\circ = -393.5 \text{ kJmol}^{-1}$$

Enthalpy of formation for 1mol of $H_2O_{(l)}$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \text{– (iv)}$$
$$\Delta_f H^\circ = -285.83 \text{ kJmol}^{-1}$$

Multiply the equation (iii) by 6 and multiply equation (iv) by 3

$$6C_{(graphite)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} \quad \text{– (v)}$$
$$\Delta_f H^\circ = -2361 \text{ kJmol}^{-1}$$

$$3H_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow 3H_2O_{(l)} \quad \text{– (vi)}$$
$$\Delta_f H^\circ = -857.49 \text{ kJmol}^{-1}$$

On adding eqns. (v) and (vi)

$$6C_{(graphite)} + 3H_{2(g)} + \frac{15}{2}O_{2(g)} \rightarrow 6CO_{2(g)} + 3H_2O_{(l)} \quad \text{– (vii)}$$
$$\Delta_f H^\circ = -3218.49 \text{ kJmol}^{-1}$$

By reversing the equation (ii)

$$6CO_{2(g)} + 3H_2O_{(g)} \rightarrow C_6H_{6(l)} + \frac{15}{2}O_2 \quad \text{– (viii)}$$
$$\Delta_r H^\circ = 3267 \text{ kJ mol}^{-1}$$

Adding eqns. (vii) and (viii)

$$6C_{(graphite)} + 3H_{2(g)} \rightarrow C_6H_{6(l)}$$
$$\Delta_f H^\circ = 3267 - 3218.49 = 48.51 \text{ kJmol}^{-1}$$

Enthalpy of Atomisation

The energy which is used to transform any substance into gaseous atoms is called enthalpy of atomization. It is defined per mole of the gaseous atoms. It is represented by $\Delta_a H^\circ$.

For example.

$$H_{2(g)} \rightarrow 2H_{(g)};\ \Delta_a H^\ominus = 435.0 \text{ kJmol}^{-1}$$

Here. on breaking the H-H bond in dihydrogen the H atoms are formed.

Bond Enthalpy

The energy which is used to break one-mole molecule's bond is called enthalpy of bond dissociation. It is defined per mole of the molecule.

It is symbolized as $\Delta_{bond}H^{\ominus}$.

$\Delta_r H^{\ominus}$ is the bond enthalpy of reactants and products in gas phase will be:

$\Delta_r H^{\ominus} = \Sigma \text{bond enthalpy}_{reactants} - \Sigma \text{ bond enthalpy}_{products}$

Bond dissociation enthalpy

Change in the enthalpy to break the covalent bond of one mole of gaseous molecules into two free radicals.

Example.

Here, one-mole dihydrogen bond splits in the diatomic molecules in the following manner:

$H_{2(g)} \rightarrow 2H_{(g)};$ $\quad \Delta_{H-H}H^{\ominus} = 435.0 \text{kJmol}^{-1}$

The enthalpy change involves in this process is the bond dissociation enthalpy of H-H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of gaseous covalent compound is broken to form products in the gas phase.

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecules let us consider a polyatomic molecule CH_4.

Mean bond enthalpy

Let's explain with an example of CH_4

$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)};$ $\quad \Delta_a H^{\ominus} = 1665 \text{ kJmol}^{-1}$

In methane, all four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ:

$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)};$ $\quad \Delta_{bond}H^{\ominus} = +427 \text{ kJmol}^{-1}$

$CH_{3(g)} \rightarrow CH_{2(g)} + H_{(g)};$ $\quad \Delta_{bond}H^{\ominus} = +439 \text{ kJmol}^{-1}$

$CH_{2(g)} \rightarrow CH_{(g)} + H_{(g)};$ $\quad \Delta_{bond}H^{\ominus} = +452 \text{ kJmol}^{-1}$

$CH_{(g)} \rightarrow C_{(g)} + H_{(g)};$ $\quad \Delta_{bond}H^{\ominus} = +347 \text{ kJmol}^{-1}$

Thus, overall equation will be:

$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)};$ $\quad \Delta_{bond}H^{\ominus} = +1665 \text{ kJmol}^{-1}$

Here, the mean bond enthalpy for C-H bond

In CH_4;

$$\Delta_{C-H}H^{\ominus} = \frac{1}{4}(\Delta_a H^{\ominus}) = \frac{1}{4}(1665 \text{ kJmol}^{-1})$$

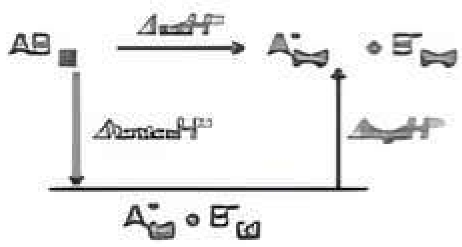
$$= 416 \text{ kJmol}^{-1}$$

Enthalpy of solution

The heat which is produced or exhausted by dissolving a mole of the compound in the excess solvent. It is denoted by $\Delta_{sol}H^{\ominus}$

$$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$$

$\Delta_{lattice}H^{\ominus}$ = lattice enthalpy, $\Delta_{hyd}H^{\ominus}$ = enthalpy of hydration



Diagrammatic representation enthalpy of solution for an AB ionic compound

Enthalpy of dilution

The enthalpy change is associated with the addition of a specific amount of solute to the specific amount of solvent at a constant temperature.

For example,

$HCl_{(g)} + 10aq \rightarrow HCl.10aq$ $\quad \Delta H = 69.0 \text{ kJ/mol}$

Let us consider the following set of enthalpy changes:

$HCl_{(g)} + 25aq \rightarrow HCl.25aq$ $\quad \Delta H = 72.03 \text{ kJ/mol}$ (i)

$HCl_{(g)} + 40aq \rightarrow HCl.40aq$ $\quad \Delta H = 72.79 \text{ kJ/mol}$ (ii)

$HCl_{(g)} + \infty aq \rightarrow HCl.\infty aq$ $\quad \Delta H = 74.85 \text{ kJ/mol}$ (iii)

The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more the solvent is used, the enthalpy of solution approaches a limiting value. That is the value in infinitely dilute solution.

If we subtract the eq (i) from the eq. (ii)

$HCl.25aq + 15aq \rightarrow HCl.40aq$

$$\Delta H = [-72.79 - (-72.03)] \text{ kJ/mol}$$

$$= -0.76 \text{ kJ/mol}$$

This value (–0.76kJ/mol) refers to enthalpy of dilution.

Neutralisation Reaction

The amount of heat evolved during the neutralization of an acid with alkali. Neutralization reaction is a reaction between a strong acid and a strong base. it is essentially the combination of one equivalent of hydrogen ions with one equivalent of hydroxyl ions.

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

Enthalpy of neutralization is the heat evolved when one gram equivalent of the acid is completely neutralized by a base in a dilute solution.

The value of enthalpy of neutralization for a strong acid and strong base is fixed which is 57.1 kJ, while the value of enthalpy of neutralization for a strong acid with a weak base or weak acid/ weak base is less than 57.1 kJ.

Example 2.10: Case Based:

Enthalpy change is the standard enthalpy of formation, which has been determined for a vast number of substances. In any general chemical reaction, the reactants undergo chemical changes and combine to give products. For any such reaction, the change in enthalpy is represented as $\Delta_r H$ and is termed as the reaction enthalpy. The reaction enthalpy is calculated by subtracting the sum of enthalpies of all the reactants from that of the products.

(A) In the standard change of enthalpy of neutralization, the reaction between the acid and alkali will form one mol of:

(a) water (b) oxygen
(c) anhydrous salt (d) nitrogen

(B) For which of the following reactions would the ΔH° for the reaction be labelled ΔH_f°?

(a) $Al_{(s)} + \frac{3}{2}H_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow Al(OH)_{3(s)}$

(b) $PCl_{3(g)} + \frac{1}{2}O_{2(g)} \rightarrow POCl_{3(g)}$

(c) $\frac{1}{2}N_2O_{(g)} + \frac{1}{4}O_{2(g)} \rightarrow NO_{(g)}$

(d) $CaO_{(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)}$

(C) What is the standard enthalpy of reaction?

(D) How is the enthalpy of sublimation represented and mention one example?

(E) **Assertion (A):** In case of strong acid and base the enthalpy of neutralisation is the same.

Reason (R): Neutralization means the formation of heat from the water.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(a) Water*

Explanation: $OH^-_{(aq)} + H^+_{(aq)} \rightarrow H_2O_{(l)}$ the standard enthalpy change of neutralization is the enthalpy change when a solution of an acid and an alkali react together under standard conditions to produce 1 mole of water.

(B) *(a)* $Al_{(s)} + \frac{3}{2}H_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow Al(OH)_{3(s)}$

Explanation: As one mole of aluminium hydroxide is formed from the reactants which are in their standard states, the heat of the reaction represents the standard heat of the formation of aluminium hydroxide ΔH_f°.

(C) If the reaction is undergoing in the standard state of substance, then the enthalpy of reaction is called as standard enthalpy.

(D) It is symbolised by $\Delta_{sub}H^\ominus$

For example,

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$
$$\Delta_{vap}H^\ominus = -6.0\ kJmol^{-1}$$

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: For the strong acid and base of enthalpy of neutralisation is 13.7 kcal, this is due to the formation of heat from water from H^+ and OH^-

Lattice Enthalpy

The change in enthalpy takes place when the dissociation of one mole of ionic compound which is transformed into a gaseous ions state. It is represented by $\Delta_{lattice}H^\ominus$

For example,

$$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$$

Born-Haber Cycle

It is difficult to find the lattice enthalpy of the ionic compound through a direct experiment. Therefore, we can have calculated them in the following manner.

$$Na_{(s)} \rightarrow Na_{(g)}$$
$$\Delta_{sub}H^\ominus = 108.4\ kJmol^{-1}$$
$$Na_{(g)} \rightarrow Na^+_{(g)} + e^-$$

Ionisation enthalpy, $\Delta_i H^\ominus = 496\ kJmol^{-1}$

$$\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)}$$

Bond dissociation enthalpy $\frac{1}{2}\Delta_{bond}H^\ominus = 121\ kJmol^{-1}$

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$$

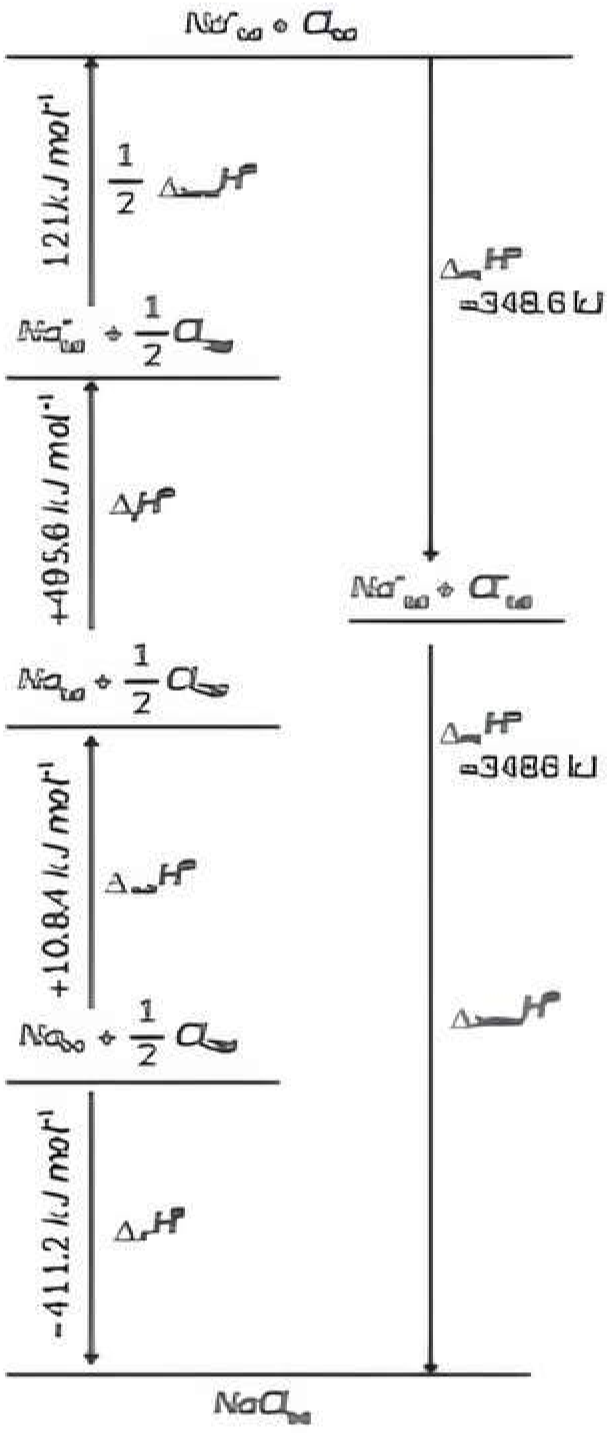
The electron gain enthalpy $\Delta_{eg}H^\ominus = 348.6\ kJmol^{-1}$

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+Cl^-_{(s)}$$

By applying Hess's Law:

$\Delta lattice\ H^\ominus = 411.2 + 108.4 + 121 + 496 - 348.6$

$\Delta lattice\ H^\ominus = 788\ kJ$



Enthalpy diagram for lattice enthalpy of NaCl

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. **What is the purpose of a bomb calorimeter?**
   (a) To determine the Latent heat of fusion
   (b) To determine the Heat of combustion
   (c) To determine the Heat of vaporisation
   (d) To determine the Specific heat capacity

Ans. *(b) To determine the Heat of combustion*

Explanation: A bomb calorimeter is a device used to calculate the heat of combustion of a process. To estimate the heat of combustion, it must resist a great deal of pressure. The process is isochoric, and the heat energy equals the internal energy.

2. **What is the mass of a substance if its specific heat capacity is denoted by c, the temperature differential (ΔT), and the heat energy is ΔQ?**

(a) $\frac{Q}{c\Delta T}$ **(b)** $\frac{c\Delta T}{Q}$

(c) $Qc\Delta T$ **(d)** $Q\Delta T$

Ans. *(a)* $\frac{Q}{c\Delta T}$

Explanation: The heat energy of a substance is denoted by ΔQ and given by the equation, $\Delta Q = mc\Delta T$ where m is the mass of the substance, c is the specific heat capacity, and ΔT is the temperature difference.

$$m = \frac{\Delta Q}{c\Delta T}$$

3. **How much heat energy is required to convert 1 kilogram of water to steam at 373 degrees Kelvin?**

(a) 273 kJ **(b) 22600 kJ**

(c) 2260 kJ **(d) 2260 J**

Ans. *(c) 2260 kJ*

Explanation: The latent heat of vaporisation of water is 2260 kJ/kg

The heat is required to convert water at 373 K to steam is $Q = mL$

where m = mass of water

L = latent heat vaporisation of water.

heat energy required = 1 kg × 2260 kJ/kg
= 2260 kJ

4. **What is the value of specific heat capacity in the adiabatic process?**

(a) 0 J **(b) Infinity**

(c) 4.2 J **(d) 4.2 kJ**

Ans. *(a) 0 J*

Explanation: The change in total energy is zero during an adiabatic process.

5. **Enthalpy of sublimation of a substance is equal to:**
   (a) enthalpy of fusion + enthalpy of vaporisation
   (b) enthalpy of fusion
   (c) enthalpy of vaporisation
   (d) twice the enthalpy of vaporisation

[NCERT Exemplar]

Ans. *(a) enthalpy of fusion + enthalpy of vaporisation*

Explanation: Enthalpy of sublimation of a substance is equal to enthalpy of fusion + enthalpy of vaporisation.

Sublimation is direct conversion of solid to vapour.

$$\text{solid} \rightarrow \text{vapour}$$

Sublimation is a two step process :

$$\text{solid} \rightarrow \text{liquid} \rightarrow \text{vapour}$$

(1) solid → liquid, requires enthalpy of fusion
(2) liquid → vapour, requires enthalpy of vaporisation

6. **The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound:**
   (a) Is always negative
   (b) Is always positive
   (c) May be positive or negative
   (d) Is never negative **[NCERT Exemplar]**

Ans. *(c) May be positive or negative*

Explanation: The enthalpy of formation of a compound may be positive or negative as it can be an exothermic or endothermic process.

7. **A system absorbs 10 kJ of heat at constant volume and its temperature rises from 270 °C to 370 °C. The value of ΔU is :**

(a) 100 kJ **(b) 10 kJ**

(c) 0 kJ **(d) 1 kJ**

Ans. *(b) 10kJ*

Explanation: At constant volume, $w = 0$.

Therefore, $\Delta U = q_v = 10$ kJ

8. **The heat of combustion of yellow phosphorous is –9.91 kJ and the red phosphorous is –8.78 kJ. The heat of transition of yellow phosphorous to red phosphorous is:**

(a) –9.91 kJ (b) –8.78 kJ
(c) –9.34 kJ (d) –1.13 kJ

[Delhi Gov. QB 2022]

Ans. *(d) –1.13 kJ*

Explanation: The heat of combustion of yellow phosphorus is given –9.91 kJ

$$P_{4(y)} + 5O_2 \rightarrow 2P_2O_5 \qquad \text{—(i)}$$

The heat of combustion of red phosphorus is given –8.78 KJ

$$P_{4(r)} + 5O_2 \rightarrow 2P_2O_5 \qquad \text{—(ii)}$$

We need the heat of transition of yellow phosphorous to red phosphorous, so subtract equation (ii) from equation (i).

$$P_{4(y)} \rightarrow P_{4(r)}$$

$$\Delta H_r = -9.91-(-8.78)\ \text{kJ}$$

$$= -1.13\ \text{kJ}$$

Thus heat of transition of yellow phosphorus to red phosphorus is –1.13 kJ.

9. The reaction

$$C_2H_6 + 3\frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$$

where the heat produces from the ethane gas, = –84.7 kJmol^{-1}, CO_2 = 393.5 kJmol^{-1}, water liquid = –285.8 kJmol^{-1}, then what is the heat combustion for ethane?

(a) –155.7 kJmol^{-1} (b) –1559.7 kJmol^{-1}
(c) –55.9 kJmol^{-1} (d) –559.7 kJmol^{-1}

Ans. *(b) –1559.7 kJmol^{-1}*

Explanation:

$$\Delta H_r = \sum \Delta H_{f\,[\text{product}]} - \sum \Delta H_{f\,[\text{reactant}]}$$

$$\Delta H_c(C_2H_6)$$

$$= 2x(-393.5\,\text{kJmol}^{-1}) + 3x(-285.8\,\text{kJmol}^{-1})$$

$$-(-84.7\,\text{kJmol}^{-1}) - \frac{7}{2}x(0\,\text{kJmol}^{-1})$$

$$= -1559.7\,\text{kJmol}^{-1}$$

10. Standard enthalpy of vaporization ΔH_{Vap} for water at 100°C is 40.66 kJmol^{-1}. The internal energy of vapourisation at 100°C (in kJ mol^{-1}) is (assume water vapour to behave like an ideal gas):

(a) 43.76 (b) 40.66
(c) 37.56 (d) –43.76

Ans. *(c) 37.56*

Explanation: For gaseous reactants and products, we have a relation between standard enthalpy of vaporisation (ΔH_{Vap}) and standard internal energy (ΔE) as:

$$\Delta H_{Vap} = \Delta E + \Delta n_g RT$$

whereas. $\Delta n_g = n_2 - n_1$. ie. difference between no. of moles of reactant and product.

For vaporisation of water.

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

Therefore $\Delta n_g = 1 - 0 = 1$

Therefore $\Delta H_{Vap} = \Delta E + \Delta n_g RT$

Therefore $\Delta H_{Vap} = \Delta E + \Delta n_g RT$

$\Rightarrow$ $\Delta E = \Delta H_{Vap} - \Delta n_g RT$

$$= 40.66 - (1 \times 8.314 \times 373)$$

$$= 37.53\ \text{kJ/mol}$$

Hence, the value of ΔE for this process will be 37.53 kJ/mol.

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

(a) –676 kJ (b) 110.5 kJ
(c) –110.5 kJ (d) 676.5 kJ

Ans. *(c) –110.5 kJ*

Explanation:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H_1 = 393.5$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H_2 = -283.0$$

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$$

$$\Delta H = \Delta H_1 - \Delta H_2$$

$$= -393.5 + 283 = -110.5\ \text{kJ}$$

12. Enthalpy changes for the reaction $4H_{(g)} \rightarrow 2H_{2(g)}$ is – 869.6 kJ. The dissociation energy of H–H bond is :

(a) –869.6 kJ (b) 869.6 kJ
(c) –434.8 kJ (d) 434.8 kJ

Ans. *(d) 434.8 kJ*

Explanation:

$$4H_{(g)} \rightarrow 2H_{2(g)}; \Delta H = -869.6\,\text{kJ}$$

$$2H_{2(g)} \rightarrow 4H_{(g)}; \Delta H = 869.6\,\text{kJ}$$

$$H_{2(g)} \rightarrow 2H_{(g)}; \Delta H = \frac{869.6}{2} = 434.8\,\text{kJ}$$

13. Consider the reactions given below. On the basis of these reactions, find out which of the algebraic relations is correct.

(i) $C_{(g)} + 4H_{(g)} \rightarrow CH_{4(g)}$; $\Delta_r H = x$ kJ mol^{-1}

(ii) $C_{(graphite)} + 2H_{2(g)} \rightarrow CH4_{(g)}$; $\Delta_r H = y$ kJ mol^{-1}

Options:

(a) x = y (b) x = 2y
(c) x > y (d) x < y

[NCERT Exemplar]

Ans. *(c) $x > y$*

Explanation: In eq. (i), no bond is being broken while in eq. (ii), 2H – H bonds are broken. So, in eq. (ii), some of the energy is used up to break the bonds. Thus, $x > y$.

14. When the conditions are identical, how many mL of 0.1 M of strong base AOH and 0.05 M strong H_2A acid solution should be mixed for a total volume of 100 mL to produce the highest rise in temperature ?

(a) 10 : 90 (b) 90 : 10

(c) 25 : 75 (d) 50 : 50

[Delhi Gov. QB 2022]

Ans. *(a) 50 : 50*

Explanation: When an equal amount of acid and bases are mixed, maximum amount of acid will be neutralized by the base, thus maximum amount of heat of neutralization will be released. The higher the amount of heat released, the higher will be the rise in temperature.

15. Calculate the change in enthalpy for the reaction:

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

If heat of formation of $H_2O_{2(l)}$ and $H_2O_{(l)}$ are −188 and −286 kJ/mol respectively:

(a) − 196 kJ/mol (b) + 196 kJ/mol

(c) + 948 kJ/mol (d) − 948 kJ/mol

Ans. *(a) −196 kJ/mol*

Explanation:

$$2H_2O_{2(l)} \rightarrow 2H_{2(l)} + O_{2(g)}$$

$$\Delta H_f[H_2O_{2(l)}] = -188 \text{ kJ/mol}$$

For 2 moles $H_2O_2 = -2 \times 188$ kJ/mol

$$\Delta H_f[H_2O_{(l)}] = -286 \text{ kJ/mol}$$

For 2 moles $H_2O = -2 \times 286$ kJ/mol

$$\Delta Hr = (2 \times -286) - (2 \times -188)$$
$$= 196 \text{ kJ/mol}$$

16. The enthalpy of neutralization of HCl and NaOH is x kJ. The heat evolved when 500 mL of 2N HCl is mixed with 250 mL of 4N NaOH will be:

(a) x (b) $\frac{x}{2}$

(c) 2x (d) $\frac{x}{4}$

Ans. *(a) x*

Explanation: No. of gram equivalent HCl

$$= \frac{500 \times 2}{1000} = 1$$

No. of gram equivalents of NaOH $= \frac{250 \times 4}{1000} = 1$

Enthalpy change of a reaction when 1 gram equivalent of acid is neutralized by one gram equivalent of base is called heat of neutralization.

17. Calculate the heat required to make 6.4 kg CaC_2 from $CaO_{(s)}$ and $C_{(s)}$ from the reaction: $CaO_{(s)} + 3C_{(s)} \rightarrow CaC_{2(s)} + CO_{(g)}$ given that $\Delta H_f(CaC_2) = -14.2$ kcal, ($\Delta H_f(CO) = -26.4$ kcal.) and $\Delta H_f(CaO) = 151.6$ kcal.

(a) 5624 kcal (b) 1.11×10^4 kcal

(c) 86.24×10^3 kcal (d) 1100 kcal

Ans. *(b) 1.11×10^4 kcal*

Explanation: $n = \dfrac{(\text{Mass})}{(\text{Molecular weight})}$

$$= \frac{(6.4 \times 10^3)}{(64)} = 100$$

For 1 mole of CaC_2

$$\Delta H = \Delta H_f(CaC_2) + H_f(CO) - H_f(CaO)$$
$$= -14.2 - 26.4 + 151.6$$
$$= 111.1 \text{ kcal}$$

For 100 moles,

$$\Delta H = 1.11 \times 10^4 \text{ kcal}$$

Assertion-Reason (A-R)

In the following question no. (18–20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

18. Assertion (A): Enthalpy of formation of HCl is equal to the bond energy of HCl.

Reason (R): Enthalpy of formation and bond energy both involve the formation of one mole of HCl from the elements.

[Delhi Gov. QB 2022]

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: $\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl$

It represents the enthalpy of formation of HCl as there only one bond is formed between H and Cl, thus it will also represent its bond enthalpy.

19. Assertion (A): The enthalpy of formation of $H_2O_{(g)}$ is lesser than that of $H_2O_{(l)}$.

Reason (R): Change in the enthalpy for $H_2O_{(g)} \rightarrow H_2O_{(l)}$ which is a condensation reaction is negative.

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: We know that gaseous molecules are at highes energy than water so enthalpy change is less negative for the condensation reaction, and because of this, the enthalpy change for the formation of $H_2O_{(l)}$ is greater than that of $H_2O_{(g)}$ in terms of numerical value.

20. Assertion (A): Combustion of all organic compounds is an exothermic reaction.

Reason (R): The enthalpies of all elements in their standard state are zero.

[NCERT Exemplar]

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: In the combustion reaction the enthalpies for the product are lesser than the reactant enthalpies.

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

21. *We can measure the movement of heat from one system to another that results in a temperature change. The magnitude of the temperature shift is determined by the substance's heat capacity. Hess's law states that the enthalpy change of reaction remains constant regardless of the number of steps. It aids in the calculation of the enthalpy of production, combustion, and other enthalpy changes. Bond enthalpies can also be used to calculate enthalpy change. Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy equals to the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure. A mole of acetone takes less heat to vaporise than one mol of water.*

(A) Which of the two liquids i.e., acetone and water has the greater vaporisation enthalpy?

(a) Acetone

(b) Water

(c) Equal

(d) Cannot be determined

(B) Calculate $\Delta_r H^\circ$ for the following reaction at 25°C:

$Fe_3O_{4(s)}$	+ $CO_{(g)}$	→ $3FeO_{(s)}$	+ $CO_{2(g)}$
$\Delta_f H^\circ$ (kJ/mol)			
–1118	–110.5	–272	–393.5

(a) –263 kJ (b) 54 kJ

(c) 19 kJ (d) –50 kJ

(C) Consider the following reaction between zinc and oxygen

$$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)};\ \Delta H = -693.8\ \text{kJ mol}^{-1}$$

(a) The enthalpy of two moles of ZnO is equal to the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(b) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.

(c) 693.8 kJ mol^{-1} energy is evolved in the reaction.

(d) 693.8 kJ mol^{-1} energy is absorbed in the reaction.

(D) Increase in the enthalpy of the surrounding environment is equal to a decrease in the system's enthalpy. When the system and its surroundings are in thermal equilibrium, will their temperatures be the same?

(a) Yes

(b) No

(c) Depends on the pressure

(d) Always the same

Ans. (A) *(b) Water*

Explanation: Acetone requires less heat to vaporise due to the weak force of attraction between molecules.

As a result, water has a higher enthalpy of vaporisation.

It can be represented as:

$$\Delta H_{vap}\ (\text{water}) > \Delta H_{vap}\ (\textit{acetone})$$

(B) *(c) 19 kJ*

Explanation: $\Delta_r H^\circ = \Delta_f H^\circ$ (products) – $\Delta_f H^\circ$ (reactants)

$= [(3 \times (-272)] + (-393.5) - (-1118 - 110.5)$

$= 19$ kJ

(C) *(c) 693.8 kJ mol^{-1} energy is evolved in the reaction.*

Explanation: As the value of heat is negative, that means heat is evolved during the reaction and heat is released when reactants have energy higher than that of products.

(D) *(a) Yes*

Explanation: Yes, when the system and its surroundings are thermally balanced, their temperatures are the same.

22. *A calorimeter is a device that is in use for measuring the warmth of chemical reactions or physical changes also as heat capacity. Normally a calorimeter consists of a thermometer. This thermometer is then attached to a metal container filled with water suspended above a combustion chamber. It is one of the measurement devices useful in the study of thermodynamics, chemistry, and biochemistry.*

For finding the enthalpy change per mole of a substance P in a reaction between two substances P and Q. Here, both the substances P and Q are separately added to a calorimeter and the initial and final temperatures are noted. Multiplying the natural process by the mass and heat capacities of the substances gives worth for the energy given off or absorbed during the reaction. Dividing the energy change by what percentage of moles of A were present gives its enthalpy change of the reaction.

$$q = C_v(T_f - T)q = Cv(T_f - T)$$

Where q is the amount of warmth consistent with the change in temperature measured in joules and C_v is the heat capacity of the calorimeter which is measured in units of energy per temperature (Joules/Kelvin).

(A) Explain the need of using a calorimeter.

(B) What is the ΔH sign of endothermic reactions, and why is it so? What is the relationship between the standard enthalpy of formation and a compound's enthalpy?

(C) What are the specific heat capacity and molar heat capacity for water? Why is the enthalpy of neutralisation lower when either the acid or the base, or both, is weak?

Ans. (A) Calorimetry is the process of measuring the amount of heat released or absorbed during a chemical reaction. It is a crucial part of thermodynamics. In order to measure the heat of a reaction, the reaction must be isolated so that no heat is lost to the environment. By knowing the change in heat, it can be determined whether or not a reaction is exothermic (releases heat) or endothermic (absorbs heat). Calorimetry also plays a large part in everyday life, controlling the metabolic rates in humans and consequently maintaining such functions like body temperature.

(B) ΔH is postive as $\Delta H = H_p - H_r$ and $H_r < H_p$

The relationship between the standard enthalpy of formation and a compound's enthalpy is that they are equal.

(C) Specific heat capacity for H_2O

$$= 4.1\ JK^{-1}g^{-1}$$

Molar heat capacity for H_2O

$$= 4.18 \times 18$$

$$= 75.24\ J\ mol^{-1}\ K^{-1}$$

A part of the heat is used up for dissociation of the weak acid or weak base or both.

Related Theory

- *Here 18 g/mol is the molar mass of water.*

The enthalpy of neutralisation is lower when either the acid or the base, or both, is weak because a part of the heat is used up for dissociation of the weak acid or weak base or both.

23. *Lattice energy is the change in the enthalpy which takes place when one mole of an ionic compound is breakdown into the gaseous ion state. Alternately, it can be defined as the energy that must be supplied to one mole of an ionic crystal in order to separate it into gaseous ions in a vacuum via an endothermic process. Therefore, this quantity always holds a positive value. Some sources define lattice energy in the opposite manner, i.e., the amount of energy released when an ionic solid is formed from its gaseous ionic constituents via an exothermic process. According to this definition, lattice energy must always hold a negative value. The two primary factors that affect the lattice energy of an ionic compound are the magnitude of charge associated with the constituent ions and the distance between the ions. Due to the electrostatic forces between them, the individual ions in an ionic lattice are attracted to each other. The strength of the electrostatic force of attraction is directly proportional to the magnitude of the charge held by the constituent ions, i.e., the greater the charge and the stronger the force of attraction, the stronger the lattice. The lattice energy of an ionic compound is inversely proportional to the distance between the ions. The further the distance between the ions in a lattice, the weaker the electrostatic forces holding them together and the lower the lattice energy. Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a Born-Haber Cycle.*

(A) Name the energy when the decomposition of NaCl transforms into a sodium ion and chloride ion during this reaction 788 $kJmol^{-1}$ energy release.

(a) Lattice energy

(b) Dilution energy

(c) Neutralization energy

(d) Translation energy

(B) Choose the correct option for analyzing the reaction energies:

(a) Chemical cycle (b) Born-Haber cycle

(c) Nitrogen cycle (d) Carbon cycle

(C) The enthalpy of dilution of a solution will be .... on the original concentration of the solution and the amount of solvent added.

(a) Independent

(b) May be dependent

(c) May be independent

(d) Dependent

(D) The enthalpy of the solution will be positive or:

(a) does not exist (b) negative

(c) zero (d) infinity

(E) For the given reaction

$$NaCl_{(s)} \rightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}$$

What is the type of enthalpy involved in the reaction?

(a) Enthalpy of atomization

(b) Enthalpy of dilution

(c) Lattice enthalpy

(d) Enthalpy of ionisation

Ans. (A) *(a) Lattice energy*

Explanation: Lattice enthalpy is the change in enthalpy that takes place when the dissociation of one mole of an ionic compound which is transformed into a gaseous ions state.

(B) *(b) Born-Haber cycle*

Explanation: It is difficult to find the lattice enthalpy of the ionic compounds through a direct experiment. Therefore, we find the enthalpy through an indirect method that is Born Haber cycle.

(C) *(d) Dependent*

Explanation: Enthalpy of dilution is dependent on the concentration of the original solution and the amount of solvent. The heat is produced or exhausted by dissolving a mole of the compound in the excess solvent.

(D) *(b) negative*

Explanation: It can be exothermic and endothermic depending on the reaction.

(E) *(c) Lattice enthalpy*

Explanation: Lattice energy can be defined as the energy required to convert one mole of an ionic solid into gaseous ionic constituents. Thus, the given reaction represents the lattice enthalpy.

24. *The amount of heat energy released or absorbed when one mole of a substance dissolves in a specified amount of solvent is known as enthalpy of solution. Enthalpies of solution may be either positive or negative, in other words, some ionic substances dissolved endothermically (for example, NaCl); others dissolve exothermically (for example, NaOH). An infinitely dilute solution is one where there is a sufficiently large excess of water that adding any more doesn't cause any further heat to be absorbed or evolved. So, when 1 mole of sodium chloride crystals is dissolved in an excess of water, the enthalpy change of solution is found to be +3.9 kJ mol^{-1}. The change is slightly endothermic, and so the temperature of the solution will be slightly lower than that of the original water. The enthalpy of solution in the infinite dilution we can observe the change in the enthalpy by dissolving the substance in the infinite amount of solvent there will be minimal interaction between the ions. The enthalpy change is associated with the addition of a specific amount of solute to the specific amount of solvent at a constant temperature. The values show general dependence of the enthalpy of solution on amount of solvent. As more solvent is used, the enthalpy of solution approaches a limiting value. That is the value in an infinitely dilute solution.*

(A) Explain the enthalpy of dilution.

(B) Is the dissolution of hydrated copper sulphate an exothermic or endothermic process? Why is copper sulphate taken in powdered form?

(C) When liquid A is mixed with liquid B, the resulting solution is found to be cooler. What do you conclude about the nature of the solution? What type of deviation is expected of a solution obtained by adding concentration H_2SO_4 to water?

Ans. (A) The enthalpy change is associated with the addition of a specific amount of solute to the specific amount of solvent at a constant temperature.

(B) When the dissolution of hydrated copper sulphate is an endothermic process. The copper sulphate is taken in powdered form to facilitate its dissolution in minimum time. Hence, preventing heat loss to the surroundings.

(C) The solution shows a positive deviation. Absorption of heat takes place. A–B interaction is weaker than A–A and B–B interaction. By adding a concentrated H_2SO_4 to water the solution shows a negative deviation. The heat is liberated and A–B interactions are stronger than A–A and B–B interactions.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

25. What is meant by reaction enthalpy?

Ans. Reactants are converted into products in a chemical reaction. The enthalpy change that occurs as a result of a reaction is referred to as the reaction enthalpy.

26. Give the significance of enthalpy change.

Ans. Measuring the change in enthalpy allows us to determine whether a reaction was endothermic (absorbed heat, positive change in enthalpy) or exothermic (released heat, a negative change in enthalpy). It is used to calculate the heat of reaction of a chemical process.

27. Define the Enthalpy of fusion.

Ans. The enthalpy changes when one mole of solid-state is converted to a liquid state at its melting point is known as enthalpy of fusion.

28. Write the applications of Hess's Law.

Ans. (1) For the enthalpy of formation calculation

(2) To determine the standard enthalpies of reactions.

29. The standard heat of formation of Fe_2O_3 is 824.2 $kJmol^{-1}$. Calculate enthalpy change for the reaction, $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_3$.

Ans. $\Delta H^\circ = \sum \Delta H^\circ_{f_{(products)}} - \sum \Delta H^\circ_{f_{(reactants)}}$

$= [2 \times \Delta H_f^\circ (Fe_2O_{3(s)})] [-4\Delta H_f^\circ (Fe_{(s)})]$

$= 2 (-824.2\ kJ) - 4(0)$

$= -1648.4\ kJ$

30. How will you calculate work done on an ideal gas in a compression, when a change in pressure is carried out in infinite steps? [NCERT Exemplar].

Ans. The work done can be calculated with the help of p–V plot. A p–V plot of the work of compression which is carried out by change in pressure in infinite steps, and shaded area represents the work done on the gas.

31. Define the concept of enthalpy.

Ans. It is defined as the overall heat content of the system.

32. Express enthalpy in mathematical form.

Ans. In terms of maths, the answer is:

$$H = U + pV.$$

where, U is internal energy.

33. When does the enthalpy change become positive or negative?

Ans. ΔH is positive for endothermic reaction which absorbs heat from the surroundings. ΔH is negative for exothermic reactions which evolve heat to the surroundings.

34. Give the isothermal reversible change expression.

Ans. For an isothermal irreversible change

$$Q = -w = p_{ex} (V_f - V_i)$$

$$= nRT \ln \frac{V_f}{V_i} = 2.303\ nRT \log \frac{V_f}{V_i}$$

35. What is the standard enthalpy of formation of graphite? [Delhi Gov. QB 2022]

Ans. Zero, as all elements in their standard states (solid carbon in the form of graphite, etc.) have a standard enthalpy of formation of zero, as there is no change involved in their formation.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

36. Calculate the enthalpy of ethylene hydrogenation using the given data.

Bond energies of C—H, C—C, C—C and H—H are 414, 347, 618 and 435 kJ mol^{-1}

Reaction can be given as:

$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

Ans. $\Delta H_r = \Sigma(\text{Bond energy})_r - \Sigma_p(\text{Bond energy})$

$\Delta H_r = (E_{C=C} + 4E_{C-H} + E_{H-H}) - (E_{C-C} + 6E_{C-H})$

$\Delta H_r = [618 + (4 \times 414) + 435) - (347 + (6 \times 414)]$

$\Delta H_r = 2709 - 2891$

$\Delta H_r = -122\ kJ\ mol^{-1}$

37. **The enthalpy of atomization for the reaction $CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}$ is 1665 $kJmol^{-1}$. What is the bond energy of C–H bond?** **[NCERT Exemplar]**

Ans. The reaction is

$$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)} \qquad \Delta_a H = 1665\ kJ\ mol^{-1}$$

By using the mean bond enthalpy for C–H, the 4 *moles* of atomisation for C–H bonds, therefore more energy.

$= 1665/4 = 416.25\ kJmol^{-1}$

38. **Calculate the enthalpy of formation of ethane at 25°, if the enthalpies of combustion of $C_{(s)}$, $H_{2(g)}$ and C_2H_6 are –94.14, –68.47, –373.3 kcal respectively.**

Ans. Given thermochemical reactions are

(i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta_r H = 94.14 Kcal$

(ii) $H_{2(g)} + \frac{1}{2}O_2 \rightarrow H_2O_{(l)} \qquad \Delta_r H = 68.47 Kcal$

(iii) $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta_r H = 373.3 Kcal$

The required reaction is

$2C_{(s)} + 3H_{2(g)} \rightarrow C_2H_{6(g)}$

The required reactions are obtained by multiplying equation (i) by 2 and equation (ii) by 3 and reversing equation (iii) and then adding, we get.

$2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} \qquad H = 188.28 kcal$

$3H_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow 3H_2O_{(l)} \qquad H = 205.41 kcal$

$2CO_{2(g)} + 3H_2O_{(l)} \rightarrow C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \qquad H = +373.3 kcal$

Therefore, we will get

$2C_{(s)} + 3H_{2(g)} \rightarrow C_2H_{6(g)} \qquad H = -20.39\ kcal$

Enthalpy of formation of ethane at 298 K is – 20.39 k cal / mol.

39. **Define the following:**

(A) Enthalpy of sublimation

(B) Enthalpy of atomisation

Ans. (A) The enthalpy change when one mole of solid at its melting point is directly transformed into the gaseous state is known as enthalpy of sublimation. It is represented by $\Delta_{sub}H^{\ominus}$.

(B) The energy which is used to transform any substance into gaseous atoms is called enthalpy of atomization. It is per mole of the gaseous atoms. It is represented by $\Delta_a H^{\ominus}$.

40. **Explain the following terms with an example:**

(A) Enthalpy of vaporisation.

(B) Enthalpy of combustion.

Ans. (A) **Enthalpy of vaporisation:** The enthalpy changes when one mole of liquid state is converted into gaseous state at its boiling point of liquid. It is symbolised by $\Delta_{vap}H^{\ominus}$.

For example.

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$
$$\Delta_{vap}H^{\ominus} = 6.0\ kJmol^{-1}$$

(B) **Enthalpy of combustion:** The enthalpy change that the one mole of substance undergoes combustion in the presence of excess air. It is denoted by $\Delta_c H^{\ominus}$

For example:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$
$$\Delta_c H^{\ominus} = 890.3\ kJmol^{-1}$$

SHORT ANSWER Type-II Questions (SA-II)

[**3** marks]

41. **Answer the following:**

(A) Why is the standard enthalpy of formation of diamond, not zero although it is an element?

(B) SO_2 and SO_3 have standard enthalpies of production of 297 kJ mol^{-1} and 396 kJ mol^{-1}, respectively. Determine the normal enthalpy of reaction for the following reaction:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

Ans. (A) If an element is present in various allotropic forms, then only the standard heat of formation of the most stable allotropic form is taken as zero. For carbon, graphite is the most stable and not diamond therefore, the enthalpy of formation of graphite is considered as zero not for diamond.

(B) $\Delta H^{\circ}_r = (\Delta H^{\circ}_f)_{products} - \Sigma(\Delta H^{\circ}_f)_{reactants}$

$\Delta H^{\circ}_r = \Delta H^{\circ}_f(SO_3) - (\Delta H^{\circ}_f(SO_2) + 1/2\ \Delta H^{\circ}_f(O_2)]$

$\Delta H^{\circ}_r = -396\ kJ\ mol^{-1}\ (-297 kJ\ mol^{-1} + 0)$

$\Delta H^{\circ}_r = -396\ kJ\ mol^{-1} + 297$

$\Delta H^{\circ}_r = -99\ kJ\ mol^{-1}$

42. **Calculate the enthalpy of formation of acetic acid, if its enthalpy of combustion is –867 kJ/mol. The enthalpies of formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are – 393.5 kJ/mol and –285.9 kJ/mol respectively.**

Ans. $\Delta H_{(reaction)} = \Delta H_{(product)} - \Delta H_{(reactant)}$

Let the enthalpy of formation of acetic acid as X.

For the reaction:

$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$

– 867 = (2 × (enthalpy of formation of CO_2)

+ 2 × (enthalpy of formation of H_2O)

– enthalpy of formation of acetic acid

$-867 = -[2 \times (-393.5) + 2 \times (-285.9)] - (X)$

$-867 = -1358.8 + X$

$X = 1358.8 - 867$

$X = 491.8$ kJ/mol

43. **Calculate the heat of combustion of ethylene (gas) to form carbon dioxide (gas) and water (gas) at 298 K and 1 atmospheric pressure. The heat of formation of carbon dioxide, water and ethylene are –393.7, –241.8, 52.3 kJ per mole respectively.**

Ans. The combustion reaction of ethylene gas is as follow:

$C_2H_4 + 3O_2 \rightarrow 2CO_{2(g)} + 2H_2O_{(g)}$

$\Delta H_f(CO_2) = -393.7$ kJ

$\Delta H_f(H_2O) = -241.8$ kJ

$\Delta H_f(C_2H_4) = +52.3$ kJ

$$\Delta H_r = \sum \Delta H_f^\circ(p) \quad \sum \Delta H_f^\circ(r)$$

$$\Delta H_r = [2 \times \Delta H_f^\circ(CO_2) + 2 \times \Delta H_f^\circ(H_2O)]$$

$$[\Delta H_f^\circ(C_2H_4) + 3 \times \Delta H_f^\circ(O_2)]$$

$$\Delta H_r = [2 \times -393.7 + 2 \times -241.8] - [52.3 + 0]$$

Enthalpy of formation is zero for elementary changes.

$\Delta H_c = -1323.3$ kJ

44. **Answer the following:**

(A) Define reaction enthalpy.

(B) Enthalpy is an extensive property. In general, if enthalpy of an overall reaction *A → B* along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... represent enthalpies of intermediate reactions leading to product B. What will be the relation between $\Delta_r H$ for overall reaction $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3$— for intermediate reactions?

[NCERT Exemplar]

Ans. (A) The amount of heat produced or given out during the chemical reaction is called reaction enthalpy. The enthalpy of reaction is denoted by $\Delta_r H$.

$\Delta_r H$ = (sum of enthalpies of product)

– (sum of enthalpies of reactants)

$$\Delta_r H = \sum_i a_i H_{product} - \sum_i b_i H_{reactants}$$

Σ Sigma is denoted for summation and a_i and b_i is represented as stoichiometric coeffcient for the reactant and product.

(B) As per Hess's law $\Delta_r H = \Delta_r H_1 . \Delta_r H_2 . \Delta_r H_3$— this due to reasons in the reaction of A→B the formation of B underwent different intermediate reactions therefore overall enthalpy is $\Delta_r H$.

45. **Briefly explain the following:**

(A) Hess's Law

(B) Will the heat released in the following two reactions be equal? Give reasons in support of your answer.

(i) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$

(ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$

Ans. (A) As per the law, the standard reaction enthalpy will be the sum of the standard enthalpies of an intermediate reaction in which total reaction occurs at the same temperature, whether the reaction occurs in one step or multiple steps.

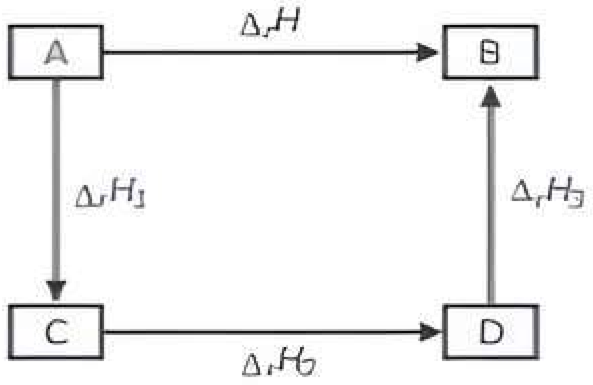
Therefore,

$A \rightarrow B$

$\Delta_r H = \Delta_r H_1 + \Delta_r H_1 + \Delta_r H_3$—

The diagrammatic representation.

$A \longrightarrow A$



(B) No, the heat released in the two reactions are not equal. The heat released in any reaction depends upon the reactants, products and their physical states. Here in reaction (i), the water produced is in the gaseous state whereas in reaction (ii) liquid is formed. As we know, when water vapours condensed to form water, heat equal to the latent heat of vaporisation is released. Thus, more heat is released in reaction (ii).

LONG ANSWER Type Questions (LA)

[4 & 5 marks]

46. 3.5 g of a gas with a molecular weight of 28 was burned in excess oxygen in a constant volume calorimeter at 298 K. The combustion process increased the temperature of the calorimeter from 298 K to 298.45 K. Assume the calorimeter constant is 2.5 kJ K^{-1}. Calculate the enthalpy of gas combustion in kJ mol^{-1}.

Ans. $T_i = 298$ K

$T_f = 298.45$ K

$K = 2.5$ kJK^{-1}

$m = 3.5$ g

$M_m = 28$

Heat evolved $= K\Delta T$

$= K(T_f - T_i)$

$= 2.45$ $kJK^{-1} \times (298.45 - 298)K$

$= 1.12$ kJ

Heat evolved for 3.5 g of a gas = 1.12 kJ

∴ Heat evolved for 28 g of gas (1 mole)

$= (1.125 \times 28)/ 3.5$

The enthalpy of combustion of the gas

$\Delta H_C = 9$ $kJmol^{-1}$

47. Calculate the lattice enthalpy of $CaCl_2$, given that:

Enthalpy of sublimation for

$Ca_{(s)} \rightarrow Ca_{(g)} = 121$ kJ mol^{-1}

Enthalpy of dissociation of

$Cl_{2(g)} \rightarrow 2Cl_{(g)} = 242.8$ kJ mol^{-1}

Ionisation energy of

$Ca_{(g)} \rightarrow Ca^{2+}_{(g)} = 2422$ kJ mol^{-1}

Electron gain enthalpy of

$2Cl \rightarrow 2Cl^{-1}$

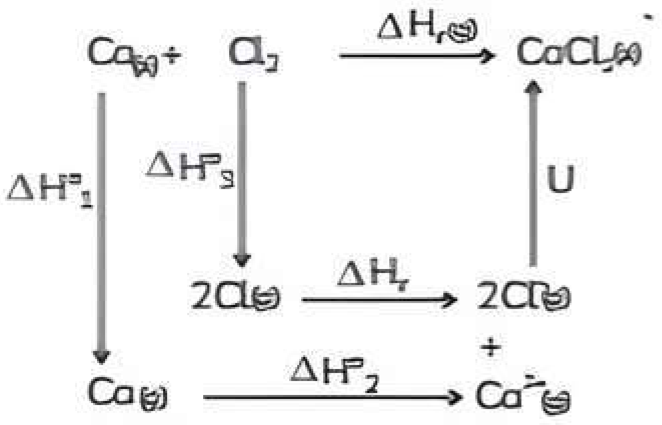
$= (2 \times -355)$ kJ mol^{-1}

$= -710$ kJ mol^{-1}

Enthalpy of formation of $CaCl_2$

$= -795$ kJ mol^{-1}

Ans.



$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + 2\,\Delta H_4 + u$

$-795 = 121 + 2422 + 242.8 + [2 \times (-355)] + u$

$-795 = 2785.8 - 710 + u$

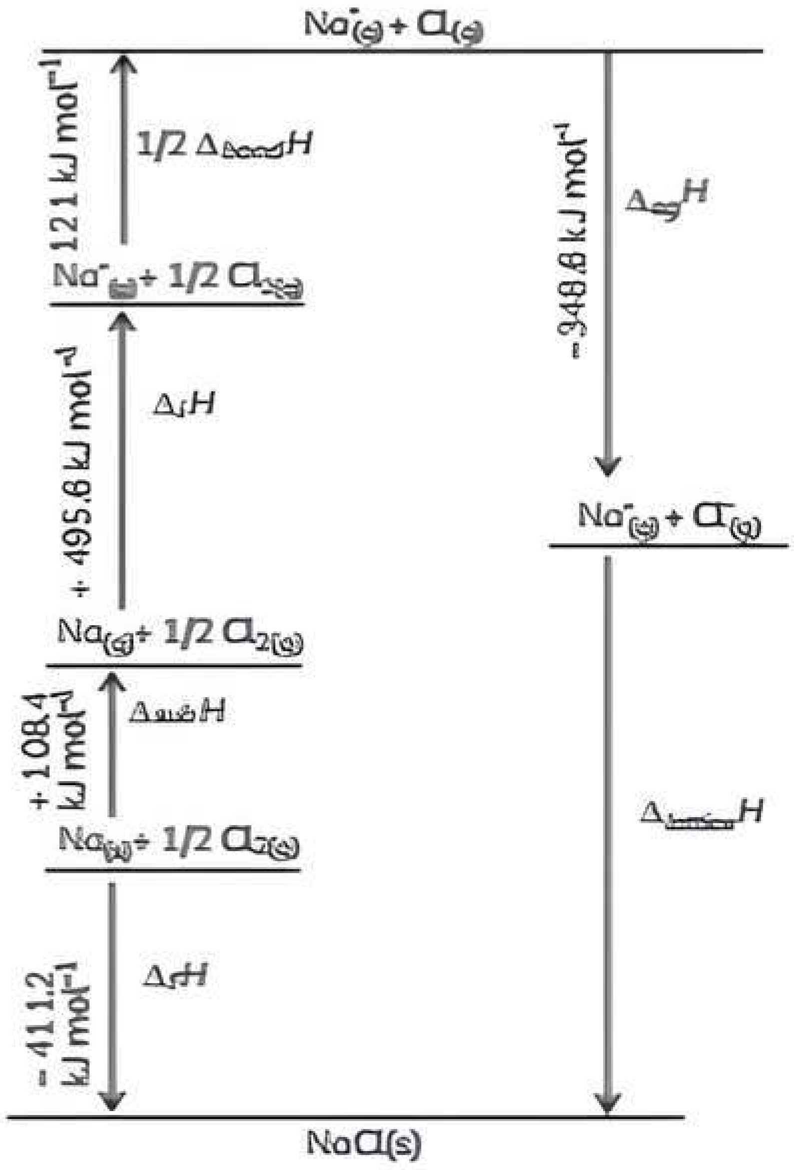
$-795 = 2075.8 + u$

$u = -795 - 2075.8$

$u = -2870.8$ kJ mol^{-1}

48. The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine by experiment. Suggest and explain an indirect method to measure lattice energy of $NaCl_{(s)}$. **[NCERT Exampler]**

Ans. The change in enthalpy takes place when the dissociation of one mole of ionic compound which is transformed into a gaseous ions state. It is represented by $\Delta_{lattice}H^\ominus$.



Enthalpy diagram for lattice enthalpy of NaCl

$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$

$\Delta_{lattice}H^\ominus = 788$ $kJmol^{-1}$

To calculate the lattice energy for NaCl following steps:

(1) Sodium metal undergoes sublimation.

$Na_{(s)} \rightarrow Na_{(g)}$

(2) Then the sodium atom undergoes ionisation

$Na_{(g)} \rightarrow Na^+_{(g)} + e^-_{(g)}$

(3) Dissociation of chlorine

$$\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)}$$

(4) Chlorine gain electron

$$Cl_{(g)} + e^-_{(g)} \rightarrow Cl^-_{(g)}$$

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$$

Therefore, the overall change in the enthalpy is zero.

49. Answer the following:

(A) A 1.25g sample of octane (C_8H_{18}) is burnt in excess of oxygen in a bomb calorimeter. The temperature of the calorimeter rises from 294.05 K to 300.78 K. If heat capacity of the calorimeter is 8.93 kJ/gK. Find the heat transferred to calorimeter.

(B) The enthalpy of reaction for the reaction: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ is $\Delta_r H^\ominus = -572$ kJ mol^{-1}. What will be standard enthalpy of formation of $H_2O_{(l)}$?

Ans. (A) $C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$

Mass of octane, $m = 1.25$ g or 0.00125 kg

Heat capacity, $c = 8.93$ kJg^{-1}K^{-1}

Change in temperature,

$$\Delta T = 300.78 - 294.05$$
$$= 6.73 \text{ K}$$

Heat transferred, $Q = mc\Delta T$

$$= 0.00125 \times 8.93 \times 6.73$$
$$= 0.075 \text{ kJ}$$

Enthalpy of combustion is enthalpy of reaction. In reaction, 1 mole of octane is used.

So, enthalpy of 1 mole of octane can be calculated as follows:

For 1.25 g heat transferred is 0.075 kJ

For 1 mole of 114 g of octane heat transferred will be $\frac{0.075}{1.25} \times 114 = 6.84$ kJ

(B) For the given reaction:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

the standard enthalpy of reaction is $\Delta_r H^\ominus = -572$ kJ mol^{-1}.

The reaction for standard enthalpy of formation of H_2O can be represented by the equation:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

so the half of $\Delta_r H^\circ$ will be the standard molar enthalpy of formation: is $\Delta_f H^\circ = \frac{1}{2}$

572 × is $\Delta_f H^\circ = \left(-\frac{572}{2}\right) = -286$ kJ mol^{-1}

LAWS OF THERMODYNAMICS, SPONTANEITY, GIBB'S ENERGY CHANGE

3

TOPIC 1

LAWS OF THERMODYNAMICS

Thermodynamics laws define the fundamental physical quantities like energy, temperature and entropy that characterise thermodynamic systems at thermal equilibrium. These thermodynamics laws represent how these quantities behave under various circumstances.

There are four laws of thermodynamics which are given below:

(1) Zeroth law of thermodynamics
(2) First law of thermodynamics
(3) Second law of thermodynamics
(4) Third law of thermodynamics

Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that-

"If two bodies are individually in equilibrium with a separate third body, then the first two bodies are also in thermal equilibrium with each other".

Important

➥ *The zeroth law of thermodynamics frames an idea of temperature as an indicator of thermal equilibrium.*

Zeroth law of thermodynamics takes into account that temperature is something worth measuring because it predicts whether the heat will transfer between objects or not. This is true regardless of how the objects interact. Even if two objects are not in physical contact, heat still can flow between them, by means of radiation mode of heat transfer. Whereas, the zeroth law of thermodynamics states that, if the systems are in thermal equilibrium, no heat flow will take place.

First Law of Thermodynamics

The first law of thermodynamics states that the energy of the universe remains the same or the energy can neither be created nor destroyed although, it may be exchanged between the system and the surroundings. This law relates to the changes in energy states due to work and heat transfer. It redefines the conservation of energy concept.

Let us consider the general case in which a change of state is brought about both by doing work and by the transfer of heat. We write change in internal energy for this case as:

$$\Delta U = q + w$$

Where,

ΔU = change in internal energy of the system.

q = algebraic sum of heat transfer between system and surroundings.

w = work interaction of the system with its surroundings.

The mathematical equation for the first law

$$\Delta U = q + w$$

For a given change in state, q and w can vary depending on how the change is carried out. However, it depends only on the initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) *i.e.*, if $w = 0$ and $q = 0$, then $\Delta U = 0$.

The equation *i.e.*, $\Delta U = q + w$ is a mathematical statement of the first law of thermodynamics, which states that

'The energy of an isolated system is constant.'

It is commonly stated as the law of conservation of energy *i.e.*, energy can neither be created nor be destroyed.

Important

➥ *(1) For an isolated system, energy (E) always remains constant.*
(2) Internal Energy is a point function and property of the system. Internal energy is an extensive property (mass-dependent) while specific energy is an intensive property (independent of mass).
(3) For an ideal gas, the internal energy is a function of temperature only.

Limitations

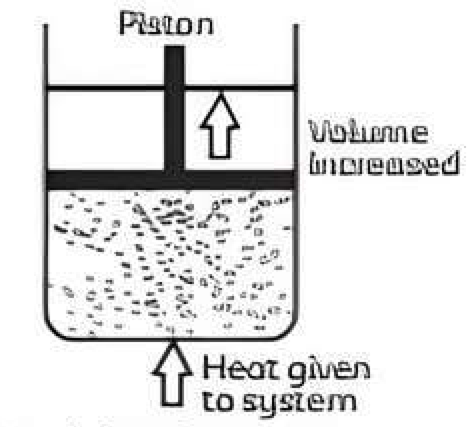
The law states that whenever a system undergoes any thermodynamic process it always holds a certain energy balance. However, the first law fails to give the feasibility of the process or change of state that the system undergoes. For instance, the first law fails to explain why heat flows from the hot end to the cold end when a metallic rod is heated at one end and not on the other and *vice versa*. The first law only quantifies the energy transfer that takes place during this process.

Example 3.1: Predict the change in internal energy for an isolated system at constant volume.

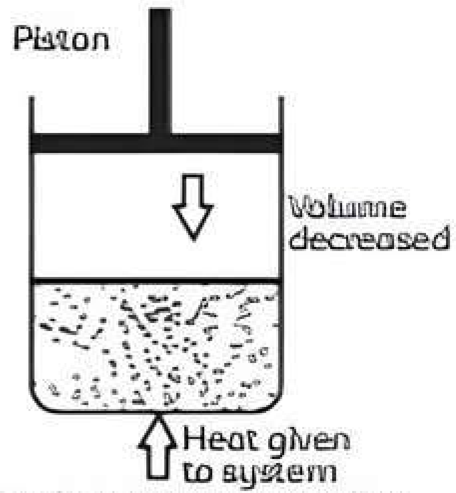
Ans. For an isolated system, no form of energy to be it heat or work can be transferred in any direction. Hence, $q = 0$ and $w = 0$. Therefore, change in internal energy for an isolated system $\Delta U = 0$.

Example 3.2: Case Based:

Given below is the diagram in which the ideal gas is enclosed in a cylinder fitted with a frictionless and weightless piston. In the first figure, work is done by system, increasing the volume and in the second work is done by surrounding, decreasing the volume of the system. Answer the asked questions.



Work done by system



Work done by surrounding

(A) The first law of thermodynamics in an isothermal process is represented by (q = heat exchanged, w=work done, ΔU=internal energy change):

(a) $q = -w$ (b) $\Delta U = w$

(c) $\Delta U = q_v$ (d) $\Delta U = -q_v$

(B) Which of the following can be explained by the first law of thermodynamics?

(a) It takes into account the law of conservation of energy.

(b) Does not indicate the direction in which change takes place.

(c) Gives no information about the extent of change.

(d) Gives no information about the heat source.

(C) What would be the sign convention for the work in both cases?

(D) During an adiabatic expansion of 3 moles of a gas, the change in internal energy was found to be equal to −100 J. Calculate the work done during the process.

(E) Assertion (A): The heat supplied to a system is always equal to the increase in its internal energy.

Reason (R): When a system changes from one thermal equilibrium to another, some heat is absorbed by it.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(a)* $q = -w$

Explanation: According to the first law of thermodynamics

$$\Delta U = q + w$$

When a thermodynamic system undergoes a physical change in such a way that its temperature remains constant, then the change is known as an isothermal process.

For an isothermal process, $\Delta U = 0$

Hence,

$$q + w = 0$$
$$q = -w$$

(B) *(a) It takes into account the law of conservation of energy.*

Explanation: The first law of thermodynamics does signify the general law of conservation of energy that the total energy of a system remains conserved.

(C) Negative, Positive

If the gas expands, $V_f > V_i$, work is done by the system and work is negative.

If the gas contracts, $V_f < V_i$, work is done on the system and work is positive.

(D) Change in internal energy, $\Delta U = -100$ J

Since it is an adiabatic process, the heat exchanged will be zero, $q = 0$

$$\Delta U = q - W$$
$$-100 = 0 - W$$
$$W = 100 \text{ J}$$

(E) *(d) (A) is false but (R) is true.*

Explanation: According to the first law of thermodynamics

$$\Delta q = \Delta U - \Delta w$$
$$= \Delta U + p\Delta V$$

If heat is supplied in such a manner that volume does not change, $\Delta V = 0$

The whole of the heat energy supplied to the system will increase internal energy only. But in any other process, it is not possible. Also, heat may be absorbed or evolved when state of thermal equilibrium changes.

Example 3.3: Three moles of an ideal gas initially at 37°C and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas at 5 atm. Calculate q, w and ΔU for the process.

Ans. Here, $n = 3$ moles, $T = 37°C = 310$ K, $p_1 = 1$ atm,
$p_2 = 5$ atm

$$w = 2.303\, nRT \log \frac{p_2}{p_1}$$
$$= 2.303 \times 3 \times 8.314 \times 310 \log \frac{5}{1}$$
$$= 12{,}464.79 \text{ J}$$
$$= 12.465 \text{ kJ}$$

For isothermal compression of an ideal gas,

$$\Delta U = 0$$
$$q = -w = -12.465 \text{ kJ}.$$

TOPIC 2

SPONTANEITY

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. However, this law doesn't talk about the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. For example, when a hot body and a cold body are placed in contact, heat flows from the hot body to the cold body. The flow of heat is unidirectional from higher temperature to lower temperature. All naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only.

But heat will not flow from a colder body to a warmer body on its own, gas cannot diffuse from low pressure to high pressure or water cannot run uphill on its own.

These and many other spontaneously occurring changes show unidirectional change. Does the question arise what is the driving force of spontaneously occurring changes? What determines the direction of a spontaneous change? In this section, we shall establish some criteria for these processes whether these will take place or not.

By two processes we take into consideration of spontaneous reaction or change.

(1) Dissolution of sugar into the water at room temperature

(2) Burning of coal in air or oxygen

You may think by your common observation that spontaneous reaction occurs immediately when contact is made between the reactants. The first process takes place by itself, although it may be slow, whereas the second process cannot take place by itself. It needs initiation i.e., coal needs to be ignited but once it is initiated it continues on its own.

Although the reaction is taking place between them, it is at an extremely slow rate. It is still called a spontaneous reaction. So spontaneity means 'having the potential to proceed without the assistance of external agency'. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. So a spontaneous process can be thus defined as:

An irreversible process that has a natural tendency to occur either on its own or after proper initiation under the given set of conditions and can be reversed by some external agency only.

Note: A spontaneous process does not mean that the process should be instantaneous. The rate of the process may vary from extremely slow to extremely fast.

A process that can neither take place by itself nor by initiation is called a non-spontaneous process.

For example, flowing of water up a hill, flowing of heat from a cold body to a hot body, diffusion of gas from low pressure to high pressure.

Is the decrease in enthalpy a criterion for spontaneity?

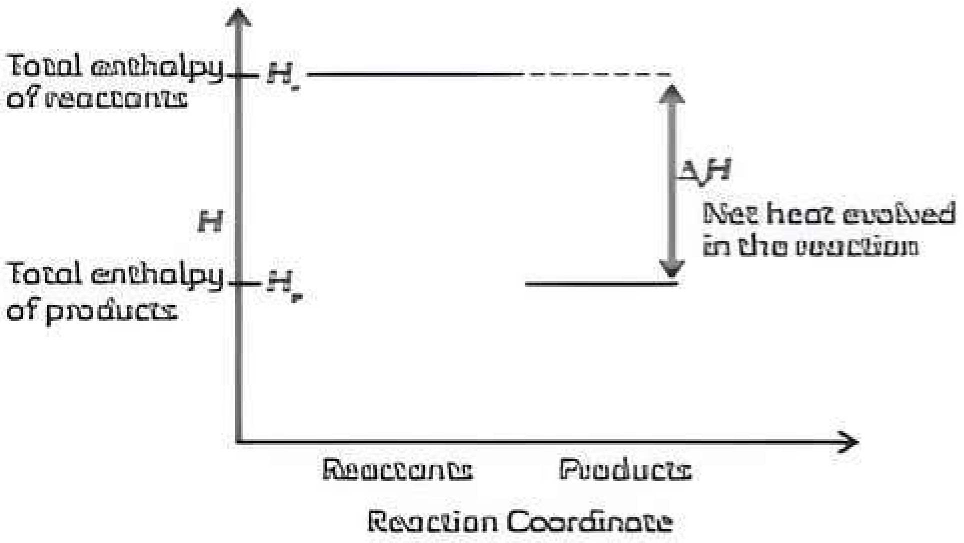
We know that all physical and chemical changes are accompanied by energy changes. If we examine the dropping of a stone from a building and the flowing of water down the hill, a net decrease in potential energy in the direction of change takes place. As we know that the stone or water possessed more potential energy at a higher level than at a lower level. This suggests that macroscopic objects proceed by a decrease of energy to undergo a spontaneous process because the state of the lowest energy corresponds to maximum stability. Similarly, chemical reactions that are exothermic have a negative enthalpy of the system and are spontaneous and a reaction will always be non-spontaneous when ΔH is positive and ΔS is negative. For example:

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)}; \quad \Delta_r H^\circ = -46.1 \text{ kJ mol}^{-1}$$

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}; \quad \Delta_r H^\circ = -92.32 \text{ kJ mol}^{-1}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}; \quad \Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$$

The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram.

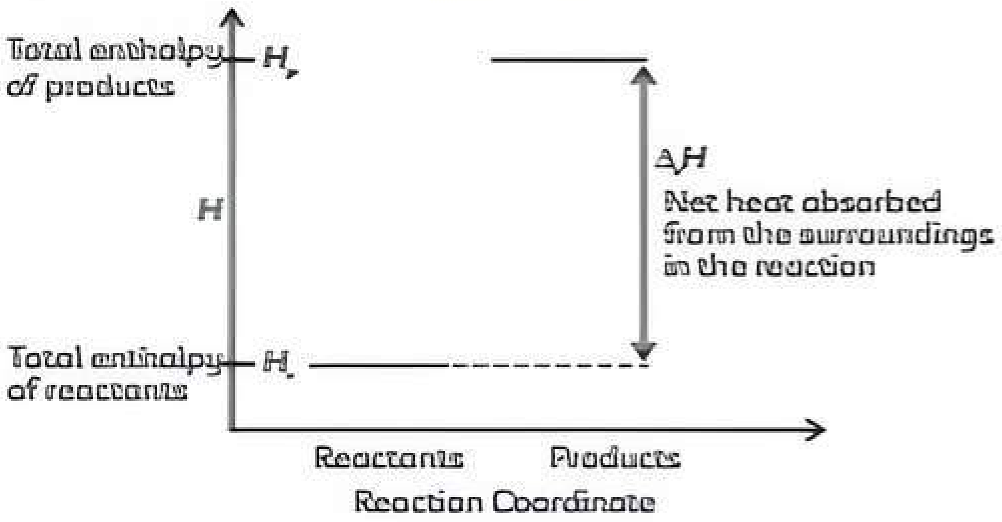


Thus, the postulate that the driving force for a chemical reaction may be due to a decrease in energy sounds "reasonable" as the basis of evidence.

$$\frac{1}{2}N_{2(g)} + O_{2(g)} \rightarrow NO_{2(g)}; \quad \Delta_f H^\ominus = +33.2\ \text{kJ mol}^{-1}$$

$$C_{(graphite,\ s)} + 2S_{(l)} \rightarrow CS_{2(l)}; \quad \Delta_r H^\ominus = +128.5\ \text{kJ mol}^{-1}$$

These reactions through endothermic are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram.

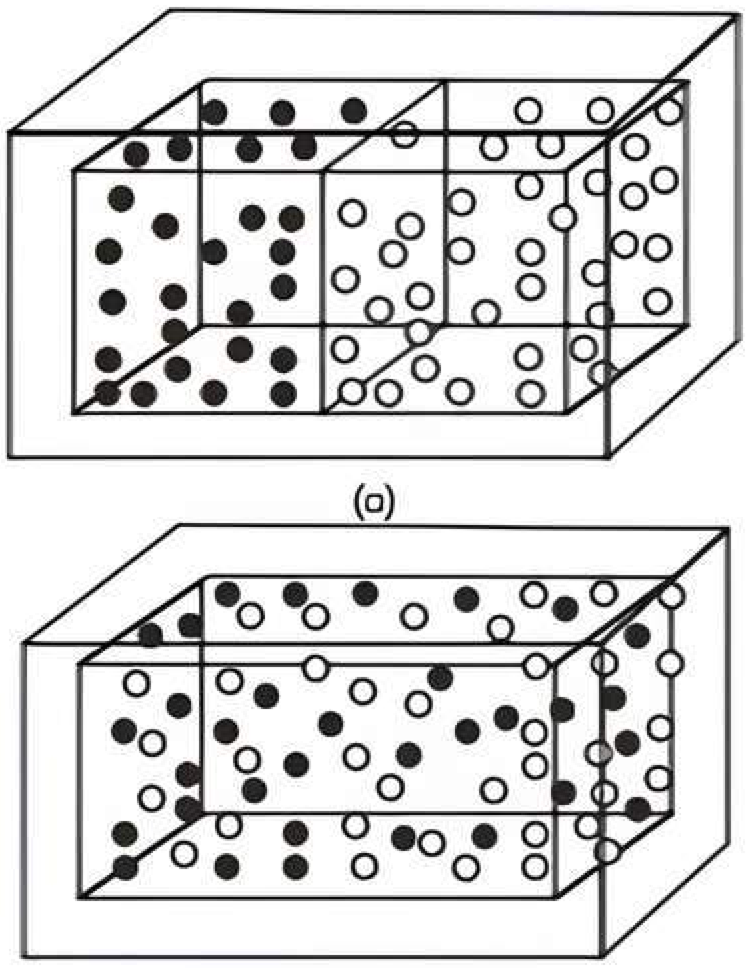


Therefore, it becomes obvious that while a decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

Entropy and spontaneity

Every system tends to attain a state of maximum stability; therefore, a more disordered state may be related to more stability. Hence, the tendency of various systems to acquire a more random state may be responsible for the spontaneity of the process. When the entropy of the universe increases during a process, Gibbs's free energy of the system decreases, and the process is spontaneous. When the entropy of the universe decreases during a process, the Gibbs free energy of the system increases, and the process does not spontaneously proceed.

What is the reason for the spontaneous process to proceed in a given direction? Let us examine such a case in which ΔH = 0, *i.e.*, there is no change in enthalpy, but still the process is spontaneous. Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in the fig.


(a)

(b)

Diffusion of two gases

The two gasses say gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition in (*a*). When the partition is withdrawn as shown in (*b*), the gases begin to diffuse into each other and after a period of time, diffusion will complete. Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly, if we were to pick up the gas molecules from the right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from the container when the partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic. We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change.

At this point, we introduce another thermodynamic function, entropy denoted as S. The above-mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As for as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much more disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. A decrease in regularity in structure would mean an increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered). The gaseous state is state of highest entropy. Now let us try to quantify entropy. We can quantify this process by heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path. Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat (q) has a randomising influence on the system. Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at a higher temperature has greater randomness in it than one at a lower temperature. Thus, temperature is the measure of average chaotic motion of particles in the system. Heat added to a system at a lower temperature causes greater randomness than when the same quantity of heat is added to it at a higher temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as :

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

The total entropy changes (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but

ΔS_{total} i.e. $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible processes, whereas ΔS does.

Example 3.4: Predict which of the following, entropy increases/decreases:

(A) A liquid crystallises into a solid.

(B) Temperature of a crystalline solid is raised from 0 K to 115 K.

Ans. (A) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

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

Gibbs energy and spontaneity

Generally, the total entropy change is the essential parameter that defines the spontaneity of any process. Since most of the chemical reactions fall under the category of a closed system and open system; we can say there is a change in enthalpy too along with the change in entropy. Since, change in enthalpy also increases or decreases the randomness by affecting the molecular motions, entropy change alone cannot account for the spontaneity of such a process. Therefore, for explaining the spontaneity of a process we use the Gibb's energy change. Gibbs' energy is a state function and an extensive property. The general expression for Gibb's energy change at constant temperature is expressed as:

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Where,

ΔG_{sys} = Gibb's energy change of the system
ΔH_{sys} = Enthalpy change of the system
ΔS_{sys} = Entropy changes of the system
T = Temperature of the system

This is known as the Gibbs equation.

For a spontaneous process, the total entropy change, ΔS_{total} is always greater than zero.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

Where,

ΔS_{total} = Total entropy change for the process
ΔS_{sys} = Entropy change of the system
ΔS_{surr} = Entropy change of the surrounding

The change in temperature between the system and the surrounding in the case of thermal equilibrium between system and surrounding is 0, i.e. ΔT= 0. Thus, enthalpy lost by the system is gained by the surrounding. Hence, the entropy change of the surrounding is given as

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

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

ΔH_{surr} = change in enthalpy of the surrounding

ΔH_{sys} = change in enthalpy of the system

Also, for a spontaneous process, the total change in entropy is 0, i.e. $\Delta S_{total} > 0$

Therefore:

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

Using the Gibb's equation, it can be said that

$$\Delta G_{sys} < 0$$

Thus, it can be inferred that spontaneity at constant pressure and temperature is obtained by

(1) If ΔG is negative < 0, the process is spontaneous.

(2) If ΔG is positive > 0, the process is non-spontaneous.

Therefore, with the help of the above relation, the spontaneity of a reaction can be easily predicted.

(1) In the case of exothermic reactions, the enthalpy of the system is negative thereby making all exothermic reactions spontaneous.

(2) In the case of endothermic reactions, Gibb's free energy becomes negative only when the temperature is very high or the entropy change is very high.

Example 3.5: A reaction, $A + B \rightarrow C + D + q$ is found to have a positive entropy change. The reaction will be:

(a) Possible at high temperature

(b) Possible only at low temperature

(c) Not possible at any temperature

(d) Possible at any temperature

Ans. *(d) Possible at any temperature*

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

For the given reaction,

ΔH = –ve as it is exothermic, ΔS = + ve, then ΔG = –ve

So, the reaction will be spontaneous at all temperatures.

Second Law of Thermodynamics and Entropy

The second law of thermodynamics states that $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$ any spontaneously occurring process will always lead to an escalation in the entropy (S) of the universe. In simple words, the law explains that an isolated system's entropy will never decrease over time.

In some cases where the system is in thermodynamic equilibrium or going through a reversible process, the total entropy of a system and its surroundings remains constant. The second law is also known as the Law of Increased Entropy.

The second law clearly explains that it is impossible to convert heat energy to mechanical energy with 100 per cent efficiency. For example, if we look at the piston in an engine, the gas is heated to increase its pressure and drive a piston. However, even as the piston moves, there is always some leftover heat in the gas that cannot be used for carrying out any other work. Heat is wasted and it has to be discarded. In this case, it is done by transferring it to a heat sink, or in the case of a car engine, waste heat is discarded by exhausting the used fuel and air mixture to the atmosphere. Additionally, heat generated from friction that is generally unusable should also be removed from the system.

'It states that the state of entropy of the entire universe, as an isolated system, will always increase over time.'

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

Important

- *If $\Delta S_{universe} > 0$, the reaction is spontaneous*
- *If $\Delta S_{universe} < 0$, the reaction is non-spontaneous*
- *If $\Delta S_{universe} = 0$, the reaction is reversible or is at equilibrium*

Mathematically, the second law of thermodynamics is represented as:

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

Where, ΔS_{univ} is the change in the entropy of the universe.

Entropy is a measure of the randomness of the system or it is the measure of energy within an isolated system. It can be considered as a quantitative index that describes the quality of energy.

Meanwhile, there are a few factors that cause an increase in entropy of the closed system. Firstly, in a closed system, while the mass remains constant there is an exchange of heat with the surroundings. This change in the heat content creates a disturbance in the system thereby increasing the entropy of the system.

Secondly, internal changes may occur in the movements of the molecules of the system. This leads to disturbances which further cause irreversibility's inside the system resulting in the increment of its entropy.

TOPIC 3

GIBBS ENERGY CHANGE AND EQUILIBRIUM

The sign and magnitude of the free energy change of a chemical reaction allow predicting:

(1) The spontaneity of the chemical reaction.

(2) The useful work that could be extracted from free energy.

The reversible under strict thermodynamic sense is in perfect equilibrium with its surroundings. The term reversible means that the given reaction can proceed in either direction simultaneously due to this a dynamic equilibrium is set up. It indicates there will be a decrease in free energy in both directions of the reactions, which appears impossible. It is possible only if the system is at equilibrium there will be minimum free energy. if it is not followed, there will be a spontaneous change in the system to the configuration of lower free energy.

So, the condition for equilibrium

$$A + B \rightleftharpoons C + D$$

$$\Delta G = 0$$

Gibbs energy, for a reaction in which all the reactants and products are in standard state, ΔG° is related to the equilibrium constant for the reaction as follows:

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

$$or\ \Delta_r G^\circ = -RT \ln K$$

$$or\ \Delta_r G^\circ = -2.303 RT \log K$$

We also know that

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

$$= -RT \ln K$$

For a strongly endothermic reaction, $\Delta_r H^\circ$ may be large and positive, the value of K is much smaller than one and the reaction produce very less product.

For exothermic reaction–$\Delta_r H^\circ$ is large and negative, the K value for this reaction will be much larger than one we may expect the reaction will be near the completion due to the large K value.

The value of $\Delta_r H^\circ$ is related to $\Delta_r S^\circ$, also the extent of chemical reaction (K) will also be affected depending on whether the $\Delta_r S^\circ$ is positive or negative.

Using the equation,

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

$$= -RT \ln K$$

(1) It is possible for the estimation of $\Delta_r G^\circ$ from the measurement of $\Delta_r H^\circ$ and $\Delta_r S^\circ$, and then K is calculated at any temperature to know the yield of the products.

(2) If K is measured in the laboratory directly, the value of $\Delta_r G^\circ$ at any other temperature can be calculated.

Table: Effect of temperature on the spontaneity of reactions

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

Note: The terms low temperature and high temperature are relative. For some reactions, the high temperature could even mean room temperature and low temperature means below the room temperature.

Third Law of Thermodynamics

The Third Law of Thermodynamics explain about entropy it states that the Entropy of a pure Crystal at Absolute Zero is Zero.

As we know that Entropy is the measure of the disorder in a system, and while a perfect Crystal is by definition perfectly ordered so that the Entropy of that Crystal is Zero.

The temperature at which all particle motion almost stops. The temperature is known as Absolute Zero, and it's the lowest possible temperature. It is equal to -273.15 degrees Celsius or 0 Kelvin.

Example 3.6: Case Based:

The enthalpy is a state function which is the sum of the system's internal energy and the product of its pressure and volume. The sign of enthalpy changes with spontaneity. There are two types of reactions that can occur when heat energy is involved, they are exothermic and endothermic.

(A) The $\Delta_r H^\circ$ value for an exothermic reaction:

(a) positive (b) negative

(c) infinite (d) integer

(B) When the K value is lower than one, then the reaction is:

(a) evaporation (b) exothermic

(c) endothermic (d) crystallisation.

(C) The burning of sugar is an example of which reaction and suggest its $\Delta_r H^\circ$ and K value ?

(D) Why endothermic reaction has a positive value of $\Delta_r H^\circ$?

(E) Assertion (A): Melting of solid salts is an endothermic process.

Reason (R): The $\Delta_r H^\circ$ value for melting of ice is positive.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(b) Negative*

Explanation: For an exothermic reaction the value of $\Delta_r H^\circ$ is negative as the enthalpy of reactants is higher than the enthalpy of products.

$\Delta H = H_p - H_r$

$H_p < H_r$. So negative value.

(B) *(c) Endothermic*

Explanation: The value of K is lower than one in the case of an endothermic reaction as the enthalpy of products is greater than the enthalpy of reactants. So, lower the value of K.

(C) When sugar was burnt, the heat energy is released to the surroundings. So, it is an example of exothermic reaction. The $\Delta_r H^\circ$ is large and negative, the K value for this reaction will be much larger than one.

(D) The endothermic reaction has a positive value of $\Delta_r H^\circ$ because the enthalpy of the products is higher than the enthalpy of the reactants of the system.

$$\Delta_r H = H_p - H_r$$

As enthalpy of products are greater than the enthalpy of reactants.

$$H_p > H_r$$

So the value of enthalpy is positive.

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Melting of solid salts is an example of endothermic process is due to the higher enthalpy of products than the enthalpy of reactants. Both statements are correct.

Example 3.7: Calculate $\Delta_r G^\circ$ for conversion of oxygen to ozone, $\frac{3}{2} O_{2(g)} \rightarrow O_{3(g)}$ at 298 K. If K_p for this conversion is 2.47×10^{-29}. [NCERT]

Ans. We know,

$\Delta_r G^\circ = -2.303 \, RT \log K_p$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

Therefore,

$$\begin{aligned}\Delta_r G^\circ &= -2.303(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &\quad (\log 2.47 \times 10^{-29}) \\ &= 163000 \text{ J mol}^{-1} \; (1 \text{ kJ} = 1000 \text{ J}) \\ &= 163 \text{ kJ mol}^{-1}\end{aligned}$$

Example 3.8: Find out the value of equilibrium constant for the following reaction at 298 K. $2NH_{3(g)} + CO_{2(g)} \rightleftharpoons NH_2CONH_{2(aq)} + H_2O_{(l)}$. The standard Gibbs energy change, $\Delta_r G^\circ$ at a given temperature is $-13.6 \text{ kJ mol}^{-1}$. [NCERT]

Ans. We know,

$$\log K = \frac{-\Delta_r G^\circ}{2.303RT}$$

$$= \frac{(-13.6 \times 10^3 \text{ J mol}^{-1})}{2.303\left(8.314 \text{ JK}^{-1} \text{ mol}^{-1}\right)(298 \text{ K})}$$

$$(1 \text{ kJ} = 10^3 \text{ J})$$

$$\log K = \frac{(-13.6 \times 10^3 \text{ J mol}^{-1})}{5705.848 \text{ J mol}^{-1}}$$

$$\log K = 2.38$$

Hence, $K = \text{antilog } 2.38$

$= 2.4 \times 10^2$

OBJECTIVE Type Questions

[**1** mark]

1. A system absorbs 500 kJ heat and performs 250 kJ work on the surroundings. The increase in internal energy of the system is:

(a) 750 kJ (b) 250 kJ

(c) 500 kJ (d) 1000 kJ

Ans. *(b) 250 kJ*

Explanation: According to the first law of thermodynamics

$$\begin{aligned}\Delta U &= q + w \\ &= 500 + (-250) \\ &= 250 \text{ kJ}\end{aligned}$$

Caution

- *If work is done on the system, its sign is positive. If work is done by the system, its sign is negative.*

2. 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

Ans. *(b) 10 J*

Explanation: Internal energy is a function of temperature. In an isothermal process, the temperature is constant. Hence, the internal energy is constant, and the net change in internal energy is zero.

So, $\Delta U = 0$ for reversible isothermal process

According to the first law of thermodynamics

$$\begin{aligned} \Delta U &= Q + W \\ 0 &= Q + W \\ W &= -Q \\ &= -10 \text{ J} \end{aligned}$$

Related Theory

- *Work is done by the system so work is negative.*

3. A system absorbs 10 kJ of heat at constant volume and its temperature rises from 270°C to 370°C. Find change in internal energy.

(a) 100 kJ　　(b) 10 kJ
(c) 0 kJ　　(d) 1 kJ

Ans. *(b) 10 kJ*

Explanation: At constant volume, $w = 0$

$\Delta U = q = 10$ kJ

4. What is the entropy change (in JK^{-1} mol^{-1}) when 1 mole of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C.

(a) 20.13　　(b) 2.013
(c) 2.198　　(d) 21.98

Ans. *(d) 21.98*

Explanation: The entropy change:

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

$$\Rightarrow \quad \Delta S = \frac{6000 \text{ Jmol}^{-1}}{273\text{K}}$$

$$\Rightarrow \quad \Delta S = 21.978 \text{ JK}^{-1} \text{ mol}^{-1}$$

5. The enthalpy of vaporization of a substance is 8400 J mol^{-1} and its boiling point is −173°C. The entropy change for vaporization is:

(a) 84 JK^{-1} mol^{-1}　　(b) 21 JK^{-1} mol^{-1}
(c) 49 J K^{-1} mol^{-1}　　(d) 12 JK^{-1} mol^{-1}

Ans. *(a) 84 JK^{-1} mol^{-1}*

Explanation: $\Delta S = \dfrac{(q_{rev})}{T}$

$$= \left(\frac{8400}{100}\right)$$

$$= 84 \text{ JK}^{-1} \text{ mol}^{-1}$$

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

$H_2O_{(l)} \leftrightarrow H_2O_{(g)}$ at 100°C and 1 atm pressure

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

Ans. *(b) $\Delta H = T\Delta S$*

Explanation: At equilibrium

Therefore,

$$\Delta G = 0 = \Delta H - T\Delta S$$

$$\text{or } T\Delta S = \Delta H$$

7. What is the molar entropy change for melting of ice at 0°C, if $\Delta H_f = 1.435$ kcal/mol?

(a) 0.526 cal/mol k　　(b) 5.26 cal/mol k
(c) 10.52 cal/mol k　　(d) 21.04 cal/mol k

Ans. *(b) 5.26 cal/mol k*

Explanation: $\Delta H = T\Delta S$

∴ The molar entropy changes for the melting of ice

$$\Delta S = \frac{\Delta H}{T} = \frac{1.435 \times 10^3}{273\text{K}}$$

$$= 5.26 \text{ cal/mol k}$$

Assertion-Reason (A-R)

In the following question no. (8–11) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

8. Assertion (A): Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason (R): Decrease in enthalpy is a contributory factor for spontaneity.

[NCERT Exemplar]

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Spontaneous processes are accompanied by a decrease in energy and an increase in randomness.

9. Assertion (A): The thermodynamic factor which determines the spontaneity of a process is free energy. For a process to be spontaneous the free energy must be negative.

Reason (R): The change in free energy is related to the change in a process that must always be positive if it is spontaneous.

Ans. *(c) (A) is true but (R) is false.*

Explanation: For a reaction to be spontaneous

$$T\Delta S > \Delta H$$

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

So, ΔG must be negative.

10. Assertion (A): For an exothermic reaction the *K* value will be much larger than one.

Reason (R): The reaction is more towards the product side.

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: The reaction shift is determined by the value of K. In the case of exothermic the K value will be much larger than one, it indicates there will be a shift in the reaction towards the right side that is product side. So, the larger the K value the more the reaction will tend towards the right and thus to completion.

Related Theory

- *For exothermic reaction $-\Delta_r H^{\ominus}$ is large and negative, the K value for this reaction will be much larger than 1. So, we may expect the reaction will be near the completion due to the large K value.*

11. Assertion (A): A spontaneous process is irreversible and can only be reversed by an external force.

Reason (R): A decrease in enthalpy is a factor that contributes to spontaneity.

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Natural processes are characterised by a loss in energy and an increase in randomness.

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

12. *Nernst stated that the entropy changes for each chemical or physical transition between condensed phases, at temperatures very close to the absolute zero , is equal to zero:*

$$\lim_{T\to 0} \Delta S = 0$$

This statement is also referred to as the Nernst heat theorem. The statement of Nernst was simplified by Planck. He stated that not only the entropy changes for processes but also the actual entropy of each condensed substance equals zero if the temperature approaches absolute zero. This statement explicitly excludes mixtures. The following statement makes the explicit exclusion of mixtures unnecessary: for each system in equilibrium, the entropy equals zero when the temperature approaches the absolute zero.

The current "extended form" of the third principle is the one introduced by Planck (1917) which admits, in two stages, that the absolute value of the thermodynamic entropy of any homogeneous solid at 0 Kelvin is: (i) "a universal constant"; (ii) "that one can set to zero without loss of generality".

This choice corresponds to the cancellation of the additive constant S_0 in the Planck-Boltzmann statistical formula. An important caution is that this definition only concerns solids, and is therefore not applicable to perfect gases. By a lack of luck, the water which constitutes an important component of the atmosphere possesses the singular property of having a residual entropy still present at 0 K. The work of Pauling (1935) completed by Nagle (1966) was used to estimate the value at $S_0 = 0.82$ cal / K / mole, by calculating the impacts due to the transfer of charges via the hydrogen bonds still at work at 0 K within the molecule H_2O. So, just for water, you need to include that difference S_0 to have a reference that is "the most stable" at zero Kelvin.

(A) Is the third law is applicable to perfect gases? What are the exceptions of the third law of thermodynamics?

(B) Why is the third law of thermodynamics important?

(C) What are the limitations of this law and under which conditions the third law of thermodynamics is not being obeyed?

Ans. (A) No, it is only applicable to solids. The third law of thermodynamics states that a system's entropy approaches a constant value as the temperature approaches absolute zero. With the exception of non-crystalline solids (glasses), the entropy of a system at absolute zero is typically close to zero.

(B) The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.

(C) **Limitations:**

(1) If any disorder like impurity or imperfection is found in a substance then the entropy of such crystal is non-zero at 0 K. For example: The entropy of pure carbon dioxide and nitric oxide is not zero at 0 K. This shows that there exists disorder in the arrangement of such molecules.

(2) This law is applicable only to pure compounds. Thus, we can say that this law is not applicable to glass which is a supercooled liquid. It is also not applicable to amorphous substance and supercooled solutions.

(3) It is impossible by any procedure, no matter how idealised, to reduce the temperature of any closed system to zero temperature in a finite number of finite operations.

13. *Melting of ice into water happens spontaneously as soon as ice is left at room temperature. Ice is a solid with an ordered crystalline structure as compared to water, which is a liquid in which molecules are more disordered and randomly distributed. All natural processes tend to proceed in a direction which leads to a state that has more random distribution of matter and energy. All of these processes take place spontaneously, meaning that once they start, they will proceed to the end if there is no external intervention. You will never witness the reverse of this process, in which water converts back to ice at room temperature. In other words, it would be inconceivable that this process could be reversed without tampering with the external conditions (you will have to put water in the freezer to force it to form ice).*

(A) This is an example of which law of thermodynamics?

(a) Zeroth law **(b) First law**

(c) Second law **(d) Third law**

(B) What determines the direction in which a process will go under a given set of conditions?

(a) Temperature **(b) Pressure**

(c) Entropy **(d) Enthalpy**

(C) Effect on entropy during this change:

(a) Increase

(b) Decrease

(c) No change

(d) Cannot be determined

(D) Melting of ice is:

(a) Endothermic process

(b) Exothermic process

(c) Equilibrium process

(d) Adiabatic process

(E) In the melting of ice, which one of the conditions will be more favourable?

(a) High temperature and high pressure

(b) Low temperature and low pressure

(c) Low temperature and high pressure

(d) High temperature and low pressure

Ans. (A) *(c) Second law*

Explanation: A crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus, the entropy of a system must increase during melting.

(B) *(c) Entropy*

Explanation: The second law of thermodynamics states that the total entropy of a chemical system and that of its surroundings always increases if the chemical or physical change is spontaneous. The preferred direction in nature is toward maximum entropy.

(C) *(a) Increase*

Explanation: When ice melts, it means solid is converting into liquid so the entropy of the system increases and the process becomes spontaneous.

(D) *(a) Endothermic process*

Explanation: Water in a higher energy state, as the liquid can rotate and vibrate while solid ice can only vibrate. This means for ice to turn into a higher energy state(water) it has to absorb energy, hence it is an endothermic process with respect to the system (surrounding temperature decreases).

(E) *(a) High temperature and high pressure*

Explanation: Since the change of ice into water is an endothermic process, hence with rising of temperature ice melts into water. Since the volume of ice is more than that of water so an increase of pressure favour melting.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

14. **The expansion of a gas in a vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of an ideal gas expands isothermally into a vacuum until its total volume is 5 litres.** **[NCERT Exemplar]**

Ans. Work done by the internal energy is

$$(-w) = p_{ext}(V_2 - V_1)$$
$$= 0 \times (5 - 1) = 0$$

For isothermal expansion $q = 0$

By the first law of thermodynamics

$$q = \Delta U + (-w)$$
$$\Rightarrow \quad 0 = \Delta U + 0$$

So, $\Delta U = 0$

15. **A system gives out 20 J of heat and also does 40 J of work. What is the internal energy change?**

Ans. Internal energy change can be calculated by the first law of thermodynamics

$$\Delta U = q + w$$
$$= -20 \text{ J} + (-40) \text{ J}$$
$$= -60 \text{ J}$$

16. **Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not.**

Ans. It is a spontaneous process. Although the change in enthalpy is zero, the change in randomness or disorder (*i.e.*, ΔS) increases. As a result, in the equation $\Delta G = \Delta H - T\Delta S$, the term $T\Delta S$ will be negative. As a result ΔG will be negative.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

17. Answer the following question in one sentence.

(A) **What are the conditions for the spontaneous reaction under any temperature?**

(B) **Considering system(s) thermodynamic parameters the criteria for the spontaneity of any process is:**

Ans. (A) $\Delta_r G° = (-)ve$, $\Delta_r H° = (-)ve$ and $\Delta_r S° = (+)ve$

(B) The criteria for the spontaneity of any process is $\Delta S_{system} + \Delta S_{surroundings} > 0$.

18. **An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than in the earlier case? (Given that 1 L bar = 100 J)** **[NCERT Exemplar]**

Ans. Work done:

Here

$$w = -p_{ext}(V_f - V_i)$$
$$= -2 \times 40$$
$$= -80 \text{ L bar}$$
$$= -8 \text{ kJ}$$

The negative sign shows that work is done by the system on the surrounding. Work done will be more in the reversible expansion because internal pressure and external pressure are almost the same at every step.

19. **The entropy change in the conversion of water to ice at 273 K for the system is $-21.85 \text{ J K}^{-1} \text{mol}^{-1}$ and that of surrounding is $+21.93 \text{ J K}^{-1} \text{mol}^{-1}$. State whether the process is spontaneous or not.**

Ans. $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$

$$= -21.85\ JK^{-1}\ mol^{-1} + (+21.93\ JK^{-1}\ mol^{-1})$$

$$= 0.08\ JK^{-1}\ mol^{-1}$$

$\Delta S_{Process} > 0$ at 273 K for freezing of ice

So, the process is spontaneous at 273 K.

20. Calculate the temperature at which Gibb's energy change (ΔG) is equal to zero.

(Given $\Delta H = -95.4$ kJ, $\Delta S = -198.3\ kJ^{-1}$)

Ans. The temperature at which the Gibb's energy change is equal to zero is:

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

$$\Delta G = 0$$

$$\Delta H - T\Delta S = 0$$

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

$$T = \frac{\Delta H}{\Delta S} = \frac{(-95.4 \times 1000\,J)}{(-198.3\,JK^{-1})} = 481\,K$$

21. During 200J work done on the system, 140J of heat is given out. Calculate the change in internal energy.

Ans. The change in internal can be calculated by the first law of thermodynamics:

$$w = 200\ J$$

$$q = -140\ J$$

$$\Delta U = q + w$$

$$\Delta U = -140 + 200$$

$$= 60\ J$$

Related Theory

- *Work is done on the system, so work is positive.*

22. Calculate the entropy change in the system and its surroundings, as well as the overall entropy change in the universe, during a process in which 245 J of heat flow from the system at 77°C to the surroundings at 33°C.

Given:

$T_{sys} = 77°C = (77 + 273) = 350$ K

$T_{surr} = 33°C = (33 + 273) = 310$ K

$q = 245$ J

Ans.

$$\Delta S_{sys} = \frac{q}{T_{sys}} = \frac{245}{350} = -0.7\ JK^{-1}$$

$$\Delta S_{surr} = \frac{q}{T_{surr}} = \frac{245}{310} = +0.8\ JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = -0.7\ JK^{-1} + 0.8\ JK^{-1}$$

$$\Delta S_{univ} = -0.1\ JK^{-1}$$

23. One mole of sodium chloride requires 30.4 kJ to melt. The change in entropy during melting is 28.4 $JK^{-1}\ mol^{-1}$. Determine sodium chloride's melting point.

Ans.

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f}$$

Melting point of NaCl

$$T_f = \frac{\Delta H_{fusion}}{\Delta S_{fusion}}$$

$$= \frac{30.4\ kJ\ mol^{-1}}{28.4\ JK^{-1}}$$

$$= \frac{30.4 \times 1000\ J\ mol^{-1}}{28.4\ JK^{-1}mol^{-1}}$$

Melting point of NaCl $T_f = 1070.4$ K

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

24. (A) Dissolution of ammonium chloride in water is endothermic but still, it dissolves in water readily. Why?

(B) What is ΔG for melting of ice at 20°C?

($\Delta_{fusion}H = 6.01$ kJ/mol and

$\Delta_{fusion}S = 220$ J/mol k)

Ans. (A) The reason for this is that the entropy change in this case is positive. i.e. ΔS is +ve.

$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

The ions that were held together in a crystalline solid are free and moving in all possible directions. Its entropy has increased and this makes $T\Delta S > \Delta H$. i.e.

$$\Delta G = -ve$$

(B) The process is changing of phase from solid to liquid.

$$H_2O_{(s)} \rightarrow H_2O_{(l)}$$

The Gibbs energy equation.

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

$$T = 20 + 273K$$

$$= 293\ K$$

Now substituting the values we get.

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

$$= 6.01\ kJ/mol - (293\ k)\ (22.0\ J/mol\ k)$$

$$= 6.01\ kJ/mol - 6.45\ J/mol\ k$$

$$= -0.44\ kJ/mol$$

25. **Predict whether the following reaction is still spontaneous at 500°C:**

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. Assume that $H = 92.22$ kJ mol^{-1} and $\Delta S = -198.75$ JK^{-1} mol^{-1}

Ans. To decide whether the reaction is still a spontaneous we have to calculate the temperature of the Kelvin scale:

$$T = 500°C + 273 = 773\ K$$

Then multiply the entropy term by this temperature and subtract this quantity from the enthalpy term:

$$\begin{aligned}\Delta G° &= \Delta H° - T\Delta S° \\ &= 92{,}220\ J - (773\ K \times -198.75\ J/K) \\ &= 92{,}220\ J - (-153{,}600\ J) \\ &= 61{,}380\ J \\ \Delta G° &= 61.4\ kJ\end{aligned}$$

Thus, the reaction is not spontaneous at 773 K because the entropy term becomes larger as the temperature increases and the reaction changes from the one which is favourable at low temperatures to one that is unfavourable at high temperatures.

26. **Answer the following:**

(A) The standard molar entropy of $H_2O_{(l)}$ is 70 JK^{-1} mol^{-1}. Will the standard molar entropy of $H_2O_{(s)}$ be more, or less than 70 JK^{-1} mol^{-1}?

(B) Which quantity out of Δ_rG and $\Delta_rG°$ will be zero at equilibrium?

(C) At 298 K, K_p for the reaction $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ is 0.98. Predict whether the reaction is spontaneous or not.

Ans. (A) The solid form of water is ice, in which the position of molecules is quite fixed as compared to liquid therefore, the disorderness or randomness in solid molecules is less than in the liquid form where the molecular orientation is more random.

Hence, entropy of $H_2O_{(s)}$ < entropy of $H_2O_{(l)}$

If the standard molar entropy of $H_2O_{(l)}$ is 70 JK^{-1} mol^{-1} then standard molar entropy of $H_2O_{(s)}$ will be less than 70 JK^{-1} mol^{-1}.

(B) At equilibrium, Δ_rG is 0

And $\Delta_rG° = -RT\ \ln K$

(C) $\Delta_rG° = -RT\ \ln K_p = -RT\ \ln(0.98)$

Since ln (0.98) is negative

$\Delta G°$ is positive

$\Rightarrow$ the reaction is non- spontaneous.

27. **Give reasons:**

(A) Evaporation of water is an endothermic process but it is spontaneous.

(B) A real crystal has more entropy than an ideal crystal.

(C) Entropy of the universe is increasing.

[Delhi Gov. QB 2022]

Ans. (A) It is because during this process entropy increases as water vapour has more entropy than liquid water. ΔG become -ve because $T\Delta S > \Delta H$.

(B) A real crystal has some disorders due to the presence of defects whereas an ideal crystal does not have any defect, thus, it has no disorder. Hence, a real crystal has more entropy than an ideal crystal.

(C) Energy always flows downhill, and this causes an increase of entropy. Entropy is the spreading out of energy, and energy tends to spread out as much as possible.

28. **Determine the temperature at which G equals zero. Predict the reaction's direction (A) at this temperature and (B) below this temperature as well.**

$\Delta H = 30.56$ kJmol^{-1} = 30560 mol^{-1}

$\Delta S = 6.66 \times 10^{-3}$ kJK^{-1}mol^{-1}

Ans. Given: $\Delta G = \Delta H - T\Delta S$

$$0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{30.56\ kJ/mol^{-1}}{6.66 \times 10^{-3}\ kJK^{-1}\ mol^{-1}}$$

$$= 4589\ K$$

(A) At 4589 K; $\Delta G = 0$, the reaction is in equilibrium.

(B) At temperature below 4589 K,

$\Delta H > T\Delta S$, $\Delta G = \Delta H - T\Delta S > 0$.

The reaction is not spontaneous in the forward direction. In other words, the response takes place in the opposite direction.

29. **Determine the equilibrium constant for the reaction $2NH_{3(g)} + CO_{2(g)} \rightarrow NH_2CONH_{2(aq)} + H_2O$ at 298K, the standard Gibbs energy change, $G°$, is 13.6 kJ mol^{-1}.**

Ans. Given:

$$T = 298\ K$$

$$\Delta_rG° = -13.6\ kJ\ mol^{-1}$$

$$\Delta G° = -2.303\ RT\ \log K_{eq}$$

$$\log K_{eq} = \frac{-\Delta G°}{2.303\ RT}$$

$$\log K_{eq} = \frac{[-(-13.6)]}{[2.303 \times 8.314 \times 10^{-3} \times 298]}$$

$$\log K_{eq} = 2.38$$

$$K_{eq} = \text{antilog}\ (2.38)$$

$$K_{eq} = 239.88$$

LONG ANSWER Type Questions (LA)

[4 & 5 marks]

30. ΔG Is net energy available to do useful work and is thus a measure of free energy. Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG. If a reaction has positive enthalpy change and positive entropy change, under what condition will be reaction be spontaneous?

Ans. For the reaction to be spontaneous:

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

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

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

For a spontaneous change $\Delta S_{total} > 0$

$$T\Delta S_{total} = \Delta H_{sys} > 0 -(\Delta H_{sys} - T\Delta S_{sys}) > 0$$

But $\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$

$\therefore \quad -\Delta G_{sys} > 0$

$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} < 0$

ΔH_{sys} = Enthalpy change of a reaction.

$T\Delta S_{sys}$ = Enthalpy which is not available to do useful work.

ΔG_{sys} = Energy available for doing useful work.

Unit of ΔG is Joule

The reaction will be spontaneous at high temperature.

31. Two moles of a perfect gas undergo the following process.

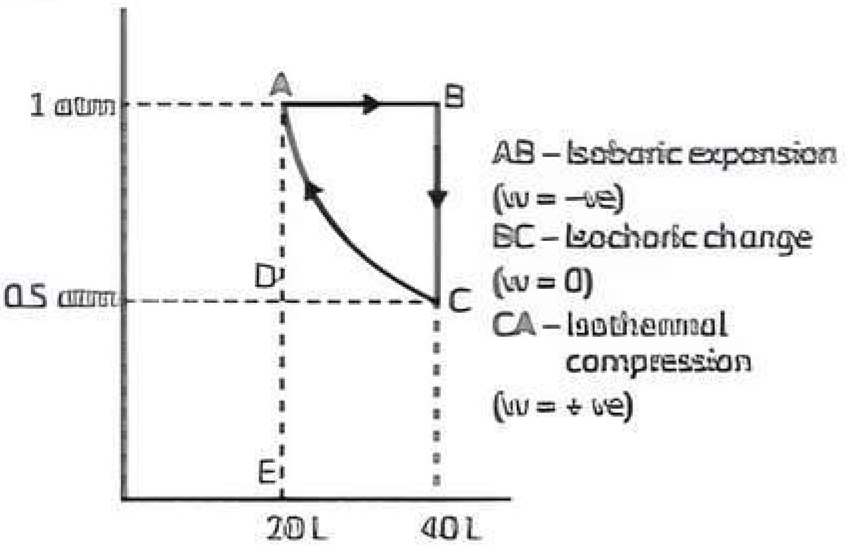
A reversible isothermal compression from (0.5 atm, 40 L) to (1.0 atm, 20 L)

(A) Sketch with labels each of the processes on the same p-V diagram

(B) Calculate the total work (w) and the total heat change (q) involved in the above process.

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

Ans. (A)



(B) Now total work.

$$w = w_{AB} + w_{BC} + w_{CA}$$

$$= -p(V_2 - V_1) + 0 + 2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -1 \times (40 - 20) + 0 + 2.303 p_1V_1 \log \frac{V_2}{V_1}$$

$$= -20 + 2.303 \times 1 \times 20 \log \frac{40}{20}$$

$$= -6.13 \text{ litre atm}$$

$$= -\frac{6.13 \times 8.314}{0.0821} \text{ J}$$

$$= -620.77 \text{ J}$$

$$= w = q = -620.77 \text{ J}$$

(C) The overall process is cyclic one i.e. initial state is regained. thus.

$\Delta U = 0$

$\Delta H = 0$

$\Delta S = 0$