CONTENTS

Introduction

In the study of chemistry the following fundamental questions need to be answered.

(i) Why does a reaction occur? That is, what is the driving force of a reaction?

(ii) How far a reaction can occur? That is, what is the extent (or progress) of the reaction?

(iii) How fast a reaction can occur? That is, what is the rate of the reaction?

We get the answer of the first two questions by the study of **thermodynamics**, while third question forms the domain of the study of chemical kinetics. In this unit we shall focus our attention mainly on thermodynamics while the study of chemical kinetics will be taken up in other unit of the book

Thermodynamics

The branch of science dealing with the relations between energy, heat, work and accompanying changes in the nature and behaviour of various substances around us is called *thermodynamics.* The principles of thermodynamics have been enunciated in the form of a few laws of thermodynamics called zeroth law, first law, second law and third law. These laws find applications in physics, chemistry, engineering, medicine, biotechnology, biochemistry, geology and space sciences. The branch of chemistry dealing with the investigation of energetics and feasibility of chemical reactions and physical changes is called ***chemical thermodynamics***. Its principles are simple, and its predictions are powerful and extensive.

The predictive power of chemical thermodynamics is based on the characteristics of thermodynamic properties namely internal energy *(U),* enthalpy *(H),* entropy (S) and free energy functions *(A* and *G)* and their variations with variables like temperature, pressure, volume and amount. The changes in these properties depend only on the initial and final states of the system, and are independent of the path followed for the system Therefore, these thermodynamic properties are called ***state functions.*** This aspect will be discussed later in this unit.

Aim of the study of chemical thermodynamics

The main aim of the study of chemical thermodynamics is to learn (i) transformation of energy from one form into another form, (ii) utilization of various forms of energy and (iii) changes in the properties of systems produced by chemical or physical effects. Therefore, this branch of science is called ***chemical energetics*** also.

Various forms of energy involved in the study of chemical thermodynamics

In the study of chemical thermodynamics most frequently we deal with the interconversions of four forms of energy namely, electrical energy, thermal energy, mechanical energy, and chemical energy. The energy involved in the chemical processes is called **chemical energy**. That is, it is the energy liberated or absorbed when chemical bonds are formed, broken or rearranged. For example, when hydrogen and oxygen combine water is formed and a large quantity of chemical energy is released. When one mole H–H and half mole O = O bonds are broken, two moles of O–H bonds are formed as H–O–H. In the process energy is required to break

H – H and O = O bonds whereas energy is liberated in the formation of O – H bonds. As a result of breaking and formation of bonds the energy equivalent to 286 kJ is released. The changes are described by the equation.

$$\mathrm{H-H} + \tfrac{1}{2}\,\mathrm{O=O} \longrightarrow \mathrm{H-O-H} + 286\ \mathrm{kJ}$$

Conversion of chemical energy into other forms

Depending upon the conditions under which the reaction proceeds, the chemical energy released can be made to appear as thermal energy, mechanical energy or electrical energy.

- If the reaction takes place in a closed vessel immersed in a water bath, the chemical energy will appear as thermal energy (**heat)*, which*** would warm the vessel, the reaction mixture and the bath.

- If the reaction proceeds in a cylinder fitted with a movable piston, the chemical energy released can be made to produce ***mechanical work*** (work of expansion) by forcing the piston to move in the cylinder against an external pressure.

- If the reaction is allowed to take place in an appropriate electrochemical cell, the chemical energy can be converted into ***electrical energy***.

Thermodynamic terms

In order to understand and appreciate the power of thermodynamics it is necessary to become familiar with the commonly used terms in thermodynamics.

System. A system is a portion of the universe which is selected for investigations. The system may be water taken in a beaker, a balloon filled with air, an aqueous solution of glucose, a seed, a plant, a flower, a bird, animal cell etc**.**

Surroundings. The rest of the universe, which can interact with the system, is called surroundings. For practical purposes the environment in the immediate vicinity of the system is called the surroundings. The boundary may be real or even imaginary

Boundary. The space that separates the system and the surroundings is called the boundary. The system and surroundings interact across the boundary.

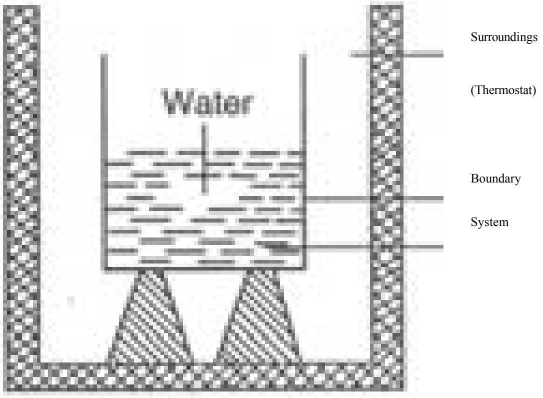


Fig. 1. Illustration of system, surroundings and boundary

Let us suppose that water is taken in a beaker and kept in a constant temperature bath (called thermostat) as shown in Fig. 1. Here water is the **system.** Each wall of the beaker is a ***boundary*** (water-air surface is another boundary). The constant temperature bath is the ***surroundings.***

Types of boundary: Depending upon the nature of the walls of the container boundary can be classified as follows.

(a) **Rigid boundary**. It is a wall whose shape and position are fixed

(b) **Impermeable boundary**: It is a wall that prevents the passage of the matter but permits the passage of energy.

(c) **Permeable boundary**. It is a wall that permits the passage of matter and energy

(d) **Adiabatic boundary**. It is a wall that prevents the passage of mass or energy.

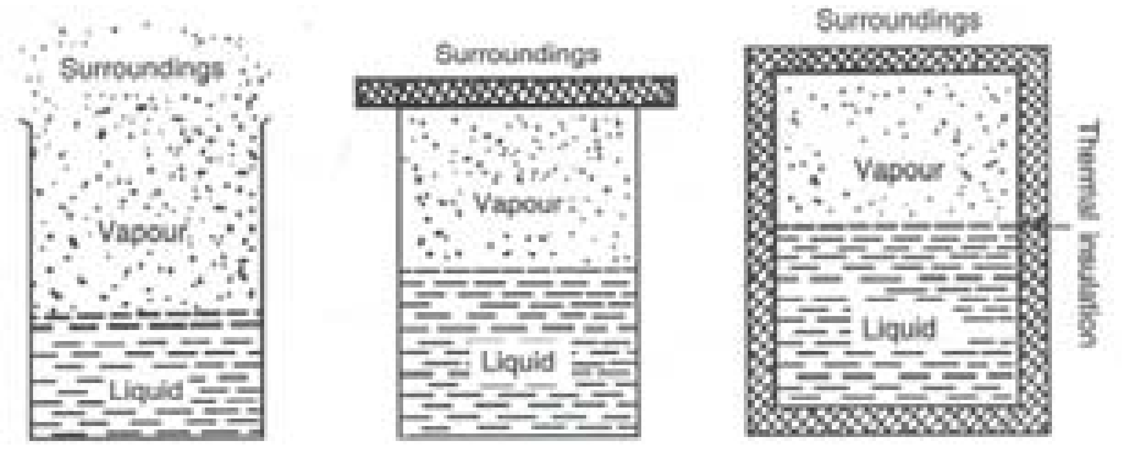
(e) **Diathermic boundary**. It is a wall that allows the passage of energy but prevents the passage of matter. That is, a diathermic boundary is impermeable but not adiabatic

Types of system

Depending upon the nature of the boundary the system can be identified as open, closed or isolated.

(i) **An open system.** It is a system which has permeable boundary across which the system can exchange both the mass (*m*) and energy (*U*) with the surroundings. Thus in an open system mass and energy may change. In terms of symbolic notation it may be stated that in an open system $\Delta m \neq 0$ and $\Delta U \neq 0$

(ii) **A closed system.** It is a system with impermeable boundary across which the system cannot exchange the mass (*m*) but it can exchange energy (*U*) with the surroundings. Thus in a closed system mass remains constant but energy may change. In terms of symbolic notation it may be stated that in an open system $\Delta m = 0$ but $\Delta U \neq 0$



Open system Closed system Isolated system

Fig. 2. Types of systems

(iii) **An isolated system.** It is a system with rigid and adiabatic boundary across which neither exchange of mass (m) nor energy (U) between the system and the surroundings is not permissible. Thus in an isolated system mass and energy remain unchanged. In **terms** of symbolic notation it may be stated that in an isolated system $\Delta m = 0$ and $\Delta U = 0$ Milk kept in a thermos flask is an example of an isolated system.

Extensive and intensive properties

Some of the properties of a system depend on its size whereas others do not depend on its size. Therefore, the properties of a system are grouped as ***extensive*** property and ***intensive*** property.

Extensive property. A property which depends directly on the size of the system is called ***extensive property.*** Volume, mass and amount (mole) are extensive properties.

Characteristics of an extensive property

- An extensive property of the entire system is greater than any of its smaller parts.

- The sum of the properties of subsystems is equal to the same property of the entire system. This means that the extensive properties are **additive.**

Intensive property. A property which does not depend on the size of the system is called ***intensive property***. Density, temperature and molarity are intensive properties.

Characteristics of an intensive property

- An intensive property of a homogeneous system is the same as that of any of its smaller parts.

- The intensive properties are nonadditive.

Illustration that volume is an extensive property but temperature is an intensive property

Take 100 mL of water in a beaker (main system A) and note its temperature (say it is 25 °C). Now divide water (the main system) into four parts as subsystems A_1 (10 mL), $A2$ (20 mL), A_3 (30 mL), and A_4 (40 mL). Here we observe that the volume of the main system A is larger than the volume of any individual subsystem. But the sum of the volumes of subsystems (10 mL + 20 mL + 30 mL+ 40 mL) is equal to the volume of the main system (100 mL). So ***volume is an extensive property***.

Record the temperature of each subsystem. It is observed that the temperature of each subsystem A_1, $A2$, A_3, and A_4 is the same as it was for the main system. Therefore, ***temperature is an intensive*** property**.**

List of extensive and intensive properties

Extensive properties	***Intensive properties***
Volume, mass, amount (mole), energy, enthalpy, entropy, free energy, heat capacity	Molar volume, density, molar mass, molarity, mole fraction, molality, specific heat capacity

A general statement: The ratio of two extensive properties is an intensive property. For example:

(1) Density is an intensive property

$$\frac{\text{Mass (extensive property)}}{\text{Volume (extensive property)}} = \text{Density (intensive property)}$$

(2) Molarity is an intensive property

$$\frac{\text{Mole of the solute (extensive property)}}{\text{Volume of solution (extensive property)}} = \text{Molarity (intensive property)}$$

Logical explanation that molarity of solution is an intensive property

When we prepare 100 mL of 0.1 molar solution of Mohr salt in a measuring flask, we say that its molarity is 0.1 mol/L (0.1 M). Now, if we take 20 mL or 10 mL of this solution, its molarity is still 0.1 mol/L. Thus, the molarity does not depend on the size (volume) of the system (solution) and it is an ***intensive property***.

State variables of the system

A system can be described by its measurable properties such as temperature (*T*), pressure *(P),* volume (*V*) and amount *(n* = moles of various species present in the system). These measurable properties *(T, P, V, n)* are called ***state variables***.

Reason: If the state variables are fixed, the other properties of the system are also fixed. If the state variables are changed the properties of the system are accordingly changed. This implies that all the state variables are not independent. That is, the state of the system may be defined by fixing a certain minimum number of variables depending on the nature of the system.

State properties of the system and state functions

A property of the system which depends only on the state variables is called ***state property*** or state function. The change in a state property depends only on the initial and final states of the system. A state property is independent of the manner in which the change is brought about. This means that the state property does not depend on the path followed by the system.

Thermodynamic properties namely energy *(U),* enthalpy *(H),* entropy (*S*), work function (*A*) free energy (G), volume *(V),* pressure *(P)* and temperature (*T*) are state functions. A state function say energy (*U*) may be mathematically represented as *U = U (T, V, n).* The mathematical representation is stated as *U* is a function of *T, V,* and *n*. That is, energy of the system depends on the state variables *T, V* and *n.* Similarly; volume of the system is a function of temperature (*T*), pressure *(P)* and amount *(n).* That is, *V = V (T, P, n).* For a system of constant composition (for a constant value of *n*) the volume of a gas is a function of temperature and pressure only i.e., *V = V (T, P).*

We can understand the meaning of state functions and state property by taking an analogy. Suppose that one wants to climb a. mountain peak 1 km above ground level. This decision defines the initial state (ground where $h = 0$) and the final state (peak where $h = h$). There may be various paths up to the mountain peak but the vertical height (*h*) of the peak from the ground is 1 km. The height of the mountain peak cannot be altered by choosing different paths though the actual distance travelled and the amount of work put in will be different if different paths are followed. Vertical distance in this analogy corresponds to a thermodynamic function.

Mathematical formulation of state property (Φ)

A thermodynamic property (**Φ**) of the system is called **state function** if it can be expressed in terms of state variables say *x* and *y* as

$$\mathbf{\Phi} = \mathbf{\Phi}\,(x, y)$$

The function Φ can represent any thermodynamic state property namely *P, V, T U, H, S, A,* and *G*

The total differential of a state function is an ***exact differential***. It is expressed in terms of partial derivatives as follows.

$$\mathrm{d}\,\Phi = \left(\frac{\partial \phi}{\partial x}\right)_y dx + \left(\frac{\partial \phi}{\partial y}\right)_x dy$$

Or, $$\mathrm{d}\,\Phi = \left(\frac{\partial \phi}{\partial y}\right)_x dy + \left(\frac{\partial \phi}{\partial x}\right)_y dx$$

In the expression for total differential

$\left(\frac{\partial \phi}{\partial x}\right)_y$ = Partial derivative of Φ with respect to *x* at constant *y* and d*x* is the small change in the variable *x*. Therefore,

$\left(\frac{\partial \phi}{\partial x}\right)_y$ d*x* = Change in the function Φ due to change in the variable *x*

Similarly,

$\left(\frac{\partial \phi}{\partial y}\right)_x$ = Partial derivative of Φ with respect to *y* at constant *x* and d*y* is the small change in the variable y and $\left(\frac{\partial\phi}{\partial y}\right)_x$ dy = Change in the function Φ due to change in the variable y

The expression for total differential implies that d Φ is the same whether Φ is differentiated first with respect x at constant y then with respect to y at constant x or first with respect to y at constant x then with respect to x at constant y. This implies that the order of differentiation of a state function is immaterial. That is,

$$\frac{\partial}{\partial y}\left[\left(\frac{\partial\phi}{\partial x}\right)_y\right]_x = \frac{\partial}{\partial x}\left[\left(\frac{\partial\phi}{\partial y}\right)_x\right]_y$$

$$\frac{\partial^2\phi}{\partial y\partial x} = \frac{\partial^2\phi}{\partial x\partial y}$$

The above relation is called **Euler's** reciprocity relation.

Simplified form of Euler's reciprocity relation

In equation for total differentia $\Phi = \left(\frac{\partial\phi}{\partial x}\right)_y dx + \left(\frac{\partial\phi}{\partial y}\right)_x dy$, let us suppose that

$$\left(\frac{\partial\phi}{\partial x}\right)_y = M(x, y)$$

and
$$\left(\frac{\partial\phi}{\partial y}\right)_x = N(x, y)$$

Now the total differential d Φ can be written as

$$\mathrm{d}\,\Phi = M(x, y)\,\mathrm{d}x + N(x, y)\,\mathrm{d}y$$

and Euler's reciprocity relation can be written as

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Exercise for proficiency. ***Describe the method to write the total differential and Euler's reciprocity relation for the volume of a fixed amount of a system.***

The volume of a fixed amount of a gas is a function of temperature and pressure. That is, $V = V(T, P)$. Total differential of V is written as

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

(i) In the above equation

dV = Total small change in the volume when temperature and pressure are changed by dT and dP respectively

$\left(\frac{\partial V}{\partial T}\right)_P$ = Rate of change of volume with temperature at constant pressure and therefore,

$\left(\frac{\partial V}{\partial T}\right)_P dT$ = Change in volume due to change in temperature only

$\left(\frac{\partial V}{\partial P}\right)_T$ = Rate of change of volume with pressure at constant temperature and therefore,

$\left(\frac{\partial V}{\partial P}\right)_T dP$ = Change in volume due to change in pressure only

Euler's reciprocity relation for volume is written as

$$\frac{\partial}{\partial P}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]_T = \frac{\partial}{\partial T}\left[\left(\frac{\partial V}{\partial P}\right)_T\right]_P$$

Or, $$\frac{\partial^2 V}{\partial P \partial T} = \frac{\partial^2 V}{\partial T \partial P}$$

Illustration of total differential and exact differential of volume of an ideal gas

The volume of an ideal gas is expressed by the equation $PV = nRT$ or, $V = nRT/P$. For one mole of a gas, $n = 1$ and

$$V = \frac{RT}{P} \qquad \text{(i)}$$

On differentiating equation (i) we get

$$\mathrm{d}V = \frac{R}{P}dT - \frac{RT}{P^2}dP \qquad \text{(ii)}$$

This equation implies that the volume of a given amount of the gas is a function of temperature and pressure

$$V = V(T, P) \qquad \text{(iii)}$$

Total differential of V is written as

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad \text{(iv)}$$

The differential dV given by equation (ii) is the same as that given by equation (iv). Thus on comparing the coefficients of dT and dP of the two equations, we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \qquad \text{(v)}$$

and $$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} \qquad \text{(vi)}$$

On differentiating equation (v) with respect to P at constant T we get

$$\frac{\partial}{P}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]_T = \frac{\partial}{P}\left(\frac{R}{P}\right)_T = -\frac{R}{P^2} \qquad \text{(vii)}$$

On differentiating equation (vi) with respect to T at constant P we get

$$\frac{\partial}{T}\left[\left(\frac{\partial V}{\partial P}\right)_T\right]_P = \frac{\partial}{T}\left(-\frac{RT}{P^2}\right)_P = -\frac{R}{P^2} \qquad \text{(viii)}$$

Comparison of equations (vii) and (viii) gives

$$\frac{\partial}{P}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]_T = -\frac{R}{P^2} = \frac{\partial}{T}\left[\left(\frac{\partial V}{\partial P}\right)_T\right]_P$$

Or, $$\frac{\partial^2 V}{\partial P \partial T} = \frac{\partial^2 V}{\partial T \partial P}$$

Conclusion: The total differential of V is an exact differential because it satisfies the Euler's reciprocity relation. Thus ***volume (V) is a state function.***

General statements

- Total differential of a state function is an exact differential.
- An exact differential follows Euler's reciprocity relation

Conversely

- If a total differential follows Euler's reciprocity relation, it is an exact differential
- If the total differential of a function is exact, then that function must represent a state property

Physical interpretation of Euler's reciprocity relation

The Euler's reciprocity relation implies that the total change in a state property is independent of the path (method) followed.

We shall illustrate this aspect by taking an example of change of volume (V) of a given amount of gas with the change of the temperature and pressure from T_1 , P_1 to T_2 , P_2. This change in volume may be carried by any of the following methods.

Method I: Both the temperature and pressure are simultaneously changed from T_1, P_1 to T_2, P_2

$$\textbf{Gas } (T_1, P_1) \xrightarrow{\text{simultaneous change of temperature and pressure}} \textbf{Gas } (T_2, P_2)$$

Initial state Final state

Volume change = Final volume of the gas – Initial volume of the gas

$$\Delta V\,(\mathrm{I}) = V\,(T_2, P_2) \; - V\,(T_1, P_1)$$

Method II: First the temperature is changed from T_1 to T_2 at constant pressure (P_1), and then the pressure is changed from P_1 to P_2 at constant temperature (T_2)

$$\textbf{Gas}\ (\boldsymbol{T_1, P_1}) \xrightarrow{\text{constant pressure}} \textbf{Gas}\ (\boldsymbol{T_2, P_1}) \xrightarrow{\text{constant temperature}} \textbf{Gas}\ (\boldsymbol{T_2, P_2})$$

Initial state Intermediate state Final state

$$\begin{aligned}\Delta V\,(\mathrm{II}) &= [\,V\,(T_2, P_1) \; - V\,(T_1, P_1)\,] + \; [\,V\,(T_2, P_2) \; - V\,(T_2, P_1)\,] \\ &= V\,(T_2, P_2) \; - V\,(T_1, P_1)\end{aligned}$$

Thus, Volume change = Final volume of the gas – Initial volume of the gas

Method III: First the pressure is changed from P_1 to P_2 at constant temperature (T_1), and then the temperature is changed from T_1 to T_2 at constant pressure (P_2)

$$\textbf{Gas}\ (\boldsymbol{T_1, P_1}) \xrightarrow{\text{constant temperature}} \textbf{Gas}\ (\boldsymbol{T_1, P_2}) \xrightarrow{\text{constant pressure}} \textbf{Gas}\ (\boldsymbol{T_2, P_2})$$

Initial state Intermediate state Final state

$$\begin{aligned}\Delta V\,(\mathrm{III}) &= [\,V\,(T_1, P_2) \; - V\,(T_1, P_1)\,] + \; [\,V\,(T_2, P_2) \; - V\,(T_1, P_2)\,] \\ &= V\,(T_2, P_2) \; - V\,(T_1, P_1)\end{aligned}$$

Thus, Volume change = Final volume of the gas – Initial volume of the gas

Experimentally it has been observed that total change in the volume of the gas is the same in all the three cases, i.e.,

$$\Delta V\,(\mathrm{I}) = \Delta V\,(\mathrm{II}) =.\ \Delta V\,(\mathrm{III})$$

Thus volume is a state property.

VOLUME IS A STATE PROPERTY– *demonstration by calculation*

Consider a given amount of an ideal gas in its initial state $T_I = 300$ K, $P_I = 1$ bar, $V_I = 20\ \mathrm{dm}^3$. Let us suppose that the state variables of the gas are changed to a final state $T_2 = 600$ K, $P_2 = 0.8$ bar, so that its final volume is V_2. The change in the state of the gas (system) may be made in the following ways.

Method 1. The gas is heated and allowed to expand simultaneously from the initial state $T_1 = 300$ K, $P_1 = 1$ bar, $V_1 = 20\ \mathrm{dm}^3$ to the final state $T_2 = 600$ K, $P_2 = 0.8$ bar, so that final volume is V_2. Now in this case the gas equation $P_1\ V_1 /\ T_1 = P_2\ V_2\ /T_2$ gives

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{1\ \mathrm{bar} \times 20\ \mathrm{dm}^3 \times 600\ \mathrm{K}}{0.8\ \mathrm{bar} \times 300\ \mathrm{K}} = 50\ \mathrm{dm}^3$$

Thus change of volume = $\Delta V(1) = V_2 - V_1 = 50\ \text{dm}^3 - 20\ \text{dm}^3 = 30\ \text{dm}^3$

Method 2. Step (a). The gas is heated at constant pressure from 300 K, 1 bar, 20 dm^3 to 600 K, 1 bar so that its volume is V_a as given by Charles's law:

$$V_a = \frac{600\ \text{K}}{300\ \text{K}} \times 20\ \text{dm}^3 = 40\ \text{dm}^3$$

$$\Delta V(2\ \text{a}) = (40 - 20)\ \text{dm}^3 = 20\ \text{dm}^3$$

Step 2(b) The gas is allowed to expand at constant temperature from 600 K, 1 bar, 40 dm^3 to 600 K, 0.8 bar so that its final volume is V_2 as given by Boyle's law

$$V_2 = \frac{1\ \text{bar} \times 40\ \text{dm}^3}{0.8\ \text{bar}} = 50\ \text{dm}^3$$

$$\Delta V(2\ \text{b}) = (50\ \text{dm}^3 - 40\ \text{dm}^3) = 10\ \text{dm}^3$$

Net change of volume in step 2 =$\Delta V(2) = \Delta V(2\text{a}) + \Delta V(2\text{b})$

$$= (20\ \text{dm}^3 + 10\ \text{dm}^3) = 30\ \text{dm}^3$$

Method 3. Step (a) The gas is allowed to expand at constant temperature from 300 K, 1 bar, 20 dm^3 to 300 K, 0.8 bar so that its final volume is V_a as given by Boyle's law

$$V_a = \frac{1\ \text{bar} \times 20\ \text{dm}^3}{0.8\ \text{bar}} = 25\ \text{dm}^3$$

$$\Delta V(3\text{a}) = (25\ \text{dm}^3 - 20\ \text{dm}^3 = 5\ \text{dm}^3$$

Step 3(b) The gas is heated at constant pressure from 300 K, 0.8 bar, 25 dm^3 to 600 K, 0.8 bar so that its final volume V_2 is given by Charles's law:

$$V_2 = \frac{600\ \text{K}}{300\ \text{K}} \times 25\ \text{dm}^3 = 50\ \text{dm}^3$$

$$\Delta V(3\text{b}) = (50\ \text{dm}^3 - 25\ \text{dm}^3) = 25\ \text{dm}^3$$

Net change of volume in step 3 =$\Delta V(3) = \Delta V(3\text{a}) + \Delta V(3\text{b})$

$$= (5\ \text{dm}^3 + 25\ \text{dm}^3)\ \text{dm}^3 = 30\ \text{dm}^3$$

Discussion: The final state of the system is reached in three different ways but the final volume in each process is the same $V_2 = 50\ \text{dm}^3$ and the net volume change for all the three paths is also the same. This proves that ***volume is a state function*** *and* $V = V(T, P)$

Other characteristics of partial derivatives of a state function (for example V)

(i) Reciprocal of a partial derivative of a state function leads to the reversal of the differentiation, i.e.,

$$\frac{1}{\left(\frac{\partial V}{\partial T}\right)_P} = \left(\frac{\partial T}{\partial V}\right)_P$$

(2) Two partial derivatives of a state function can be multiplied and their numerators and denominators can be cancelled provided their constraints (subscripts) are the same. For example

$$\left(\frac{\partial V}{\partial P}\right)_T \times \left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial V}{\partial V}\right)_T = 1$$

(3) Partial derivatives of a state function obey cyclic rule. For example

$$\left(\frac{\partial P}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial T}\right)_P \times \left(\frac{\partial T}{\partial P}\right)_V + 1 = 0$$

Or, $$\left(\frac{\partial P}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial T}\right)_P \times \left(\frac{\partial T}{\partial P}\right)_V = -1$$

Note: To remember the cyclic rule write *PVT* in a line and differentiate *P* with respect to *V* at constant *T (remember PVT),* differentiate *V* with respect to *T* at constant *P (remember VTP*), differentiate *T* with respect to *P* at constant *V (remember TPV*), multiply these derivative and equate to –1.

Physical significance of partial derivatives of volume

(i) $\left(\frac{\partial V}{\partial T}\right)_P$ = Rate of change of volume with change of temperature at constant pressure

$= \alpha V$

Or, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

where α is called ***isobaric coefficient of thermal expansion***, its dimension is T^{-1}

(ii) $\left(\frac{\partial V}{\partial P}\right)_T$ = Rate of hange of volume with change of pressure at constant temperature

$= -k V$

Or, $k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

where k is called ***isothermal compressibility*** coefficient, its dimension is P^{-1}

A negative sign with the derivative tells that volume of the system decreases with increase of pressure at constant temperature.

Relation between α and k

(a) $$\frac{\alpha}{\kappa} = \left(\frac{\partial P}{\partial T}\right)_V$$

(b) $$\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P$$

Path dependent function and its differential

A thermodynamic quantity is called a ***path function*** if its value depends on the path followed. For example, work done depends on the path followed by the system. For the same initial and final states of a system the work done is different under reversible and irreversible conditions as given below.

(i) $w_{\text{reversible}}$ (ideal gas) = $-2.303\ nRT \ln (P_1/P_2)$

(ii) $w_{\text{irreversible}}$ (ideal gas) = $-\ nRT\,(1-\frac{P_2}{P_1})$

It is clear from the above relations that w (reversible) $\neq$ w (irreversible)

Differential of a path function is inexact and it does not follow Euler's reciprocity relation. For example, work (w) is a path dependent quantity and its differential is inexact and is represented by $đw$

Justification that *đw* is an inexact differential *(Optional)*

The work done is given by

$$đw = -\,P\mathrm{d}V \qquad \text{(i)}$$

But V is a state function $V = V(T, P)$ and its total differential is given by

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad \text{(ii)}$$

From equations (i) and (ii), we have

$$đw = -\,P\left(\frac{\partial V}{\partial T}\right)_P dT \;-\; P\left(\frac{\partial V}{\partial P}\right)_T dP \qquad \text{(iii)}$$

At constant T, $\mathrm{d}T = 0$ and therefore, equation (iii) gives

$$\left(\frac{\partial w}{\partial P}\right)_T = -\,P\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{(iv)}$$

Differentiation of equation (iv) with respect to T at constant P gives

$$\frac{\partial^2 w}{\partial T \partial P} = -\,P\left(\frac{\partial^2 V}{\partial T \partial P}\right) \qquad \text{(v)}$$

At constant P, dP = 0 and therefore, equation (iii) gives

$$\left(\frac{\partial w}{\partial T}\right)_P = - P\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{(vi)}$$

Differentiation of equation (vi) with respect to P at constant T gives

$$\frac{\partial^2 w}{\partial P \partial T} = -\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial^2 V}{\partial P \partial T}\right) \qquad \text{(vi)}$$

Let us suppose that w were state function and dw were exact differential. In such a case Euler's reciprocity relation should be valid and

$$\frac{\partial^2 w}{\partial T \partial P} = \frac{\partial^2 w}{\partial P \partial T}$$

Or, $$- P\left(\frac{\partial^2 V}{\partial T \partial P}\right) = -\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial^2 V}{\partial P \partial T}\right) \qquad \text{(vii)}$$

But V is a state function and dV is exact differential therefore,

$$\frac{\partial^2 V}{\partial P \partial T} = \frac{\partial^2 V}{\partial T \partial P} \qquad \text{(viii)}$$

From equations (vii) and (viii) we should have

$$\left(\frac{\partial V}{\partial T}\right)_P = 0 \qquad \text{(ix)}$$

The above equation implies that volume is independent of temperature at constant pressure. But this result is against the experimental observation (Charles's law requires that volume of a given amount of a gas is directly

proportional to absolute temperature at constant pressure).

Conclusion

- We arrived at a wrong result because of the wrong assumption of considering work as state function and dw as exact differential. Hence đw ***is inexact differential and w is a path dependent quantity.***

- In the same way it can be proved that đq is inexact differential and heat (q) is path dependent quantity.

Thermodynamic process

The method of operation which can bring about the change in the system is called *thermodynamic process.* Heating, cooling, expansion, compression, fusion, vaporization etc., are some examples of thermodynamic process.

Types of process

A change can be carried in different ways and under different conditions. Therefore, the processes can be classified as follows:

Isothermal process. A process is said to be *isothermal* when the temperature of the system is kept constant

during various operations. That is, there is no change of temperature ($dT = 0$) in an isothermal process. Isothermal condition is attained either by supplying heat to the system or by removing heat from the system. For this purpose the experiment is performed in a thermostat (constant temperature bath).

Adiabatic process. A process is said to be adiabatic if there is no exchange of heat (q) between the system and surroundings during various operations. That is, $q = 0$ in an adiabatic process. This condition is attained by thermally insulating the system. In an adiabatic process if work is done by the system its temperature decreases, if work is done on the system its temperature increases.

Isobaric process. A process is said to be ***isobaric*** if the pressure remains constant during the change. That is, $dP = 0$ in an isobaric process. (bar is the SI unit of pressure, therefore, isobaric means same pressure))

Isochoric process. A process is said to be ***isochori****c* if the volume of the system remains constant during the change. That is, $\mathrm{d}V = 0$ in an isochoric process. Combustion of a fuel in a bomb calorimeter is an example of isochoric process.(the term chore is used for space, therefore, isochoric means same space or same volume)

Quick view of the process and its condition

Process	*Isothermal*	*Adiabatic*	*Isobaric*	*Isochoric*
Condition	$dT = 0$	$q = 0$	$dP = 0$	$dV = 0$

Reversible process. A process is said to be ***reversible*** if the change can take place in both the forward and back directions by a small change in its state variables. In a reversible change the system can be brought back to its initial state without altering the properties of surroundings to an appreciable extent. In a reversible process the change takes place very slowly so that the system and surroundings are nearly at equilibrium (called quasiequilibrium).

Illustrations of a reversible process

Let us consider a gas taken in a cylinder which is fitted with a movable piston. Suppose that an external pressure (P_{ext}) is applied on the gas by keeping sufficient quantity of sand grains on the piston. In this situation the pressure of the gas (P_1) is balanced by the external pressure on the gas, that is, $P_1 = P_{\text{ext}}$

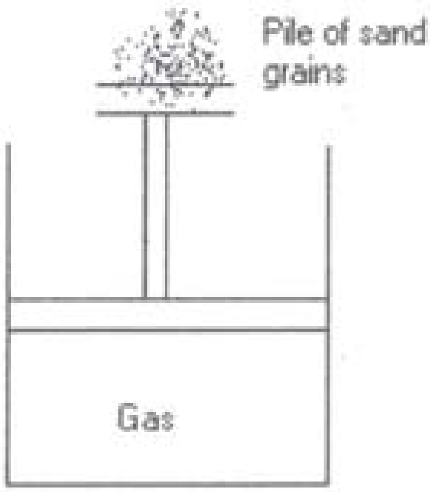


Fig. 3 Illustration of reversible process

Suppose that one grain of the sand is removed from the piston. The removal of the sand grain will cause a very small decrease in the external pressure. Now the pressure of the gas becomes slightly greater than the external pressure. Because of this difference of pressure the gas will expand till the pressure of the gas becomes equal to the pressure on the gas. This expansion will result in an infinitesimally small work done by the gas on the surroundings. The work is so small that no appreciable change is observed in the properties of the system or surroundings. On the other hand, if the same grain of sand is placed again on the piston, the external pressure will increase and the gas will be compressed to its initial stage. In this case also infinitesimally small work will be done by the surroundings on the system, which will not cause any appreciable change in the properties of the system and surroundings. Therefore, the change is said to be ***reversible.*** However, by removing the sand grains continuously from the piston (by lowering the pressure) the gas will expand by a definite volume

Irreversible process. A process is said to be ***irreversible*** if the change takes place in one direction. In an irreversible process the system cannot be brought back to its original state without affecting the surroundings. All the natural changes are irreversible and hence spontaneous.

Cyclic process. It is a process in which the initial state of the system is restored after undergoing a series of changes

Path. Path is the representation of steps of changes starting from initial state and then reaching the final state through various intermediate states (if any).

Concept of internal energy, work and heat

Thermodynamics has been defined as the branch of science wherein we study the interconversions of heat, work and energy and various possible relations between these quantities. Therefore, it is essential to learn the meaning of these terms.

Concept of internal energy (U)

Internal energy is a characteristic property of a system which decides its nature and behaviour**.** It is denoted by symbol U. Internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The energy of a molecule is equal to translational energy (U_t), vibrational energy (U_v), rotational energy (U_r), bond energy (U_b), electronic energy (U_e), energy due to molecular interactions (V_T) and the relativistic energy ($U = \Delta m \times c^2$ which is very large and hence it is not considered in chemical reactions). Thus:

$$U = U_t + U_{\mathrm{v}} + U_r + U_b + U_{\mathrm{e}} + V_{\mathrm{T}}$$

The total energy of all the molecules of the system is called ***internal energy*** or *intrinsic energy*. The internal energy is the cause of existence of various types of distinct substances. In thermodynamic studies one is more concerned with the change in internal energy (ΔU) rather than the absolute value of energy.

Importance of internal energy: The internal energy possessed by a substance differentiates it from other substances. For example, the allotropes of carbon namely graphite (C) and diamond (C), differ from each other because they possess different internal energies and have different structures. This is the reason that internal energy is also called ***inherent energy*** or *hidden energy* or more appropriately ***intrinsic energy.***

Characteristics of internal energy

- Internal energy of a system is an ***extensive*** property. It depends on the amount of the substances present in the system. If the amount is doubled, energy is also doubled.

- Internal energy of a system is a ***state property***. It depends only upon the state variables *(T, P, V, n)* of the system. The change in internal energy of a fixed amount the system is expressed as:

$$\Delta U = U_2\,(T_2, P_2, V_2) - U_1\,(T_1, P_1, V_1)$$

Or,

$$\Delta U = U_2 - U_1 = \int_1^2 \mathrm{d}U$$

- The change in internal energy does not depend on the path by which the final state is reached.

- In a cyclic process, there is no energy change. ΔU (cycle) = 0

Or,

$$\oint \mathrm{d}U = 0$$

Methods by which the energy of a system can be changed. The energy of a system can be changed by all or any of the following processes:

- The system undergoes either a chemical change or a physical change.
- Heat is given to the system or heat is removed from the system.
- Work is done by the system or work is done on the system. Therefore, ***internal energy of a system is also defined as its capacity to do work***

Concept of work in thermodynamics

Work is a result of action against an opposing force. It is equal to the force multiplied by displacement

$$w = -F \times \Delta x$$

where Δx is the path length over which action is taken and F is the force against which work has to be done.

- If $F = 0$, then $w = 0$. That is, if there is no opposing force, then the motion itself cannot produce any work.
- If $\Delta x = 0$, then $w = 0$. That is, if there is no motion, even the strongest opposing force cannot generate any work.

Mechanical work involving gas

In a system when gases are involved, the mechanical work is equal to pressure *(P)* multiplied by change of volume (ΔV).

$$w = -F \times \Delta x$$

$$= \frac{F}{A} \times A \times \Delta x$$

$$= -P \times \Delta x$$

Here $P = \frac{F}{A}$ = Force per unit area = pressure

and $\Delta V = A \times \Delta x$ = Area × displacement = change of volume

Significance of minus sign in the expression $w = -P \times \Delta V$

- As per IUPAC recommendations the symbol w has to be used for work done on the system.
- During compression work is done on the system thus volume decreases and ΔV is negative. Therefore, work done on the system is positive as is clear from the relation $w = -P \times \Delta V$
- During expansion volume increases and ΔV is positive so the work done on the system is negative as is clear from the relation $w = -P \times \Delta V$. But in this case work done by the system is positive during expansion as given by $-w = P \times \Delta V$..

Characteristics of *w*

- A system does not possess any work. Work appears across the boundary during change only.
- The work is zero if there is no change.
- Work is path dependent quantity.

- Work is manifestation of energy.
- When work is done by the system its energy decreases.
- When work is done on the system its energy increases.

Illustration of work and sign of its value

(i) w = + 200 kJ implies that 200 kJ work is done on the system. This will increase the energy of the system. Since the work done on the system is positive, it represents compression.

(ii) w = –250 kJ implies that - 250 kJ work is done on the system. That is, in the process the energy of the system would decrease. A decrease in energy suggests that the work is done by the system. Thus w = - 240 kJ stands for - w = 240 kJ = work done by the system and the given value corresponds to a process of expansion.

An analogy of sign of work done on the system and work done by the system

It is the recommendation of the IUPAC that the symbol w should be used for the work done on the system by the surrounding. Therefore, for the work done by the surrounding on the system the symbol –w can be used. Let us understand it by an analogy of an account in a bank.

Suppose a person deposits a sum of Rs. 400. 00 on December 2005 and withdraws a sum of Rs. 150.00 on December 8, 2005. Now these statements can be shown as follows

Particulars	Amount deposited		Amount withdrawn		Balance	
	Rs.	Paise	Rs.	Paise	Rs.	Paise
2 - 12 - 2005	400	00	nil		400	00
8 - 12 - 2005	nil		150	00	250	00

Suppose that in the register of bank there is column for amount deposited only and there is no column for amount withdrawn. In that case the amount withdrawn will be indicated as – 150.00 under the amount deposited and the above statement of account may be shown as follows:

Expressions for work under different conditions

It has been stated that work is a path dependent quantity. It has different values if the change is brought under different experimental conditions. For example, for the changes between the same initial state and same final state of a system

(i) work done under isothermal condition is different from the work done under adiabatic condition.

(ii) work done under isothermal reversible condition is different from the work done under isothermal irreversible condition.

(iii) work done for free expansion is different from the work done under any other condition

(A) Work done under isothermal reversible condition

Let us consider *n* moles of a gas in a cylinder confined by a frictionless and weightless movable piston. Let us suppose that

P_{ext} = External pressure acting on the gas

P_{int} = Internal pressure of the gas.

The change in the state of the gas will depend on the relative values of P_{ext} and P_{int}. Thus

(a) When $P_{\text{ext}} > P_{\text{int}}$ the gas will be compressed

(b) When $P_{\text{int}} > P_{\text{ext}}$ the gas will expand

When $P_{\text{ext}} = P_{\text{int}} \pm \mathrm{d}P$, where d*P* is a small change in the pressure then the change is reversible. This type of situation is shown in Fig. 4. (a) for the expansion of a gas. In the figure the dotted lines show the position of the piston for a small volume change d*V* of the gas.

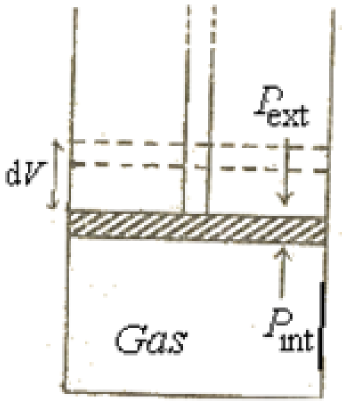


Fig. 4 (a) Reversible - isothermal expansion of an ideal gas in a cylinder fitted with a movable piston

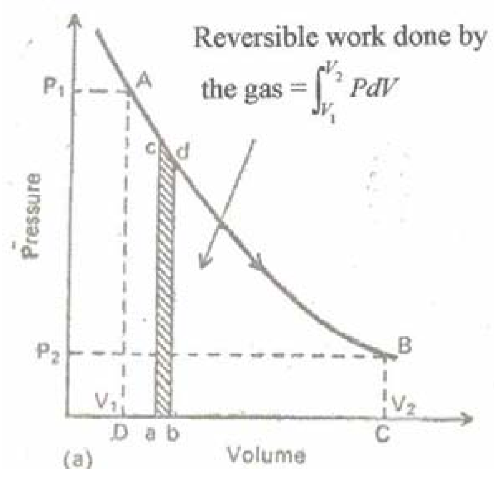


Fig. 4 (b) Pressure versus volume indicator diagram for reversible - isothermal expansion of an ideal gas. Work = Area ABCD

Calculation of work done for isothermal reversible process from *P* versus *V* indicator diagram

When the change is isothermal and reversible the pressure and volume both are changed slowly so that equilibrium is maintained between the system and surrounding at each stage of the change. For such a process the variation of volume with pressure is shown by an indicator diagram in Fig. 4 (b).

Suppose that the pressure is slightly lowered by d*P* (from c to d) so that there is infinitesimally small increase in volume by d*V* (from a to d). For such a small volume change the small work done by the gas is given by

$$đw \text{ (rev)} = (P - dP)\, dV$$

The change of pressure from point c to point d is very small as it is clear from the indicator diagram.

Therefore, it can be assumed that pressure on the gas (P– dP) is very near to the pressure of the gas (P). That is,

$P - dP \approx P$ and thus work done by the gas is given by

$$-\,đw \text{ (rev)} = P\, dV$$

From the indicator diagram it is seen that

$$P\, dV = ac \times ab = \text{Area of the thin strip abcd}$$

$$-dw(\text{rev}) = P\, dV = \text{Area abcd}$$

For a finite isothermal reversible change of state of the system, the total work done is equal to the sum of the areas of all such thin strips as *abcd*. Now the reversible change is very slow and continuous therefore, the work done by the gas is equal to the integral of $P dV$. Thus

$$-\,w(\text{rev}) = \int_{V_1}^{V_2} P dV = \text{Area ABCD} \quad \text{refer to Fig. 5 (a)}$$

Comments. ***Reversible work of expansion is the maximum work which can be obtained from a system.*** Let us see how and why? For expansion the pressure on the gas should be less than pressure of the gas. That is $P_{ext} < P_{int}$ and work done by the gas is given by

$$-\,đw = P_{ext} \times dV$$

In a reversible change the internal pressure is only slightly greater that the external pressure

$$P_{ext} = P_{int} - dP \approx P_{int}$$

Now to cause expansion, P_{ext} cannot be greater than P_{int}. At most these two pressures may approach each other. In other words, it may be stated that P_{ext} is the limiting maximum pressure against which the gas can expand. If the external pressure exceeds this limiting value the gas will not expand rather it will be compressed. Therefore, the product $P_{ext} \times dV = P_{int} \times dV$ should have the maximum possible value and thus the reversible work of expansion is maximum.

(B) Work done under isothermal irreversible condition

Let us consider *n* moles of a gas in a cylinder confined by a frictionless and weightless movable piston. Let us suppose that the piston is held in position by a pin Fig. 5 (a) and the internal pressure of the gas is greater than the external pressure on the gas.

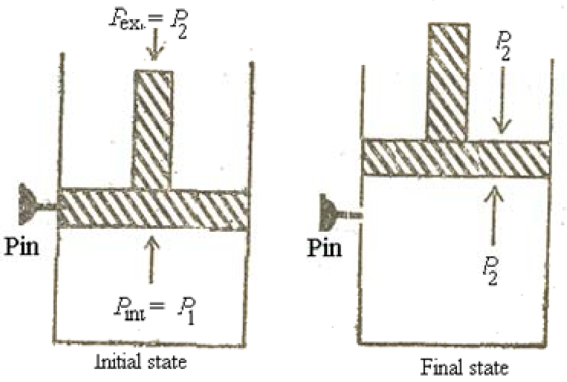


Fig. 5 (a) Irreversible-isothermal expansion of an ideal gas in a cylinder fitted with a piston
Initial state: Piston held by a pin ($P_{\text{int}} > P_{\text{ext}}$)
Final state: When pin is removed the gas expands so that $P_{\text{int}} = P_{\text{ext}}$

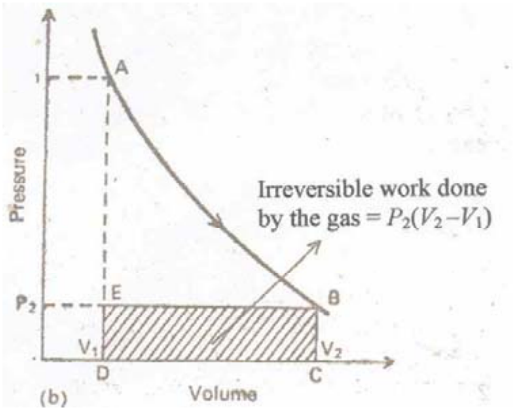


Fig. 5 (b) Pressure versus volume indicator diagram for irreversible-isothermal expansion of an ideal gas.
Work = Area BCDE

Calculation of work done for isothermal irreversible process from *P* versus *V* indicator diagram

In an irreversible process the pressure is suddenly released from initial value of P_1 to a final value of P_2. Therefore, the gas expands from initial volume V_1 to final volume V_2 against the new lower constant pressure P_2 Thus

$$-w(\text{irr}) = \int_{V_1}^{V_2} P dV$$

Since final pressure is constant and $P = P_2$, therefore,

$$-w(\text{irr}) = P_2 \int_{V_1}^{V_2} dV$$

$$= P_2 [V_2 - V_1]$$

$$= \text{DE} \times \text{DC} = \text{Area BCDE} \qquad \text{refer to Fig 5 (b)}$$

Conclusions: From the above illustrations it is quite clear that area ABCD is larger than the area BCDE. Therefore

(a) Work done is different under different conditions for the same initial state and same final state.

(b) Isothermal reversible work is greater than isothermal irreversible work.

Concept of heat in thermodynamics

The change in the internal energy of the system due to difference of temperature of the system and its surroundings is called ***heat***. The symbol of heat is *q*. Heat flows from higher temperature towards lower temperature. The energy of the system increases when it is brought into contact with the surroundings which is at a higher temperature. On the other hand, when the temperature of the system is higher than that of the surroundings the heat flows from the system to the surroundings and the internal energy of the system decreases. Thus:

- When heat is absorbed by the system its energy increases. That is, ΔU is positive. Such a change is called ***endothermic.***
- When heat is given out by the system its energy decreases. That is, ΔU is negative. Such a change is called ***exothermic***.

Characteristics of heat

- A system does not possess any heat. It possesses only energy
- The concept of heat comes into picture across the boundary during the change only.
- If there is no difference of temperature between the system and surroundings there is no flow of heat.
- Heat is a path dependent quantity.
- Heat is manifestation of energy.
- When heat flows into the system its energy increases.
- When heat flows out of the system its energy decreases.

Sign conventions for heat (*q*)

- When *q* has a positive value, then we say that heat is absorbed by the system from the surroundings. This change is endothermic
- When *q* has a negative value, then we say that heat is given out by the system to the surroundings. This change is exothermic

Illustration

(i) $q = +200$ kJ implies that 200 kJ heat is absorbed by the system from the surroundings

(ii) $q = -300$ kJ implies that 300 kJ heat is given out by the system to the surroundings

Discussion

- Heat is not a material or fluid.
- A system does not possess heat and work.

- When it is stated that heat flows it means that the energy is exchanged between the system and surroundings due to temperature difference

- When it is stated that mechanical work is done it means that energy is exchanged because of pressure gradient between the system and the surroundings.

- In reality the heat and work are manifestation of energy.

Units of energy, heat and work

- The energy of a system is expressed as joules (J) or kilojoules (kJ). The change of energy is also expressed in J or kJ. Since heat and work are manifestation of energy, these are also expressed in the units of J or kJ.

- Calories (cal) and kilocalories (kcal) are non-SI units of energy

- These units are related as follows:

(i) 1000 J = 1 kJ or 10^{-3} kJ = 1 J

(ii) 1000 cal = 1 kcal or 10^{-3} kcal = 1 cal

(iii) 1 cal = 4.198 J = 4.2 J (for approximate calculations)

A molecular picture of flow of heat or exchange of heat. The internal energy of the system can be changed by supplying heat to the system or by removing heat from the system. The energy of the system increases when it is brought into contact with the surroundings which is at a higher temperature.

Explanation. In this case heat energy flows from the surroundings into the system because of temperature difference. The flow of heat from the surroundings to the system continues until both attain the same temperature. The exchange of heat between the system and surroundings is due to the collisions of the molecules on the walls of the system. The molecules in the surroundings have more energy because they are at higher temperature.When these energetic molecules hit the boundary they transfer their energy which is transmitted to the system. This causes an increase in the internal energy of the system.

When the temperature of the system is higher its molecules hit the boundary and transfer their energy to the surroundings. Thus, the heat flows from the system to the surroundings and the internal energy of the system decreases.

Example. State which of the following will cause decrease and increase of the internal energy of the system:

(a) Heat transferred to the surroundings

(b) Work done by the system

(c) Work done on the system.

Solution.

(a) Heat transferred to the surroundings will cause a decrease in the energy of the system.

(b) Work done by the system will cause a decrease in its energy.

(c) Work done on the system will cause an increase in is energy.

THERMAL EQUILIBRIUM

The law of thermal equilibrium is called the ***zeroth law of thermodynamics***. This law states that if two systems A and B are separately in thermal equilibrium with a third system C, then A and B will also be in the thermal equilibrium with each other. That is,

If A = C ... thermal equilibrium between A and C

and B = C ... thermal equilibrium between B and C

Then A = B ... thermal equilibrium between A and B

Zeroth law of thermodynamics forms the basis of measurement of temperature of a system by a thermometer. When a thermometer is brought in contact with a system both attain thermal equilibrium. Thus, the thermometer records a constant temperature of the system

CONFIDENCE BUILDING QUESTIONS ON FUNDAMENTAL TERMS

(A) Complete the following statements using a correct word/term from the list given below:

[zero, extensive, boumdary, volume, temperature, isobaric, adiabatic, isothermal, closed, intensive, path dependent, cyclic, state, on]

1. The space separating the system from the surroundings is called the -------------

2. Temperature is kept constant in an ----------------- process

3. In an isothermal process ------------------ remains constant.

4. In an adiabatic process ------------ is not exchanged between the system and the surroundings.

5. In ------------- process heat is not exchanged between the system and surroundings.

6. An ------------ property is independent of the amount of substance.

7. An ------------ property depends on the amount of substance.

8. A -------------- property is independent of the path

9. Change of internal energy is ----------- in a cyclic process

10. In an isochoric process ------------ is constant.

11. Pressure is constant in an ------------ process

12. Mass cannot be exchanged between the system and surroundings in a ------------- system

13. Work is a ----------------- property

14. The change of a state property in a -------------process must be zero.

15. The sign of work is positive when work is done --------- the system.

(B) Give a very brief answer of the following questions.

1.Write the main aim of the study of thermodynamics.

2. Define an extensive property.

3. Volume is an extensive property. Give reason.

4. Define an intensive property.

5. Density is an intensive property. Explain.

6. Use the relation $PV = nRT$ to prove that volume is a state function.

7. Select intensive and extensive properties from the following:

volume, pressure, density, mass, internal energy, heat capacity, mole, mole fraction, molarity, molar mass

8. State the condition under which a thermodynamic property $\Phi(x, y)$ is a state function and $\mathrm{d}\Phi$ is an exact differential.

(C) Select true and false statements

1. In an adiabatic process volume is kept constant.
2. In an isothermal process temperature is kept constant
3. Density is an intensive property.
4. Both heat and matter are exchanged between the system and surroundings in an isolated system.
5. Total differential of a state function is an exact differential.
6. Heat is state property of the system.
7. The internal energy is a state function.
8. In an open system both heat and matter are exchanged with the surroundings.
9. State functions are perfect differentials.
10. All natural processes are irreversible.

Answers

True: 2, 3, 5,7, 9, 10 **False** 1, 4, 6, 8:

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is popularly called the law of ***conservation of energy***. This law is stated as follows:

Energy can be neither created nor destroyed. If it disappears in one form it must reappear in some other equivalent form.

This statement also implies that the ***energy of the universe is constant.*** If there is an increase in the energy of the system, there must be a decrease in the energy of the surroundings and *vice versa.*

Statement of the first law of thermodynamics

Mathematical formulation of the law of conservation of energy is called the ***first law of thermodynamics***. In terms of energy, heat and work the first law of thermodynamics is written as:

$$\Delta U = q + w$$

Here: ΔU = Change in the internal energy of the system

$= U\text{ (final)} - U\text{ (initial)}$

q = Heat absorbed by the system

w = Work done on the system (it includes all possible types of work)

Formulation of the relation $\Delta U = q + w$

Let us suppose that U_1 is the initial internal energy of the system. Again let us suppose that work *(w)* is done on the system and at the same time heat *(q)* is supplied to the system so that its energy is increased from initial value U_1 to a final value U_2. According to the law of conservation of energy, the final energy of the system is equal to the sum of its initial energy *(U_1),* work done on it *(w)* and heat absorbed by it *(q).*

Final energy = Initial energy + Heat absorbed by the system +Work done on the system

$$U_2 = U_1 + q + w \qquad \text{(i)}$$

Or, $U_2 - U_1 = q + w$

$$\Delta U = q + w$$

That is, increase in internal energy = Heat absorbed by the system + Work done on the system

The equation $\Delta U = q$ + w is a mathematical statement of the first law of thermodynamics. In this equation ΔU is the change in the internal energy of the system, q is the heat absorbed by the system and w is the work done on the system.

Meaning of symbol Δ in Δ*U*. Symbol Δ is called **delta.** It signifies a change. Thus, ΔU is the change in the internal energy of the system and $\Delta U = U_2 - U_1$.

Delta (Δ) is not used before *q* and w

Reason. q and w depend on path and there is no initial and final heat or work of the system. The concept of heat or work comes into picture only during the change. If there is no change, there is no heat or work. But the system has energy.

Important information derived from the first law of thermodynamics ($\Delta U = q + w$)

- If no work is done, $w = 0$, and first law of thermodynamics reduces to

$$\Delta U = q \qquad \text{when } w = 0$$

This relation tells that change in internal energy is equal to the heat exchanged between the system and the surroundings. That is, if heat is absorbed by the system there is increase in its internal energy. On the other hand, if heat is released by the system there is decrease in its internal energy

- If there is no exchange of heat between the system and surroundings, $q = 0$ and the first law reduces to

$$\Delta U = w \qquad \text{when } q = 0$$

This relation is true for ***adiabatic process***. It implies that if work is done on the system its internal energy will increase. On the other hand, if work is done by the system its internal energy will decrease. That is, ***in an adiabatic process work is done by the system at the expense of its internal energy.*** This is the reason that in adiabatic expansion of a gas cooling effect is observed and during adiabatic compression heating effect is observed.

- If there is no change in the internal energy of the system, $\Delta U = 0$ and the first law may be written as

$$q = -w \qquad \text{when } \Delta U = 0$$

But $-w$ represents the work done by the system. Thus, when the energy of the system is kept constant then heat absorbed by the system is equal to the work done by the system.

The relation $q = -w$ may also be written as $w = -q$. Thus when the energy of the system is kept constant and work is done on the system, then heat must flow from the system to the surroundings.

Change in internal energy and heat exchanged in an isochoric process

The change in internal energy is equal to the heat exchanged between the system and surrounding at constant volume. Let us prove it.

The first law of thermodynamics states that $\Delta U = q + \mathrm{w}$ where ΔU is the change of internal energy, q is the heat exchanged between the system and surroundings and w is the work done against an opposing force. The mechanical work at constant pressure due to volume change is given by

$$w = -P \times \Delta V$$

where ΔV is the volume change and P is the constant pressure. For such a case the first law of thermodynamics can be written as:

$$\Delta U = q + w = q - P \times \Delta V$$

In an isochoric process volume is constant and $\Delta V = 0$, therefore, the product $P \times \Delta V$ is also zero. Thus, for an **isochoric** process the first law of thermodynamics can be written as

$$\Delta U = q \qquad \text{at constant volume}$$

Or $\Delta U = q_V$

Here subscript *'V'* in q_V indicates that volume (V) is constant. The relation $\Delta U = q_V$ is a link between the chemical energy (ΔU) and thermal energy *(q)*.

Example: ***In an experiment 400 kJ heat is absorbed by the system so that its internal energy increases by 250 kJ. How would you apply the law of conservation of energy to this system?***

Solution. Law of conservation of energy in the form of first law of thermodynamics requires that

$$\Delta U = q + w$$

Or, $-w = q - \Delta U$

$= 400 \text{ kJ} - 250 \text{ kJ}$

$= 150 \text{ kJ}$ = work done by the system

Measurement of ΔU

The energy change in a chemical reaction is measured in a bomb calorimeter. Fig. 6 illustrates an experimental set up.

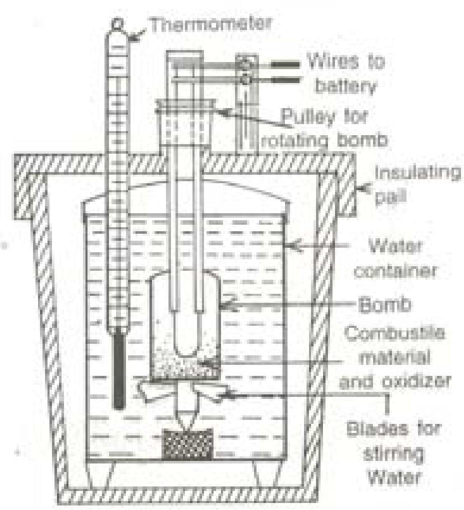


Fig. 6. Measurement of ΔU in a bomb calorimeter

In this experiment a known mass of the combustible material and sufficient quantity of an oxidizer are taken in the bomb. The bomb is immersed in a vessel containing known mass of water (it will act as surroundings). The water is stirred by rotating blades and its initial temperature (t_i) is recorded.

An electric current is passed to ignite the mixture taken in the bomb. As the reaction takes place, chemical energy is released which is used to warm water and the calorimeter. When the temperature of water reaches a constant value, the final reading of thermometer (t_2) is noted. Thus, change in temperature ($\Delta T = t_2 - t_1$) of water and the calorimeter (surroundings) is recorded.

The heat exchanged between the system (reaction) and surroundings (water + calorimeter) is calculated from the equation

$$q \text{ (water + calorimeter)} = (m \times s + C) \times \Delta T = q \text{ (surroundings)}$$

In the above equation

m =mass of water

s = specific heat capacity of water

C = heat capacity of the calorimeter

The heat liberated in the reaction is calculated as heat appearing in the surroundings. Thus

$$\Delta U = q \text{ (system)} = -q \text{ (surroundings)} \qquad \text{at constant volume}$$

Difficulties in the experimental determination of Δ*U*

When the experiment is performed at constant volume in a bomb calorimeter and if a large quantity of heat is liberated in a reaction then there is a danger of explosion. *Why?* Because the heat liberated during the reaction will make the gaseous products to expand. Since the vessel is closed the gas cannot expand. This will cause a build up of high pressure inside the bomb calorimeter. If the walls of the vessel are not strong enough to withstand the high pressure developed, an explosion may take place.

Need of a new thermodynamic property- the enthalpy

In the laboratory usually the experiments are performed at constant atmospheric pressure and the volume is allowed to change. So the measured value of ΔU cannot account for the actual heat exchanged between the system and surroundings at constant pressure. Hence, there is a need of new function that can account for the total heat content. That is, we need a function that must reflect as to how much heat is absorbed or liberated in the process at constant pressure. This new property is called heat content or ***enthalpy.***

Definition of enthalpy (*H*)

The enthalpy (H) is defined by

$$H = U + \mathrm{PV}$$

where U is the internal energy, P is the pressure and V is the volume.

Comments:

(i) The enthalpy is a Greek word which means heat in *(en* = in, thalpos = heat) and was formerly called ***heat content***. The symbol of enthalpy is *H. Why?* Because *H* is the first letter of heat content.

(ii) The name heat content was dropped to avoid confusion with heat capacity but the symbol *H* is retained to represent enthalpy.

Characteristics of enthalpy

- Enthalpy is an extensive property. Its value depends on the amount of the substances present in the system. Larger the amount larger is the value of *H*.

- Enthalpy of a system is a state property. For a given amount of the system it depends only on the state variables (T, P, V). If the state variables are changed from T_1, P_1, V_1 to T_2, P_2, V_2 the enthalpy of a given amount (fixed n) of the system is changed from H_1 to H_2. The change in enthalpy is represented as:

$$\Delta H = H(T_2, P_2, V_2) - H(\mathrm{T_I}, P_1, V_1) \qquad \text{when } n = \text{constant}$$

Since T, P, V are related by a suitable equation of state, out of $T, P, V,$ if two are known the third is also known for a constant amount of the system. Therefore, enthalpy is considered as a function of T and P for a fixed amount, *i.e.,*

$$H = H(T, P)$$

and
$$\Delta H = H(T_2, P_2) - H(T_I, P_1)$$

- The change in enthalpy (ΔH) does not depend on the path by which the final state of the system is reached.

Sign conventions of ΔJI

- When heat is absorbed by the system at constant pressure its enthalpy is increased so the value of ΔH is positive. When ΔH is positive, the process is said to be ***endothermic***.

- When heat is liberated by the system at constant pressure its enthalpy is decreased so the value of ΔH is negative. When ΔH is negative, the process is said to be ***exothermic.***

Illustration:

(i) $\Delta H = 310$ kJ implies that during the change 310 kJ heat is absorbed by the system from the surroundings at constant pressure. The process is ***endothermic***. Since heat absorbed by the system is heat lost by surroundings, a cooling effect is observed in the surroundings.

(ii) $\Delta H = -\ 175$ kJ implies that during the change 175 kJ heat is released by the system into the surroundings at constant pressure. The process is ***exothermic***. Since heat released by the system is heat gained by the surroundings, a heating effect is observed in the surroundings.

Relation between ΔH and q

The enthalpy is defined by

$$H = U + PV$$

For a change in the states of the system

$$\Delta H = \Delta\,(U + PV)$$

$$= \Delta U + (P\times\Delta V + V\times\Delta P) \qquad \text{(i)}$$

First law of thermodynamics states that

$$\Delta U = q + w = q - P\times\Delta V \qquad \text{(ii)}$$

From equations (i) and (ii), we get

$$\Delta H = (q - P\times\Delta V) + (P\times\Delta V + V\times\Delta P)$$

$$= q + V\times\Delta P$$

When pressure is constant, $\Delta P = 0$, and thus $V\times\Delta P = 0$, therefore

$$\Delta H = q \qquad \text{. .. at constant pressure}$$

Or, $\Delta H = q_p$

Here subscript *'P'* in q_p is used to state that pressure is constant in the process.

Comparison of ΔH and ΔU

(i) The change of enthalpy (ΔH) of the system accounts for both the energy change (ΔU) and the pressure-volume changes of the system. $\Delta H = \Delta U + P\times\Delta V + V\times\Delta P$

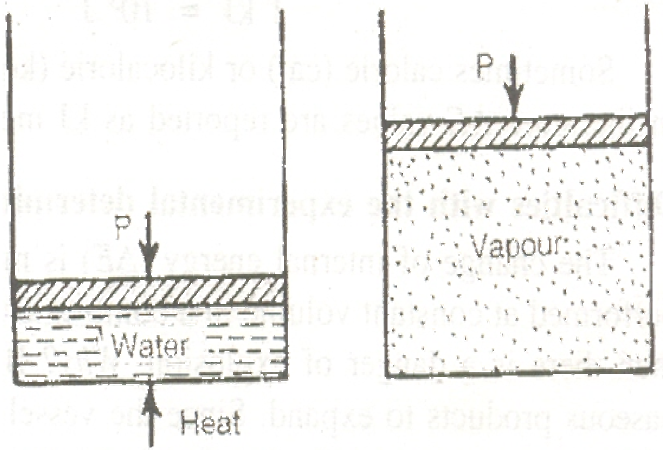
(ii) ΔH and ΔU have different values for different types of changes. Enthalpy change is equal to the heat exchanged between the system and the surroundings at constant pressure $\Delta H = q_p$ whereas energy change is equal to the heat exchanged between the system and surroundings at constant volume $\Delta U = q_v$

(iii) If the experiment is performed at constant pressure and at the same time there is no volume change then

$$P\times\Delta V + V\times\Delta P = 0 \quad \text{and} \quad \Delta H = \Delta U.$$

Illustration of enthalpy change and heat exchanged at constant pressure

Consider water taken in a cylinder which is fitted with a movable piston. When water is heated its temperature increases and thus the energy of each molecule of water increases. Consequently water vaporizes. The energetic molecules of water vapour hit the piston which is pushed and thus vapour expands against the constant atmospheric pressure *(P)* (Fig. 7).



(a) Heating of a liquid (b) Expansion of vapour
Fig.7. Illustration of enthalpy change in terms of heat absorbed at constant pressure

During expansion work is done by the vapour and at the same time energy is increased from U_1 to U_2

Work done by vapour $= -w = P\times (V_2 - V_1) = P\times\Delta V$

Suppose q_p is the heat absorbed by the system at constant pressure, so that there is an increase in the energy of the system *by* ΔU and $P\times\Delta V$ work is done by the system. For this process the law of conservation of energy (first law of thermodynamics) requires that

Heat absorbed = Increase in energy + work done by vapour

$$q_p = \Delta U + P\times\Delta V$$

Now, $\Delta U = U_2 - U_1$

and $\Delta V = V_2 - V_1$

Therefore, $q_p = U_2 - U_1 + P V_2 - PV_1$

$$= (U_2 + PV_2) - (U_1 + PV_1)$$

The relation $H = U + PV$, guides us to write

$$H_2 = U_2 + PV_2$$

and $H_1 = U_I + PV_t$

Thus $q_p = H_2 - H_I = \Delta H$

q_p = Total heat absorbed by water at constant pressure

But $H_2 = U_2 + PV_2$ = Enthalpy of the vapour after expansion

and $H_1 = U_l + PV_t$ = Enthalpy of water before heating

Therefore, $\Delta H = H_2 - H_1$ = Difference of enthalpies of water vapour and liquid water

= Change of enthalpy of the system

The relation $\Delta H = q_p$ is a link between the chemical energy (ΔH) and thermal energy (q_p).

Heat capacity

The quantity of heat needed to cause unit rise in the temperature of a substance is called its ***heat capacity***. It is denoted by symbol *C* and defined by.

$$\text{Heat capacity} = \frac{\text{Heat needed}}{\text{Increase of temperature}}$$

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

Units of heat capacity. Heat (*q*) is expressed in joules (J) and temperature in kelvin (K). Therefore, heat capacity is expressed in the units of ***joules per kelvin*** (J K^{-1}). Heat capacity is an extensive property because the heat needed to raise the temperature of the system depends on its size.

Note: ***Change of temperature expressed in kelvin is equal to the change of temperature expressed in degree celsius***. *How*? Suppose that the initial temperature of a system is 25 °C and its final temperature is 32 °C, then

The change of temperature in degree celsius = 32 °C – 25 °C = 7 °C

The change of temperature in kelvin = (32 + 273) K – (25 + 273) K

= 305 K – 298 K = 7 K

Molar heat capacity. It is defined as the quantity of heat needed to cause unit rise in the temperature of one mole of a substance. Molar heat capacity is denoted by C_m. Thus,

$$\text{Molar heat capacity} = \frac{\text{Heat capacity of the substance}}{\text{Amount of the substsnce}}$$

$$C_m = \frac{C}{n}$$

Units of molar heat capacity. Heat capacity is expressed as J K^{-1} and the amount is expressed as mol. Therefore, molar heat capacity is expressed as $\boldsymbol{J\ K^{-1}\ mol^{-1}}$ (pronounced as joule per Kelvin per mol). ***It should never be written as J/K/mol.***

Molar heat capacity is an ***intensive*** property, because it is a ratio of two extensive properties.

Specific heat capacity. It is defined as the quantity of heat needed to cause unit rise in the temperature of unit mass of a substance. Specific heat capacity is denoted by small *c* or small *s*. It is expressed in the units of $J\ K^{-1}\ g^{-1}$

Example. Calculate the thermal energy needed to raise the temperature of 10.0 g of iron from 298 K to 773 K. It is given that the specific heat capacity of iron is 0.45 $J\ K^{-1}\ g^{-1}$

Solution. Data given:

Mass of iron = m = 10 g

Specific heat capacity of iron = $C_s = 0.45\ JK^{-1}\ g^{-1}$

Temperature change = $\Delta T = 773\ K - 298\ K = 475\ K$

Therefore, $q = m \times C_s \times \Delta T$

$$= 10\ g \times 0.45\ JK^{-1}\ g^{-1} \times 475\ K = 2173.5\ J = 2.1\ kJ$$

Heat capacity at constant volume and at constant pressure

From the first law of thermodynamics we know that the heat exchanged between the system and surroundings depends on the experimental conditions, For example,

(i) Heat exchanged at constant volume = $q_V = \Delta U$

(ii) Heat exchanged at constant pressure = $q_P = \Delta H$

Therefore, depending on the experimental conditions the following two types of heat capacities are defined.

(1) **Heat capacity at constant volume**

$$C_V = \frac{q_v}{\Delta T} = \frac{\Delta U}{\Delta T}$$

For small temperature change the heat capacity at constant volume is expressed as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Molar heat capacity at constant volume = $C_{V,m} = \frac{C_V}{n}$

and $C_V = n \times C_{V,m}$

(2) **Heat capacity at constant pressure**

$$C_P = \frac{q_P}{\Delta T} = \frac{\Delta H}{\Delta T}$$

For small temperature change the heat capacity at constant pressure is expressed as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Molar heat capacity at constant pressure = $C_{P,m} = \dfrac{C_P}{n}$

and $C_P = n \times C_{P,\,m}$

Relation between C_P and C_V

(i) Ratio of heat capacities = $C_{P,m}/C_{V,\,m} = \gamma$

(a) For monotomic gas such as He: $C_{P,\,m}/C_{V,\,m} = \gamma = 1.67$

(b) For diatomic gas such as H_2: $C_{P,\,m}/C_{V,\,m} = \gamma = 1.40$

(c) For triatomic gas such as CO_2: $C_{P,\,m}/C_{V,\,m} = \gamma = 1.33$

(ii) Difference between C_P and C_V

(a) For an ideal gas: $C_P - C_V = nR$ where R is gas constant and n is the amount of the substance.

(b) For 1 mole of an ideal gas: $C_{P,\,m} - C_{V,\,m} = R$

(c) For a solid or a liquid: $C_{P,\,m} \approx C_{V,\,m}$

Derivation of the relation between C_P and C_V

$H = U + PV$ Definition of enthalpy

Differentiation of above equation with respect to T an constant P gives

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{(i)}$$

Heat capacity at constant pressure is defined by

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{(ii)}$$

For an ideal gas

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \text{(iii)}$$

where, C_V = Heat capacity at constant volume

Differentiation of ideal gas equation of state $PV = nRT$ with respect to T at constant P, gives

$$P\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} = nR\left(\frac{\partial T}{\partial T}\right)_{\mathrm{P}} = nR \times 1 = nR \qquad \text{(iv)}$$

On putting the expressions for various derivatives in to equation (i) we get

$$C_{\mathrm{p}} = C_{\mathrm{V}} + nR$$

$$C_{\mathrm{p}} - C_{\mathrm{V}} = nR$$

Variation of heat capacity with temperature

The variation of heat capacity with temperature are given by the following general equations

(i) $C_{\mathrm{P,\,m}} = \alpha + \beta T + \gamma T^2$

(ii) $C_{\mathrm{V,\,m}} = \alpha' + \beta' T + \gamma' T^2$

where values of the parameters α, β, γ ... α', β', γ' are characteristics of a substance. These values are available in the thermodynamic tables.

Variation of internal energy with temperature and volume

Internal energy of given amount of system is a function of temperature and volume

$$U = U(T, V)$$

For a small change in T and V the change in internal energy is expressed as its total differential

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \mathrm{d}V$$

$$= C_{\mathrm{V}}\,\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \mathrm{d}V$$

where, $C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}}$ = Heat capacity at constant volume

The change in internal energy can be calculated provided the values of C_{V} and $(\partial U/\partial V)_{\mathrm{T}}$ of the system are known. The value of C_{V} is obtained by calorimetric method and the value of $(\partial U/\partial V)_{\mathrm{T}}$ is given by Joule's law.

Joule's Law

Joule's law states that the internal energy of an ideal gas is independent of its volume at a constant temperature. Mathematically it is expressed as

$$\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} = 0 \qquad \ldots \textit{\textbf{Joule's law}}$$

This law also means that internal energy of a given amount of an ideal gas depends on its temperature only. Thus at a constant temperature there is no change in the internal energy of an ideal gas as the volume is changed.

Experimental verification of Joule's law

Joule performed an experiment to demonstrate the law that for a gas $(\partial U/\partial V)_T = 0$. The experimental setup is sown in Fig.8.

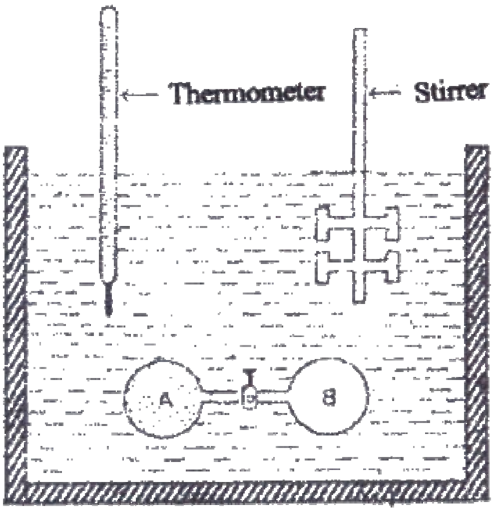


Fig. 8. Joule's experiment of expansion of air from vessel A into an evacuated vessel B

A glass bulb *A* was filled with air and connected through a stopcock to an evacuated bulb *B*. The assembly was placed in a water bath and its initial temperature was recorded. When the stopcock was opened the gas expanded into the bulb B and thus occupied both the bulbs. The final temperature of the water bath was recorded but no change in the temperature was observed.

Interpretation of the observations: From this experiment Joule argued as follows.

(i) There is no change of temperature showing that there is no exchange of heat between the system and surroundings. That is, $q = 0$.

(ii) The gas expands into an evacuated vessel where $P_{ext} = 0$. Therefore, no work is done in the process and $w = -P_{ext} \times \Delta V = -0 \times \Delta V = 0$.

(iii) From the first law of thermodynamics, therefore, it is obvious that $\Delta U = q + w = 0 + 0 = 0$ or $\mathrm{d}U = 0$. Thus

$$\mathrm{d}U = C_V\,\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = 0$$

Or,

$$\left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = -C_V\,\mathrm{d}T$$

Now, $\mathrm{d}T = 0$ (because there is no change of temperature in Joule's experiment) but $C_V \neq 0$, therefore, $C_V\,\mathrm{d}T = 0$. Thus

$$\left(\frac{\partial U}{\partial V}\right)_T dV = 0$$

Now, $dV \neq 0$ (as the gas expands and occupies both the bulbs). Therefore, the above equation is valid only when

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \text{… \textbf{\textit{Joule's law}}}$$

Physical interpretation of Joule's law: The derivative $(\partial U/\partial V)_T$ is called ***internal pressure*** **(π_T)**. It is a measure of the molecular force of attraction. For a nonideal gas obeying van der Waals equation of state the internal pressure is given by $(\partial U/\partial V)_T = a/V^2$. When the molecular force of attraction is strong, the internal pressure is large. In an ideal gas the molecular force of attraction is absent, therefore, its internal pressure is zero. Thus $(\partial U/\partial V)_T = 0$ is a thermodynamic definition of an ideal gas.

Variation of enthalpy with temperature and pressure

Enthalpy of given amount of system is a function of temperature and pressure

$$H = H(T, P)$$

For a small change in T and P the change in enthalpy is expressed as its total differential

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$= C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

where, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ = Heat capacity at constant pressure

The change in enthalpy can be calculated provided the values of C_P and $(\partial H/\partial P)_T$ of the system are known. The value of C_p is obtained by calorimetric method and the value of $(\partial H/\partial P)_T$ can be calculated from ***Joule- Thomson coefficient.***

Joule – Thomson Coefficient

The change of temperature with change of pressure of a gas at constant enthalpy is called ***Joule – Thomson coefficient.*** It is denoted by the symbol $\mu_{J\text{-}T}$ and defined as

$$\mu_{J\text{-}T} = (\partial T/\partial P)_H$$

Measurement of $\mu_{J\text{-}T}$

Joule in collaboration with Thomson performed porous plug experiment to study the change of temperature with change of pressure of a gas at constant enthalpy. Fig. 9 shows the experimental setup.

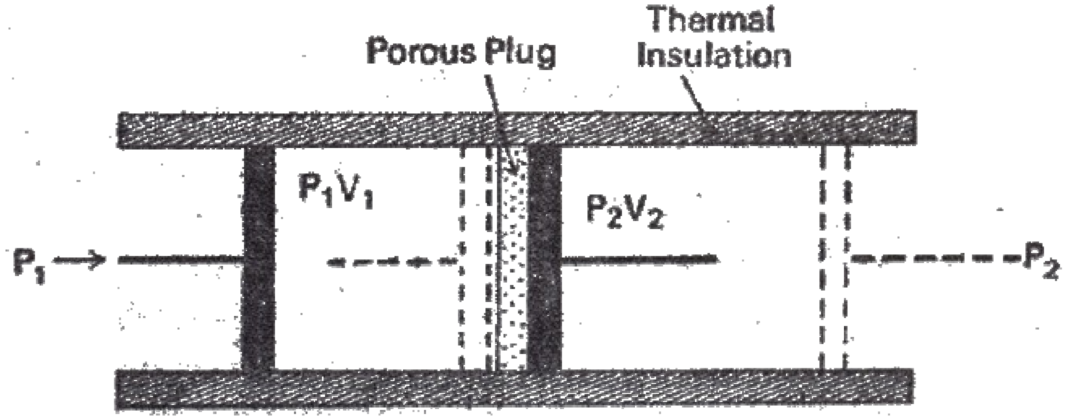


Fig. 9. Joule – Thomson porous plug experiment (Dotted lines represent the final position of piston in each compartment)

The entire experimental assembly is insulated from the surroundings so that adiabatic condition is maintained. In this experiment the gas is compressed by applying a high pressure (P_1) and forced to pass through the pores of porous plug. The gas escaping through the porous plug is allowed to expand against a constant pressure (P_2). The change of temperature with the change of pressure is recorded and thus Joule-Thomson coefficient $(\partial T/\partial P)_H$ is determined.

Justification of isenthalpic condition in Joule-Thomson experiment

In J-T experiment the enthalpy of the system remains constant ($H_2 - H_1 = \Delta H = 0$) though there is change of temperature and pressure. It is explained below.

In the left chamber the gas is compressed at a constant pressure P_1 from initial volume V_1 to a state that the piston touches the porous plug and thus final volume of the gas in the left chamber is zero (because the gas passes into the right chamber). Thus

Work done on the gas in the left chamber = $w_1 = P_1V_1$

In the right chamber the gas expands against a constant external pressure P_2 from zero initial volume to a final volume V_2. Thus

Work done by the gas in the right chamber = $w_2 = -P_2V_2$

Total work done in the process = $w = w_1 + w_2 = P_1V_1 - P_2V_2$

Joule – Thomson experiment is carried adiabatically and thus $q = 0$. Therefore, the first law of thermodynamics gives

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

or, $$\Delta U - w = 0$$

or, $$(U_2 - U_1) - (P_1V_1 - P_2V_2) = 0$$

$$(U_2 + P_2V_2) - (U_1 + P_1V_1) = 0$$

But $H = U + PV$, therefore

$$\Delta H = H_2 - H_1 = 0$$

Significance of Joule – Thomson coefficient $\mu_{J\text{-}T} = (\partial T/\partial P)_H$

- Joule-Thomson effect and the value of $\mu_{J\text{-}T}$ form the basis of liquefaction of gases.

- A positive value of the Joule-Thomson coefficient ($\mu_{J\text{-}T}$) corresponds to a cooling effect when a compressed gas is allowed to pass through small holes

- A negative value of the Joule-Thomson coefficient ($\mu_{J\text{-}T}$) corresponds to a heating effect when a compressed gas is allowed to pass through small holes

- A zero value of the Joule-Thomson coefficient ($\mu_{J\text{-}T}$) corresponds to no thermal change when a compressed gas is allowed to pass through small holes

Summary of the significance of the values of

Joule – Thomson coefficient($\mu_{J\text{-}T}$)

Sign of the Value of $\mu_{J\text{-}T}$	*Effect observed*
❖ Positive	Cooling
❖ Negative	Heating
❖ Zero	Neither heating nor cooling

Inversion temperature: The temperature at which the Joule-Thomson coefficient is zero is called the ***inversion temperature***. At this temperature neither cooling nor heating effect is observed during Joule Thomson expansion, below this temperature, cooling effect is observed while above this temperature, heating effect is observed.

Evaluation of $(\partial H/\partial P)_T$ from Joule-Thomson coefficient

The change of enthalpy is given by

$$dH = C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Joule – Thomson experiment is isenthalpic process (constant enthalpy) , that is, dH = 0 and thus

$$C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0 \qquad \text{when } H \text{ is constant}$$

or, $$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} \mathrm{d}P = -C_{\mathrm{P}}\,\mathrm{d}T$$

$$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} = -C_{\mathrm{P}}\left(\frac{\partial T}{\partial P}\right)_{\mathrm{H}}$$

But $$\left(\frac{\partial T}{\partial P}\right)_{\mathrm{H}} = \mu_{J\text{-}T} = \text{Joule-Thomson coefficient}$$

$$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} = -C_{\mathrm{P}} \times \mu_{J\text{-}T}$$

- The value of $(\partial H/\partial P)_{\mathrm{T}}$ can be calculated if the values of C_{P} and $\mu_{J\text{-}T}$ are known.

- For an ideal gas $\mu_{J\text{-}T}$ is zero. Therefore, $(\partial H/\partial P)_{\mathrm{T}}$ is also zero. This implies that the enthalpy of a given amount of an ideal gas is independent of pressure and it depends on temperature only. Thus at a constant temperature there is no change in the enthalpy of an ideal gas as the pressure is changed.

Calculation of thermodynamic preperties from first law

(A) Calculation of *w*, *q*, ΔU and ΔH for isothermal and reversible changes in the states of an Ideal gas

Points to be remembered

- **Isothermal change:** Temperature is constant

- **Reversible change**: Change is slow but pressure and volume both are changed

- **Ideal gas**: $PV = n\,RT$

(1) Calculation of *w*

For an infinitesimally small change in volume ($\mathrm{d}V$) of a gas the small quantity of mechanical work ($đw$) is defined by

$$đw = -P\mathrm{d}V \qquad \text{(i)}$$

For an ideal gas $PV = nRT$ and $P = nRT/V$. Thus

$$đw = -\frac{nRT}{V}\,\mathrm{d}V = -nRT\,\mathrm{d}\,ln\;V$$

For a finite reversible change of volume of a fixed amount of the gas from an initial volume of V_1 to a final volume V_2 at a constant temperature, the work is obtained by integrating equation (ii)

$$w = -nRT\int_{V_1}^{V_2}\mathrm{d}\ln V$$

$$= -nRT\ \ln[V]_{V_1}^{V_2}$$

$$= -nRT\ \ln\frac{V_2}{V_1} = nRT\ \ln\frac{V_1}{V2}$$

For an ideal gas at constant temperature, $P_1V_1 = P_2V_2$ and $V_2/V_1 = P_1/P_2$. Thus

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

The value of w can be calculated on substituting the values of n, R, T, V_1,, V_2 (or P_1, P_2) in the above equation.

(2) Calculation of ΔU

The internal energy (U) of an ideal gas is a function of temperature only and is independent of volume (***Joule's law***). Therefore, for an isothermal process when temperature is constant internal energy of an ideal gas is also constant. Thus

$$U_2 - U_1 = \Delta U = 0 \qquad \ldots \text{ for an ideal gas at constant } T$$

(3) Calculation of q

From the first law of thermodynamics we have

$$\Delta U = q + w$$

For isothermal change, $\Delta U = 0$ for an ideal gas, therefore,

$$q = -w = 2.303\ nRT\log\frac{V_2}{V_1} = 2.303\ nRT\log\frac{P_1}{P_2}$$

(4) Calculation of ΔH

Change of enthalpy = Final enthalpy – Initial enthalpy

$$\Delta H = H_2 - H_1$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= U_2 - U_1 + (P_2V_2 - P_1V_1)$$

For an ideal gas at constant temperature

$$U_2 - U_1 = \Delta U = 0$$

and $$P_2V_2 = P_1V_1$$

Therefore, $$\Delta H = 0$$

Summary : For isothermal reversible change of states of an ideal gas

(i) $w = -2.303\ nRT \log \frac{V_2}{V_1} = -2.303\ nRT \log \frac{P_1}{P_2}$

(ii) $q = -w$ (iii) $\Delta U = 0$ and (iv) $\Delta H = 0$

Example: Two moles of an ideal gas undergo the following changes:

(a) Reversible isobaric expansion from state *x* (1.0 bar, 20.0 dm^3) to state *y* (1.0 bar, 40.0 dm^3)

(b) Reversible isochoric change from state *y* (1.0 bar, 40.0 dm^3) to state *z* (0.5 bar, 40.0 dm^3)

(c) Reversible isothermal compression from state *z* (0.5 bar, 40.0 dm^3) to *x* (1.0 bar, 20.0 dm^3).

Calculate

(i) The work done in each step and the total work (*w*) done

(ii) **Total heat exchanged (*q*) in the above processes**

(iii) **The values of *ΔU* and *ΔH* for the overall process**.

Solution.

(i) **Calculation of work (*w*)**

Process (a):

2 mol Ideal gas (1.0 bar, 20.0 dm^3) → 2 mol Ideal gas (1.0 bar, 40.0 dm^3)

For a reversible isobaric process

Work done = $w = -P\times \Delta V = -P(V_2 - V_1)$ when P is constant

Therefore, $w(a) = -1 \text{ bar } (40 \text{ dm}^3 - 20 \text{ dm}^3) = -20 \text{ bar dm}^3$

Since 1 bar dm^3 =101.325 J

Therefore, $w(a) = -20 \text{ bar dm}^3 \times 101.325 \text{ J/bar dm}^3 = -2026.5 \text{ J}$

In this process the work done on the system is negative thus the work is done by the system

Process (b) : 2 mol Ideal gas (1.0 bar, 40.0 dm^3) → 2 mol Ideal gas (0.5 bar, 40.0 dm^3)

$w(b) = -0.5 \text{ bar } (40 \text{ L} - 40 \text{ L}) = -0{,}5 \text{ bar} \times 0 = 0$

In this process no work is done because the volume is constant

Process (c) 2 mol Ideal gas (0.5, 40.0 L) → 2 mol Ideal gas (1.0 bar, 20.0 L)

For an isothermal reversible process

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

But for an ideal gas $nRT = PV$

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

On substituting the values of various quantities in the above equation, we have

$w(c) = -(0.5 \text{ bar} \times 40 \text{ dm}^3) \ln (20 \text{ L}/40 \text{ dm}^3)$

$= 13.86 \text{ bar dm}^3$

$= (13.86 \text{ bar L}) \times (101.325 \text{ J/ bar dm}^3)$

$= 1404.4 \text{ J}$

In this process, the work is done on the system.

Total work done = $w = w(a) + w(b) + w(c)$

$= -2026.5 \text{ J} + 0 \text{ J} + 1404.4 \text{ J}$

$= -622.1 \text{ J}$

(ii) Calculation of heat exchanged (q)

From the first law of thermodynamics we know that $\Delta U = q + w$. Now the given processes constitute a cycle for which the internal energy is constant. That is, ΔU is zero for the cyclic process *x y z x*. Thus

$\Delta U = q + w = 0$

and $q = -w = -(-622.1 \text{ J}) = 622.1 \text{ J}$

In the given cyclic process heat is absorbed by the system

(iii) Calculation of *ΔU* and *ΔH*

U and *H* are state functions and depend only on the initial and final states of the system. Now, in the give processes *a, b* and *c* the system is restored to its initial state. Therefore, there is no change in *U* and *H*. Thus ΔU (cycle) = 0 and ΔH(cycle) = 0

(B) Calculation of *w*, *q*, Δ*U* and Δ*H* for adiabatic and reversible changes in the states of an Ideal gas

Points to remember

- **Adiabatic change:** $q = 0$
- **Reversible change:** Change is slow and *T, P,* and V are changed
- **Ideal gas:** $PV = n RT$

(1) Calculation of *q*

The change is adiabatic, therefore, $q = 0$

(2) Calculation of ΔU

In adiabatic process there is change of temperature and for a small change of temperature ($\mathrm{d}T$) the change of internal energy is given by

$$\mathrm{d}U = C_v \,\mathrm{d}T$$

For a finite change of temperature of a fixed amount of the gas from an initial value of T_1 to a final value of T_2 the change of internal energy is obtained on integrating equation. Thus when C_v is constant

$$U_2 - U_1 = C_v(T_2 - T_1)$$

Or, $$\Delta U = C_v \times \Delta T = n\, C_{v.\,m} \times \Delta T$$

where, $C_{V.\,m}$ = molar heat capacity of the gas at constant volume and n is the amount of the gas

(3) Calculation of *w*

For a small change in volume ($\mathrm{d}V$) of a gas the small quantity of mechanical work ($\mathrm{d}w$) is given by $\mathrm{d}w = -P\mathrm{d}V$

For an ideal gas $PV = nRT$ and $P = nRT/V$. Thus

$$\mathrm{d}w = -\frac{nRT}{V}\mathrm{d}V$$

A direct calculation of work (w) is not possible because the integration of the above equations is difficult as in an adiabatic reversible process each one of T, P and V will change.

Calculation of *w* from ΔU: For adiabatic process $q = 0$ and first law of thermodynamic gives $\Delta U = w$. Thus

$$w = \Delta U = C_v \times \Delta T = n\, C_{v.\,m} \times \Delta T$$

(4) Calculation of ΔH

$$\Delta H = H_2 - H_1$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

Since, $$U_2 - U_1 = \Delta U = C_V\,(T_2 - T_1)$$

and $$(P_2V_2 - P_1V_1) = (n\,RT_2 - n\,RT_1)$$

Therefore,

$$\Delta H = C_V\,(T_2 - T_1) + n\,R(T_2 - T_1)$$

$$= (C_V\ + n\,R)\,(T_2 - T_1)$$

$$= C_P\ (T_2 - T_1)$$

$$= n\,C_{P,\,m}\ (T_2 - T_1)$$

Here, $(C_V\ + n\,R) = C_P = n\,C_{P.\,m}$

Derivation of *T–P–V* relations for adiabatic and reversible process

Purpose of derivation: The relation $w{=}\Delta U = C_V\ (T_2 - \ T_1)$ is used to calculate the desired quantities when T_2 and T_1 are known. When instead of T_2 the values of P_1, V_1, T_1 and P_2 , V_2 are given, we need relations between *T, P* and *V*.

Main equations to be remembered

- $C_V\,\mathrm{d}T\ =\ -P\mathrm{d}V$
- $PV = n\,RT$

(1) ***T – V* relation:** For an adiabatic process

$$C_V\,\mathrm{d}T\ =\ -P\mathrm{d}V$$

Now, $P = \dfrac{nRT}{V}$

$$C_V\,\mathrm{d}T\ = -\frac{nRT}{V}\ \mathrm{d}V$$

or, $\dfrac{dT}{T}\ =\ -\ \dfrac{nR}{C_V}\,\dfrac{dV}{V}$

$$\mathrm{d}\ln T\ = -(\gamma - 1)\ \mathrm{d}\ln V$$

or, $\mathrm{d}\ln T = \ -\,\mathrm{d}\ln(V)^{\gamma-1}$

where $\gamma\ = \tilde{C}_P C_V$ and $\gamma\ - 1 = nR\,/\,C_V\ = (C_P - C_V\,)/\ C_V$

On integrating between the limits $T\ =\ T_1$, $T\ =\ T_2$ and $V\ =\ V_1$, $V\ =\ V_2$, we get

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

On taking antilog we shall get

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

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

(2) ***T* – *P* relation:** For an adiabatic process

$$C_V\,\mathrm{d}T = -P\mathrm{d}V \qquad \ldots \text{(i)}$$

For ideal gas $PV = n\,RT$

and $$P\,\mathrm{d}V + V\,\mathrm{d}P = n\,R\,\mathrm{d}T$$

or, $$-P\mathrm{d}V = V\,\mathrm{d}P - n\,R\,\mathrm{d}T = \frac{nRT}{P}\,\mathrm{d}P - n\,R\,\mathrm{d}T \qquad \ldots \text{(ii)}$$

From equations (i) and (ii) we get

$$(C_V + n\,R)\ \frac{dT}{T} = nR\frac{dP}{P}$$

or, $$\mathrm{d}\ln T = \frac{nR}{C_V + nR}\,\mathrm{d}\ln P = \mathrm{d}\ln (P)^{(\gamma-1)/\gamma}$$

where $\gamma = C_P/C_V$ and $\gamma - 1 = nR/C_V = (C_P - C_V)/C_V$

On integrating between the limits $T = T_1$, $T = T_2$ and $P = P_1, P = P_2$,we get

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$

On taking antilog we shall get

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

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

(3) ***P* – *V* relation:** For an adiabatic process

$$C_V\,\mathrm{d}T = -P\mathrm{d}V \qquad \ldots \qquad \text{(i)}$$

For ideal gas $PV = n\,RT$

and $$P\,\mathrm{d}V + V\,\mathrm{d}P = n\,R\,\mathrm{d}T$$

$$\frac{nRT}{V}\,\mathrm{d}V + \frac{nRT}{P}\,\mathrm{d}P = n\,R\,\mathrm{d}T$$

or, $$\mathrm{d}T = T\,\frac{dV}{V} + T\,\frac{dP}{P} = T\,(\mathrm{d}\ln V + \mathrm{d}\ln P)$$

On substituting dT in to equation (i) we get

$$C_V \times T\,(\mathrm{d}\ln V + \mathrm{d}\ln P) = -P\mathrm{d}V = -\frac{nRT}{V}\,\mathrm{d}V = -nRT\,\mathrm{d}\ln V$$

or, $(C_V + nRT)\,\mathrm{d}\ln V = -C_V\,\mathrm{d}\ln P$

or, $\mathrm{d}\ln (V)^{\gamma} = -\mathrm{d}\ln P$

On integrating between the limits $V = V_1$, $V = V_2$ and $P = P_1$, $P = P_2$ then taking antilog we shall get

$$\left(\frac{V_2}{V_1}\right)^{\gamma} = \frac{P_1}{P_2}$$

and $P_1 V_1^{\gamma} = P_2\,V_2^{\gamma} = \text{constant}$

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

EXPRESSIONS FOR REVERSIBLE ADIABATIC WORK UNDER DIFFERENT CONDITIONS

(A) When T_1, V_1 and V_2 are given

$$w = \Delta U = n\,C_{\mathrm{v,\,m}}(T_2 - T_1)$$

$$= n\,C_{\mathrm{v,\,m}}\,T_1\left(\frac{T_2}{T_1} - 1\right)$$

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

Therefore, $$w = n\,C_{\mathrm{v,\,m}}\,T_1\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right]$$

(B) When T_1, P_1 and P_2 are given

$$w = \Delta U = n\,C_{\mathrm{v,\,m}}(T_2 - T_1)$$

$$= n\,C_{\mathrm{v,\,m}}\,T_1\left(\frac{T_2}{T_1} - 1\right)$$

But $$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\gamma-1/\gamma}$$

Therefore, $$w = n\,C_{\mathrm{v,\,m}}\,T_1 \left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right]$$

(C) When P_1, V_1 and P_2, V_2 are given

$$w = \Delta\, U$$

$$= n\,C_{\mathrm{v,\,m}}\,(T_2 - T_1)$$

For an ideal gas $P_1V_1 = nRT_1$ and $P_2V_2 = nRT_2$

Or, $T_1 = P_1V_1/nR$

and $T_2 = P_2V_2/nR$

With these values of T_1 and T_2 in the expression for w is written as

Therefore, $$w = \frac{C_{V,m}}{R}\,(P_2V_2 - P_1V_1)$$

But, $$\frac{C_{V,m}}{R} = \frac{C_{V,m}}{C_{P,m} - C_{V,m}} = \frac{1}{\gamma - i}$$

Therefore, $$w = \frac{P_2V_2 \text{ - } P_1V_1}{\gamma - i}$$

Note: In the same way the values of ΔU and ΔH can be calculated for reversible adiabatic process under different conditions.

Example: One mole of an ideal gas at 300 K and 1 bar is allowed to expand under reversible and adiabatic conditions to 0. 1 bar. Calculate the final temperature (T_2), w, ΔU, ΔH when $C_{\mathrm{V,m}} = 1.5\,R$.

Solution. Data given:

$n = 1$ mol, $C_{\mathrm{v,\,m}} = 1.5\,R$, $T_1 = 300$ K, $P_1 = 1$ bar and $P_2 = 0.1$ bar

Final temperature = $T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\gamma-1/\gamma}$

$$\gamma = C_{\mathrm{P,m}} / C_{\mathrm{V,\,m}} = (1.5\,P + R) / 1.5R = 2.5/1.5$$

and $$\frac{\gamma-1}{\gamma} = \frac{(2.5/1.5)-1}{2.5/1.5} = 0.4$$

Therefore, $T_2 = 300\text{ K} \times [(0.1\text{ bar}/\ 1\text{ bar})^{0.4} - 1]$

$$= 120\ \text{K}$$

The change is adiabatic. Therefore, $q = 0$ and thus from the first law of thermodynamics we have

$$w = \Delta U = nC_{\text{V, m}}\,(T_2 - T_1)$$

$$= n \times 1.5\,R \times (120\ \text{K} - 300\ \text{K})$$

$$= -1\ \text{mol} \times 1.5 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 180\ \text{K}$$

$$= -2245\ \text{J}$$

$$\Delta H = C_{\text{P, m}}\,(T_2 - T_1)$$

$$= n \times 2.5\,R(T_2 - T_1)$$

$$= 1\ \text{mol} \times 2.5 \times 8.314\ \text{J K}^{-1-}\ \text{mol}^{-1}\ (120\ \text{K} - 300\ \text{K})$$

$$= -3741\ \text{J}$$

Example: One mole of a gas at 2 bar occupies a volume of 100 cm^3 and kept in an adiabatic container. Its pressure increases steeply to 100 bar followed by a decrease of volume to 98 cm^3 at a constant pressure of 100 bar. Calculate the values of *ΔU* and *ΔH* for the change of state.

Solution. (a) Adiabatic and isochoric change of pressure

$$1\ \text{mol gas}\ (2\ \text{bar}, 100\ \text{cm}^3) \longrightarrow 1\ \text{mole gas}\ (100\ \text{bar}, 100\ \text{cm}^3)$$

Work done = $w = -P \times \Delta V = -100\ \text{bar} \times 0\ \text{mL} = 0$

For adiabatic process, $q = 0$ Therefore, from the first law of thermodynamics we have

$$\Delta U(\text{a}) = q + w = 0 + 0 = 0$$

(b) Adiabatic isobaric volume change

$$1\ \text{mol gas}\ (100\ \text{bar}, 100\ \text{cm}^3) \longrightarrow 1\ \text{mole gas}\ (100\ \text{bar}, 96\ \text{cm}^3)$$

Work done = $w = -P \times \Delta V = -100\ \text{bar} \times (98\ \text{cm}^3 - 100\ \text{cm}^3) = 200\ \text{bar cm}^3$

For adiabatic process, $q = 0$, therefore, from the first law of thermodynamics we have

$$\Delta U(\text{b}) = q + w = 0 + 200\ \text{bar cm}^3 = 200\ \text{bar cm}^3$$

$$= 200\ \text{bar cm}^3 \times (10^5\ \text{N m}^{--2} / \text{bar})\ (10^{-6}\ \text{m}^3 / \text{cm}^3) = 20\ \text{N m} = 20\ \text{J}$$

(c) Calculation of ΔU and ΔH for the change of state

$$\Delta U = \Delta U(\text{a}) + \Delta U(\text{b}) = 0 + 20\ \text{J} = 20\ \text{J}$$

$\Delta H = \Delta U \;+ \Delta PV)$

$. = \Delta U + P_2V_2 \;— P_1V_1)$

$= 200$ bar mL + (100 bar ×98 cm^3 — 2 bar × 100 cm^3)

$= 200$ bar cm^3 + 9600 bar cm^3 = 9800 bar cm^3

$= 9800$ bar cm^3 ×(10^5 N m^{--2} / bar) ($10^{—6}$ m^3 / cm^3)

= 980 N m = 980 J

Example. When one mole of a monotomic ideal gas initially at a temperature of *T* K undergoes adiabatic expansion under a constant external pressure of 1 atm the volume changes from 1 L to 2 L. Which one of the following options would be a correct expression for the final temperature of the gas when *R* = 0.0821 atm L K^{-1} mol^{-1}.

(A) $\dfrac{T}{2^{273}}$

(B) T

(C) $T + \dfrac{2}{3 \times 0.0821}$

(D) $T - \dfrac{2}{3 \times 0.0821}$

Solution. Option (D) is correct

Justification. For an adiabatic process, $q = 0$ and therefore, from the first law of thermodynamics we have

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

For one mole of a monotomic ideal gas

$$\Delta U = C_{\text{v, m}}\,(T_{\text{final}} - T_{\text{initial}}) = (3/2)\,R(T_{\text{final}} - T_{\text{initial}})$$

and $w = -\,P_{\text{ext}}(V_2 - V_1) = -\,1$ atm (2 L mol^{-1} – 1 L mol^{-1}) = – 1 atm L mol^{-1}

Therefore, $\quad 3/2\; R\;(T_{\text{final}} - T_{\text{initial}}) = -\,P_{\text{ext}}(V_2 - V_1)$

$$T_{\text{final}} = \frac{-P_{\text{ext}}(V_2 - V_1)}{(3/2)R} + T_{\text{initial}}$$

On substituting the known data we get

$$T_{\text{ final}} = \frac{-1\,\text{atm L mol}^{-1}}{(3/2) \times 0.0821\,\text{atm L K}^{-1}\ \text{mol}^{-1}} + T\,\text{K}$$

$$= T + \frac{2}{3 \times 0.0821}$$

Discussion. In adiabatic expansion the final temperature is lower than the initial temperature. Therefore, options (B) and (C) are not possible. Out of the others, option (A) is valid if the adiabatic change is reversible and option (D) is correct if the adiabatic change is irreversible.

Now, the given problem refers to an irreversible adiabatic volume change at a constant pressure. therefore, option (D) is correct..

Comparison of isothermal and adiabatic reversible expansion of an ideal gas

An indicator diagram of the variation of volume with pressure for an ideal gas under iothermal and adiabatic reversible conditions is shown in Fig. 10.

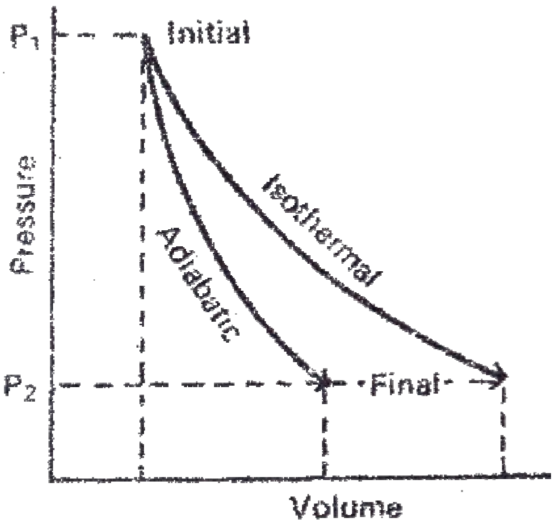


Fig. 10. Comparison of isothermal and adiabatic reversible expansion of an ideal gas

Form the figure it is observed that:

- The final volume (V_2) in isothermal reversible expansion is greater than that of adiabatic expansion for the same final pressure (refer to Fig. 10).

Explanation: For isothermal change $P_{iso}V_{iso}$ = constant

For adiabatic change $P_{ad}\ V_{ad}^{\ \gamma}$ = constant

Or, $P_{iso}V_{iso} = P_{ad}\ V_{ad}^{\ \gamma}$

Since $P_{iso} = P_{ad}$ = Final pressure. Therefore,

$V_{iso} = V_{ad}^{\ \gamma}$

Now, $\gamma > 1$, therefore. $V_{iso} > V_{ad}$

- Isothermal reversible work of expansion is greater than adiabatic reversible work of expansion as shown in Fig, 10 (area under isothermal curve is greater than the area under adiabatic curve).

Isothermal irreversible changes in the states of an ideal gas

In an irreversible change the pressure acting on the gas is suddenly released and then the gas expands against the constant pressure P_{ext}. Due to expansion the state variables of the gas are changed from P_1, V_1 to P_2, V_2

(1) Calculation of *w*

The work done on the gas is given by

$$w = -\int_{V_1}^{V_2} P_{\text{ext}}\, dV = -P_{\text{ext}} \int_{V_1}^{V_2} dV$$

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

For an ideal gas $PV = nRT$ and $V = nRT/P$. Therefore, for an isothermal process

$$w = -P_{\text{ext}}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$= -nRT\left(\frac{P_{ext}}{P_2} - \frac{P_{ext}}{P_1}\right)$$

When $P_{\text{ext}} = P_2$ = final pressure of the gas, the work done is given by

$$w = -P_2\,(V_2 - V_1)$$

$$= -nRT\left(1 - \frac{P_2}{P_1}\right)$$

Work of compression under isothermal irreversible condition

To bring back the gas to its initial state (P_1, V_1) from the expanded state (P_2, V_2) it must be compressed by applying pressure higher than P_2 and equal to P_1. Thus, work of compression is given by

$$w = -\int_{V_2}^{V_1} P_{\text{ext}}\, dV = -P_{\text{ext}} \int_{V_2}^{V_1} dV$$

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

When $P_{\text{ext}} = P_1$ = pressure of the compressed gas

$$w = -P_1\,(V_1 - V_2)$$

$$= -\,nRT\left(1 - \frac{P_1}{P_2}\right) \qquad \text{(ii)}$$

Comparison of irreversible work due to expansion and compression

In an irreversible process the work obtained from the system (work of expansion) is smaller than the work done on the system (work of compression). That is, to bring back the gas to its initial state more work has to be done than the work produced on expansion.

Jusification:

$$w_{\mathrm{by}}(\exp) = P_2 (V_2 - V_1)$$

and $$w_{\mathrm{on}} (\mathrm{com}) = -P_1 (V_1 - V_2)$$

Since $P_1 > P_2$ and $(V_2 - V_1) = -(V_1 - V_2)$

Therefore, $-P_1 (V_1 - V_2) > P_2 (V_2 - V_1)$

and $$w_{\mathrm{on}}(\mathrm{com}) > w_{\mathrm{by}}(\exp)$$

(2) **Calculation of Δ*U***

The internal energy (U) of an ideal gas is a function of temperature only and is independent of volume (***Joule's law***). Therefore, for an isothermal process when temperature is constant internal energy of an ideal gas is also constant. Thus

$$U_2 - U_1 = \Delta U = 0 \qquad \ldots \text{ for an ideal gas at constant } T$$

(3) Calculation of *q*

From the first law of thermodynamics we have

$$\Delta U = q + w$$

For isothermal change, $\Delta U = 0$ for an ideal gas, therefore,

$$q = -w = nRT\left(1 - \frac{P_t}{P_1}\right)$$

(4) Calculation of Δ*H*

$$H = U + PV \qquad \text{... definition of enthalpy}$$

Change of enthalpy = Final enthalpy – Initial enthalpy

$$\Delta H = H_2 - H_1$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= U_2 - U_1 + (P_2V_2 - P_1V_1)$$

For an ideal gas at constant temperature

$$U_2 - U_1 = \Delta U = 0 \quad \text{and} \quad P_2V_2 = P_1V_1$$

Therefore, $\Delta H = 0$

(D) Isothermal free expansion of an ideal gas

Free expansion is a process in which the gas is allowed to expand against zero external pressure into an evacuated vessel (as in Joule's experiment).

(1) Calculation of *w*

The work done by the gas is given by

$$-w = \int_{V_1}^{V_2} P_{\text{ext}} dV = P_{\text{ext}} \int_{V_1}^{V_2} dV$$

Since $P_{\text{ext}} = 0$, therefore,

Therefore, $-w = 0 \times \int_{V_1}^{V_2} dV = 0$

(2) Calculation of ΔU

The internal energy (U) of an ideal gas is a function of temperature only and is independent of volume (***Joule's law***). Therefore, for an isothermal process when temperature is constant internal energy of an ideal gas is also constant. Thus

$U_2 - U_1 = \Delta U = 0$ … for an ideal gas at constant T

(3) Calculation of *q*

From the first law of thermodynamics we have

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

(4) Calculation of ΔH

$H = U + PV$ ... definition of enthalpy

Change of enthalpy = Final enthalpy – Initial enthalpy

$$\Delta H = H_2 - H_1$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= U_2 - U_1 + (P_2V_2 - P_1V_1)$$

For an ideal gas at constant temperature

$$U_2 - U_1 = \Delta U = 0$$

and $P_2V_2 = P_1V_1$

Therefore, $\Delta H = 0$

Summary: In an isothermal free expansion of an ideal gas

(i) $w = 0$ (ii) $q = 0$ (iii) $\Delta U = 0$ (iv) $\Delta H = 0$

Example: ***One mole of an ideal gas is held under a piston in a cylinder at a pressure of 10 bar and 300 K. The pressure is suddenly released to 0.5 bar and the gas expands isothermally.***

(i) ***Calculate* w, *q, ΔU and ΔH***

(ii) ***Calculate the work required to bring back the gas to its initial state.***

Solution. Sudden release of pressure implies that the expansion is irreversible.

(i) Data give: $n = 1$ mol, $P_1 = 10$ bar, $P_{\text{ext}} = 0.5$ bar $= P_2$, $T = 300$ K

$$w = -nRT\left(1 - \frac{P_2}{P_1}\right)$$

$$= -1\ \text{mol} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}\left(1 - \frac{0.5\ \text{bar}}{10\ \text{bar}}\right)$$

$$= -\,2369.49\ \text{J}$$

For isothermal change of an ideal gas

$\Delta U = 0$ and $\Delta H = 0$

From the first law of thermodynamics $\Delta U = q + w = 0$ and

$q = -w = 2369.49$ J

(ii) For isothermal irreversible compressible

$$w = -nRT\left(1 - \frac{P_1}{P_2}\right)$$

$$= -\,1\ \text{mol} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}\left(1 - \frac{10\ \text{bar}}{0.5\ \text{bar}}\right)$$

$$= 47389.8\ \text{J}$$

Note: From this calculation it is observed that the work done by the surroundings on system (47389.8 J) during compression is much greater than the work done by the system on surroundings (2369.49 J) during expansion.

First law of thermodynamic applied to Carnot cycle

A cyclic process in which each step operates under reversible conditions is called a ***Carnot cycle*** (*pronounce Carnot as Karno*). With the help of paper and pencil, Sadi Carnot (an engineer by profession) explained that a reversible engine should have the highest efficiency. **Four steps of Carnot cycle.** The Carnot cycle for a fluid involves the following four reversible operations which are shown in Fig. also as P-V indicator diagram for a gas.

1. Isothermal reversible expansion along path AB
2. Adiabatic reversible expansion along path BD
3. Isothermal reversible compression along path CD

Adiabatic reversible compression along path DA

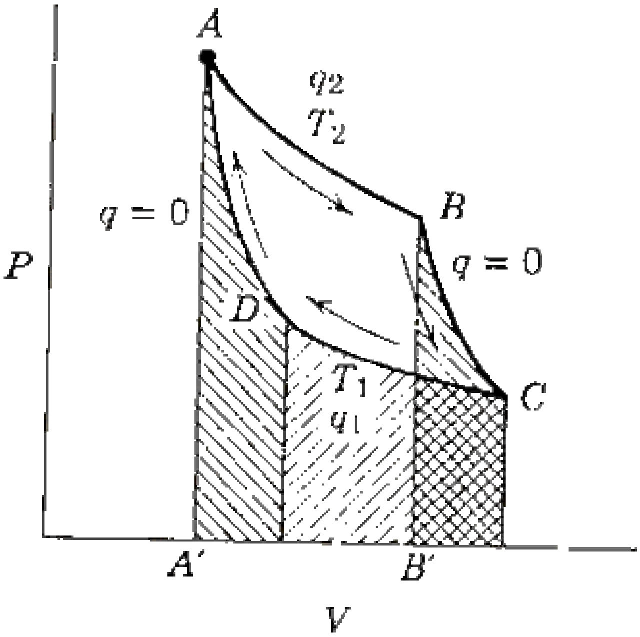


Fig. 11. Pressure – volume indicator diagram of the four steps of Carnot cycle (shaded area gives the work for the corresponding change)

Example. ***One mole of an ideal gas undergoes reversible changes in a Carnot cycle. Without doing calculations, predict the sign of each one of ΔT, ΔV, ΔP, ΔU and ΔH in each step of the cycle.***

Solution. The four steps of Carnot cycle and the corresponding changes are given below

Step	ΔT	ΔV	ΔP	ΔU	ΔH
(a) Isothermal reversible expansion	0	+	–	0	0
(b) Adiabatic reversible expansion	–	+	–	–	–
(c) Isothermal reversible compression	0	–	+	0	0
(d) Adiabatic reversible compression	+	–	+	+	+

Efficiency of Carnot cycle

The efficiency of Carnot cycle is defined as the fraction of the heat q_2 absorbed at the higher temperature which is converted into work in the cycle. It is denoted by symbol □ (eta) and expressed as

$$\eta = \frac{\text{Net work done by the system}}{\text{Total heat absobed by the system}} = \frac{W_{\text{by}}\,(\text{cycle})}{q_2}$$

A machine that converts heat into work is called heat engine. Suppose that a heat engine absorbs heat q_2 from a source at a higher temperature T_2 and reject a part q_1 to the surroundings at a lower temperature T_1. Since in a cyclic process $\Delta U = 0$, therefore, from the first law of thermodynamics we have $q_2 - q_1 = w_{\text{by}}$ (cycle) and

$$\eta = \frac{q_2 - q_1}{q_2} = 1 - \frac{q_1}{q_2}$$

From the above equation it is clear that efficiency of a machine is always less than one.

Calculation of work and heat for each step of Carnot cycle involving an ideal gas

1. Isothermal reversible expansion. The gas absorbs heat q_2 and expands reversibly at a higher temperature T_2 so that its volume changes from V_1 to V_2 along path AB of the indicator diagram. The work done by the gas $(-w_1)$ is given by

$$(-w_1) = nRT_2 \ln (V_2/V_1) = \text{Area } A'ABA`$$

or, $$w_1 = -nRT_2 \ln (V_2/V_1)$$

For an ideal gas at constant temperature, $\Delta U_1 = 0$, therefore, first law of thermodynamics gives

$$q_2 = (-w_1) = nRT_2 \ln (V_2/V_1)$$

2. Adiabatic reversible expansion. The gas expands reversibly and adiabatically so that its volume changes from V_2 to V_3 along path BC of the indicator diagram. In this step no heat is exchanged and $q = 0$ thus temperature falls

from T_2 to T_1. Therefore, according to the first law of thermodynamics the work done by the gas $(-w_2)$ is equal to decrease of internal energy. That is,

$$-w_2 = \Delta U_2 = C_V(T_1 - T_2) \text{ or } w_2 = C_V(T_1 - T_2)$$

3. Isothermal reversible compression. The gas is compressed reversibly and isothermally at lower temperature T_1 so that its volume changes from V_3 to V_4 along path CD of the indicator diagram. During isothermal compression heat q_1 is given out by the system and work (w_3) is done on the system. Thus $\Delta U_3 = 0$ and from first law of thermodynamics we have.

$$w_3 = -q_1 = -nRT_1 \ln (V_4/V_3)$$

4. Adiabatic reversible compression. The gas is compressed reversibly and adiabatically so that its volume changes from V_4 to V_1 along path DA of the indicator diagram and the system reaches its original state. In this step no heat is exchanged and $q = 0$ thus temperature increases from T_1 to T_2. Therefore, according to the first law of thermodynamics the work done on the gas (w_4) is equal to increase of internal energy. That is,

$$w_4 = \Delta U_4 = C_V (T_2 - T_1)$$

In the Carnot cycle

Net heat absorbed = Q (cycle)

= Heat taken from the hot source – Heat rejected to the surroundings

$= q_2 - q_1$

Net work done = W (cycle)

$$= w_1 + w_2 + w_3 + w_4$$

$$= - nRT_2 \ln (V_2/V_1) + C_V (T_1 - T_2) - nRT_1 \ln (V_4/V_3) + C_V (T_2 - T_1)$$

For second and fourth steps of Carnot cycle $C_V (T_1 - T_2) = - C_V (T_2 - T_1)$

Therefore, $W \text{ (cycle)} = - nRT_2 \ln (V_2/V_1) - nRT_1 \ln (V_4/V_3)$

Or, $W_{by} \text{ (cycle)} = - W_{by} \text{ (cycle)} = nRT_2 \ln (V_2/V_1) + nRT_1 \ln (V_4/V_3)$ (i)

For adiabatic changes along BC and DA

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$$

Or, $$\frac{V_1}{V_2} = \frac{V_4}{V_3}$$

and $$\ln \frac{V_4}{V_3} = \ln \frac{V_1}{V_2} = - \ln \frac{V_2}{V_1}$$

On substituting the above equality in equation (i), we get

$$W_{by} \text{ (cycle)} = nRT_2 \ln (V_2/V_1) - nRT_1 \ln \frac{V_2}{V_1}$$

$$= nR (T_2 - T_1) \ln \frac{V_2}{V_1}$$

Net energy change $= \Delta U$ (cycle) = 0 since internal energy is a state function

From the first law of thermodynamics we have

$$\Delta U\,(\text{cycle}) = Q\,(\text{cycle}) + W\,(\text{cycle}) = 0$$

$$Q\,(\text{cycle}) = -\,W\,(\text{cycle}) = W_{\text{by}}\,(\text{cycle})$$

Or, $$W_{\text{by}}\,(\text{cycle}) = Q\,(\text{cycle}) = q_2 - q_1$$

$$\text{Efficiency} = \eta = = \frac{W_{by}\,(cycle)}{q_2}$$

$$= \frac{nR\,(T_2 - T_1)\ln(V_2/V_1)}{nRT_2\ln(V_2/V_1)}$$

$$= \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

Example. ***One mole of an ideal gas undergoes reversible changes in a Carnot cycle.First it expands isothermally from a most compressed state of 10 bar and 600 K to a pressure of 1 bar then adiabatically to most expanded state at 300 K. Finally it is brought back to its initial state via isothermal compression and adiabatic compression respectively. Calculate q, w and ΔU for each step and the efficiency of the cycle. $C_{V,m}$= 25 JK^{-1} mol^{-1}***

Solution: Data given:

$T_1 = 300$ K, $T_2 = 600$ K, $C_{\text{V, m}} = 25$ JK^{-1} mol^{-1}

(a) Step 1: Reversible isothermal expansion at 600 K from a pressure of 10 bar to a pressure of 1 bar

$$w_1 = -2.303\;n\,RT_2\;\log\frac{P_1}{P_2}$$

$$= -2.303\times 1\text{ mol}\times 8.314\text{ JK}^{-1}\text{ mol}^{-1}\times 600\text{ K}\times\;\log\frac{10\text{ bar}}{1\text{ bar}}$$

$$= -11488\text{ J}$$

and $$q_2 = -\,w_1 = 11488\text{ J}\quad\text{since }\Delta U = 0$$

(b) Step 2. Reversible adiabatic expansion so that temperature decreases from 600 K to 300 K

$$q = 0$$

and from the first law of thermodynamics we have

$$w_2 = \Delta U_2 = n\,C_{\text{V, m}}\,(T_1 - T_2)$$

$$= 1\text{ mol}\times 25\text{ JK}^{-1}\text{ mol}^{-1}\times(300\text{ K} - 600\text{ K})$$

$$= -\,7500\text{ J}$$

(c) Step 3: Reversible isothermal compression at 300 K from a pressure of 1 bar to a pressure of 10 bar

$$w_3 = -2.303\ nRT_1\ \log \frac{P_1}{P_2}$$

$$= -2.303 \times 1 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log \frac{1 \text{ bar}}{10 \text{ bar}}$$

$$= 5744 \text{ J}$$

and $q_1 = -w_3 = -5744$ J since $\Delta U_3 = 0$

(d) Step 4. Reversible adiabatic compression so that temperature increases from 300 K to 600 K

$$q = 0$$

and from the first law of thermodynamics we have

$$w_4 = \Delta U_4 = n\ C_{\text{V, m}}\ (T_2 - T_1)$$

$$= 1 \text{ mol} \times 25 \text{ JK}^{-1} \text{ mol}^{-1} \times (600 \text{ K} - 300 \text{ K})$$

$$= +\ 7500 \text{ J}$$

For the entire cycle

$$\Delta U(\text{cycle}) = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4$$

$$= 0 + (-7500 \text{ J}\ ) + 0 + 7500 \text{ J}\ ^{1} = 0$$

$$W(\text{cycle}) = w_1 + w_2 + w_3 + w_4$$

$$= -\ 11488 \text{ J}\ \ -7500 \text{ J}\ ^{1} -5744 \text{ J}\ \ +7500 \text{ J}$$

$$= -\ 5744 \text{ J}$$

$$W_{\text{by}}(\text{cycle}) = -\ W(\text{cycle}) = 5744 \text{ J}$$

$$\text{Efficiency} = \eta = = \frac{W_{by}\,(cycle)}{q_2}$$

$$= \frac{5744 \text{ J}}{11488 \text{ J}} = 0.5$$

Comments: The efficiency is also calculated by

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{300 \text{ K}}{600 \text{ K}} = 1 - 0.5 = 0.5$$

A critical discussion: It is observed that in a cyclic process the total heat absorbed is not converted in to work. *Why?* Where has that remaining heat been utilized? We can explain this aspect of the subject by the study of the second law of thermodynamics which introduces the concept of entropy a measure of randomness and unavailable energy.

Carnot theorem

(i) Carnot theorem states that the efficiency of a reversible engine depends only on the higher temperature (T_2) and lower temperature (T_1) and is independent of the nature of the substance. Therefore, efficiency of a reversible engine may be expressed as

$$\text{Efficiency} = \eta = \frac{W_{\text{by}}\,(\text{cycle})}{q_2}$$

$$= \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

(ii) Carnot theorem may also be stated that for the same higher and same lower temperatures all reversible engines should have same efficiency.

Further discussion of Carnot theorem

The relation $\eta = 1 - \frac{T_1}{T_2}$ suggests that

(1) The efficiency of an engine is less than 1

(2) The efficiency will be equal to 1 only when $T_1/T_2 = 0$. It is possible only when either. $T_1 = 0$, or $T_2 = \infty$ But both these conditions are impossible to achieve experimentally.

(3) The efficiency of an engine can be increased by increasing the difference of the temperature of the source and the sink

(4) The efficiency of a machine operating in Carnot cycle is maximum because the work obtained from the system under reversible conditions is the highest possible work which a system can perform.

Thermodynamic scale of temperature

Lord Kelvin defined the thermodynamic scale of temperature by assigning the triple point of water exactly equal to 273.16 K. On this scale one kelvin (1 K) is defined as the fraction 1/273.16 of the thermodynamic temperature of triple point of water**.** This temperature can be conveniently realized, maintained and measured in the laboratory. The measurement of temperature is independent of the method followed. That is, the temperature of a system is the same whether it is measured using a mercury thermometer or thermocouple or thermistor. The temperature on thermodynamic scale (kelvin scale) is always positive. There is no negative value of temperature on kelvin scale

Comments: Triple point of water is the state when the three phases of water namely, solid (ice), liquid (water) and gas (vapour) exist together in equilibrium. The triple point of water is 273.16 K, which is greater than its melting point.

Zero value of kelvin temperature in terms of efficiency of Carnot cycle

Zero value of kelvin temperature is defined in terms of the efficiency (η, which is independent of the working substance in the cycle) of Carnot cycle as

$$T_1 = T_2 (1 - \eta)$$

When $\eta = 1$

$$T_1 = T_2 (1 - 1) = 0 \text{ K}$$

That is, the efficiency of the Carnot cycle is unity if the temperature of the surroundings (sink) is 0 K. In other words, we may state that the lowest temperature of thermodynamic scale corresponds to unit efficiency of Carnot cycle. This lowest temperature is written as $T =$ 0 K which is equal to –273.16 ^{o}C.

CONFIDENCE BUILDING QUESTIONS ON THE FIRST LAW OF THERMODYNAMICS

(A) Complete the following statements using a correct word/term from the list:

[by, increases, first, internal energy, adiabatic, enthalpy, constant, greater, zero, lower, adiabatic]

1. The relation $\Delta U = q + w$ represents the …………law of thermodynamics
2. Work done on the system ………….. its internal energy.
3. Work done … the system decreases its internal energy.
4. In the equation $H = U + PV,$ the term H is called -------------
5. The relation PV^{γ} tant is valid when an ideal gas undergoes ………….. reversible process..
6. In an adiabatic reversible process for an ideal gas $TV^{\gamma-1}$ = --------------
7. The value of w is ------------ in an adiabatic process than that in an isothermal process.
8. The value of w is ------------ in an isothermal reversible process than that in an isothermal irreversible process.
9. The efficiency of a Carnot cycle is one when T_1/T_2 is -----------
10. $\Delta U = w$ for an ------------ process

(B) Short Answer Questions:

1. Write the mathematical statement of the first law of thermodynamics.
2. Write the relation between work, heat and change in internal energy.
3. Write the first law of thermodynamics for an adiabatic process.
4. Name the process for which the first law of thermodynamics is written as $\Delta U = w$
5. Write the missing terms in the equation $H = U +$ --------
6. Mention the conditions when (a) $\Delta U = q_V$ and (b) $\Delta H = q_P$
7. Mention the conditions when $\Delta U = \Delta H$
8. Define heat capacity, specific heat capacity and molar heat capacity.
9. Write the relation between C_P and C_V for an ideal gas.
10. The relation $C_P - C_V = nR$ is valid for which type of system?
11. State Joule's law.

12. The relation $(\partial U/\partial V)_T = 0$ is known as which law?

13. A positive value of Joule-Thomson coefficient corresponds to which type of effect cooling or heating or no thermal change?

14. A zero value of Joule-Thomson coefficient corresponds to which type of effect cooling or heating or no thermal change ?

15. A negative value of Joule-Thomson coefficient corresponds to which type of effect cooling or heating or no thermal change ?

16. Derive an expression for work (w) when an ideal gas undergoes isothermal and reversible volume change.

17. Derive the expressions for w, q, ΔU and ΔH when n mol of an ideal gas undergoes adiabatic and reversible expansion.

18. Derive a relation between temperature and volume in adiabatic reversible expansion of an ideal gas.

19. Derive a relation between temperature and pressure in adiabatic reversible expansion of an ideal gas.

20. Name the system and conditions when $PV^{\square}$ is constant.

21. Derive the following relation for an ideal gas undergoing adiabatic reversible process

(a) $TV^{\gamma-1}$ = constant (b) TP^{-R/C_p} = constant

22. What is the value of work (w) when an ideal gas is allowed to expand in to an evacuated vessel?

23. In which type of process adiabatic or isothermal the value of work (w) done is more?

24. Calculate the value of ΔU and ΔH in the isothermal and reversible expansion of 4 g of hydrogen gas at 300 K from an initial volume of 20 dm^3 to a final volume of 60 dm^3. Assume that hydrogen gas obeys ideal gas law.

(C) Numerical problems

1. One mole of an ideal gas is heated at constant pressure from 273 K to 373 K. Calculate w, q ΔU and ΔH when $C_{p,.\,m} = 3.5\,R$ **[Ans: $w = -P_{ext}(V_2 - V_1) = -nR(T_2 - T_1) = -831.4$ J. $\Delta U = 2078.5$ J, $q = 2909.9$ J $= \Delta H$]**

2. One mole of an ideal gas at 300 K and 10^6 Pa expands to 10^5 Pa under isothermal and reversible conditions. Calculate w, q ΔU and ΔH .**[Ans: $w = -5744$ J $q = 5744$ J. $\Delta U = 0$, $\Delta H = 0$**

3. One mole of an ideal gas at 300 K and 10^6 Pa expands to 10^5 Pa under isothermal and irreversible conditions Calculate w, q ΔU and ΔH .**[Ans: $w = -2245$ J $q = 2245$ J. $\Delta U = 0$, $\Delta H = 0$]**

4. One mole of an ideal gas at 300 K and 10^6 Pa expands to 10^5 Pa under adiabatic and reversible conditions. Calculate final temperature, w, q ΔU and ΔH (Given that $C_{V,.\,m}$ = 1.5 R)..**[Ans:Final temperature = 119.4 K, *q* = 0 ΔU = *w*= –2252 J, ΔH = – 3753 J]**

5. A sample of 1.6 mole of an ideal gas ($C_{V,\,.m}$ = 2.5 *R*) at 300 K were allowed to expand adiabatically from 5 bar to a final pressure of 2 bar against a constant external pressure of 1 bar. Calculate final temperature, *q, w,* ΔU and ΔH. **[Ans: Final temperature = 270 K , *q* = 0, *w*= ΔU = – 997.68 J. ΔH = –1396.7]**

6. A sample of 0.175 mol of an ideal gas is allowed to expand under adiabatic and reversible conditions from a volume of 5.0 dm^3 at a pressure of 303975 N/m^2 and 298 K until the volume becomes 10.0 dm^3. Calculate the final pressure and final temperature of the gas and the values of *q, w,* ΔU and ΔH.for the process**.** (Given that $C_{p,.\,m}$ = 29.1 JK^{-1} mol^{-1})..**[Ans**: **Final pressure = 115186.5 N/m^2, final temperature = 226 K , *q* = 0, *w* = ΔU = – 261.9 J. ΔH = –366.6 J]**

7. One mole of an ideal gas is held by a piston at 0 °C and under a pressure of 10 kPa. The pressure is suddenly released to 0. 4 kPa and the gas is allowed to expand isothermally. Calculate *q, w,* ΔU and ΔH.for the process**. Hint:** The change is irreversible**. [Ans: ΔU = 0, ΔH = 0, *w* = –2179 J =*q*]**

Thermochemistry

The branch of chemistry dealing with the measurement and computation of energy changes *(ΔU)* and enthalpy changes *(ΔH)* of various types of physical transformations and chemical reactions is called ***thermachemistry.*** Now ΔU and ΔH are related to the heat exchanged between the system and the surroundings, Therefore, these properties are also called as **heat of reactions**.

Types of heat of a reaction

Depending on the experimentsl conditionsthe heat of a reaction is classified as follows.

- When the reaction is performed at constant volume the accompanying energy change *(ΔU)* is called ***heat af reaction at canstant volume*** (q_v)

$$\Delta U = q_v = \text{Heat of reaction at constant volume}$$

- When the reaction takes place at constant pressure the accompanying enthalpy change *($\Delta.H$)* is called the ***heat af reactian at canstant pressure***

$$\Delta H = q_p = \text{Heat of reaction at constant pressure}$$

Since most of the experiments are performed at constant pressure, the enthalpy change (ΔH) *is* used to describe the thermal changes in various types of chemical reactions and physical transformations.

Type of enthalpy changes. The enthalpy changes are classified as follows

(1) Enthalpy changes in reactions ($\Delta_r H$)	**(2) Enthalpy changes in chemical physical transformation ($\Delta_{trss} H$)**
(a) Enthalpy of formation ($\Delta_f H$)	(i) Enthalpy of vaporization ($\Delta_{vap} H$)
(b) Enthalpy of combustion ($\Delta_c H$)	(ii) Enthalpy of fusion ($\Delta_{fus} H$)
(c) Bond enthalpy ΔH(A –B)	(iii) Enthalpy of sublimation ($\Delta_{sub} H$)
(d) Enthalpy of neutralization ($\Delta_n H$)	(iv) Enthalpy of solution ($\Delta_{sol} H$)

Enthalpy of reaction ($\Delta_r H$)

The enthalpy of a reaction is defined as ***the heat absorbed or liberated when the reactants are completely converted into products as represented by the balanced chemical equation at a given temperature and pressure.***. It is also called as the ***heat of reaction*** at constant pressure. Enthalpy of reaction is denoted by $\Delta_r H$ and expressed in the units of kJ mol^{-1}. For example,

(i) When hydrogen gas is burnt in oxygen, a chemical reaction takes place. As a result of the reaction water is formed and 285.8 kJ heat is liberated. The reaction is represented by the equation

$$H_2\,g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O(l) \qquad \Delta_rH = -\,285.8\ \text{kJ mol}^{-1}$$

Interpretation of the above equation : The above equation tells that 286 kJ heat is liberated when 1 mole (2 g) of hydrogen gas completely reacts with half mole (16 g) of oxygen gas so that 1 mole (18 g) of water is formed. Thus heat of the reaction as represented by the above balanced chemical equation is –285.8 kJ mol^{-1}

(ii) When methane gas is burnt in oxygen, a chemical reaction takes place. As a result of the reaction carbon dioxide and water are formed and 890 kJ heat is liberated. The reaction is represented by the equation

$$CH_4(g) + 2O_2\,(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta_rH = -\,890\ \text{kJ mol}^{-1}$$

Interpretation of the above equation : The above equation tells that 890 kJ heat is liberated when 1 mole (16 g) of methane gas completely reacts with 2 moles (64 g) of oxygen gas so that 1 mole CO_2 (44 g) and 2 moles (36 g) of water are formed. Thus heat of the reaction as represented by the above balanced chemical equation is -890 kJ mol^{-1}

Role of mole to report the value of the enthalpy of reaction

- Enthalpy of reaction is always reported as kJ mol^{-1}. Here per mole (mol^{-1}) corresponds to per mole of the extent (progress) of reaction. Thus Δ_rH is the change of enthalpy with the extent of reaction. For example,

(i) The enthalpy of reaction

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

is –890 kJ mol^{-1}. This value tells that when one mole of methane gas reacts completely with 2 moles of oxygen gas to produce one mole of CO_2 (g) and 2 moles of $H_2O(l)$ then progress of reaction is said to be hundred percent. In this case we state that one mole of reaction has occurred

(ii) The enthalpy of reaction

$$2\,CH_4g) + 4\,O_2(g) \longrightarrow 2\,CO_2\,(g) + 4\,H_2O(l)$$

is –1780 kJ mol^{-1} This value tells that when two moles of methane react completely with 4 moles of oxygen to produce two moles of CO_2 and 4 moles H_2O then progress of this reaction is hundred percent. In this case we state that one mole of reaction as represented by the balanced chemical equation has occurred.

Notes:

(i) While reporting the enthalpy of combustion of a fuel, the value is given as kJ per mole of the substance burnt. In the given example the enthalpy of combustion is 890 kJ mol^{-1} of methane

(ii) Enthalpies of formation, vaporisation, fusion etc. are reported as kilojoules per mole (kJ mol^{-1}) of the substance concerned.

Standard state

The enthalpy change depends on temperature, pressure and the physical states of the reactants and products. Therefore, it is the recommendation of the IUPAC to mention the standard experimental condition while reporting the values of the enthalpy changes.

Standard states of different forms of matter

Physical state	***Notation***	***Conditions of standard states***
(1) Gas	(g)	Ideal gas at 1 bar at the specified temperature*
(2) Liquid	(l)	Pure liquid at 1 bar at the specified temperature*
(3) Solid	(s)	Pure crystalline and reactive form# at 1 bar and temperature *T*
(4) Solution in water	(aq)	Unit molarity (1 mol /dm^3) at 1 bar and temperature *T*

*The conventional temperature for thermodynamic tables is specified as 298.15 K

#graphite is taken as the standard state of carbon

#rhombic form is taken as the standard state of sulphur

Standard enthalpy of formation ($\Delta_f H^\upsilon$)

Standard enthalpy of formation is defined as ***the heat absorbed or liberated when one mole of a substance is formed from its constituent elements in their respective standard states.*** Standard enthalpy of formation is denoted by $\Delta_f H^\upsilon$ .and it is called standard ***heat of formation*** also. It is expressed in the units of kJ mol^{-1}. For example, the standard enthalpy of formation of water is – 285.8 kJ mol^{-1}. It is written as $\Delta_f H^\upsilon$ (H_2O) = – 285.8 kJ mol^{-1}. This enthalpy change is described as follows:

$$H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l) \qquad \Delta_f H^\upsilon (H_2O) = -285.8 \text{ kJ mol}^{-1}$$

Ideal gas Ideal gas Pure liquid

1 bar, 298 K 1 bar, 298 K 1 bar, 298 K

Notes:

(i) It is not always necessary to mention the standard conditions with the reactants and products in the balanced chemical equation, because $\Delta_f H^\upsilon$ itself tells that the value refers to standard state

The values of standard enthalpy of formation of some substances are given in table 1

Table 1- a. Standard enthalpy of formation ($\Delta_f H^\Theta$) of some inorganic compounds

Substance	$\Delta_f H^\Theta$ ***/kJ mol^{-1}***	***Substance***	$\Delta_f H^\Theta$ ***/kJ mol^{-1}***
H_2O (l)	- 285.8	NO (g)	90.4
H_2O (g)	- 241.8	N_2O (g)	81.5
H_2O_2 (l)	- 188.0	N_2O_4 (g)	9.6
HF (g)	- 268.6	NO_2 (g)	33.8
HCl (g)	-92.3	NH_3 (g)	-46.2
HBr (g)	-36.2	HNO_3 (l)	- 173.2
HI (g)	25.9	NH_4Cl (s)	-315.4
HIO_3(s)	- 238.6	LiCl(s)	- 408.8
H_2S (g)	- 20.1	NaCl(s)	- 411.0
H_2SO_4 (l)	- 814.0	KCl (s)	- 435.8
SO_2 (g)	- 296.9	AgCl (s)	- 127.0
SO_3 (g)	- 395.2	Br_2 (g)	30.7
CO (g)	- 110.5	O_3 (g)	+ 142.3
CO_2 (g)	- 393.5	Na_2CO_3	-1131.0

Table 1-b. Standard enthalpy of formation ($\Delta_f H^{\ominus}$) of some organic compounds

Compound	**Formula**	$\Delta_f H^{\ominus}$ **/ kJ mol^{-1}**
Methane	CH_4 (g)	- 74.85
Ethane	C_2H_6 (g)	- 84.67
Propane	C_3H_8 (g)	- 103.50
n-Butane	C_4H_{10} (g)	- 124.30
Ethene	C_2H_4 (g)	+ 52.30
Ethyne	C_2H_2 (g)	+ 226.70
Benzene	C_6H_6 (l)	+ 49.03
Benzene	C_6H_6 (g)	+ 82.93
Methanol	CH_3OH (l)	- 238.6
Ethanol	C_2H_5OH (l)	- 227.6
Ethanal	CH_3CHO (l)	- 166.3
Tetrachloromethane	CCI_4 (l)	- 139.8
Trichloromethane	$CHCI_3$ (l)	- 131.8
Urea	$(NH_2)_2CO$ (s)	- 333.2
Glucose	$C_6H_{12}O_6$ (s)	- 1270.0
Cyclohexane	C_6H_{12} (l)	- 123.1

(A) Standard enthalpy of formation of an element

The standard enthalpy of formation of an element is taken as zero.. That is, $\Delta_f H^{\upsilon}$ (element) = 0

Reason: An element can not be synthesized or decomposed by chemical or physical methods. For example, let us suppose that we want to represent the standard enthalpy of formation of element $H_2(g)$ by a balanced chemical equation. Now, according to the definition of $\Delta_f H^{\theta}$ it will be represented by

$$\underset{\text{(reactant)}}{H_2(\text{g, 1 bar, 298 K})} \longrightarrow \underset{\text{(product)}}{H_2(\text{g, 1 bar,298 K})} \qquad \Delta_r H = \Delta_f H^{\theta}\ (H_2, g) = 0$$

It is quite clear that there will not be any change of enthalpy for the formation of $H_2(g)$ from $H_2(g)$. It is to be kept in mind that $\Delta_f H^{\theta}$ $(H_2, g) = 0$, but $\Delta_f H^{\theta}$ $(H, g) \neq 0$. That is, the standard enthalpy of formation of hydrogen atom is not zero because atomic hydrogen is not the standard state of H_2. Similarly, we can write that:

(1) $\Delta_f H^{\upsilon}(O_2, g) = 0$ (2) $\Delta_f H^{\upsilon}(N_2, g) = 0$ (3) $\Delta_f H^{\upsilon}(I_2, s)) = 0$ but $\Delta_f H^{\upsilon}(I_2, g)) \neq 0$ because gaseous iodine is not its standard state.

(B) Standard enthalpy of formation of a gaseous atom

The heat absorbed when 1 mole of a gaseous atom is formed from its element in its standard state is called the ***standard enthalpy of formation*** of that atom. For example:

- The standard enthalpy of formation of gaseous hydrogen atom is equal to the enthalpy change for the following reaction.

$$\tfrac{1}{2} H_2(g) \longrightarrow H(g) \qquad \Delta_r H^{\theta} = \Delta_f H^{\theta}(H, g) = 218 \text{ kJ mol}^{-1}$$

- The standard enthalpy of formation of gaseous carbon atom is equal to the enthalpy change for the following reaction.

$$C(\text{graphite}) \longrightarrow C(g) \qquad \Delta_r H^{\theta} = \Delta_f H^{\theta}(C, g) = 716.67 \text{ kJ mol}^{-1}$$

Enthalpy of combustion ($\Delta_c H$)

The enthalpy of combustion is the ***heat liberated at a constant pressure when one mole of a fuel is completely burnt in oxygen***. It is denoted by notation $\Delta_c H$ and expressed in the units of kJ mol^{-1}. Enthalpy of combustion is called heat of combustion also.

A combustion reaction is always **exothermic**. For example, when one mole of methane burns completely in the presence of oxygen, one mole of CO_2 and two moles of H_2O are formed and 890 kJ heat is liberated.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \quad \Delta_r H = \Delta_c H(CH_4, g) = -890 \text{ kJ mol}^{-1}$$

Relation between standard enthalpy of reaction and standard enthalpy of formation

Standard enthalpy of reaction ($\Delta_r H^{\theta}$) and standard enthalpy of formation ($\Delta_f H^{\theta}$) are related by

$$(\Delta_r H^{\theta}) = \Sigma V_p \, \Delta_f H^{\theta}(\text{products}) - \Sigma V_r \, \Delta_r H^{\theta}(\text{reactant})$$

where,

V_p = Stoichiometric coefficient of product

V_r = Stoichiometric coefficient of reactant

For a general chemical reaction

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

$\Sigma \square_p \, \Delta_f H^{\upsilon}(\text{products}) = c\,\Delta_f H^{\upsilon}(C) + d\,\Delta_f H^{\upsilon}(D)$

$\Sigma v_r \, \Delta_f H^{\theta}(\text{reactants}) = a\,\Delta_f H^{\theta}(A) + b\,\Delta_f H^{\theta}(B)$

Thus

$$(\Delta_r H^\theta) = [c\ \Delta_f H^\theta(\text{C}) + d\ \Delta_f H^\theta(\text{D})] - [a\ \Delta_f H^\theta(\text{A}) + b\ \Delta_f H^\theta(\text{B})]$$

Comments:

- The above equation can be used to calculate any one of the quantities if others are known
- In the calculation it is assumed that $\Delta_f H^\theta$ (element) = 0
- The values of $\Delta_f H^\theta$ for other substances are taken from the table of thermodynamic data.

Example: Use the given values of $\Delta_f H^\theta$ to calculate the enthalpy of the following reaction

$$2\ \text{H}_2\text{S (g)} + 3\ \text{O}_2\ \text{(g)} \longrightarrow 2\ \text{SO}_2\text{(g)} + 2\ \text{H}_2\text{O (l)}$$

Substance	**H_2S (g)**	**SO_2(g)**	**H_2O (l)**
$\Delta_f H^\theta$/kJ mol^{-1}	**– 20.1**	**–296.9**	**– 285.8**

Solution: Enthalpy of a reaction is related to the standard enthalpy of formation as

$$(\Delta_r H^\theta) = \sum \nu_p\ \Delta_f H^\theta\ \text{(products)} - \sum \nu_r\ \Delta_r H^\theta\ \text{(reactant)}$$

For the given reaction

$$(\Delta_r H^\theta) = [\,2\ \Delta_f H^\theta(\text{SO}_2, \text{g}) + 2\ \Delta_f H^\theta(\text{H}_2\text{O, l})] - [2\ \Delta_f H^\theta(\text{H}_2\text{S, g}) + 3\ \Delta_f H^\theta(\text{O}_2, \text{g})]$$

On substituting the given $\Delta_f H^\theta$ values and assuming $\Delta_f H^\theta(\text{O}_2, \text{g}) = 0$, we get

$$(\Delta_r H^\theta) = 2\times(-296.9\ \text{kJ mol}^{-1}) + 2\times(-\,285.8\ \text{kJ mol}^{-1}) - [2\times(-\,20.1\ \text{kJ mol}^{-1}) - 3\times 0\ \text{kJ mol}^{-1})$$

$$= -\,1125.2\ \text{kJ mol}^{-1}$$

Example: Use the standard enthalpies of formation of various species to calculate the enthalpy change (*$\Delta_r H^0$*) for the reaction $\text{CH}_2\text{Cl}_2 \longrightarrow \text{C(g)} + 2\ \text{H (g)} + 2\ \text{Cl(g)}$

Species	**CH_2Cl_2 (g)**	**C(g)**	**H(g)**	**Cl(g)**
$\Delta_f H^0$/ kJ mol^{-1}	**– 1162.4715.0**	**218.0**	**121.3**	

Solution. For the reaction $\text{CH}_2\text{Cl}_2 \longrightarrow \text{C(g)} + 2\ \text{H (g)} + 2\ \text{Cl(g)}$

$$\Delta_r H^\theta = [\Delta_f H^\theta(\text{C, g}) + 2\Delta_f H^\theta(\text{H, g}) + 2\ \Delta_f H^\theta(\text{Cl, g})] - \Delta_f H^\theta(\text{CH}_2\text{Cl}_2, \text{g})$$

$$= [\,715.0 + 2\times 218.0 + 2\times 121.3]\ \text{kJ mol}^{-1} - (-1162.4\ \text{kJ mol}^{-1})$$

$$= 1556.0\ \text{kJ mol}^{-1}$$

Difference between the enthalpy of formation and enthalpy of reaction

- The enthalpy change accompanying the formation of one mole of a compound from its constituent elements in their respective standard stable states is called *standard enthalpy of formation* . It is denoted by $\Delta_f H^\ominus$.

- The enthalpy change in any type of chemical reaction namely combination, combustion, hydrogenation, bond dissociation or neutralization is called the *enthalpy of reaction.* It is denoted by $\Delta_r H^\ominus$.

  Important statements: *Enthalpy of formation is always equal to the enthalpy of reaction representing the formation of that compound. But the enthalpy of every reaction need not be the enthalpy of formation* For example,

- Reaction $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$ describes the formation of one mole of liquid water from its constituent elements. It also describes the combustion of hydrogen gas in the presence of oxygen to produce one mole of liquid water. Therefore, the enthalpy change of this reaction is equal to the enthalpy of combustion of hydrogen and also the standard enthalpy of formation of H_2O (l). Thus

$$\Delta_r H^\ominus = \Delta_C H^\ominus (H_2, g).= \Delta_f H^\ominus (H_2O, l)$$

- The enthalpy of the reaction

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \quad \Delta_r H^\ominus = -178.9 \text{ kJ mol}^{-1}$$

does not represent the standard enthalpy of formation of NH_4Cl (s). That is,

$$\Delta_r H^\ominus \neq \Delta_f H^\ominus (NH_4Cl, s)$$

Reason. The reactants NH_3 (g) and HCl (g) are not elements.

- The enthalpy change for the reaction

$$C(g) + 4H(g) \longrightarrow CH_4(g) \qquad \Delta_r H^\ominus = -1664 \text{ kJ mol}^{-1}$$

does not represent the standard enthalpy of formation of one mole of methane. That is,

$$. \Delta_r H^\ominus \neq \Delta_f H^\ominus (CH_4, g)$$

Reason. The reactants C (g) and H(g) are not the elements in their standard states.

Exercise. ***Identify and justify the thermochemical equations representing standard enthalpy of formation and standard enthalpy of reaction in the following list.***

(1) $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\ominus = -286 \text{ kJ mol}^{-1}$

(2) $C(g) + 4\ H(g) \longrightarrow CH_4(g) \qquad \Delta H^\ominus = -1664 \text{ kJ mol}^{-1}$

(3) $2H_2(g) + O_2(g) \longrightarrow 2\ H_2O(l) \qquad \Delta H^\ominus = -572 \text{ kJ mol}^{-1}$

(4) $C_2H_4\ (g) + H_2(g) \longrightarrow C_2H_6(g)$ $\Delta H^\Theta = -137\ kJ\ mol^{-1}$

(5) $C\ (graphite) + 2\ H_2(g) \longrightarrow CH_4\ (g)$ $\Delta H^\Theta = -74.8\ kJ\ mol^{-1}$

(6) $CaO(s) + CO_2\ (g) \longrightarrow CaCO_3(s)$ $\Delta H^\Theta = -178.3\ kJ\ mol^{-1}$

(7) $NH_3\ (g) + HCl\ (g) \longrightarrow NH_4Cl\ (s)$ $\Delta H^\Theta = -178.9\ kJ\ mol^{-1}$

(8) $C\ (graphite) + O_2(g) \longrightarrow CO_2\ (g)$ $\Delta H^\Theta = -\ 393.5\ kJ\ mol^{-1}$

Hint: (i) Enthalpy of formation : (1), (5), (8) (ii) **Enthalpy of reaction**: Each one including 1, 5 and 8

Enthalpy of neutralization

The heat liberated when one mole of hydrogen ions (H^+) is completely neutralized by a base in dilute aqueous solution at constant temperature and constant pressure is called ***enthalpy of neutralization***. It is called the heat of neutralization also.

$$H^+\ (aq) + Base \longrightarrow Salt + Water + Heat$$

For example, at 25 °C and 1 atm when one mole HCl (aq) and one mole NaOH (aq) react, 57 kJ heat is liberated as represented by

$$HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (1) \qquad \Delta H = -57\ kJ\ mol^{-1}$$

In aqueous solution each one of HCl (aq), NaOH (aq) and NaCl (aq) is completely ionized. Therefore, the neutralization reaction may be represented as

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-\ (aq) + H_2O(l) \qquad \Delta H = -57\ kJ\ mol^{-1}$$

Since equal number of Na^+ (aq) and Cl^-(aq) ions appear on both the aides of the neutralization reaction they may be dropped while writing the balanced chemical equation so that we have

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O\ (l) \qquad \Delta H = -57\ kJ\ mol^{-1}$$

That is, the neutralization reaction between HCl (aq) and NaOH (aq) is essentially the reaction between H^+ (aq) and OH^- (aq) to form unionized H_2O This is exclusively valid for strong and strong base pair.

Comments*:*

(i) It is true that the neutralization reaction between a strong acid-base pair is the combination of H^+ (aq) and OH^- (aq) ions to form H_2O (l). But the value of heat of neutralization is different for various acid-base pairs at different concentrations. For example, the heat of neutralization of sulphuric acid and NaOH is 62 kJ at 25 °C and 1 atm.

(ii) In very dilute solutions the heat of neutralization of strong acid and strong base pair is constant and equal to about 57 kJ mol^{-1} at 298 K and 1 atm. If the acid and base are of appreciable concentrations (more than 1.0 M*),* then ΔH value is different.

(iii) For weak acid and strong base pair ($CH_3COOH + NaOH$), or strong acid and weak base pair ($HCl + NH_4OH$), the heat of neutralization is less than 57 kJ. *Why?* Because part of the heat liberated is utilized to cause the ionization of the weak acid or weak base.

Example: The enthalpy of neutralization of ethanoic acid and NaOH is – 55.8 kJ mol^{-1} and that of hydrochloric acid and NaOH is – 57.3 kJ mol^{-1}. Give a suitable reason for the difference in the two values.

Solution. The enthalpy changes may be represented by the following equations.

(i) $Na^+ OH^- (aq) + H^+ Cl^- (aq) \longrightarrow Na^+Cl^- (aq) + H_2O (l)$ $\Delta H = -57.3$ kJ mol^{-1}

Or, $OH^-(aq) + H^+(aq) \longrightarrow H_2O$ $\Delta H = -57.3$ kJ mol^{-1}

(ii) $Na^+OH^- (aq) + CH_3COOH(aq) \longrightarrow CH_3COO^- Na^+ (aq) + H_2O(l)$ $\Delta H = -55.8$ kJ mol^{-1}

Or, $OH^-(aq) + CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$ $\Delta H = -55.8$ kJ mol^{-1}

Ethanoic acid is a weak acid and is only partially ionized. Therefore, a part of the enthalpy change on neutralization is used in the ionization of CH_3COOH. Thus the magnitude of ΔH for the reaction (ii) is lower than that for the reaction (i)

Calculation of enthalpy of ionization of CH_3COOH

(i) $Na^+ OH^- (aq) + H^+ Cl^- (aq) \longrightarrow Na^+Cl^- (aq) + H_2O (l)$ $\Delta H(i) = -57.3$ kJ mol^{-1}

(ii) $Na^+OH^- (aq) + CH_3COOH(aq) \longrightarrow CH_3COO^- Na^+ (aq) + H_2O(l)$ $\Delta H(ii) = -55.8$ kJ mol^{-1}

On subtracting equation (i) from equation (ii) we get

(A) $CH_3COOH (aq) \longrightarrow CH_3COO^-(aq) + H^+(aq)$

$$\Delta H(A) = \Delta H(ii) - \Delta H(i) = -55.8 \text{ kJ mol}^{-1} - (-57.3 \text{ kJ mol}^{-1}) = +1.8 \text{ kJ mol}^{-1}$$

Enthalpy on ionization of $CH_3COOH = 1.8$ kJ mol^{-1}

Hess's law of constant heats summation

This law was formulated in 1840 by the Swiss-Russian chemist Germain Henri Hess and is stated as follows

The heat of a reaction (reaction enthalpy) is the same whether the reaction takes place in one step or in several steps under the same conditions.

Illustration of the statement of the Hess's law

Let us consider the calculation of the standard enthalpy of formation of carbon dioxide. The formation of CO_2 may be described in the following two ways:

Method 1. A calculated quantity of carbon (graphite) is burnt directly in the presence of oxygen to form carbon dioxide

(i) $\text{C (graphite)} + O_2(g) \longrightarrow CO_2\ (g)$ $\Delta H°(i) = -395\ \text{kJ mol}^{-1}$

Method 2. A calculated quantity of carbon (graphite) is burnt in limited supply of oxygen to form cabron monoxide: then allowing CO to combine with oxygen and form carbon dioxide

(ii) $\text{C (graphite)} + \frac{1}{2}\ O_2(g) \longrightarrow CO(g)$ $\Delta H°(ii) = -110\ \text{kJ mol}^{-1}$

(iii) $CO(g) + \frac{1}{2}\ O_2(g) \longrightarrow CO_2\ (g)$ $\Delta H°(\text{iii}) = -\ 285\ \text{kJ mol}^{-1}$

On adding equations (ii) and (iii) alongwith the ΔH^θ values we get

$$\text{C (graphite)} + \frac{1}{2}\ O_2(\ g) + CO(g) + O_2(\ g) \longrightarrow CO(g) + CO_2(\ g)$$

and $\Delta H^\theta\ (ii) + \Delta H^\theta\ (iii) = -\ 110\ \text{kJ mol}^{-1} + (\ -\ 285\ \text{kJ mol}^{-1}\ ) = -\ 395\ \text{kJ mol}^{-1}$

On cancelling the common species on both the sides of the above equation we have

(iv) $\text{C (graphite)} + O_2(g) \longrightarrow CO_2(g)$ $\Delta H^\theta\ (iv) = -\ 395\ \text{kJ mol}^{-1}$

Since the chemical equations (i) and (iv) are the same, their enthalpy changes are also the same. Thus

$$\Delta H^\theta\ (i) = \Delta H^\theta\ (\text{ii}) + \Delta H^\theta\ (iii) = \Delta H^\theta\ (iv) = -\ 395\ \text{kJ mol}^{-1}$$

Conclusion: From this illustration it is concluded that the standard enthalpy of formation of carbon dioxide is the same whether it is produced by burning graphite in sufficient quantity of oxygen or first burning graphite in limited supply of oxygen to form carbon monoxide then burning carbon monoxide to produce carbon dioxide

Discussion

(1) ***Hess's law is a direct consequence of the law of conservation of energy.*** Suppose in the above reaction the enthalpy changes in the two steps of the second method were greater than that of the first method *i.e.,* $\Delta H^\theta\ (\text{ii}) + \Delta H^\theta\ (\text{iii}) > \Delta H^\theta\ (\text{i})$. This would mean that energy is not conserved though the amounts of the reactants and the product are the same in both the methods of performing the experiments. This would be contrary to the conservation law. Thus the enthalpy changes estimated by the two should be the same.

(2) Hess's law is also in line with the fact that enthalpy is a state function. Therefore, the

change of enthalpy will depend only on the initial and final states, and not on the path followed by the change. It implies that we cannot alter the enthalpy of a reaction by choosing different paths.

Applications of Hess's law of constant heat summation

(i) This law provides a practical method for computing the enthalpy change of a reaction from the enthalpy changes of other reactions.

(ii) Hess's law is used to calculate the reaction enthalpies even for those reactions which are otherwise difficult to carry out in the laboratory

(iii) According to Hess's law the thermochemical equations may be treated as algebraic equations.

Working rules of applications of Hess's law

- ***When a chemical equations is reversed, the sign of the enthalpy change is also reversed but magnitude remains the same.*.** For example, the standard enthalpy of formation of H_2O is given by the reaction

$$. H_2(g) + ½ O_2(g) \longrightarrow H_2O(l) \qquad \Delta_f H^\theta (H_2O) = –285.8 \text{ kJ mol}^{-1}$$

Now, according to the Hess's law, the enthalpy of decomposition of H_2O is represented by

$$H_2O(l) \longrightarrow H_2(g) + ½ O_2(g) \qquad \Delta_d H^\theta (H_2O) = - \Delta_f H^\theta (H_2O) = + 285.8 \text{ kJ mol}^{-1}$$

- ***When an equation is multiplied by a number, the enthalpy change is also multiplied by the same number***. For example

If $H_2(g) + ½ O_2(g) \longrightarrow H_2O(l) \qquad \Delta_r H^\theta (i) = –285.8 \text{ kJ mol}^{-1}$

then $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(l)$

$$\Delta H^\theta (ii) = 2 \times \Delta_r H^\theta (i) = 2\times(–285.8 \text{ kJ mol}^{-1}) = –571.6 \text{ kJ mol}^{-1}$$

- ***When equations are added, the enthalpy changes are also added accordingly with proper signs.*** For example

$$\text{(a) } C(\text{graphite}) + ½ O_2(g) \longrightarrow CO(g) \qquad \Delta H^\theta (a) = –110 \text{ kJ mol}^{-1}$$

$$\text{(b) } CO(g) + ½ O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta (b) = – 285 \text{ kJ mol}^{-1}$$

On adding equations (a) and (b) we get

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$$

According to the Hess's law the enthalpy of reaction (c) is given by

$\Delta H^{\upsilon}\ (c)\ = \Delta H^{\upsilon}\ °(a) + \Delta H^{\upsilon}(b)$

$= – 110\ \text{kJ mol}^{–1} + (– 285\ \text{kJ mol}^{–1})$

$= – 395\ \text{kJ mol}^{–1}$

Example: Apply Hess's law to calculate the enthalpy change ($\Delta_r H^\theta$) of the following reaction

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

Data given:

(i) C (graphite) + O_2(g) $\longrightarrow$ CO_2(g) **$\Delta_r H^\theta$ (i) = – 393.5 kJ mol$^{–1}$**

(ii) H_2 (g) + 0.5 O_2(g) $\longrightarrow$ H_2O(l) **$\Delta_r H^\theta$ (ii) = – 285.8 kJ mol$^{–1}$**

(iii) CH_4 (g) + 2 O_2(g) $\longrightarrow$ CO_2(g) +2 **H_2O(l)** **$\Delta_r H^\theta$ (iii) = – 890.3 kJ mol$^{–1}$**

Solution. Our aim

(A) C (graphite) + 2 H_2(g) $\longrightarrow$ CH_4(g) $\Delta_r H^\theta$ (A) = ?

Operations: On multiplying equation (ii) by 2 and reversing equation (iii) we get

(iv) 2H_2 (g) + O_2(g) $\longrightarrow$ 2H_2O(l) $\Delta_r H^\theta$ (iv) = – 2×285.8 kJ mol$^{–1}$

(v) CO_2(g) + H_2O(l) $\longrightarrow$ CH_4 (g) + 2 O_2(g) $\Delta_r H^\theta$ (v) = + 890.3 kJ mol$^{–1}$

On adding equations (i), (iv) and (v) along with corresponding $\Delta_r H^{\upsilon}$ values, we get equation (vi)

(vi) [C (graphite) + O_2(g)] + [2H_2 (g) + O_2(g)] + [CO_2(g) +2 H_2O(l)]

$\longrightarrow$ CO_2 (g) + 2 H_2O(l) +[CH_4(g) + 2 O_2(g)]

$\Delta_r H^\theta$ (vi) = $\Delta_r H^\theta$ (iv) + $\Delta_r H^\theta$ (v) + $\Delta_r H^\theta$ (i)

= (– 393.5 + (– 2×285.8 + 890.3) kJ mol$^{–1}$

= –74.8 kJ mol$^{–1}$

On canceling the common terms on the two sides of equation (vi), we get equation (vii)

(vii) C (graphite) + 2H_2 (g) $\longrightarrow$ CH_4(g) $\Delta_r H^{\upsilon}$ (vii) = –74.8 kJ mol$^{–1}$

It is observed that equations (A) and (vii) are the same. Therefore, according to Hess's law their enthalpies should also be the same. Thus

$\Delta_r H^{\ominus}$ (A) $= \Delta_r H^{\ominus}$ (vii) $= -74.8$ kJ mol^{-1}

Example. Use the following combustion data to calculate the enthalpy change for the hydrogenation of ethene as represented by the reaction C_2H_4 (g) + H_2 (g) $\longrightarrow$ C_2H_6(g)

Combustion data:

(i) C_2H_4 (g) + $3O_2$ (g) $\longrightarrow$ $2CO_2$ + $2H_2O$(g) $\Delta_c H^0 = -1410$ kJ mol^{-1}

(ii) C_2H_6 (g) + 3.5 O_2 (g) $\longrightarrow$ $2CO_2$ + $3H_2O$(g) $\Delta_c H^0 = -1550$ kJ mol^{-1}

(iii) H_2 (g) + $0.5O_2$ (g) $\longrightarrow$ H_2O(l) $\Delta_c H^0 = -286.0$ kJ mol^{-1}

Solution. Our aim is to calculate $\Delta H^{\ominus}$ for the reaction

$$C_2H_4\,(g) + H_2\,(g) \longrightarrow C_2H_6\,(g) \quad \Delta H^{\ominus}\,(A) = ?$$

Operations: Subtract equation (ii) from the sum of equations (i) and (iii) to get

eq (i) + eq (iii) – eq (ii)

$$[C_2H_4\,(g) + 3O_2\,(g)] + [H_2\,(g) + 0.5O_2\,(g)] — [C_2H_6\,(g) + 3.5\,O_2\,(g)]$$

$$\rightarrow [2\,CO_2 + 2H_2O(g)] + H_2O(l) — [2CO_2 + 3H_2O(g)]$$

On canceling the common terms on the two sides of the above equation we get

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

and $\Delta_r H^{\ominus}\,(A) = \Delta_r H^{\ominus}\,(i) + \Delta_r H^{\ominus}\,(iii) - \Delta H^{\ominus}\,(ii)$

$$= -1410 \text{ kJ mol}^{-1} + (-286 \text{ kJ mol}^{-1}) - (-1550 \text{ kJ mol}^{-1})$$

$$= -137 \text{ kJ mol}^{-1}$$

Relation between $\Delta_r H$ AND $\Delta_r U$

$H = U + PV$ Definition of enthalpy

$\Delta H = \Delta U + P\,\Delta V + V\,\Delta P$ For changes in the states of the system

$= \Delta U + P\,\Delta V$ At constant pressure

And for a chemical reaction the above relation can be written as $\Delta_r H = \Delta_r U + P\,\Delta_r V$

(i) For solids and liquids, the volume change in the reaction ($\Delta_r V$) is generally very small. Therefore, under atmospheric pressure $P\Delta_r V$ is negligible as compared to $\Delta_r H$ and $\Delta_r U$. Hence,

$\Delta_r H = \Delta_r U$ For reactions involving solids and liquids only

(ii) For gases $\Delta_r V$ is large and hence $P\,\Delta_r V$ has appreciable value. Thus

$\Delta_r H = \Delta_r U + P\Delta_r V$ For gases at constant pressure

(iii) In a chemical reaction involving gases

$$\Delta_r V = \Sigma\text{volume of products} - \Sigma\text{volume of reactants}$$

$$= \Sigma V\,(\text{products}) - \Sigma V\,(\text{reactants})$$

For a general reaction involving gases

$$a\text{A (g)} + b\text{B(g)} \longrightarrow c\text{C (g)} + d\text{D (g)}$$

$$\text{Reactants} \longrightarrow \text{Products}$$

$\Sigma V\,(\text{reactants}) = aV_m\,(\text{A}) + bV_m\,(\text{B})$

$\Sigma V\,(\text{products}) = cV_m\,(\text{C}) + dV_m\,(\text{D})$

Where, V_m = Molar volume of gas

For an ideal gas $PV = nRT$ and $V/n = RT/P$. Therefore, $V_m = RT/P$. .

If temperature (T) and pressure (P) are kept constant, we shall have

$$\Sigma V\,(\text{reactants}) = a \times \frac{RT}{P} + b \times \frac{RT}{P} = \frac{RT}{P}\ (a + b)$$

$$\Sigma V\,(\text{products}) = c \times \frac{RT}{P} + d \times \frac{RT}{P} = \frac{RT}{P}\ (c + d)$$

$$\Delta_r V = \Sigma V\,(\text{products}) - \Sigma V\,(\text{reactants})$$

$$= \frac{RT}{P}\ [(c + d) - (a + b)]$$

Therefore, $$P\Delta_r V = P \times \frac{RT}{P}\ [(c + d) - (a + b)]$$

$$= RT[(c + d) - (a + b)]$$

$$= \Delta n_g RT$$

Where, $\Delta n_g = (c + d) - (a + b)$

$= \Sigma$coefficients of gaseous products – Σ coefficients of gaseous reactants

Thus $\Delta_r H = \Delta_r U + P\Delta V = \Delta_r U + \Delta n_g RT$

Or, $\Delta_r U = \Delta_r H - \Delta n_g RT$

For the reaction $N_2\text{ (g)} + 3\,H_2\text{ (g)} \longrightarrow 2\,NH_3\text{ (g)}$

$$\Delta n_g = 2 - (1 + 3) = -2$$

and $\quad \Delta_r H = \Delta_r U - 2\,RT$

Or, $\quad \Delta_r U = \Delta_r H + 2\,RT$

Remarks:

(i) It must be noted that Δn_g is a number and it is not mole because it is the change in the moles of the substances per mole of the reaction occurred. Thus mole divided by mole is a number.

(ii) For a reaction $\Delta_r H = q_p$ and $\Delta_r U = q_v$, thus, the relation $\Delta_r H = \Delta_r U + \Delta n_g\,RT$ may be written as

$$q_p = q_v + \Delta n_g\,RT$$

(iii) For a reaction such as $H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$, $\Delta n_g = 0$. Therefore, $\Delta_r H = \Delta_r U$ and $q_p = q_v$

Example: For a reaction $CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$, $\Delta_r H^{\ominus} = -\,890.3$ kJ mol^{-1} at 298 K and 1 bar. Find the value of $\Delta_r U$ for the same reaction at the same temperature and pressure.

Solution: For the reaction $CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2(g) + 2\,H_2O\,(l)$

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

Therefore, $\quad \Delta_r H^{\ominus} = \Delta_r U^{\ominus} - 2\,RT$

Or, $\quad \Delta_r U^{\ominus} = \Delta_r H^{\ominus} + 2\,RT$

$$= -\,890.\,35 \text{ kJ mol}^{-1} + 2 \times 8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{ K}^{-1} \times 298 \text{ K}$$

$$= -\,890.\,35 \text{ kJ mol}^{-1} + 4.95 \text{ kJ mol}^{-1}$$

$$= -\,885.4 \text{ kJ mol}^{-1}$$

Example. The enthalpy change ($\Delta_r H$) for the reaction $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ is – 92.38 kJ mol^{-1} at 298 K. Calculate the value of $\Delta_r U$ at 298 K.

Solution. For the reaction $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$

$$\Delta \nu = 2 - (1 + 3) = -\,2$$

$$\Delta_r H = -\,92.38 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K}$$

Therefore, $\quad \Delta_r U = \Delta_r H - \Delta \nu\,RT$

$$= -\,92.38 \text{ kJ mol}^{-1} - (-2) \times 8{,}314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$$= -92.38 \text{ kJ mol}^{-1} + 4.95 \text{ kJ mol}^{-1}$$

$$= -\ 87.43 \text{ kJ mol}^{-1}$$

Example. Calculate the value of $\Delta_r H$ at 298 K for the reaction OF_2 (g) + H_2O(g) → 2 HF(g) + O_2(g). It is given that the value of $\Delta_r U$ is –320.9 kJ mol^{-1} at 298 K.

Solution. For the reaction $OF_2(g) + H_2O(g) \rightarrow 2\,HF(g) + O_2\,(g)$

$$\Delta\nu = (2 + 1) - (1 + 1) = 1$$

$$\Delta_r U = -\ 320.9 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K}$$

Therefore,

$$\Delta_r H = \Delta_r U \ + \Delta\nu RT$$

$$= -\ 320.9 \text{ kJ mol}^{-1} + 1 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$$= -92.38 \text{ kJ mol}^{-1} + 2.477 \text{ kJ mol}^{-1}$$

$$= -\ 318.423 \text{ kJ mol}^{-1}$$

Example. When a sample of 1.25 g of gaseous chlorofluorocarbon ($C_2Cl_2F_2$) at a constant atmospheric pressure of 1 atm was cooled from 320 K to 293 K there was a decrease in its volume from 274 cm^3 to 248 cm^3. Calculate the values of $\Delta_r H$ and $\Delta_r U$ for the process. The molar heat capacity of $C_2Cl_2F_2$ is 80.7 JK^{-1} mol^{-1}.

Solution. Data given :

Heat capacity of $C_2Cl_2F_2$ at constant pressure = C_p = 80.7 JK^{-1} mol^{-1}

Initial temperature = T_1 = 320 K , Final temperature = T_2 = 293 K

Therefore,

$$\Delta T = T_2 - T_1 = 293 \text{ K} - 320 \text{ K} = -27 \text{ K}$$

(i) Calculation of ΔH

$$\Delta H_m = C_p \times \Delta T$$

$$= 80.7 \text{ JK}^{-1} \text{ mol}^{-1}. \times (-\ 27 \text{ K})$$

$$= -\ 2178.9 \text{ J mol}^{--1}$$

ΔH (to cool 1.25 g of $C_2Cl_2F_2$)

$$= \Delta H \text{ per mole of } C_2Cl_2F_2 \times \text{mole of } C_2Cl_2F_2 \text{ in } 1.25 \text{ g}$$

$$\text{Mole of } C_2Cl_2F_2 = \frac{\text{Mass of } C_2Cl_2F_2}{\text{Molar mass of } C_2Cl_2F_2} = \frac{1{,}25 \text{ g}}{133 \text{ g/mol}}$$

Therefore,

$$\Delta H = -2178.9 \text{ kJ mol}^{--1} \times \frac{1{,}25 \text{ g}}{133 \text{ g/mol}} = --\ 20.478 \text{ J}$$

(ii) Calculation of *ΔU*

$\Delta H = \Delta U + P\Delta V$ gives

$\Delta U = \Delta H - P\Delta V$

Data given

$P = 1\ \text{atm} = 101325\ \text{N / m}^2$

$V_1 = 274\ \text{cm}^3 = 274 \times 10^{-6}\ \text{m}^3$

$V_2 = 248\ \text{cm}^3 = 248 \times 10^{-6}\ \text{m}^3$

Therefore, $\Delta V = V_2 - V_1 = 248 \times 10^{-6}\ \text{m}^3 - 274 \times 10^{-6}\ \text{m}^3 = -26 \times 10^{-6}\ \text{m}^3$

and $P \times \Delta V = 101325\ \text{N m}^{-2} \times (-26 \text{ x } 10^{-6}\ \text{m}^3) = --2.634\ \text{N m}^{-2} = 2.364\ \text{J}$

Thus

$\Delta U = \Delta H - P\Delta V$

$= -20.478\ \text{J} -- (-2.364\ \text{J})$

$= -20.478\ \text{J} + 2.364\ \text{J} = -18.114\ \text{J}$

Example. When the sample of 0.562 g of graphite was burnt in a bomb calorimeter in the presence of excess of oxygen at 298 K and 1 bar pressure the following reaction took place $C\ (s) + O_2(g) \rightarrow CO_2\ (g)$. During the reaction an increase of temperature from 298 K to 298.8 K was observed. Calculate the molar enthalpy change for the above reaction. It is given that the heat capacity of the calorimeter and its content is 20.7 kJ K^{-1}.

Solution. $q\ (\text{calorimeter}) = C(\text{calorimeter}) \times \Delta T$

$= 20.7\ \text{kJ K}^{-1} \times (298.8\ \text{K} - 298.0\ \text{K})$

$= 18.423\ \text{kJ}$

$q\ (\text{reaction}) = -\,q(\text{calorimeter})$

$= -18.423\ \text{kJ}$

= Heat liberated on burning 0.562 g of graphite

Heat liberated per mole of graphite $= \dfrac{q(\text{reaction})}{\text{mole of graphite}}$

$$= \frac{-18.423\ \text{kJ}}{0.562\ \text{g}/12\ \text{g mol}^{-1}}$$

$$= -393.378\ \text{kJ mol}^{-1}$$

(i) Calculation of ΔU: The experiment is carried in a bomb calorimeter

Therefore, q (reaction) /mol = ΔU (reaction)./mol = $-$ 393.378 kJ mol^{-1}

(ii) Calculation of $\Delta H = \Delta U + \Delta \nu_g RT$

For the reaction C (s) + O_2(g) → CO_2 (g

$$\Delta \nu_g = 1 - 1 = 0$$

Therefore, $\Delta \nu_g RT = 0 \times RT = 0$

and $\Delta H = \Delta U = -$ 393.378 kJ mol^{-1}

Bond enthalpy

When a chemical bond is formed heat is liberated. This heat liberated at constant pressure is referred to as ***enthalpy of bond formation***. On the other hand, the heat needed to cause the breaking of a chemical bond at a constant pressure is called the ***bond dissociation enthalpy.*** Thus, the bond formation is an exothermic process whereas bond dissociation is an endothermic process. For example:

When two hydrogen atoms unite to form a covalent bond in hydrogen molecule as H–H, the heat liberated is 436 kilo joule per mole of bond formed. That is, the enthalpy of formation of one mole of H–H bond is – 436 kJ. It is written as follows

$$\text{H (g)} + \text{H(g)} \longrightarrow \text{H} - \text{H(g)} \qquad \Delta H^{\upsilon} = -436 \text{ kJ mol}^{-1}$$

On the other hand, when one mole of H – H covalent bonds are broken, 436 kJ heat is absorbed and is given as

$$\text{H} - \text{H (g)} \longrightarrow 2\text{H (g)} \qquad \Delta H^{\upsilon} = +436 \text{ kJ mol}^{-1}$$

The enthalpy of dissociation of one mole of H–H bonds is 436 kJ mol^{-1}

Preference of bond dissociation enthalpy over bond formation enthalpy

Bond formation enthalpy is a conceptual term. It is not possible to estimate directly its experimental value. *Why?* Because we cannot isolate the free gaseous atoms and force them to combine. On the other hand, bond dissociation enthalpy is an operational term. It is convenient to collect a sample of the substance and fragment (atomize) its molecules to produce the constituent atoms and then to estimate the heat needed to break the bonds.

Bond enthalpy of a diatomic molecule

. The bond dissociation enthalpy of a diatomic molecule is equal to the heat needed to break the bonds in one mole of molecules so that free gaseous atoms are produced. For example:

(i) The bond enthalpy of H –H bond is equal to the enthalpy change for breaking one mole of H–H bonds in H_2 molecules and to produce free gaseous H atoms

$$H - H\,(g) \longrightarrow 2\,H(g) \qquad \Delta H\,(H\text{–}H) = 436\ \text{kJ mol}^{-1}$$

(ii) The bond enthalpy of O = O bond is equal to the enthalpy change for breaking one mole O = O bonds in O_2 molecules and to produce free gaseous O atoms.

$$O = O\,(g) \longrightarrow 2\,O\,(g) \qquad \Delta H\,(O{=}O) = 498\ \text{kJ mol}^{-1}$$

(iii) The bond enthalpy of H–Cl bond is equal to the enthalpy change in breaking one mole H–Cl bonds in HCl molecules so that 1 mole H atoms and 1 mole Cl atoms are produced.

$$H\text{–}Cl\,(g) \longrightarrow H(g) + Cl(g) \quad \Delta H\,(H\text{–}Cl) = 432\ \text{kJ mol}^{-1}$$

Enthalpy of bond dissociation in polyatomic molecules

In a polyatomic molecule the energy needed to break the same type of bond is different in different chemical situations. For example, in H_2O there are two O–H bonds written as H–O–H (simplified). Both the O–H bonds are equivalent in length and strength. But, the experiment shows that the enthalpy change to break one mole O – H bonds in H – O –H is 498 kJ mol^{-1}. On the other hand, the enthalpy change to break one mole O – H bond in hydroxyl group (OH) is 430 kJ mol^{-1}

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

and

$$O\text{–}H\,(g) \longrightarrow O(g) + H(g) \qquad \Delta H = 430\ \text{kJ mol}^{-1}$$

Thus the enthalpy of bond dissociation is defined as ***the enthalpy change to breaking a given bond in specified chemical environment.***

Bond enthalpy. *Average of bond dissociation enthalpies of a given bond in different dissociating species is called its bond enthalpy.* For example, in water molecule (H–O–H) the average of the two O–H bond dissociation enthalpies is called O–H bond enthalpy.

$$\Delta H\,(O - H) = \frac{498\ \text{kJ mol}^{-1} + 430\ \text{kJ mol}^{-1}}{2} = 464\ \text{kJ mol}^{-1}$$

Illustrative examples: Use the following bond dissociation enthalpies to compute the C–H bond enthalpy in methane (CH_4)

(i) $CH_4\,(g) \longrightarrow CH_3\,(g) + H(g) \qquad \Delta H(i) = 425\ \text{kJ mol}^{-1}$

(ii) $CH_3(g) \longrightarrow CH_2\,(g) + H(g) \qquad \Delta H(ii) = 470\ \text{kJ mol}^{-1}$

(iii) $CH_2\,(g) \longrightarrow CH(g) + H(g) \qquad \Delta H(iii) = 416\ \text{kJ mol}^{-1}$

(iv) $CH(g) \longrightarrow C(g) + H(g \qquad \Delta H(iv) = 335\ \text{kJ mol}^{-1}$

On adding equations (i), (ii), (iii) and (iv) and canceling the common terms on the two sides, we get

$$CH_4\,(g) \longrightarrow C\,(g) + 4\,H(g)) \qquad \Delta H = 1646\ \text{kJ mol}^{-1}$$

This is the sum of the individual C–H bond dissociation enthalpies. But bond enthalpy is equal to the average of the bond dissociation enthalpies. Therefore, the C–H bond enthalpy is given by

$$\Delta H\,(\text{C–H}) = \frac{(425\ \ + 470 + 416 + 335)\ \text{kJ mol}^{-1}}{4} = 411.5\ \text{kJ mol}^{-1}$$

A discussion of bond enthalpy and bond energy

Bond enthalpy and bond energy of a chemical bond A&B are related by

$$\Delta H^{\theta}\ \text{A\&B}) = \Delta U^{\theta}\,(\text{A\&B})\ + P\,\Delta V$$

If the bonded species A—B and its fragments A and B are assumed to obey ideal gas equation, then $P\,\Delta V = \Delta\Delta n_g\,RT$. Therefore,

$$\Delta H^{\theta}\ \ (\text{A\&B}) = \Delta U^{\theta}\,(\text{A\&B})\ + \Delta n_g\ \ RT$$

or, $$\Delta U^{\theta}\ \ (\text{A\&B}) = \Delta H^{\theta}\,(\text{A–B})\ \&\ \Delta n_g\ \ RT$$

The dissociation of bond A&B is represented by

$$\text{A\&B (g)} \longrightarrow \text{A(g)}\ \ +\ \text{B(g)}$$

Therefore, $\Delta n_g\ = 1 + 1 - 1\ = 1$. Thus,

$$\Delta U^{\theta}\ \ (\text{A\&B}) = \Delta H^{\theta}\,(\text{A\&B})\,\&\ RT$$

- At 0 K, $RT = 8.314 \times 10^{\ --3}$ kJ mol $^{\&1}\times$ 0 K = 0. Therefore,

$$\Delta U^{\theta}\ \ (\text{A\&B}) = \Delta H^{\theta}\,(\text{A\&B})$$

- At 298 K,

$$RT = 8.314\ \text{x}\ 10^{\ --3}\ \text{kJ mol}^{\ --1} \times 298\ \text{K} = 2.4775\ \text{kJ mol}^{\ --1} = 2.5\ \text{kJ mol}^{\ --1}.$$

Therefore, $\Delta U^{\theta}\ \ (\text{A\&B}) = \Delta H^{\theta}\,(\text{A\&B})\ \&2.5\ \text{kJ mol}^{\ --1}$.

For example, for H & H bond in H_2, $\Delta H^{\theta}\,(\text{H\&H}) = 436\ \text{kJ mol}^{--1}$. Therefore,

$$\Delta U^{\theta}\ \ (\text{H\&H}) = 436\ \text{kJ mol}^{--1} - 2.5\ \text{kJ mol}^{\ --1}.= 433.5\ \text{kJ mol}^{--1}$$

From the above example it is clear that in general the values of ΔH^{θ} (A&B) and ΔU^{θ} (A&B) differ only slightly. Therefore, for all practical purposes the two terms are used interchangeably.

Enthalpy of atomization

The enthalpy change in converting one mole of a substance into its constituent atoms in gaseous states is called the ***enthalpy of atomization*** or heat of atomization of that substance.

(1) Enthalpy of atomization of a diatomic molecule. The enthalpy of atomization of a diatomic molecule is equal to its enthalpy of dissociation $\Delta_d H$ Thus:

$$H_2\,(g) \longrightarrow 2\,H\,(g) \qquad \Delta_a H\,(H_2) = 436\text{ kJ mol}^{-1}$$

$$O_2\,(g) \longrightarrow 2\,O\,(g) \qquad \Delta_a H\,(O_2) = 498\text{ kJ mol}^{-1}$$

(2) Enthalpy of atomization of a polyatomic molecule

The enthalpy of atomization of a polyatomic molecule of a compound is equal to the enthalpy change to breaking all the covalent bonds so that gaseous constituent atoms are produced. The enthalpy of atomization of CH_4 is 1664 kJ mol^{-1}. which is equal to the enthalpy change associated with the breaking of the four C–H bonds per mole of CH_4 molecules.

$$CH_4\,(g) \longrightarrow C(g) + 4\,H(g) \qquad \Delta_a H\,(CH_4) = 1664\text{ kJ mol}^{-1}$$

(3) The **enthalpy of atomization** of a solid element is equal to its heat of sublimation.

$$C\text{ (graphite, solid)} \longrightarrow C\text{ (gas)} \qquad \Delta_a H = 716.67\text{ kJ mol}^{-1} = \Delta_{sub}H(C)$$

(A) Calculation of C–H bond energy from thermochemical data

The simplest molecule involving only C–H bonds is methane (CH_4) Therefore, the bond energy of C–H bond is calculated from the thermochemical data (enthalpy of atomization) of methane.

$$CH_4\,(g) \longrightarrow C\,(g) + 4\,H(g) \qquad \text{....(A)}$$

$$\Delta H(\text{C–H}) = \frac{\Delta_a H(CH_4)}{4}$$

But the enthalpy of atomization of methane is equal to the enthalpy of reaction (A)

$$\Delta_a H\,(CH_4) = \Delta_r H\,(A)$$

Now, $\Delta_r H\,(A) = \Delta_f H\,(C, g) + 4\,\Delta_f H\,(H) - \Delta_f H\,(CH_4)$

$$= 716.\,7\text{ kJ mol}^{-1} + 4\times 218\text{ kJ mol}^{-1} - (-74.8\text{ kJ mol}^{-1})$$

$$= 1663.5\text{ kJ mol}^{-1} = \Delta_a H\,(CH_4)$$

Therefore, $\Delta H(\text{C–H}) = \dfrac{\Delta_a H(CH_4)}{4}$

$$= \frac{1663.5\text{ kJ mol}^{-1}}{4}$$

$$= 415.87\text{ kJ ml}^{-1}$$

The actual value of ΔH(C–H) is 414 kJ mol^{-1}

(B) Calculation of C–C bond energy from thermochemical data

The simplest molecule involving C – C bond (along with 6 C–H bonds) is ethane (C_2H_6) Therefore, the value of enthalpy of C– C bond is calculated from the thermochemical data (enthalpy of atomization) of ethane and C–H bond enthalpy (= 414 kJ mol^{-1}).

$$H_3C - CH_3\,(g)\,. \longrightarrow 2\,C\,(g) + 6\,H(g) \qquad .(B)$$

But $\Delta_a H\,(C_2H_6) = \Delta_r H\,(B)$

Now enthalpy of reaction (B) is the enthalpy of atomization of ethane which is the energy needed to break one mole C–C bonds and six moles C–H bonds in one mole of ethane. Thus

$$\Delta_a H\,(C_2H_6) = \Delta_r H\,(B) = \Delta H(C\text{–}C) + 6\,\Delta H(C\text{–}H)$$

Therefore, $\Delta H(C\text{–}C) = \Delta_r H\,(B) - 6\,\Delta H(C\text{–}H)$

Now $\Delta_r H\,(B) = 2\,\Delta_f H\,(C, g) + 6\,\Delta_f H\,(H) - \Delta_f H\,(C_2H_6, g)$

$$= 2\times716.7 \text{ kJ mol}^{-1} + 6\times 218 \text{ kJ mol}^{-1} - (-85.6 \text{ kJ mol}^{-1})$$

$$= 2827 \text{ kJ mol}^{-1}$$

Therefore, $\Delta H(C\text{–}C) = \Delta_r H\,(B) - 6\,\Delta H(C\text{–}H)$

$$= 2827 \text{ kJ mol}^{-1} - 6\times214 \text{ kJ mol}^{-1}$$

$$= 2827 \text{ kJ mol}^{-1} - 2484 \text{ kJ mol}^{-1} = 343 \text{ kJ mol}^{-1}$$

(C) Calculation of C=C bond energy from thermochemical data

The simplest molecule involving C = C bond along with 4 C–H bonds is ethene (C_2H_4) Therefore, enthalpy of C = C bond is calculated from the thermochemical data (enthalpy of atomization) of ethene and C–H bond enthalpy.

$$H_2C = CH_2\,(g) \longrightarrow 2\,C\,(g) + 4\,H(g) \qquad \text{….(C)}$$

The enthalpy of reaction (*C*) is the enthalpy of atomization of ethene which is the energy needed to break one mole C = C bonds and four moles C–H bonds in one mole of ethene. Thus

$$\Delta_a H\,(C_2H_4) = \Delta_r H\,(C) = \Delta H\,(C = C) + 4\,\Delta H\,(C\text{–}H)$$

Therefore, $\Delta H(C = C) = \Delta_r H\,(C) - 4\Delta\,H(C\text{–}H)$

Now, $\Delta_r H\,(C) = 2\,\Delta_f H\,(C, g) + 4\,\Delta_f H\,(H) - \Delta_f H\,(C_2H_4, g)$

$$= 2\times716.7 \text{ kJ mol}^{-1} + 4\times 218 \text{ kJ mol}^{-1} - (+52.3 \text{ kJ mol}^{-1})$$

$$= 2253 \text{ kJ mol}^{-1}$$

Therefore, $\Delta H(\mathrm{C{=}C}) = \Delta_r H\,(C) - 4\,\Delta H(\mathrm{C{-}H})$

$= 2827\ \mathrm{kJ\ mol^{-1}} - 4 \times 414\ \mathrm{kJ\ mol^{-1}}$

$= 597\ \mathrm{kJ\ mol^{-1}}$

The actual value of $\Delta H(\mathrm{C{=}C})$ is 611 kJ $\mathrm{mol^{-1}}$

(D) Calculation of C ≡C bond energy from thermo chemical data

The simplest molecule involving C ≡ C bond (along with 2 C–H bonds) is ethyne (C_2H_2) Therefore, enthalpy of C≡C bond is calculated from the thermochemical data (enthalpy of atomization) of ethyne and C–H bond enthalpy

$$\mathrm{H - C \equiv C - H\,(g)} \longrightarrow \mathrm{2\,C\,(g) + 2\,H(g)} \qquad \text{(D)}$$

The enthalpy of reaction (D) is the enthalpy of atomization of ethyne which is the energy needed to break one mole C≡C bonds and two moles C–H bonds in one mole of ethyne. Thus

$$\Delta_a H\,(C_2H_2) = \Delta_r H\,(\mathrm{D}) = \Delta H(\mathrm{C{\equiv}C}) + 2\,\Delta H(\mathrm{C{-}H})$$

Therefore, $\Delta H(\mathrm{C{\equiv}C}) = \Delta_r H\,(\mathrm{D}) - 2\Delta H(\mathrm{C{-}H})$

Now, $\Delta_r H\,(\mathrm{D}) = 2\,\Delta_f H\,(\mathrm{C, g}) + 2\,\Delta_f H\,(\mathrm{H}) - \Delta_f H\,(C_2H_{2,}\,\mathrm{g})$

$= 2 \times 716.67\ \mathrm{kJ\ mol^{-1}} + 2 \times 218\ \mathrm{kJ\ mol^{-1}} - (+226.7\ \mathrm{kJ\ mol^{-1}})$

$= 1642.7\ \mathrm{kJ\ mol^{-1}}$

Therefore, $\Delta H(\mathrm{C \equiv C}) = \Delta_r H\,(\mathrm{D}) - 2\,\Delta H(\mathrm{C{-}H})$

$= 1642.7\ \mathrm{kJ\ mol^{-1}} - 2 \times 414\ \mathrm{kJ\ mol^{-1}}$

$= 814.7\ \mathrm{kJ\ mol^{-1}}$

The actual value of $\Delta H(\mathrm{C \equiv C})$ is 837 kJ $\mathrm{mol^{-1}}$

Table 2. Single bond enthalpy data (ΔH^{Θ}) expressed in kJ mol $^{-1}$

A –B	**H**	**C**	**N**	**O**	**F**	**Si**	**P**	**S**	**Cl**	**Br**	**I**
H	436				569			339	431	368	297
C	414	347	293	351	439	289	264	259	330	276	238
N	389			201	272		209		201	243	
O	464			138	184				205		
F					159						
Si	293	289		368	540	176	213	226	360	289	213
P	318	264		351	490		213	230	331	272	213
S		259			327			213	251	213	
Cl				205	255				243		
Br					197				218	192	
I				201					209	180	151

Method to find the enthalpy of a bond from the table

- In the table the values of bond enthalpy are given for the bonds which are written as A – B, for example as

  C – C, N – H, O – H, H – Cl, S – F

- Select the first atom (A) of the desired bond from the vertical column and the second atom (B) of the bond from the horizontal row.
- The value on the right side of the first atom and below the second atom is the bond enthalpy of the desired bond.

Illustration of the method: To find the bond enthalpy of the S – F bond, select S from the vertical column and F from the horizontal row. The value on the right of S and below F is the bond enthalpy of S – F bond. Thus,

ΔH^{θ} (S – F) = 327 kJ mol $^{--1}$

Table 3. Bond enthalpy data (ΔH^{Θ}) expressed in kJ mol $^{-1}$ for double and triple bonds

Bond	C=C	C=O	C=N	N=N	O=O	C≡C	C≡O	N≡N	C≡N
ΔH^{Θ}	611	741	615	418	498	837	1070	946	891

Note: The bond energy of a bond is assumed to be the same irrespective of the type of the molecule in which this bond is present. For example, the bond energy of a C – H bond is assumed to be the same whether it is present in a hydrocarbon or carboxylic acid or alcohol or aldehyde etc.

CALCULATION OF ENTHALPY OF REACTIONS FROM BOND ENTHALPY DATA

. The enthalpy of a reaction is given by the relation

. $\Delta_r H^\ominus = \sum$Bond enthalpy of reactants – $\sum$Bond enthalpy of products

Example: Use the bond enthalpy data to calculate the enthalpy change for the combustion of *n*-propane (C_3H_8) represented by the reaction

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

Bond	**C –C**	**C –H**	**O –H**	**C = O**	**O = O**
ΔH $^\ominus$ **(bond)/ kJ mol**$^{-1}$	**347**	**414**	**464**	**741**	**498**

Solution. The given reaction $C_3H_8(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$ may be represented in terms of breaking of bonds in reactants and formation of bonds in products as follows:

$$CH_3 — CH_2 — CH_3 + 5\,O = O \longrightarrow 3\;\; O = C = O \;+\; 4\,H–O–H$$

The enthalpy of reaction ($\Delta_r H^\ominus$) and bond enthalpies of reactant and product are related by

. $\Delta_r H^\ominus = \Sigma$ Bond enthalpy of reactants $- \Sigma$ Bond enthalpy of products

The given reaction involves breaking of three C–C bonds, eight C–H bond in C_3H_8 and five O = O bond in O_2. Therefore,

$$\Sigma\text{Bond enthalpy of reactants} = 3\,\Delta H^\ominus(C–C) + 8\,\Delta H^\ominus(C–H) + 5\,\Delta H^\ominus(O = O)$$

$$= 3 \times 347\ \text{kJ mol}^{-1} + 8 \times 414\ \text{kJ mol}^{-1} + 5 \times 498\ \text{kJ mol}^{-1}$$

$$= 6843\ \text{kJ mol}^{-1}$$

The given reaction involves formation of six C=O bonds in CO_2, four O–H bonds in H_2O. Therefore,

$$\Sigma\text{Bond enthalpy of products} = 6\,\Delta H^\ominus(C = O) + 8\,\Delta H^\ominus(O – H)$$

$$= 6 \times 741\ \text{kJ mol}^{-1} + 8 \times 464\ \text{kJ mol}^{-1}$$

$$= 8158\ \text{kJ mol}^{-1}$$

Therefore, . $\Delta_r H^\Theta = \Sigma$ Bond enthalpy of reactants $- \Sigma$ Bond enthalpy of products

. . $= 6843 \text{ kJ mol}^{-1} - 8158 \text{ kJ mol}^{-1}$

$= -1315 \text{ kJ mol}^{-1}$

Enthalpy of physical transformation

The process by which a substance is changed from one physical state into its another physical state is called ***physical transformation*** or phase transformation. Here we shall discuss the processes of vaporization, fusion and sublimation and the related enthalpy changes.

(A) Enthalpy of vaporization

The quantity of heat absorbed for complete conversion of one mole of a liquid in to vapour at its boiling point is called its ***enthalpy of vaporization***. It is denoted by $\Delta_{vap}H$. The enthalpy of vaporization is called the ***heat of vaporization*** also..

The enthalpy of vaporization per mole of water at 373 K is 40.70 kJ

$$H_2O(l) \longrightarrow H_2O(v) \qquad \Delta_{vap}H = 40.70 \text{ kJ mol}^{-1}$$

Latent heat of vaporization: The heat absorbed to convert one gram liquid into vapour is called ***latent heat*** of vaporization. The latent heat of vaporization of water is 2.26 kJ per gram at 100 ^oC. This means that 1 g of liquid water at 100 ^oC will absorb 2.26 kilojoules of heat to be converted into 1 g of water vapour at 100 ^oC. Since no change of temperature is involved the absorbed heat is stored in water molecules in vapour state. That is why this is called latent heat.

(B) Enthalpy of fusion

The quantity of heat absorbed for complete conversion of one mole of solid into liquid.at its melting point is called its ***enthalpy of fusion***. The enthalpy of fusion is denoted by $\Delta_{fus}H$ It is called heat of fusion also. The enthalpy of fusion of water is 6.01 kJ mol^{-1} at 273 K and 1 atm.

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta_{fus}H = 6.01 \text{ kJ mol}^{-1}$$

Latent of fusion of ice is 334 J g^{-1}

(C) Enthalpy of sublimation

The quantity of heat absorbed for complete conversion of one mole of solid directly into vapour is called ***enthalpy of sublimation*** or heat of sublimation. The enthalpy of sublimation of a substance is denoted by $\Delta_{sub}H$

According to Hess's law of constant heat summation, the enthalpy of sublimation is equal to the sum of the enthalpy of fusion and the enthalpy of vaporization of the same substance (all the quantities refer to same temperature)

$$\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$$

For example, the enthalpy of sublimation of naphthalene is computed as follows.

Aim : Naphthalene(s) $\longrightarrow$ Naphthalene (v) $\Delta_{sub}H = ?$ (to be calculated

Data given

Naphthalene(s) $\longrightarrow$ Naphthalene(l) $\Delta_{fus}H = 22.4$ kJ mol^{-1} (i)

Naphthalene(l) $\longrightarrow$ Naphthalene(v) $\Delta_{vap}H = 48.5$ kJ mol^{-1} (ii)

On adding equations (i) and (ii) we get

Naphthalene(s) + Naphthalene(l) $\longrightarrow$ Naphthalene(l) + Naphthalene(v)

On canceling the common terms on the two sides of the above equation, we have

Naphthalene(s) $\longrightarrow$ Naphthalene (v) (iii)

and $\Delta H(\text{iii}) = \Delta H(\text{i}) + \Delta H(\text{i})$

or, $\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$

$= 22.4 \text{ kJ mol}^{-1} + 48.5 \text{ kJ mol}^{-1}$

$=70.9 \text{ kJ mol}^{-1}$

Temperature dependence of reaction enthalpy (Kirchhoff's equation)

Statement Variation of reaction enthalpy (ΔrH, heat of reaction) with temperature is called ***Kirchhoff's equation.*** It is stated as follows

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_P = \Delta_r C_P$$

$d\Delta_r H = \Delta_r C_p \, dT$ at constant pressure

Where

$\Delta_r H$ = reaction enthalpy (heat of reaction at constant pressure)

and $\Delta_r C_p$ = reaction heat capacity at constant pressure

$= \Sigma\, C_p(\text{products}) - \Sigma C_p\,(\text{reactants})$

Similarly, for the heat of reaction at constant volume the Kirchhoff's equation is given by

$d\,\Delta_r U = \Delta_r C_V \, dT$ at constant volume

Relevance of Kirchhoff's equation Standard enthalpy of reaction (heat of reaction at 298 K and at 1 bar) is calculated using the standard enthalpy of formation data of reactants and products given in the International tables. But when it is required to find the enthalpy of reaction at other temperatures then we use Kichhoff's equation.

Derivation of Kirchhoff's equation

Let us consider a familiar reaction of synthesis of ammonia from nitrogen and hydrogen as represented by chemical equation

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

The standard enthalpy of this reaction is given by

$$\Delta_r H^{\upsilon} = 2\times H^{\Theta}_{m}(NH_3) - [H^{\Theta}_{m}(N_2) + 3\times H^{\Theta}_{m}(H_2)$$

On differentiating the above equation with respect to T at constant P, we get

$$\left(\frac{\partial \Delta_r H^{\Theta}}{\partial T}\right)_P = 2\left(\frac{\partial H^{\Theta}_{m}(NH_3)}{\partial T}\right)_P - \left[\left(\frac{\partial H^{\Theta}_{m}(N_2)}{\partial T}\right)_P + 3\left(\frac{\partial H^{\Theta}_{m}(H_2)}{\partial T}\right)_P\right]$$

By definition

$$\left(\frac{\partial H^{\Theta}_{m}}{\partial T}\right)_P = C^{\Theta}_{p,m} = \text{Standard molar heat capacity at constant pressure}$$

Therefore, $$\left(\frac{\partial \Delta_r H^{\Theta}}{\partial T}\right)_P = 2\,C^{\Theta}_{p,m}(NH_3) - [C^{\Theta}_{p,m}(N_2) + 3\,C^{\Theta}_{p,m}(H_2)]$$

$$= \Sigma\, C^{\Theta}_{p}\,(\text{products}) - \Sigma\, C^{\Theta}_{p}\,(\text{reactants})$$

$$= \Delta_r C^{\Theta}_{p}$$

Or, $$d\,\Delta_r H^{\upsilon} = \Delta_r C^{\Theta}_{p}\, dT$$

It is differential form of Kirchhoff's equation

Integarated form of Kirchhoff's equation

Case I. When heat capacity is independent of temperature, $\Delta_r C^{\Theta}_{p}$ is constant and integration of Kirchhoff's equation gives

$$\int_1^2 d\Delta_r H^{\Theta} = \Delta_r C^{\Theta}_{p} \int_1^2 dT$$

Or, $$\Delta_r H^{\upsilon}\ (\text{at } T_2) - \Delta_r H^{\upsilon}\ (\text{at } T_1) = \Delta_r C^{\Theta}_{p}(T_2 - T_1)$$

Or, $$\Delta_r H^{\upsilon}\ (\text{at } T_2) = \Delta_r H^{\upsilon}\ (\text{at } T_1) + \Delta_r C^{\Theta}_{p}(T_2 - T_1)$$

It is integrated form of Kirchhoff's equation. From this equation the value of enthalpy of reaction at any temperature T_2 can be calculated provided its value at a temperature T_1 is known and the molar heat capacities of reactants and products are also known

Similarly, the Kirchhoff's equation for heat of reaction at constant volume is given by

$$\Delta_r U^{\upsilon} \text{ (at } T_2) = \Delta_r U^{\upsilon} \text{ (at } T_1) + \Delta_r C_v^{\Theta} (T_2 - T_1)..$$

Kirchhoff's equation for any general reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

is given by

$$\Delta_r H^{\upsilon} \text{ (at } T_2) = \Delta_r H^{\upsilon} \text{ (at } T_1) + \Delta_r C_p^{\Theta} (T_2 - T_1)$$

where,

$$\Delta_r C_p^{\Theta} = \Sigma\, C_p^{\Theta} \text{ (products)} - \Sigma\, C_p^{\Theta} \text{ (reactants)}$$

$$= [c\,C_{p,m}^{\Theta}(\mathrm{C}) + d\, C_{p,m}^{\Theta}(\mathrm{D})] - [a\,C_{p,m}^{\Theta}(\mathrm{A}) + b\,C_{p,m}^{\Theta}(\mathrm{B})]$$

Case II. When molar heat capacity depends on temperature as

$$C_{p,m}^{\Theta} = \alpha + \beta T + \gamma T^2$$

the heat capacity of reaction is given by

$$\Delta_r C_{p,m}^{\Theta} = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2$$

where

$$\Delta\alpha = [c\alpha + d\,\alpha\,] - [a\,\alpha + b\,\alpha\,]$$

$$\Delta\,\beta = [c\,\beta + d\,\beta\,] - [a\,\beta + b\,\beta\,]$$

$$\Delta\,\gamma = [c\,\gamma + d\,\gamma\,] - [a\,\gamma + b\,\gamma\,]$$

On ignoring integrating Kirchhoff's equation we shall get

$$\int_1^2 \mathrm{d}\Delta_r H^{\Theta} = \int_1^2 \Delta_r C_p^{\Theta}\, \mathrm{d}T$$

$$= \int_1^2 \Delta\,\alpha\, \mathrm{d}T + \int_1^2 \Delta\,\beta\, T\mathrm{d}T + \int_1^2 \Delta\,\gamma\; T^2\mathrm{d}T$$

$$\Delta_r H^{\upsilon} \text{ (at } T_2) - \Delta_r H^{\upsilon} \text{ (at } T_1) = \Delta\,\alpha\,(T_2 - T_1) + \frac{1}{2}\,\Delta\beta\; T_2^2 - T_1^2 + \frac{1}{3}\,\Delta\gamma\; T_2^3 - T_1^3$$

Or, $$\Delta_r H^{\upsilon} \text{ (at } T_2) = \Delta_r H^{\upsilon} \text{ (at } T_1) + \Delta\alpha\,(T_2 - T_1) + \frac{1}{2}\,\Delta\beta\; T_2^2 - T_1^2 + \frac{1}{3}\,\Delta\gamma\; T_2^3 - T_1^3$$

This equation is used to calculate accurate value of reaction enthalpy at any temperature T_2 when the value at a temperature T_1 and the values of heat capacities of reactants are known

Example: The enthalpy of decomposition of gaseous water at 298 K and 1 bar is 241.75 kJ mol^{-1}. Calculate its value at 348 K. The molar heat capacity values in JK^{-1} mol^{-1} are: $C^{\Theta}_{p,m}$ (H_2O) = 33.56, $C^{\Theta}_{p,m}$ (O_2) = 29.12, $C^{\Theta}_{p,m}$ (H_2) = 28.82.

Solution. Kirchhoff's equation $\Delta_r H^{\upsilon}$ (at T_2) = $\Delta_r H^{\upsilon}$ (at T_1) + $\Delta_r C^{\Theta}_{p}(T_2 - T_1)$ is used to perform the calculation

For the decomposition of water $H_2O\,(g) \longrightarrow H_2\,(g) + \frac{1}{2}\,O_2\,(g)$

$$\Delta_r H^{\upsilon} \text{ (298 K)} = 241.75 \text{ kJ mol}^{-1}$$

$$\Delta_r C^{\Theta}_{p} = C^{\Theta}_{p,m}(H_2) + \tfrac{1}{2}\, C^{\Theta}_{p,m}(O_2) - C^{\Theta}_{p,m}(H_2O)$$

$$= 28.82 \text{ JK}^{-1}\text{ mol}^{-1} + \tfrac{1}{2}\,(29.12 \text{ JK}^{-1}\text{ mol}^{-1}) - 33.56 \text{ JK}^{-1}\text{ mol}^{-1}$$

$$= 9.83 \text{ JK}^{-1}\text{ mol}^{-1} = 9.83 \times 10^{-3} \text{ k JK}^{-1}\text{ mol}^{-1}$$

Therefore, $$\Delta_r H^{\upsilon} \text{ (348 K)} = \Delta_r H^{\upsilon} \text{ (298 K)} + \Delta_r C^{\Theta}_{p}(T_2 - T_1)$$

$$= 241.75 \text{ kJ mol}^{-1} + 9.83 \times 10^{-3} \text{ kJK}^{-1}\text{ mol}^{-1}\ (348 \text{ K} - 248 \text{ K})$$

$$= 242.24 \text{ kJ mol}^{-1}$$

CONFIDENCE BUILDING QUESTIONS ON THERMOCHEMISTRY

(A) Complete the following statements using a correct word/term from the list:

[exothermic, ΔH, endothermic, ΔU, negative, positive, element, bond enthalpy, enthalpy of fusion, sublimation, liberated, zero, $\Delta \nu_g RT$, diatomic, Kirchhoff's, exothermic]

1. Heat of reaction at constant pressure is equal to ----------------

2. Heat of reaction at constant volume is equal to the change of ----------------

3. Heat is liberated in an …………. thermic process

4. In an exothermic reaction the value of ΔH is ----------------

5. The standard enthalpy of formation of ……………. is zero.

6. The average of bond dissociation enthalpies of a bond in different chemical species is called its …………

7. In a combustion reaction heat is …………..

8. Cooling in the surroundings is observed in an ………….thermic process

9. Enthalpy of sublimation = enthalpy of vaporization + --------

10. In an endothermic process ΔH is ---------------

11. ΔH is negative in an -------------------- process.

12. The standard enthalpy of formation of an element is ------------

13. In -------------- molecules the bond dissociation enthalpy is equal to bond enthalpy.

14. The enthalpy change for the process C (graphite) $\longrightarrow$ C (gas) is called the enthalpy of -------------

15. The difference of ΔH and. ΔU in a chemical reaction is equal to ---------------

16. The expression $\mathrm{d}\,\Delta_r H^{\ominus} = \Delta_r C_p^{\ominus}\,\mathrm{d}T$ is the differential form of ------------- equation

(B) Short answer questions:

1. Define the following

(a) Enthalpy of sublimation

(b) Enthalpy of combustion

(c) Standard enthalpy of formation of a compound

(d) Enthalpy of neutralization

(e) Enthalpy of atomization

2. What is the basic difference between the heat of formation and heat of reaction?

3. Enthalpy of formation is enthalpy of reaction but every enthalpy of reaction need represent enthalpy of formation. Illustrate with suitable examples.

4. Give a very brief description of exothermic and endothermic reactions.

5. State the Hess's law of constant heat summation.

6. Write a relation between the reaction enthalpy ($\Delta_r H$) and the standard enthalpies of formation of reactants and products for $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

7. Write a relation between the change in enthalpy ($\Delta_r H$) and the change in internal energy ($\Delta_r U$) for the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

8. Derive the relation between q_p and q_v in a chemical reaction involving gaseous species.

9. How are the bond dissociation enthalpies and bond enthalpy of C–H bond in methane (CH_4) are related?

10. An exothermic reaction is allowed to occur very rapidly in air. Will the temperature of air increase or decrease?

11. An endothermic reaction is allowed to occur very rapidly in air. Will the temperature of air increase or decrease?

12. Evaporation of acetone causes cooling effect in the surroundings. Is this process endothermic or exothermic?

13. Illustrate the following with suitable examples :

(i) Exothermic process

(ii) Endothermic process

(iii) Standard state of a gas

(iv) Thermochemical equation

(v) Hess's law of constant heat summation

(vi) Enthalpy of hydrogenation

14. Write the relationship showing the variations of enthalpy of reaction with temperature

(C) Numerical problems

1. Calculate the enthalpy of combustion of glucose from the following data :

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

(ii) $H_2(g) + 0.5\ O_2(g) \longrightarrow H_2O\ (l)$ $\Delta_r H = -\ 286$ kJ mol^{-1}

(iii) $6\ C\ (\text{graphite}) + 6\ H_2(g) + 3\ O_2(g) \longrightarrow C_6H_{12}O_6\ (s)$ $\Delta_r H = -1260$ kJ mol^{-1}

[Ans. Application of Hess's law gives $\Delta_c H = -2817$ kJ mol^{-1}]

2. Calculate the enthalpy change of the reaction $C_2H_2\ (g) + H_2\ (g) \longrightarrow C_2H_4\ (g)$at 298 K when the enthalpy of combustion data are $\Delta_c H\ (H_2, g) = -286$ kJ mol^{-1}, $\Delta_c H\ (C_2H_2, g) = -1300$ kJ mol^{-1}, $\Delta_c H\ (C_2H_4, g) = -\ 1411$ kJ mol^{-1} **[Ans: – 175 kJ mol^{-1}]**

3. The standard enthalpy of formation of CH_4 (g), CO_2(g) and H_2O (g) are –74.8, – 393.5 and – 241.6 kJ mol^{-1} respectively. Calculate the enthalpy change on burning 1 m^3 of methane measured under standard conditions. **[Ans. $\Delta_r H = -\ 35799.1$ kJ mol^{-1}]**

4.. Calculate the enthalpy of formation of ethane when its enthalpy of combustion is – 1560 kJ mol^{-1} and $\Delta_f H\ (CO_2) = -393.5$ kJ mol^{-1} and $\Delta_f H\ (H_2O) = -285.8$ kJ mol^{-1}

[Ans: $\Delta_f H\ (C_2H_6) = -\ 84.4$ kJ mol^{-1}]

5. What is the difference between $\Delta_r H$ and $\Delta_r U$ at 298 K for the reaction

$$2\ C_6H_6(l) + 15\ O_2\ (g) \longrightarrow 12\ CO_2\ (g) + 6H_2O\ (l)$$

[Ans. – 7.43 kJ mol^{-1}]

6. Using the given data calculate the C–H bond energy in CH_4 :

Species :	CH_4 (g)	C (g)	H (g)
$\Delta_f H$ /kJ mol^{-1} :	– 74.8	716.7	218

[Ans. 415.87 kJ mol^{-1}]

7.. If the enthalpy of the reaction $H_2\ (g) + Cl_2\ (g) \longrightarrow HCl\ (g)$ at 293 K is – 91.2 kJ mol^{-1} what will be its value at 313 K. The molar heat capacities at constant pressure of H_2 (g), Cl_2 (g) and HCl (g) are 29.3, 34.7 and 28.9 JK^{-1} mol^{-1} respectively. **[Application of Kirchhoff's equation gives $\Delta_r H$ (313 K) = – 91.324 kJ mol^{-1}]**

8. The enthalpy of reaction $N_2 + 3\ H_2 \longrightarrow 2\ NH_3$ at 27 ^{0}C was found to be – 91.94 kJ mol^{-1}. What will be its value at 50 ^{o}C. The molar heat capacities at constant pressure and at 27 ^{o}C for N_2, H_2 and NH_3 are 28.45, 28.32 and 37.07 J K^{-1} mol^{-1} respectively.

[Ans: Application of Kirchhoff's equation gives $\Delta_r H$ (313 K) = – 92.843 kJ mol^{-1}]

9. The enthalpy of neutralization of CH_3COOH with NaOH is –51.63 kJ mol^{-1} Calculate the enthalpy of ionization of CH_3COOH. Assume that the enthalpy of neutralization of HCl with NaOH is –57.35 kJ mol^{-1}.

[Ans: For $CH_3COOH(aq) \leftrightarrows H^+ (aq) + CH_3COO^- (aq)$, $\Delta_r H = 5.72$ kJ mol^{-1}]

10. Calculate the enthalpy change for the polymerization of ethyne to benzene at 298 K as represented by the reaction. $3\ C_2H_2\ (g) \longrightarrow C_6H_6(l)$ when

$$C_6H_6\ (l) + 7.5\ O_2 \longrightarrow 3H_2O\ (l) + 6CO_2\ (g) \qquad \Delta_c H^{\ominus} = -3267.70 \text{ kJ mol}^{-1}$$

$$C_2H_2\ (g) + 2.5\ O_2(g) \longrightarrow 2CO_2\ (g) + H_2O(l) \qquad \Delta_c H^{\ominus} = -1299.55 \text{ kJ mol}^{-1}$$

[Ans: Application of Hess's law gives $\Delta_r H^{\ominus} = -630.95$ kJ mol^{-1}]

11. Calculate the standard enthalpy of formation of methane using the following data:

(i) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta_c H^{\ominus} = -890.35$ kJ mol^{-1}

(ii) $H_2(g) + \frac{1}{2}O_2 \rightarrow 2H_2O(l) \qquad \Delta_c H^{\ominus} = -285.84$ kJ mol^{-1}

(iii) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_c H^{\ominus} = -393.50$ kJ mol^{-1}

[Ans: Application of Hess's law gives $\Delta_f H^{\ominus}$ (CH_4) = 74.83 kJ mol^{-1}]

12. Find an expression for the variation of heat capacity of a reaction with temperature if the variation of its enthalpy change with temperature is expressed by $\Delta_r H^{\ominus} = A - BT - CT^2 - \frac{D}{T}$, where *A, B, C, D* are constants.

[**Ans:** $\Delta_r C_p^{\ominus} = \left(\frac{\partial \Delta_r H^{\ominus}}{\partial T}\right)_P = -B - 2\,CT + \frac{D}{T^2}$]

13. The standard enthalpy of combustion of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are – 241, – 3800 and – 3920 kJ mol^{-1} respectively at 298 K. Calculate the enthalpy of hydrogenation of cyclohexene in to cyclohexane. **[Ans. –121 kJ mol^{-1}]**

SECOND LAW OF THERMODYNAMICS

Limitations of the first law of thermodynamics and Need of the second law

The first law of thermodynamics enables us to compute the energy changes (ΔU) and enthalpy changes (ΔH) for different types of chemical reactions and physical transformations. But this law is not capable of predicting the direction of a process. From the first law of thermodynamics we cannot get the answers of the following type of questions:

- Why do changes take place in a particular direction?
- How and why the systems are aware to proceed only in the particular direction?
- What are the driving forces which lead the process in a given direction?

Therefore, to answer such questions we need a second law of thermodynamics. This law introduces the concept of entropy and the methods of evaluating entropy changes which in turn act as driving force for spontaneous processes in isolated systems..

Different statements of the second law of thermodynamics

The second law of thermodynamics has been stated in different ways. But each statement is related to human experiences and is in agreement with experimental observations.

1. Heat cannot spontaneously pass from a colder to a warmer body. – ***R.J.E. Clausius***
2. Every system left to itself changes rapidly or slowly in such a way to approach definite final state of rest. No system of its own will change away from the state of equilibrium except through the influence of external agencies –***G. N. Lewis***
3. Entropy is time's arrow. –***A. Edington***
4. The state of maximum entropy is the most stable state for an isolated system. –***Enrico Fermi***
5. In an irreversible process the total entropy of all bodies concerned is increased. –***G.N. Lewis***
6. The entropy function of a system of bodies tends to increase in all possible processes occurring in nature, if we include in the system all such bodies which are affected by the changes. – ***M.N. Saha***
7. There exists a characteristic thermodynamic property called entropy. The difference in entropies of the system in states 1 and 2 is given by

$$S_2 - S_1 = \int \frac{dq_{\text{rev}}}{T} \qquad \text{over a reversible path}$$

$$S_2 - S_1 > \int \frac{dq_{\text{irr}}}{T} \qquad \text{over an irreversible path}$$

The entropy is property of state only. Its value for an isolated system never decreases. – ***R. E. Gibson***

Concept of entropy

Entropy is a Greek word which stands for *trope* meaning chang*e;* a prefix 'en' is written to identify it as a thermodynamic property which belongs to the family of energy and enthalpy. This term was introduced by Clausius. He denoted entropy by the symbol *S* in the honour of Sadi Carnot (*S* from *Sadi).*

We know that energy is defined as the capacity of a system to do work. But entropy of a system is considered as an index of exhaustion of its capacity to do work. Thus entropy is a measure of unavailable portion of energy. On this basis entropy has been used to represent randomness. Greater is the randomness larger is the value of entropy. More regular is the molecular arrangement lower is the value of entropy. Thus, the entropy of a substance in gaseous state is greater than in the liquid state and that is greater than in its solid state. That is,

$$S\text{ (gas)} > S\text{ (liquid)} > S\text{ (solid)}$$

Characteristics of entropy

1. Entropy is an extensive property. Its value depends upon the amount of the substances present in the system.

2. Entropy of a system is a state function. It depends only on the state variables *(T, P, V, n).* Thus, the change of entropy is given by $\Delta S = S$ (final) – S (initial)

3. Entropy change of system (ΔS_{system}) does not depend on the path followed by the change, but the entropy change of the surroundings ($\Delta S_{\text{surronnd1ngs}}$) depends upon the path.

4. The total entropy change of an isolated system is equal to the sum of the entropy change of system and the entropy change of the surroundings.

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

The total entropy change of an isolated system is also called the entropy change of the ***univers***e ($\Delta S_{\text{universe}}$)

5. In a reversible process $\Delta S_{\text{system}} = -\Delta S_{\text{urroundings}}$

6. In an irreversible process $\Delta.S_{\text{total}} > 0$. This implies that in spontaneous changes there is increase of entropy of universe.

Entropy is the ratio of heat and temperature. Since heat is expressed as joule (J) and temperature is expressed in kelvin (K), therefore, the entropy and change in entropy is expressed as Joules per kelvin ≡J K^{-1}

Notes

(i) If the amount of the substance is one mole, then entropy and its changes are expressed as joules per kelvin per mole (J K^{-1} mol^{-1}).

(ii) Calories per kelvin = cal K^{-1} is the non-SI unit of entropy.

Background of using $dS = \frac{dq_{rev}}{T}$ *as definition of entropy change of the system*

Historically the above relation was introduced by Clausius via Carnot cycle. . But in the present discussion we shall give another logical basis of introducing the definition of entropy in view of the Euler's reciprocity relations for exact differential of state function. First we shall prove that dq_{rev} is inexact differential and then show that dq_{rev} divided by T *i.e.,* dq_{rev} /T is an exact differential

Proof I: dq_{rev} is inexact differential

For a reversible process the first law of thermodynamics is written as

$$\mathrm{d}q_{rev} = \mathrm{d}U + P\,\mathrm{d}V \quad \text{when only } P\text{-}V \text{ work is considered}$$

For an ideal gas $P = n\,RT/V$ and for a monotomic gas $U = 1.5\,n\,RT$ (from kinetic theory of gases) and thus

$$\mathrm{d}U = 1.5\,R\,dT$$

Therefore, $$\mathrm{d}q_{rev} = 1.5\,n\,R\,\mathrm{d}T + \frac{nRT}{V}\mathrm{d}V \qquad \text{(i)}$$

$$= M\,\mathrm{d}T + N\,\mathrm{d}V \qquad \text{in the form of total differential}$$

Where, $M = 1.5\,n\,R$ and $N = \frac{nRT}{V}$

On differentiating M with respect to V at constant T and N with respect to T at constant V, we get

$$\left(\frac{\partial M}{\partial V}\right)_T = \frac{\partial}{\partial V}(1.5\,n\,R\;)_T = 0$$

and $$\left(\frac{\partial N}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)_V = \frac{nR}{V}$$

It is seen that

$$\left(\frac{\partial M}{\partial V}\right)_T \neq \left(\frac{\partial N}{\partial T}\right)_V$$

and thus Euler's reciprocity relation is not valid. Therefore, dq_{rev} is ***inexact differential*** and q_{rev} is a path dependent quantity

Proof II: dq_{rev} */T is exact differential* Let us divide both sides of equation (i) by T to get

$$\frac{dq_{\text{rev}}}{T} = 1.5\, n\, R\, dT + \frac{nR}{V}\,\mathrm{d}V$$

$$= M\,\mathrm{d}T + N\,\mathrm{d}V$$

Where, $M = 1.5\, n\, R$ and $N = \frac{nR}{V}$

On differentiating M with respect to V at constant T and N with respect to T at constant V, we get

$$\left(\frac{\partial M}{\partial V}\right)_T = \frac{\partial}{\partial V}(1.5\, n\, R\,)_{\mathrm{T}} = 0$$

and $$\left(\frac{\partial N}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{nR}{V}\right)_V = 0$$

It is seen that

$$\left(\frac{\partial M}{\partial V}\right)_T = 0 = \left(\frac{\partial N}{\partial T}\right)_V$$

and Euler's reciprocity relation is valid. Therefore, $\mathrm{d}q_{\text{rev}}/T$ is ***an exact differential***

Logical discussion: $\mathrm{d}q_{\text{rev}}/T$ is an exact differential. Therefore, it should represent a total differential of a state function. This state function is represented by S and thus $\mathrm{d}S = \mathrm{d}q_{\text{rev}}/T$

.**Notes**

(i) We have presented the discussion for an ideal gas but the same is applicable for reversible process involving any type of system.

(ii) $\mathrm{d}q_{\text{rev}}$ is an inexact differential and q is path dependent quantity but when it is multiplied by $1/T$, then $\mathrm{d}q_{\text{rev}}/T$ represents a term $\mathrm{d}S$ which is an exact differential. Therefore, $1/T$ is called the ***integrating factor.***

Statement: ***dq_{irr}/T is inexact differential therefore,*** $\mathrm{d}S \neq \mathrm{d}q_{\text{irr}}/T$.

Proof: For an irreversible process the first law of thermodynamics is written as

$$\mathrm{d}q_{\text{irr}} = \mathrm{d}U + P\,\mathrm{d}V$$

For an ideal monotomic gas $\mathrm{d}U = C_{\mathrm{V}}\,\mathrm{d}T = 1.5\, n\, R\, dT$ and in irreversible process $P = P_{\text{ext}}$ =constant

Therefore, $$\mathrm{d}q_{\text{irr}} = 1.5\, n\, R\,\mathrm{d}T + P_{\text{ext}}\,\mathrm{d}V \qquad \text{(i)}$$

Let us divide both sides of equation (i) by T to get

$$\frac{dq_{\text{irr}}}{T} = 1.5\,\frac{nR}{T}\,dT + \frac{P_{\text{ext}}}{T}\,\mathrm{d}V$$

$$= M\,\mathrm{d}T + N\,\mathrm{d}V$$

Where, $M = 1.5\,\frac{nR}{T}$ and $N = \frac{P_{\mathrm{ext}}}{T}$

On differentiating M with respect to V at constant T and N with respect to T at constant V, we get

$$\left(\frac{\partial M}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{nR}{T}\right)_{\mathrm{T}} = 0$$

and $$\left(\frac{\partial N}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{P_{\mathrm{ext}}}{T}\right)_V = -\frac{P_{\mathrm{ext}}}{T^2}$$

It is seen that

$$\left(\frac{\partial M}{\partial V}\right)_T \neq \left(\frac{\partial N}{\partial T}\right)_V$$

That is, Euler's reciprocity relation is not valid. Therefore $\mathrm{d}q_{\mathrm{irr}}/T$ is an inexaxt differential. Hece, $\mathrm{d}S \neq q_{\mathrm{irr}}/T$

Entropy as a state function – a detailed discussion

Entropy (S) is a state function if $\mathrm{d}S$ is an exact differential and $\mathrm{d}S$ is an exact differential if it obeys Euler's reciprocity relation. To prove it let us start with the first law of thermodynamics applied to an ideal gas undergoing a reversible change

$$\mathrm{d}U = \mathrm{d}q_{\mathrm{rev}} - P\mathrm{d}V$$

$$\mathrm{d}q_{\mathrm{rev}} = \mathrm{d}U + P\mathrm{d}V \qquad \text{(i)}$$

Now, energy is a function of temperature and volume, $U = U(T, V)$ and its total differential is given by

$$\boldsymbol{d}\mathbf{U} = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} \mathbf{d}\boldsymbol{T} + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \mathbf{d}\boldsymbol{V}$$

$$= C_{\mathrm{V}}\,\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \mathrm{d}V \qquad \text{(ii)}$$

where, $C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{T}}$ = Heat capacity at constant volume

From equations (i) and (ii), we get

$$\mathrm{d}q_{\mathrm{rev}} = C_{\mathrm{V}}\,\mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \mathrm{d}V + P\mathrm{d}V \qquad \text{(iii)}$$

For an ideal gas

$(\partial U/\partial V)_T = 0$,Joule's law

and $P = nRT/V$

Therefore, $$\mathrm{d}q_{\mathrm{rev}} = C_V\,\mathrm{d}T + \frac{nRT}{V}\mathrm{d}V$$

Or, $$\frac{dq_{\mathrm{rev}}}{T} = \frac{C_V}{T}\,\mathrm{d}T + \frac{nR}{V}\,\mathrm{d}V$$

By definition $\frac{dq_{\mathrm{rev}}}{T} = \mathrm{d}S$

Therefore, small change in entropy (d*S*) is given by the relation

$$\mathrm{d}S = \frac{C_V}{T}\,\mathrm{d}T + \frac{nR}{V}\,\mathrm{d}V \qquad \text{(iv)}$$

From equation (iv) it is clear that change in entropy (d*S*) depends on changes in *T* and *V* . Thus entropy is a function of *T* and *V* and $S = S(T, V)$

Total differential of *S* is given by

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V \qquad \text{(v)}$$

On comparing the coefficients of d*T* in equations (iv) and (v), we get

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \text{(vi)}$$

On differentiating equation (vi) with respect to *V* at constant *T,* we get

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial}{\partial V}\left(\frac{C_V}{T}\right)_T = 0 \qquad \text{(vii)}$$

On comparing the coefficients of d*V* in equations (iv) and (v), we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V} \qquad \text{(viii)}$$

On differentiating the equation (viii) with respect to *T* at constant *V,* we get

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{nR}{V}\right)_V = 0 \qquad \text{(ix)}$$

From equation (vii) and (ix), it is observed that

$$\frac{\partial^2 S}{\partial V \partial T} = 0 = \frac{\partial^2 S}{\partial T \partial V}$$

That is, dS obeys Euler's reciprocity relation. Therefore, dS is an exact differential and S is a state function

Logical proof that entropy (*S*) is a state function

For an ideal gas under reversible condition

$$\frac{dq_{\text{rev}}}{T} = \mathrm{d}S = C_V \,\mathrm{d}\ln T + nR\,\mathrm{d}\ln V$$

Integration of the above equation for a change from initial state 1 to final state 2 gives

$$\int_1^2 \mathrm{d}S = C_V \int_1^2 d\ln T + nR \int_1^2 d\ln V$$

$$= C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

Discussion: The right hand side of the above equation depends on the state variables (T_1, V_1, T_2 V_2) of the system. Therefore, the left hand side should also depend on the state variables. That is, left hand side should describe the change in a state property. Now left hand side represents the change of entropy. Therefore, we conclude that entropy is a state property and change of entropy is given by

$$\int_1^2 \frac{dq_{\text{rev}}}{T} = \int_1^2 \mathrm{d}S = S_2\,(T_2, V_2) - S_1(T_1, V_1)$$

and $$\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

Relaation between energy and entropy

The change of internal energy is given by the first law of thermodynamics as

$$\mathrm{d}U = \mathrm{d}q - P\mathrm{d}V \qquad \text{(i)}$$

The change of entropy is given by the second law of thermodynamics as

$$\frac{dq_{\text{rev}}}{T} = \mathrm{d}S$$

Or, $$\mathrm{d}q_{\text{rev}} = T\mathrm{d}S \qquad \text{(ii)}$$

On substituting the expression for dq from equation (ii) in to equation (i), we get

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \qquad \text{(iii)}$$

Or, $$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V \qquad \text{(iv)}$$

Equations (iii) and (iv) represent the combined form of first and second laws of thermodynamics.

Applications of the combined form of first and second laws of thermodynamics *(Optional)*

The relation $TdS = dU + PdV$ is useful to derive various other thermodynamic relations.

(A) Thermodynamic equation of state

A relation between the change in a thermodynamic property (say U) and state variables (PVT) s called thermodynamic equation of state.

The combined form of first and second laws of thermodynamics states that

$$TdS = dU + PdV$$

Or, $$dS = \frac{1}{T}\, dU + \frac{1}{T}\, PdV \qquad \text{(i)}$$

Energy of a given amount of a system is a function of temperature and volume, $U = U(T, V)$, and its total differential is given by

$$\boldsymbol{d}\mathbf{U} = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} \mathbf{d}\boldsymbol{T} + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \mathbf{d}\boldsymbol{V} \qquad \textit{(ii)}$$

Therefore, $$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} + P\right] dV \qquad \text{(iii)}$$

From equation (iii) it is seen that entropy is a function of T and V and $S = S(T, V)$ The total differential of S is given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}} dT + \left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} dV \qquad \text{(iv)}$$

On comparing the coefficients of dT in equations (iii) and (iv), we get

$$\left(\frac{\partial S}{\partial T}\right)_{V} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} \qquad \text{(v)}$$

On differentiating equation (iv) with respect to V at constant T, we get

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\,\frac{\partial^2 U}{\partial V \partial T} \qquad \text{(vi)}$$

On comparing the coefficients of dV in equations (iii) and (vi), we get

$$\left(\frac{\partial S}{\partial V}\right)_{T} = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} + P\right] \qquad \text{(vii)}$$

On differentiating equation (vii) with respect to T at constant V, we get

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} + P\right\}\right]_{\mathrm{V}}$$

$$= -\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} \qquad \text{(viii)}$$

Now S is a state function , therefore, Euler's reciprocity relation must be valid and

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

In view of the above condition equations (vi) and (viii) give

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} - \frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} \qquad \text{(ix)}$$

Now U is a state function , therefore, Euler's reciprocity relation must be valid and

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V}$$

In view of the above equality condition, equation (ix) gives

$$-\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} - \frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} = 0$$

Or, $$\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} = T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} - P \qquad \text{(x)}$$

Equation (x) is called ***thermodynamic equation of state***. It provides an expression for the internal pressure $(\partial U/\partial V)_{\mathrm{T}}$ in terms of state variable of a system. This equation is valid for both the ideal and nonideal systems.

(B) Internal pressure of an ideal gas

Internal pressure is given by thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} = T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} - P \qquad \text{(i)}$$

For an ideal gas $PV = nRT$ and $P = nRT/V$, therefore,

$$\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} = \frac{nR}{V} = \frac{P}{T} \qquad \text{(ii)}$$

From equations (i) and (ii), we get

$$\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} = T\frac{P}{T} - P = 0$$

Comclusions

1. The internal pressure $(\partial U/\partial V)_T$ of an ideal gas is zero.
2. The relation $(\partial U/\partial V)_T = 0$ is a thermodynamic definition of ideal gas
3. The relation $(\partial U/\partial V)_T = 0$ gives a thermodynamic proof of ***Joule's law***

(C) Internal pressure of a nonideal gas *(a gas obeying van der Waals equation)*

Internal pressure is given by thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{(i)}$$

van der Waals equation of state is written as

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \qquad \text{(ii)}$$

Now, $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb} \qquad \text{(iii)}$$

From equations (i), (ii) and (iii), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V - nb} - \frac{nRT}{V - nb} + \frac{an^2}{V^2}$$

Or, $$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$$

This relation reveals that internal pressure of a gas is large when the value of the van der Waals constant a is large *i.e.,* when the molecular force of attraction is strong.

Relation between enthalpy and entropy

Enthaly is defined by $H = U + PV$ and

$$\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P \qquad \text{(i)}$$

From the combined form of first and second laws of thermodynamics we have

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V \qquad \text{(ii)}$$

From equations (i) and (ii), we have

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P \qquad \text{(iii)}$$

Or, $$T\mathrm{d}S = \mathrm{d}H - V\mathrm{d}P \qquad \text{(iv))}$$

Equations (iii) and (iv) represent a combined form of the first and second laws of thermdynamics in terms of enthalpy and entropy changes.

(A) Thermodynamic equation of state in terms of enthalpy change (*Optional)*

A relation between the change in a thermodynamic property (say *H*) and state variables (*PVT*) s called thermodynamic equation of state.

The combined form of first and second laws of thermodynamics in terms of enthalpy states that

$$T\mathrm{d}S = \mathrm{d}H - V\mathrm{d}P$$

Or, $$\mathrm{d}S = \frac{1}{T} \quad \mathrm{d}H - \frac{1}{T} \; V\mathrm{d}P \qquad \text{(i)}$$

Enthalpy of a given amount of a system is a function of temperature and pressure, *H = H(T, P),* and its total differential is given by

$$\boldsymbol{d}\mathbf{H} = \left(\frac{\partial H}{\partial T}\right)_{\mathrm{P}} \mathbf{d}\boldsymbol{T} + \left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} \mathbf{dP} \qquad \textbf{\textit{(ii)}}$$

Therefore, $$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{\mathrm{P}} \mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} - V\right]\mathrm{d}P \qquad \text{(iii)}$$

From equation (iii) it is seen that entropy is a function of *T* and *P* and *S* = *S*(*T, P*) and its total differential of *S* is given by

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_{\mathrm{P}} \mathrm{d}T + \left(\frac{\partial S}{\partial P}\right)_{\mathrm{T}} \mathrm{d}P \qquad \text{(iv)}$$

On comparing the coefficients of d*T* in equations (iii) and (iv), we get

$$\left(\frac{\partial S}{\partial T}\right)_{P} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{\mathrm{P}} \qquad \text{(v)}$$

On differentiating equation (v) with respect to *P* at constant *T,* we get

$$\frac{\partial^2 S}{\partial P \partial T} = \frac{1}{T}\frac{\partial^2 H}{\partial P \partial T} \qquad \text{(vi)}$$

On comparing the coefficients of d*P* in equations (iii) and (iv), we get

$$\left(\frac{\partial S}{\partial P}\right)_{T} = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} - V\right] \qquad \text{(vii)}$$

On differentiating equation (vii) with respect to *T* at constant *P,* we get

$$\frac{\partial^2 S}{\partial T \partial P} = \frac{\partial}{\partial T}\left[\frac{1}{T}\left\{\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} - V\right\}\right]_{\mathrm{V}}$$

$$= -\frac{1}{T^2}\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} + \frac{1}{T}\frac{\partial^2 H}{\partial T\partial P} + \frac{V}{T^2} - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} \qquad \text{(viii)}$$

Now S is a state function , therefore, Euler's reciprocity relation must be valid and

$$\frac{\partial^2 S}{\partial P\partial T} = \frac{\partial^2 S}{\partial T\partial P}$$

In view of the above condition equations (vi) and (viii) give

$$\frac{1}{T}\frac{\partial^2 H}{\partial P\partial T} = -\frac{1}{T^2}\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} + \frac{1}{T}\frac{\partial^2 H}{\partial T\partial P} + \frac{V}{T^2} - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} \qquad \text{(ix)}$$

Now H is a state function , therefore, Euler's reciprocity relation must be valid and

$$\frac{\partial^2 H}{\partial P\partial T} = \frac{\partial^2 H}{\partial T\partial P}$$

In view of the above equality condition, equation (ix) gives

$$-\frac{1}{T^2}\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} + \frac{V}{T^2} - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} = 0$$

Or, $$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} = V - T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} \qquad \text{(x)}$$

Equation (x) is called thermodynamic equation of state in terms of enthalpy change with change of pressure at constant temperature.

Calculation of $(\partial H/\partial P)_{\mathrm{T}}$ for an ideal gas

For an ideal gas $PV = nRT$ and $PV = nRT/P$. Therefore,

$$\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} = \frac{nR}{P} = \frac{V}{T}$$

$$\left(\frac{\partial H}{\partial P}\right)_{\mathrm{T}} = V - T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} = V - T\,\frac{V}{T} = 0$$

Entropy as a function of T and V

From the combined form of first and second laws of thermodynamics we know that

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V$$

Or, $$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{1}{T}\,P\mathrm{d}V \qquad \text{(i)}$$

But U is a state function and thus

$$\boldsymbol{d}\mathbf{U} = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}} \boldsymbol{d}\mathbf{T} + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \boldsymbol{d}\mathbf{V}$$

$$= C_{\mathrm{V}}\, \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \mathrm{d}V \qquad \text{(ii)}$$

where, $C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{V}}$ = Heat capacity at constant volume

From equations (i) and (ii), we get

$$\mathrm{d}S = \frac{C_{\mathrm{V}}}{T}\mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} + P\right]\mathrm{d}V \qquad \text{(iii)}$$

For an ideal gas $(\partial U/\partial V)_{\mathrm{T}} = 0$ and $P/T = nRT/V$. Therefore,

$$\mathrm{d}S = \frac{C_{\mathrm{V}}}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V \qquad \text{(iv)}$$

From equation (iv) it is seen that entropy is a function of T and V and

$S = S(T, V)$

The total differential of S is given by

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}} \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} \mathrm{d}V \qquad \text{(v)}$$

Evaluation of partial derivatives of *S* for an ideal gas

(i) On comparing the coefficients of dT in equations (iv) and (v) we get

$$\left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}} = \frac{C_{\mathrm{V}}}{T} \qquad \text{(vi)}$$

$\left(\frac{\partial S}{\partial T}\right)_{\mathrm{V}}$ = Partial derivative of S with T at constant V

= Rate of change of entropy with temperature at constant volume

Conclusion: In equation (vi), C_{V}/T is positive. Therefore, $(\partial S/\partial T)_{\mathrm{V}}$ is also positive. Thus it is concluded that the entropy of the system increases with increase of temperature at constant volume and decreases with decrease of temperature.

(ii) On comparing the coefficients of dV in equations (iv) and (v), we get

$$\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} = \frac{nR}{V} = \frac{P}{T} \qquad \text{(vii)}$$

$\left(\frac{\partial S}{\partial V}\right)_T$ = Partial derivative of S with V at constant T

= Rate of change of entropy with volume at constant temperature

Conclusion: In equation (vii), P/T is positive. Therefore, $(\partial S/\partial V)_T$ is also positive. Thus it is concluded that the entropy of the system increases with increase of volume at constant temperature and decreases with decrease of volume.

Entropy as a function of *T* and *P*

The combined form of first and second laws of thermodynamics in terms of enthalpy states that

$$T\mathrm{d}S = \mathrm{d}H - V\mathrm{d}P$$

Or, $$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}H - \frac{1}{T}\,V\mathrm{d}P \qquad \text{(i)}$$

Enthalpy of a given amount of a system is a function of temperature and pressure, $H = H(T, P)$, and its total differential is given by

$$\boldsymbol{d}\mathbf{H} = \left(\frac{\partial H}{\partial T}\right)_P \mathbf{d}\boldsymbol{T} + \left(\frac{\partial H}{\partial P}\right)_T \mathbf{dP}$$

$$= C_P\,\mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_T \mathrm{dP} \qquad \text{(ii)}$$

where, $\left(\frac{\partial H}{\partial T}\right)_P = C_P$ = Heat capacity at constant pressure

Therefore, $$\mathrm{d}S = \frac{C_P}{T}\,\mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\mathrm{d}P \qquad \text{(iii)}$$

For an ideal gas $(\partial H/\partial P)_T = 0$ and $V/T = nR/\mathrm{P}$. Therefore,

Therefore, $$\mathrm{d}S = \frac{C_P}{T}\,\mathrm{d}T - \frac{V}{T}\,\mathrm{d}P \qquad \text{(iv)}$$

From equation (iii) it is seen that entropy is a function of T and P and $S = S(T, P)$ and its total differential of S is given by

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial S}{\partial P}\right)_T \mathrm{d}P \qquad \text{(v)}$$

Evaluation of partial derivatives of *S* for an ideal gas

(i) On comparing the coefficients of dT in equations (iv) and (v) we get

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad \text{(vi)}$$

$\left(\frac{\partial S}{\partial T}\right)_P$ = Partial derivative of S with T at constant P

= Rate of change of entropy with temperature at constant pressure

Conclusion: In equation (vi), C_P/T is positive. Therefore, $(\partial S/\partial T)_P$ is also positive. Thus it is concluded that at constant pressure the entropy of the system increases with increase of temperature and decreases with decrease of temperature

(ii) On comparing the coefficients of dP in equations (iv) and (v) we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{V}{T} \qquad \text{(vi)}$$

$\left(\frac{\partial S}{\partial P}\right)_T$ = Partial derivative of S with P at constant T

= Rate of change of entropy with pressure at constant temperature

Conclusion: In equation (vi), V/T is positive. Therefore, right hand side is negative. Thus left hand side should also be negative and hence $(\partial S/\partial P)_T$ is negative.. It is therefore, concluded that at constant temperature the entropy of the system decreases with increase of pressure and increases with decrease of pressure.

Entropy changes for change of states of an ideal gas

The combined form of first and second laws of thermodynamics is useful to calculate the entropy changes under different conditions. Here we shall describe the calculations of ΔS for an ideal gas for two types of processes.

(i) When T and V are changed

(ii) When T and P are changed

(A) **Entropy change for isochoric reversible temperature change of an ideal gas**

The variation of entropy with temperature and volume for an ideal gas is given by

$$\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V \qquad \text{(i)}$$

In an isochoric process, volume is constant and dV = 0, therefore,

$$\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T = C_V \,\mathrm{d}\ln T \qquad \text{(ii)}$$

For the change of state from initial state 1 to final state 2, the entropy change is obtained on integrating equation (iii) [assuming that C_V is independent of temperature]

$$\int_1^2 \mathrm{d}S = C_V \int_1^2 d \ln T$$

Or, $$S_2 - S_1 = C_V \ln \frac{T_2}{T_1}$$

Thus, for an isochoric process the change of entropy with change of temperature of an ideal gas is given by

$$\Delta S \text{ (isochoric)} = C_V \ln \frac{T_2}{T_1} = nC_{V,\,m} \times 2.303 \log \frac{T_2}{T_1}$$

Conclusions

- Entropy of an ideal gas increases when it is heated at constant volume because $T_2 > T_1$ and log. T_2 / T_1 is positive.
- Entropy of an ideal gas decreases when it is cooled at constant volume because T_2Therefore,T_1 and log. T_2 / T_1 is negative

(B) Entropy change for isothermal reversible volume change of an ideal gas

In an isothermal process the temperature is constant and $\mathrm{d}T = 0$. Therefore,

$$\mathrm{d}S = \frac{nR}{V} \mathrm{d}V = nR \, \mathrm{d} \ln V$$

For the change of state from initial state 1 to final state 2, the entropy change is obtained on integrating the above equation

$$\int_1^2 \mathrm{d}S = n R \int_1^2 d \ln V$$

Or, $$S_2 - S_1 = \Delta S \text{ (isothermal)} = n R \ln \frac{V_2}{V_1} \; n R \times 2.303 \log \frac{V_2}{V_1}$$

Conclusions

- Entropy of an ideal gas increases when it is allowed to expand at constant temperature because $V_2 > V_1$ and

  log. V_2 / V_1 is positive
- **Entropy of an ideal gas decreases when it is compressed at constant temperature. because $V_2 < V_1$ and log. V_2 / V_1 is negative (C) Entropy change when both the temperature and volume of an ideal gas are changed simultaneously**

The variation of entropy with temperature and volume for an ideal gasis given by

$$dS = C_V \, d \ln T + nR \, d \ln V$$

For the change of state from initial state 1 to final state 2, the entropy change is obtained on integrating the above equation

$$\int_1^2 dS = C_V \int_1^2 d \ln T + n R \int_1^2 d \ln V$$

Or, $$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$$

$$\Delta S = nC_{V,m} \times 2.303 \log \frac{T_2}{T_1} + nR \times 2.303 \log \frac{V_2}{V_1}$$

(D) Entropy change for isobaric reversible temperature change of an ideal gas

The variation of entropy with temperature and pressure is given by

$$dS = \frac{C_P}{T} dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right] dP \qquad \text{(i)}$$

For an ideal gas $(\partial H/\partial P)_T = 0$ and $V/T = nR/P$. Therefore,

$$dS = \frac{C_P}{T} dT - \frac{nR}{P} dP \qquad \text{(ii)}$$

In an isobaric process, pressure is constant and $dP = 0$, therefore,

$$dS = \frac{C_P}{T} dT = C_P \, d \ln T \qquad \text{(iii)}$$

For the change of state from initial state 1 to final state 2, the entropy change is obtained on integrating equation (iii) [assuming that C_P is independent of temperature]

$$\int_1^2 dS = C_P \int_1^2 d \ln T$$

Or, $$S_2 - S_1 = C_P \ln \frac{T_2}{T_1}$$

Thus, for an isobaric process the change of entropy with change of temperature of an ideal gas is given by

$$\Delta S \text{ (isobaric)} = C_P \ln \frac{T_2}{T_1} = nC_{P,m} \times 2.303 \log \frac{T_2}{T_1}$$

Conclusions

- Entropy of an ideal gas increases when it is heated at constant pressure because $T_2 > T_1$ and log. T_2/ T_1 is positive.
- Entropy of an ideal gas decreases when it is cooled at constant pressure because T_2Therefore,T_1 and log. T_2/ T_1 is negative

Example: Calculate the change inentropy when 2 moles of an ideal gas are heated from 300 K to 600 K at a constant pressure under reversible condition. It is given that $C_{P,\,m}$ = 25 JK^{-1} mol^{-1}

Solution: For isobaric heating of an ideal gas

$$\Delta S\text{ (isobaric)} = n\, C_{P,\,m} \times 2.303 \log \frac{T_2}{T_1}$$

Data given: $n = 2$ mol, $C_{P,\,m} = 25\ JK^{-1}\ mol^{-1}$, $T_1 = 300$ K, $T_2 = 600$ K

$$T_2/\ T_1 = 600\text{ K}/\ 300\text{ K} = 2$$

$$\log T_2/\ T_1 = \log 2 = 0.301$$

Therefore, $\Delta S\text{ (isobaric)} = 2\text{ mol} \times 25\ JK^{-1}\ mol^{-1} \times 2.303 \times 0.301$

$$= 34.6\ JK^{-1}$$

(E) Entropy change for isothermal reversible pressure change of an ideal gas

The variation of entropy with temperature and pressure for an ideal is given by

$$dS = \frac{C_P}{T} dT - \frac{nR}{P} dP$$

In an isothermal process, temperature is constant and dT = 0, therefore,

$$dS = -\frac{nR}{P} dP = -nR\, d \ln P$$

For the change of state from initial state 1 to final state 2, the entropy change is obtained on integrating the above equation

$$\int_1^2 dS = -nR \int_1^2 d \ln P$$

Or, $$S_2 - S_1 = -nR \ln \frac{P_2}{P_1}$$

Thus, for an isobaric process the change of entropy with change of temperature of an ideal gas is given by

$$\Delta S\,(\text{isothermal}) = -nR\ln\frac{P_2}{P_1} = nR\ln\frac{P_1}{P_2} = nR\times 2.303\log\frac{P_1}{P_2}$$

Conclusions

- Entropy of an ideal gas increases when it is allowed to expand at constant temperature because $P_1 > P_2$ and $P_1/P_2 > 1$ thus $\log P_1/P_2 > 0$ (positive).
- Entropy of anideal gas decreases when it is compressed at constant temperature because $P_1/P_2 < 1$ thus $\log P_1/p_2 < 0$ (negative).

(F) Entropy change when temperature and pressure of an ideal gas are changed simultaneously

The variation of entropy with temperature and pressure for an ideal is given by

$$dS = C_P\, d\ln T - nR\, d\ln P$$

For the change of state from initial state 1 to final state 2, the entropy change is obtained on integrating the above equation

$$\int_1^2 dS = C_P\int_1^2 d\ln T - nR\int_1^2 d\ln P$$

Or, $$S_2 - S_1 = C_P\ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$$

$$= nC_{P,\,m}\times 2.303\log\frac{T_2}{T_1} + nR\times 2.303\log\frac{P_1}{P_2}$$

(G) Entropy change for an ideal gas under reversible -adiabatic conditions

In adiabatic reversible process there is no entropy change that is, $\Delta S = 0$. This is proved as follows.

For simultaneous change of temperature and volume the entropy is of an ideal gas (system) is given by

$$\Delta S = C_V\ln\frac{T_2}{T_1} + nR\log\frac{V_2}{V_1} \qquad \text{(i)}$$

For an ideal gas undergoing adiabatic reversible change the temperature and volume are related by

$$\left(\frac{T_2}{T_1}\right)^{C_V/nR} = \frac{V_1}{T_2}$$

Therefore, $$\frac{C_V}{nR}\ln\frac{T_2}{T_1} = \ln\frac{V_1}{V_2}$$

Or, $$. C_V \ln \frac{T_2}{T_1} = nR \ln \frac{V_1}{V_2} = - nR \ln \frac{V_2}{V_1} \qquad \text{(ii)}$$

On replacing the first term of the right hand side of equation (i) by the right hand side term of equation (ii), we find that

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

Discussion

Zero entropy change ($\Delta S = 0$) for an adiabatic reversible change of state of an ideal gas suggests that

(i) During adiabatic reversible expansion the increase of entropy due to increase of volume is exactly balanced by the decrease of entropy due to lowering of temperature.

(ii) During adiabatic reversible compression the decrease of entropy due to decrease of volume is exactly balanced by the increase of entropy due to increase of temperature.

Entropy changes involved in the Carnot cycle

The Carnot cycle involves alternating isothermal and adiabatic expansion and alternating isothermal and adiabatic compression respectively. For a gas the steps of the changes of temperature and entropy are shown as *T–S* indicator diagram in Fig. 12.

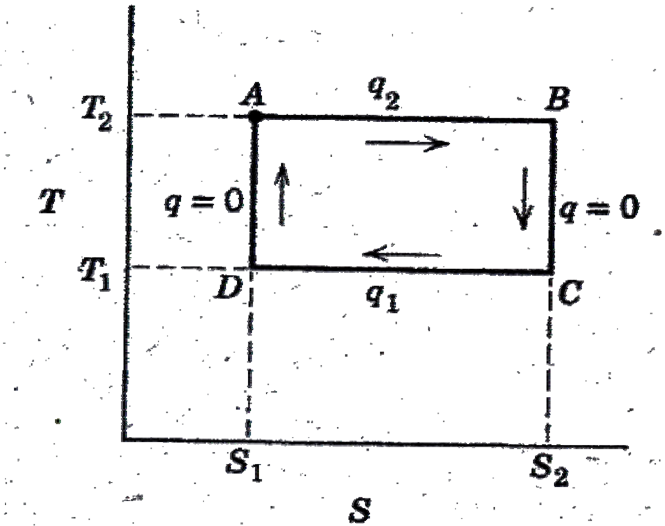


Fig. 12. Indicator diagram of Carnot cycle in terms of temperature (*T*) and entropy (*S*).

The isothermal reversible expansion is represented by the horizontal line *AB* which tells that *T* is constant and *S* increases whereas the isothermal reversible compression is represented by horizontal line *CD* which tells that entropy decreases during compression. The reversible adiabatic expansion is represented by vertical line *BC* which tells that temperature decreases but entropy remains constant, whereas adiabatic compression is represented by vertical line *DA* which tells that temperature increases but entropy remains constant (as $q_{\text{rev}} = 0$).

$$\Delta S\,(1) = \frac{q_2}{T_2} = nR \times 2.303 \log (V_2/V_1)$$

isothermal reversible expansion

$$\Delta S\,(2) = \frac{q_{\text{rev}}}{T} = \frac{0}{T} = 0 \qquad \text{adiabatic reversible expansion}$$

$$\Delta S\,(3) = -\frac{q_1}{T_1} = nR \times 2.303 \log (V_4/V_3)$$

isothermal reversible compression

$$\Delta S\,(4) = \frac{q_{\text{rev}}}{T} = \frac{0}{T} = 0 \qquad \text{adiabatic reversible compression}$$

For the entire cycle the entropy change is given by

$$\Delta S\,(\text{cycle}) = \Delta S\,(1) + \Delta S\,(2) + \Delta S\,(3) + \Delta S\,(4)$$

$$= nR \times 2.303 \log (V_2/V_1) + 0 + nR \times 2.303 \log (V_4/V_3) + 0$$

But $\log \frac{V_4}{V_3} = -\log \frac{V_2}{V_1}$

Therefore, $\Delta S\,(\text{cycle}) = nR \times 2.303 \log (V_2/V_1) - nR \times 2.303 \log (V_2/V_1) = 0$

Conclusions:

(1) Entropy increases during isothermal reversible expansion but decreases during isothermal compression in Carnot cycle.

(2) The increase of entropy for isothermal reversible expansion is equal and opposite to the decrease in entropy for isothermal reversible compression in Carnot cycle.

(3) The total entropy change in Carnot cycle is zero.

Important deduction: For Carnot cycle we have shown that

$$\Delta S(\text{cycle}) = \frac{q_2}{T_2} + 0 - \frac{q_1}{T_1} + 0 = 0$$

That is, $\frac{q_2}{T_2} = \frac{q_1}{T_1}$

Or, $\frac{q_1}{q_2} = \frac{T_1}{T_2}$

Efficiency of Carnot cycle is defined as

$$\eta = 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2} \qquad \text{(i)}$$

In this expression T_1 and T_2 are the absolute temperatures defined on thermodynamic scale. Now, it is observed that the expression (i) is the same as that derived in the previous part where T_1 and T_2 were the absolute temperatures defined in terms of ideal gas temperatures. From this similarity it is concluded that the ***temperatures on the two scales are proportional to each other.***

Entropy of isothermal mixing of ideal gases

Let us consider two ideal gases A and B kept in two separate compartments separated by a very thin partition of a container and maintained at constant temperature. Further suppose that n_A and n_B are the amounts and V_A and V_B are the initial volumes of gases A and B respectively. When the thin partition is removed, both the gases mix and occupy a final total volume $V_A + V_B$. Therefore, the mixing process can be assumed that gas A expands from its initial volume V_A to a final volume of $V_A + V_B$..

The entropy change of gas A at constant temperature is given by

$$\Delta S\,(A) = n_A R \times 2.303 \log \frac{V_A + V_B}{V_A}$$

Similarly, gas B expands from its initial volume V_B to a final volume of $V_A + V_B$. The entropy change of gas B at constant temperature is given by

$$\Delta S\,(B) = n_B R \times 2.303 \log \frac{V_A + V_B}{V_B}$$

The total entropy change is equal to the sum of the entropy changes of gas A and gas B on mixing.

$$\Delta S\,(\text{mixing}) = \Delta S\,(A) + \Delta S\,(B)$$

$$= n_A R \times 2.303 \log \left(\frac{V_A + V_B}{V_A}\right) + n_B R \times 2.303 \log \left(\frac{V_A + V_B}{V_B}\right)$$

Now, $\left(\frac{V_A}{V_A + V_B}\right) = x_A$ = Mole fraction of gas A

and $\left(\frac{V_B}{V_A + V_B}\right) = x_B$ = Mole fraction of gas B

Therefore, $$\Delta S\,(\text{mixing}) = n_A R \times 2.303 \log \left(\frac{1}{x_A}\right) + n_B R \times 2.303 \log \left(\frac{1}{x_B}\right)$$

$$= -\mathbf{R} \times 2.303\,[\mathbf{n}_A \log \mathbf{x}_A + \mathbf{n}_B \log \mathbf{x}_B]$$

Discussion

(i) $x_A < 1$ and thus $\log x_A$ is negative, similarly $\log x_B$ is also negative. Therefore, each term within bracket of right side of the above equation is negative and thus entire right side is positive. Hence entropy of mixing the gases is positive and mixing process is spontaneous.

(ii) For more than two gases (say k gases) the entropy of mixing is given by

ΔS (mixing) = $-R \times 2.303\ \Sigma n_k \log x_k$, where k represents different type of gases A, B, C, D etc.

Entropy changes in phase transformations

The change of entropy accompanying the transformation of one mole of a substance from one physical state into another physical state at its transition temperature is called entropy of a phase transformation or entropy of transition. It is denoted by $\Delta_{\text{trans}}S$.

The phase transformation may involve change from liquid to vapour (L □ V) or solid to liquid (S□L) or in general from αphase to □-phase (α □□) Accordingly, we can define different types.of entropy of transitions. Since, transformation from one phase into another phase at the transition temperature of a substance is a reversible process, the entropy change can be calculated as

$$\Delta_{\text{trans}}S = \frac{q_{\text{transition}}}{T_{\text{transition}}}$$

For a process at constant pressure $q_p = \Delta H$, therefore,

$$\Delta_{\text{trans}}S = \frac{\Delta_{\text{trans}}H}{T_{\text{transi}}}$$

Important note: In the above equation if any two quantitie are known the third can be calculated. Thus

(i) $\Delta_{\text{trans}}S = \frac{\Delta_{\text{trans}}H}{T_{\text{trans}}}$ (ii) $T_{\text{trans}} = \frac{\Delta_{\text{trans}}S}{\Delta_{\text{trans}}S}$ (iii) $\Delta_{\text{trans}}H = T_{\text{trans}} \times \Delta_{\text{trans}}S$

(A) Entropy of vaporization $\Delta_{\text{vap}}S$

The change of entropy accompanying the conversion of one mole of a liquid into vapour at its boiling point is called ***entropy of vaporization***. It is denoted by $\Delta_{\text{vap}}S$. It is equal to enthalpy of vaporization divided by the boiling point

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b}$$

$\Delta_{\text{vap}}S$ = Entropy in the final state – Entropy in the initial state

= Entropy of vapour phase – Entropy of the liquid phase

= S (vapour) $- S$ (liquid)

$\Delta_{\text{vap}}H$ = Enthalpy of vaporization of the liquid = Heat of vaporization of the liquid

T_b = Boiling point (in Kelvin) of the liquid

Example. Calculate the entropy change when one mole of liquid water is converted into vapour at 100 °C. The enthalpy of vaporization is 40.850 kJ mol^{-1}

Solution. The phase transformation is represented by

$H_2O(l)$ □ $H_2O(v)$

Data given:

$\Delta_{\text{vap}}H = 40.850 \text{ kJ mol}^{-1} = 40850 \text{ J mol}^{-1}$

Boiling point = $T_b = 100 + 273 = 373$ K

Therefore, $$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b}$$

$$= \frac{40850 \text{ J mol}^{-1}}{373\text{K}} = 109.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Remarks. Here it is observed that:

$\Delta_{\text{vap}}S$ = Entropy of vapour phase – Entropy of the liquid phase = 109.5 J K^{-1} mol^{-1}

Therefore, Entropy of vapour phase = Entropy of liquid phase + 109.5 J K^{-1} mol^{-1}

This observation is in line with the fact that in the vapour phase there is more randomness as compared to the liquid phase.

Exercise 1. Calculate the entropy of vaporization of a liquid if $\Delta_{\text{vap}}H$.= 42400 J mol^{-1}and T_b = 351.4 K

($\Delta_{\text{vap}}S$. = 42400 J mo1^{-1} / 351.4 K = 120.66 J K^{-1} mol^{-1})

Exercise 2. Calculate the entropy of vaporization of a liquid which boils at 110.6 °C when $\Delta_{\text{vap}}H$. is 35.2 kJ mol^{-1} ($\Delta_{\text{vap}}S$ = 35200 J mol^{-1} / 383.6 K = 91.76 J K^{-1} mol^{-1})

Trouton's rule. For nonpolar liquids Trouton observed that entropy of vaporization is between 80 to 90 JK^{-1} mol^{-1} . Therfore, he suggested that entropy of vaporization of such liquids may be approximately taken equal to 85 JK^{-1} mol^{-1} which is called Trouton's rule.

According to Trouton's rule

(i) $$\frac{\Delta_{\text{vap}}H}{T_b} = 85 \text{ JK}^{-1} \text{ mol}^{-1}$$

(ii) $$\Delta_{\text{vap}}H. = T_b \times 85 \text{ JK}^{-1} \text{ mol}^{-1}$$

(iii) $T_b = \dfrac{\Delta_{vap}H}{85\ \text{kJ mol}^{-1}}$

Molar entropy of vaporization of liquids at their normal boiling points

Liquid	Benzene	Cyclohexane	Methane	Methanol	Ethanol	Water
$\boldsymbol{\Delta_{vap}S/\ JK^{-1}\ mol^{-1}}$	87	85	83	104	110	109

Remarks. Trouton's rule is not obeyed by the liquids (such as ethanol C_2H_5OH and water H_2O) involving dipole – dipole interaction and hydrogen bonding

(B) Entropy of fusion $\Delta_{fus}S$

Tbe change of entropy accompanying the conversion of 1 mole of a solid into liquid at its melting point is called entropy of fusion. It is denoted by $\Delta_{fus}S$ and calculated as follows.

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_m}$$

$\Delta_{fus}S$ = Entropy of liquid phase – Entropy of solid phase

= S (liquid) – S (solid)

$\Delta_{fus}H$ = Enthalpy of fusion of the solid

T_m = Melting point (in kelvin) of solid

Example. ***Calculate the entropy of fusion of ice if its enthalpy of fusion is 6.01 kJ mol⁻¹ at its melting point of 273 K.***

Solution. The phase transformation is represented by

H_2O (s) □ H_2O (l)

and entropy change in this phase transformation is equal to the entropy of fusion of ice.

Data given:

$\Delta_{fus}H = 6.01\ \text{kJ mol}^{-1} = 6010\ \text{J mol}^{-1}$

$T_m = 273\ \text{K}$

Therefore, $\Delta_{fus}S = \dfrac{\Delta_{fus}H}{T_m} = 22\ \text{J K}^{-1}\ \text{mol}^{-1}$

Remarks. The entropy of fusion is positive. This suggests that the entropy of liquid water is greater than that of ice. Thus

Entropy of water = Entropy of ice + 22 J K^{-1} mol^{-1}

Relation between entropy and randomness in terms of entropy change

Entropy is a measure of randomness. Greater is randomness in a system, larger is its entropy. Let us illustrate it for fusion and vaporization processes.

- For the the process H_2O (s) $\rightarrow$ H_2O (l)

$\Delta_{fus}S$ = S (liquid) – S (solid) = 22 J K^{-1} mol^{-1}1

Or, S (liquid) = S (solid) + 22 J K^{-1} mol^{-1}

Thus the entropy of liquid water is greater than the entropy of ice by 22 J K^{-1} mol^{-1}. But there is more randomness in liquid water than in ice. Therefore, entropy is a measure of randomness.

- For the process H_2O(l) $\rightarrow$ H_2O(v)

$\Delta_{vap}S$ = S (vapour) – S (liquid) = + 109.5 J K^{-1} mol^{-1}Therefore,

S (vapour) = S (liquid) + 109.5 J K^{-1} mol^{-1}

The entropy of water vapour is greater.than the entropy of liquid water by 109.5 J K^{-1} mol^{-1}. But, there is more randomness in vapour phase than in liquid phase. Therefore entropy is a measure of randomness.

The data:

S (vapour) = S (liquid) + 109.5 J K^{-1} mol^{-1}

and S (liquid) = S (solid) + 22 J K^{-1} mol^{-1}

suggest that the difference in the randomness between water vapour and liquid water is much larger (equivalent to 109.5 J K^{-1} mol^{-1}) as compared to the difference in the randomness between water (liquid) and ice (solid) which is equivalet to only 22 J K^{-1} mol^{-1}.This discussion confirms the correlation

S (vapour) >> S(liquid) > S (solid)

Example. Justify that a decrease in entropy is observed as a gas condenses into liquid. Compare it with decrease of entropy when a liquid sample is converted into solid.

Solution. For the process Gas $\longrightarrow$ Liquid (a)

ΔS (a) = S(final) – S(initial) =S(liquid) –S(gas) = –ve

Justification. There is more randomness in a gas as compared to its liquid form. Therefore, entropy of a gas is greater than its liquid state. Thus ΔS is negative, that is, entropy decreases when a gas condenses.

For the process Liquid $\longrightarrow$ Solid (b)

ΔS(b) = S(final) – S(initial) = S(solid) – S(liquid) = –ve

Comparison. The increasing order of entropy S(Gas) >> S (Liquid) > S(Solid) suggests that the value of ΔS(a) is more negative as compared to the value of ΔS(b)

Example. Predict with justification the entropy change for each one of the following processes.

(a) Dissolution of iodine in a solvent

(b) HCl is added to $AgNO_3$ solution and precipitate of AgCl is obtained

(c) A partition is removed to allow two gases to mix

Solution. The entropy change is given by the relation

$$\Delta S = S(\text{final}) — S(\text{initial})$$

(a) For the process $I_2(s) \longrightarrow I_2(\text{solution})$

$$\Delta S = S(I_2, \text{solution}) — S(I_2, \text{solid}) = +\text{ve}$$

Justification. There is more randomness hence more entropy in the dissolved state as compared to the solid state of iodine. Thus dissolution of iodine in a solvent is accompanied by an increase in entropy.

(b) For the process $HCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + HNO_3(aq)$

$$\Delta S = S(\text{final}) — S(\text{initial}) = -\text{ ve}$$

Justification. The entropy on the product side is lower because of the presence of a solid and a solution as compared to the reactants where both the reactants are solution

(c)For the process $\boxed{\text{Gas A} \mid \text{Gas B}} \longrightarrow \boxed{\text{Mixture of A+B.}}$

$$\Delta S = S(\text{final}) — S(\text{initial}) = +\text{ ve}$$

Justification. In the mixture each gas has to move in a larger volume and thus there is more randomness and larger entropy as compared to that in isolated gases before mixing

Example. Predict the sign of the entropy change for each of the following :

(a) $Hg(l) \longrightarrow Hg(g)$ (b) $AgNO_3(s) \longrightarrow AgNO_3(aq)$

(c) $I_2(g) \longrightarrow I_2(s)$ (d) $C(\text{graphite}) \longrightarrow C(\text{diamond})$

Solution. Entropy change is positive when there is more randomness and hence large entropy in the final state as compared to the initial state. Thus

(a) For the process $Hg(l) \longrightarrow Hg(g)$,

$$\Delta S = S(\text{final}) - S(\text{initial}) = S(\text{Hg, gas}) - S(\text{Hg, liqiid}) = +\text{ ve}$$

Reason. The entropy of gaseous mercury is greater than that of the liquid mercury

(b) For the process $AgNO_3(s) \longrightarrow AgNO_3(aq)$

$$\Delta S = S(\text{final}) - S(\text{initial}) = S(AgNO_3,\text{ aq}) - S(AgNO_3,\text{ s}) = +\text{ ve}$$

Reason. The entropy of $AgNO_3$ in solution is greater than that of a solid $AgNO_3$.

(c) For the process $I_2(g) \longrightarrow I_2(s)$

$$\Delta S = S(\text{final}) - S(\text{initial}) = S(I_2,\text{ s}) - S(I_2,\text{ g}) = -\text{ ve}$$

Reason. The entropy of I_2 in solid state is lower than that of I_2(gas).

(d) For the process C(graphite) $\longrightarrow$ C(diamond)

$$\Delta S = S(\text{final}) - S(\text{initial}) = S(\text{Diamond}) - S(\text{graphite}) = -\text{ ve}$$

Reason. There is less randomness and hence the entropy of diamond is lower than that of graphite in which there is more randomness

Clausius inequality statement

Clausius stated that in an isolated system the entropy change is greater than zero under irreversible condition but under reversible condition it is equal to zero. In terms of symbolic notations the Clausius inequality is stated as follows

$$\Delta S_{\text{irreversible}} > 0$$

and $$\Delta S_{\text{reversible}} = 0$$

Or, $$\Delta S \geq 0$$

Justification of Clausius inequality (Nonevaluative)

For reversible and irreversible processes the first law of thermodynamics is stated as

$$\Delta U_{\text{irr}} = q_{\text{irr}} + w_{\text{irr}} \qquad \text{(i)}$$

and $$\Delta U_{\text{rev}} = q_{\text{rev}} + w_{\text{rev}} \qquad \text{(ii)}$$

We know that internal energy is a state function and dU is exact differential. Therefore, change in internal energy is the same whether a process occurs under reversible or irreversible condition. Thus

$$\Delta U_{\text{rev}} = \Delta U_{\text{irr}} \qquad \text{(iii)}$$

From equations (iii), (ii) and (i). we get

$$q_{\text{rev}} + w_{\text{rev}} = q_{\text{irr}} + w_{\text{irr}}$$

Or, $$q_{\text{rev}} - q_{\text{irr}} = -w_{\text{rev}} + w_{\text{irr}}$$

$$= - w_{\text{rev}} - (- w_{\text{irr}})$$

$$= w_{\text{rev}}\text{ (by)} - w_{\text{irr}}\text{ (by)} \quad \text{(iv)}$$

The work done by the system under reversible condition is greater than that under irreversible condition. That is,

$$w_{\text{rev}}\text{ (by)} > w_{\text{irr}}\text{ (by)}$$

Or, $$w_{\text{rev}}\text{ (by)} - w_{\text{irr}}\text{ (by)} > 0 \qquad \text{(v)}$$

From equations (iv) and (v). we get

$$q_{\text{rev}} - q_{\text{irr}} > 0$$

Or, $$q_{\text{rev}} > q_{\text{irr}} \qquad \text{(vi)}$$

On dividing both side of equation (vi) by T, we get

$$\frac{q_{\text{rev}}}{T} > \frac{q_{\text{irr}}}{T}$$

But from the second law of thermodynamics

$$\Delta S = \frac{q_{\text{rev}}}{T} \qquad \text{(vii)}$$

Therefore, $$\Delta S > \frac{q_{\text{irr}}}{T} \qquad \text{(viii)}$$

But first law of thermodynamics states that

$$q = \Delta U - w$$

Therefore, $$\Delta S = \frac{\Delta U - w_{\text{rev}}}{T} \qquad \text{(ix)}$$

and $$\Delta S > \frac{\Delta U - w_{\text{irr}}}{T} \qquad \text{(x)}$$

In an isolated system, there is no exchange of heat, energy and work between the system and surroundings. Therefore,

$q = 0$, $\Delta U = 0$ and $w = 0$ in isolated system

On introducing these conditions in to equations (ix) and (x), we get

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

$$\Delta S\text{irr} > 0$$

Or, ΔS (isolated) >= 0

where > refers to irreversible change and = refers to reversible change.

For infinitesimal change the Clausius inequality is given by

$$dS \text{ (isolated)} >= 0$$

Comments: From the relation ΔS (isolated) >=0 it appears that entropy is not a state function because it is different for reversible and irreversible processes. But we know that entropy is a state function. Thus there appears to be contradiction. This contradiction was explained by Clausius that an isolated system includes both the system under investigation and the surroundings in its immediate vicinity. Therefore, the entropy change of an isolated system is equal to the entropy changes of the system and surroundings.

$$\Delta S \text{ (isolated)} = \Delta S \text{ (system)} + \Delta S \text{ (surroundings)}$$

Calculation of Entropy Changes of systems and surroundings

While calculating the entropy change, we must take into account the entropy changes in the system and surroundings. The combination of system and surroundings constitutes an ***isolated system***. The total entropy change of an isolated system is called the entropy change of the ***universe***

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}}$$

Nature of surroundings. The surroundings are considered to be any one of the following:

(a) Heat reserviour which can exchange heat with the system *i.e.,* which can either add heat to the system or extract heat from the system

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

(b) Mechanical device which can accept work from the system or which can do work on the system.

$$w_{\text{system}} = -w_{\text{surroundings}}$$

Entropy change of system (ΔS_{system})

The entropy change of the system can be calculated from the mathematical statement of the second law of thermodynamics

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

The methods of calculation of entropy changes for an ideal gas under different conditions have already been described. For irreversible processes the entropy change of the system is the same as that for reversible process

$$\Delta S_{\text{system}}^{\text{reversible}} = \Delta S_{\text{system}}^{\text{irreversible}}$$

But it is not equal to the heat exchanged between the system and surroundings divided by temperature. That is,

$$\Delta S_{\text{system}}^{\text{irreversible}} \neq q_{\text{irr}}/T$$

Entropy change of the surroundings ($\Delta S_{\text{surroundings}}$)

The entropy change of the surroundings is calculated as

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T}$$

For surroundings, this relation is valid whether the change is reversible or irreversible.

Now the heats exchanged between the system and the surroundings are related by

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

Therefore, $$\Delta S_{\text{surrounding}}: = \frac{q_{\text{surroundings}}}{T} = - \frac{q_{\text{system}}}{T}$$

But $$\Delta S_{\text{ssurroundings}}^{\text{reversible}} \neq \Delta S_{\text{ssurroundings}}^{\text{irreversible}}$$

Comments

(i) In a reversible process

$$\Delta S_{\text{system}}^{\text{reversible}} = \frac{q_{\text{rev}}}{T} = - \Delta S_{\text{surroundings}}$$

Therefore, $$\Delta S_{\text{total}}^{\text{reversible}} = \Delta S_{\text{system}}^{\text{reversible}} + \Delta S_{\text{ssurroundings}}^{\text{reversible}} = 0$$

(ii) In an irreversible process

$$\Delta S_{\text{system}} \neq \Delta S_{\text{surroundings}}$$

Example: Mention the methods to calculate the entropy change for the following process?

$$\mathbf{H_2O\ (\mathit{l}, 298\ K, 1\ bar) \longrightarrow H_2O\ (v, 398\ K, 0.8\ bar)}$$

Solution: The given process involves phase change, change of temperature and change of pressure for which a single formula cannot be used. Therefore, we shall split the given process in to several steps for which entropy changes an be determined. Thus

(i) Liquid water is heated at constant pressure from 298 K to 373 K (the boiling point of water)

$$H_2O\ (l, 298\ K, 1\ bar) \xrightarrow{\text{Heat}} H_2O\ (l, 373\ K, 1\ bar)$$

$$\Delta S(\text{i}) = C_{\text{P, m}}(\text{l}) \times 2.303 \log \frac{373\ \text{K}}{298\ \text{K}}$$

(ii) Liquid water is allowed to vaporize under isothermal and isobaric conditions at 373 K

$$H_2O\ (\text{l, 373 K, 1 bar}) \xrightarrow{\text{Vaporize}} H_2O\ (\text{v, 373 K, 1 bar})$$

$$\Delta S(\text{ii}) = \Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{373\ \text{K}}$$

(iii) Water vapour is heated at constant pressure from 373 K to 398 K

$$H_2O\ (\text{v, 373 K, 1 bar}) \xrightarrow{\text{Heat}} H_2O\ (\text{v, 398 K, 1bar})$$

$$\Delta S(\text{iii}) = C_{\text{P, m}}(\text{v}) \times 2.303 \log \frac{398\ \text{K}}{373\ \text{K}}$$

(iv) Water vapour is allowed to expand isothermally at 398 K from 1 bar to 0.8 bar

$$H_2O\ (\text{v, 398 K, 1 bar}) \xrightarrow{\text{Expansion}} H_2O\ (\text{v, 398 K, 0.8 bar})$$

$$\Delta S(\text{iv}) = R \times 2.303 \log \frac{1\ \text{bar}}{0.8\ \text{bar}}$$

On adding equations of steps (i) to (iv) and canceling the common terms on the two sides, we shall get

$$H_2O\ (\text{l, 298 K, 1 bar}) \longrightarrow H_2O\ (\text{v, 398 K, 0.8 bar})$$

and $\Delta S\ (\text{system}) = \Delta S(\text{i}) + \Delta S(\text{ii}) + \Delta S(\text{iii}) + \Delta S(\text{iv})$

$$= C_{\text{P, m}}(\text{l}) \times 2.303 \log \frac{373\ \text{K}}{298\ \text{K}} + \frac{\Delta_{\text{vap}}H}{373\ \text{K}}$$

$$+ C_{\text{P, m}}(\text{v}) \times 2.303 \log \frac{398\ \text{K}}{373\ \text{K}} + R \times 2.303 \log \frac{1\ \text{bar}}{0.8\ \text{bar}}$$

On substituting the values of various quantities the entropy change can be calculated

Entropy as criteria of spontaneity and equilibrium

A process is said to be spontaneous if it has a tendency to occur. All natural processes are spontaneous. It is an experimental observation that in a spontaneous process total entropy increases as the change progresses. When a state of equilibrium is attained the entropy becomes maximum. At any other stage the entropy is lower than its equilibrium value. These statements may be proved starting with the combined form of the first and second laws of thermodynamics.

- For an irreversible process (spontaneous process) when only *P-V* work is considered

$$dS > \frac{dU + PdV}{T}$$

In an isolated system energy and volume are constant that is, $dU = 0$ and $dV= 0$, therefore,

$$(dS)_{U,V} > 0$$

- In a reversible processes (equilibrium)

$$dS = \frac{dU + PdV}{T}$$

In an isolated system energy and volume are constant that is, $dU = 0$ and $dV= 0$, therefore,

$$(dS)_{U,V} = 0$$

- The combined result is written as $(dS)_{U,V} >= 0$
- For finite changes $(\Delta S)_{U,V} >= 0$

Thus in an isolated system at constant energy and constant volume *the entropy is maximum at equilibrium*

Discussion: Why the entropy should be maximum at equilibrium? This can be explained like this. Equilibrium is the state when the progress of the change has stopped, that is, the system has exhausted to undergo further change in the desired direction. Now any property which increases as the change progresses must attain its limiting value when the system has exhausted to undergo further change. It is a common experience that the limiting value of an increasing property is its highest or maximum value. Hence entropy is maximum at equilibrium

Spontaneity and equilibrium in terms of internal energy

Combined form of first and second laws of thermodynamics states that for an irreversible process

$$T\,dS > dU + PdV_{\text{irr}}$$

Or, $$dU < TdS - PdV_{\text{irr}}$$

At constant entropy $dS = 0$ and at constant volume $dV= 0$. Therefore,

$$(dU)_{S,V} < 0 \qquad \text{for spontaneous change}$$

For a reversible change

$$dU = TdS - PdV_{\text{rev}}$$

At constant entropy $dS = 0$ and at constant volume $dV= 0$. Therefore,

$$(dU)_{S,V} = 0 \qquad \text{at equilibrium}$$

For finite changes $(\Delta U)_{S,V} \leq 0$

Conclusion: The result $(\Delta U)_{S,\,V} \leq 0$ implies that for a spontaneous process at constant entropy and constant volume the internal energy decreases and attains a minimum value at equilibrium.

Spontaneity and equilibrium in terms of enthalpy

Combined form of first and second laws of thermodynamics in terms of enthalpy change states that for an irreversible process

$$T\,\mathrm{d}S > dH - VdP$$

Or, $$dH < TdS + VdP$$

At constant entropy $\mathrm{d}S = 0$ and at constant pressure $\mathrm{d}P = 0$. Therefore,

$$(dH)_{S,\,P} < 0 \quad \text{for spontaneous change}$$

For a reversible change

$$dH = TdS + VdP$$

At constant entropy $\mathrm{d}S = 0$ and at constant pressure $\mathrm{d}P= 0$. Therefore,

$$(dH)_{S,\,P} = 0 \quad \text{at equilibrium}$$

For finite changes $(\Delta H)_{S,\,P} \leq 0$

Conclusion: The result $(\Delta H)_{S,\,P} \leq 0$ implies that for a spontaneous process at constant entropy and constant pressure the enthalpy decreases and attains a minimum value at equilibrium.

A critical comment: In the chemistry laboratories the experiments are seldom carried at constant entropy and constant volume or at constant entropy and constant pressure. Therefore, decrease of internal energy or decrease of enthalpy is not a suitable criterion of spontaneity of a process. Then what next? Refer to free energy functions.

THIRD LAW OF THERMODYNAMICS

The first law of thermodynamics provides methods of calculation of the energy changes (ΔU) and enthalpy changes (ΔH). On the other hand, the second law of thermodynamics helps in the calculation of entropy changes (ΔS). But this law as such cannot be used to calculate the absolute value of entropy. Therefore, we need a new law of thermodynamics which can guide us to evaluate the absolute value of entropy of different type of substances. This new law is called the ***Third law of thermodynamics*** which is also called *Nernst heat theorem* in a limited perspective.

Nernst heat theorem

In 1906 Nernst stated the heat theorem that in the vicinity of absolute zero all processes should take place without any change in entropy and heat capacity. In terms of symbolic notations Nernst heat theorem may be stated as

$$\lim_{T \to 0} \Delta S \to 0 \quad \text{and} \quad \lim_{T \to 0} \Delta C_P \to 0$$

In 1913 Plank extended heat theorem in the form of third law of thermodynamics

Statement of the third law of thermodynamics

Every substance has a finite positive entropy but at 0 K (absolute zero) the entropy *may become zero and does so become in case of a perfectly crystalline substance*

This statement also implies that

At absolute zero the entropy of a perfect crystal is zero

That is, when $T = 0$ K then $S = 0$

Molecular basis of third law of thermodynamics

We know that entropy is a measure of randomness. Greater the randomness larger is the value of entropy. Lower is radomness smaller is the value of entropy. If the randomness is reduced to zero the entropy is also reduced to zero. This implies that when there is perfect order in the system its entropy is zero. It is in tune with the third law of thermodynamics which states that at absolute zero the entropy of a perfect crystal is zero. This is true because at absolute zero of temperature there is complete order in a perfect crystal and no chaos hence entropy is zero. The correlation between entropy and molecular arrangement is given by Boltzmann equation

$$S = k \ln W \qquad \text{(i)}$$

Here, S = Entropy

k = Boltzmann constant = $\dfrac{\text{Gas constant}}{\text{Avogadro constant}} = \dfrac{R}{N_A}$

W = Number of ways of molecular arrangements

From equation (i) it is clear that larger is the value of W higher is entropy (S). At absolute zero ($0 \text{ K} \equiv 273.16\ ^{o}\text{C}$) all types of motions cease. Therefore, molecules (atoms and ions) can arrange themselves in one way only. That is, $W = 1$ and there is perfect order. Therefore,

$$S = k \ln W = k \ln 1 = k \times 0 = 0$$

Thus entropy is zero at absolute zero. At temperatures higher that 0 K, the molecules can have different types of motions and they arrange themselves in more than one ways. That is, $W > 0$ and therefore, $\ln W > 0$ and hence S is positive.

Concept of residual entropy

There are certain substances which have positive entropy even at absolute zero. The value of entropy possessed by a substance at 0 K is called its **residual entropy**.

Origin of residual entropy: The residual entropy arises because the molecules can arrange themselves in more that one ways. For example, in case of carbon monoxide (CO) the molecules can have the following type of arrangements even at 0 K.

$$\text{CO} \quad \text{CO} \quad \boxed{\text{CO}} \quad \text{CO}$$

Or, $$\text{CO} \quad \text{CO} \quad \boxed{\text{OC}} \quad \text{CO}$$

This suggests that each CO molecule can have two orientations. Thus $W = 2$ for each molecule.

Calculation of residual entropy: In a system containing one Avogadro number of molecules (one mole) the entropy is given by

$$S = N_A \times k \times 2.303 \log W = R \times 2.303 \log W$$

Now, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. Therefore, when $W = 2$ we shall have

$$S = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 2.303 \log 2$$

$$= 5.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

The experimental value of residual entropy is lower $5.7 \text{ J K}^{-1} \text{ mol}^{-1}$

Remarks: Substances such as CO, N_2O, H_2O, H_2 have residual entropy. Therefore, in the reactions where one or more of such substances are involved the entropy change is finite even at absolute zero. This type of observation is called as exception to the third law or limitation of third law.

Evaluation of absolute entropy

The absolute entropy of a system can be evaluated using the relations derived from the second law of thermodynamics and then applying the third law. From the second law of thermodynamics we know that the entropy

change of a system is related to its heat capacity at constant pressure by

Calculation of absolute entropy from heat capacity by evaluation of $\int_{0\,\mathrm{K}}^{T\,\mathrm{K}} \frac{\mathrm{C_P}}{T}\mathrm{d}T$

$$\mathrm{d}S = \frac{\mathrm{C_P}}{T}\mathrm{d}T \qquad \text{(i)}$$

On integration equation (i) between the limits $T = T_1$, $S = S_1$ and $T = T_2$, $S = S_2$, we get

$$\int_{S_1}^{S_2} \mathrm{d}S = \int_{T_1}^{T_2} \frac{\mathrm{C_P}}{T}\mathrm{d}T$$

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{\mathrm{C_P}}{T}\mathrm{d}T$$

Or, $$S_2 = S_1 + \int_{T_1}^{T_2} \frac{\mathrm{C_P}}{T}\mathrm{d}T \qquad \text{(ii)}$$

On introducing the third law of thermodynamics that

when $T_1 = 0$ K, $S_1 = 0$

and when $T_2 = T$ K, $S_2 = S^o(T)$ = Absolute entropy at temperature T

equation (ii) gives

$$S^o(T) = \int_{0\,\mathrm{K}}^{T\,\mathrm{K}} \frac{\mathrm{C_P}}{T}\mathrm{d}T \qquad \text{(iii)}$$

The value of absolute entropy $S^o(T)$ can be evaluated provided the integral on right side of equation (iii) is known.

Note: Absolute entropy $S^o(T)$ is also called ***third law entropy***, because it is calculated by assuming the validity of the third law of thermodynamics that at $T = 0$ K, $S^o(T) = 0$.

The value of above integral is evaluated by the method of extrapolation. In this method the heat capacities of the substance are measured at different temperatures. The experiment is carried up to a lower temperature of 10 K (because the measurements can not be made right up to 0 K). These experimental values of C_P/T are plotted against the corresponding temperatures.(T). The curve thus obtained is extended up to $T = 0$ K. The area under the curve from $T = 0$ to $T = T$ (the temperature of interest) gives the value of integral and thus the value of absolute entropy $S^o(T)$ is evaluated.

Note: The heat capacity from 0 K to 10 K may also be estimated by Debye equation

$$C_V = 3R[\, \frac{3}{4}\pi r^4 (T/\theta)^3] = a(T/\theta\,)$$

It is assumed that for a solid $C_V = C_P$ at and near 0 K

Method of calculation of absolute entropy of a gaseous substance *A* at 298 K which also exists in α and β physical modifications in solid state

The method of calculation of absolute entropy may be considered to involve the calculation of entropy change for the following process

$$\text{A(s, 0 K, 1 atm)} \longrightarrow \text{A(g, 298 K, 1 atm)} \qquad \text{(I)}$$

$$\Delta S\,(\text{I}) = S^{\circ}\,(\text{A, g, 298 K, 1 atm}) - S^{\circ}\,(\text{A, s, 0 K, 1 atm})$$

But $\quad S^{\circ}\,(\text{A, s, 0 K, 1 atm}) = 0 \quad$ .. third law

Therefore, $\quad \Delta S\,(\text{I}) = S^{\circ}\,(\text{A, g, 298 K, 1 atm})$ = Absolute entropy of A

To calculate the value of ΔS (I) and thus S° (A, g, 298 K, 1 atm) let us assume that the main process (I) takes place in to the following steps.

(1) Heating solid A from T= 0 K to T= T_t (transition temperature)

(2) Transition from α to β at T= T_t

(3) Heating of β from $T = T_t$ to T= T_m (melting point)

(4) Melting of solid A (□) at T= T_m

(5) Heating of liquid A from $T = T_m$ to T= T_b (boiling point)

(6) Evaporation of liquid A at T= T_b

(7) Heating of gas A from T= T_b to T = 298 K

The entropy is a state function and change in entropy is the same whether the change is carried in a single step as indicated by (I) or in several steps as indicated by steps (1) to (7). Thus

$$\begin{tikzcd}
\text{A(s, 0 K, 1 atm)} \arrow[rr, "\text{(I)}"] \arrow[d, "(1)"] & & \text{A(g, 298 K, 1 atm)} & & & \text{A(g, } T_b\text{)} \arrow[lll, "(7)"'] \\
\text{A}(\alpha, T_t) \arrow[r, "(2)"] & \text{A}(\square, T_t) \arrow[r, "(3)"] & \text{A}(\square, T_m) \arrow[r, "(4)"] & \text{A(l, } T_m\text{)} \arrow[r, "(5)"] & \text{A(l, } T_b\text{)} \arrow[ur, phantom] & \\
\end{tikzcd}$$

$$\Delta S^{\circ}(\text{I}) = S^{\circ} = \Delta S^{\circ}\,(1) + \Delta S^{\circ}\,(2) + \Delta S^{\circ}\,(3)$$

$$+ \Delta S^{\circ}\,(4) + \Delta S^{\circ}\,(5) + \Delta S^{\circ}\,(6) + \Delta S^{\circ}\,(7)$$

$$= \int_0^{T_t} \frac{C_P(\alpha)}{T}\,dT + \frac{\Delta_t H}{T_t} + \int_{T_t}^{T_m} \frac{C_P(\beta)}{T}\,dT + \frac{\Delta_{\text{fus}} H}{T_m}$$

Step **S^{υ} /JK^{-1} mol^{-1}**

$$+ \int_{T_m}^{T_b} \frac{C_P(l)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{298\,K} \frac{C_P(g)}{T} dT$$

The calculation of absolute entropy (S^{υ}) of nitrogen gas at 298 K and 1 atm is summarized below and the values for other substances are given in table 4.

Steps of evaluation of S^{υ} of nitrogen

(1) Heating solid N_2 from T= 0 K to T= 35.61 K	$\int_{0}^{35.61\,K} \frac{C_P(\alpha)}{T} dT = 27.2$
(2) Transition from α to β at 35.61 K	$\frac{\Delta_t H}{T_t} = \frac{228.9}{35.61} = 6.4$
. □Heating β from 35.61 K to 63.14 K	$\int_{T_t}^{T_m} \frac{C_P(\beta)}{T} dT = 23.4$
(4) Melting at T_m = 63.14 K	$\frac{\Delta_{fus}H}{T_m} = \frac{720.9}{63.14} = 11.4$
(5) Heating liquid N_2 from T_m to T_b	$\int_{T_m}^{T_b} \frac{C_P(l)}{T} dT = 12.4$
(6) Evaporation of liquid N_2 at T_b	$\frac{\Delta_{vap}H}{T_b} = \frac{5535}{77.32} = \mathbf{71.6}$
(7) Heating N_2 gas from T_b to 298 K	$\int_{T_b}^{298\,K} \frac{C_P(g)}{T} dT = \mathbf{39.2}$
(I) $N_2(s, 0\,K, 1\,atm) \longrightarrow N(g, 298\,K, 1\,atm)$	191.6

Substance	S^{Θ} / JK^{-1} mol^{-1}
H_2 (g)	130.6
He (g)	126.0
N_2 (g)	191.5
O_2 (g)	205.0
Halogens	
F_2 (g)	203.3
CI_2 (g)	223.0
Br_2 (l)	152.3
I_2(s)	116.7
Hydrogen halides	
HF (g)	173.7
HCI (g)	186.7
HBr (g)	198.5
HI (g)	206.3
Common substances	
CO(g)	197.9
CO_2(g)	213.6
H_2O (g)	188.7
H_2S (g)	205.6
NH_3 (g)	192.5
SO_2 (g)	248.5
SO_3 (g)	256.2

Substance	S^{Θ} / JK^{-1} mol^{-1}
S (rhombic)	31.9
NO_2 (g)	240.5
N_2O (g)	304.3
NaCl (s)	72.4
KCI (s)	82.7
$CaCO_3$ (s)	92.9
Al_2O_3 (s)	51.0
AgCl (s)	96.1
Allotropes of carbon	
C (graphite)	5.7
C (diamond)	2.4
Hydrocarbons	
CH_4 (g)	186.2
C_2H_6 (g)	229.5
C_3H_8 (g)	270.9
C_4H_{10} (g)	310.8
C_2H_4 (g)	219.0
C_2H_2 (g)	201.0
Compounds with	**OH group**
HOH (l)	69.9
CH_3OH (l)	126.8
C_2H_5OH (l)	160.7

Discussion of absolute entropies

The values of absolute entropy of substances reveal the following interesting facts:

(1) The entropy of graphite (5.7 J K^{-1} mol^{-1}) is greater than that of diamond (2.4 J K^{-1} mol^{-1}). This is in tune with the fact that diamond has a compact structure than graphite. That is, there is less randomness in the lattice of diamond as compared to that in graphite.

(2) The absolute entropies of halogens (Cl_2 = 223 JK^{-1} mol^{-1}, Br_2 = 152 JK^{-1} mol^{-1}, I_2 = 117 JK^{-1} mol^{-1}) confirm the trend $S(\text{gas}) > S(\text{l}) > S(\text{s})$ which suggests that there is more randomness in gas as compared to liquid and solid

(3) The entropy hence randomness increases with increasing molar mass in a family of compounds. This is clear from the trends in the S° values of alkanes.

Alkane	CH_4	C_2H_6	C_3H_8	C_4H_{10}
S°/ JK^{-1} mol^{-1}	186.2	229.5	270.9	310.8

(4) The entropy of hydrogen (130.6 JK^{-1} mol^{-1}) is greater than the entropy of helium (126 JK^{-1} mol^{-1}) though the molar mass of He is twice the molar mass of H_2. This suggests that in H_2 (a diatomic molecule) the entropy arises due to translational, rotational and vibrational motions of the H–H system, while in He (a monotomic molecule) there is only translational motion

Need of a new thermodynamic property

The change of internal energy or change of enthalpy or the change of entropy of the system alone cannot be used as a criterion to decide the direction of a process because of the following reasons.

(i) The use of change of the internal energy $[(\Delta U)_{S,\,V} \leq 0]$ or change of enthalpy $[(\Delta H)_{S,\,P} \leq 0]$ requires the condition of constant entropy which is not easy to maintain.

(ii) The use of total entropy change $(\Delta S_{\text{universe}} \geq 0)$ requires the calculation of entropy changes for both the system and surroundings. Here again one may not like to bother directly about the surroundings while concentrating on the investigation of the system.

In view of the above limitations of the use of the changes in U, H and S separately, we need new thermodynamic function or functions of the system which should satisfy the following requirements:

(i) The new function must be able to predict the direction of the process

(ii) It should automatically incorporate the internal energy / enthalpy and entropy changes of the system.

(iii) If required the changes in new function of the system should also account for the changes of entropies of both the system and surroundings.

Two thermodynamic functions namely Gibbs energy (G) and Helmholtz energy (A) are introduced which fulfill the above requirements. The change in Gibbs energy (ΔG) serves as driving force at constant temperature and constant pressure while Helmholtz energy (ΔA) acts as driving force at constant temperature and constant volume.

Comments:

(i) The function G is called Gibbs free energy or free energy or ***Gibbs energy.***

(ii) The function A is called Helmholtz free energy or work function or ***Helmholtz energy***

(iii) The use of the last name of each function is the IUPAC recommendation.

Gibbs energy

Gibbs energy is an important thermodynamic property which automatically accounts for the enthalpy and entropy of the system. It was introduced by American physicist J.W. Gibbs and is therefore, called Gibbs energy function denoted by symbol G in the honour of the scientist. Gibbs energy function is defined by

$$G = H - TS$$

where H = Enthalpy of the system

S = Entropy of the system

T = Temperature on kelvin scale

Characteristics of Gibbs energy *(G)*

1. Gibbs energy is an extensive property. Its value depends on the amount of the system.

2. Gibbs energy of a system is a state property. For a known amount of the system it depends only on the state

variables (T, P, V). If the state variables are changed the Gibbs energy is also changed.

3. The change in Gibbs energy (ΔG) does not depend on the path by which the final state of the system is reached.

4. The change in Gibbs energy of the system is related to the entropy change of the universe as

$$\Delta G_{\text{system}} = -\,[T\Delta S_{\text{system}} + T\Delta S_{\text{surroundings}}] = -\,T\Delta S_{\text{total}} = -\,T\Delta S_{\text{universe}}$$

5. For a spontaneous process there is decrease in Gibbs energy and $\Delta G_{\text{system}} < 0$

6. In an isothermal reversible process the decrease in Gibbs energy is equal to the net useful work that can be obtained from the system.

Gibbs energy change and useful work

By useful work we mean the total possible work minus the mechanical work involved in a system.

w (useful) = w (total) – w (mechanical)

= w (net)

At constant T and P in a reversible process the free energy change (ΔG) and w (net) are related by

$$\Delta G = w \text{ (net)}$$

Derivation of the equation $\Delta G = w$ (net)

We shall start with the definitions of thermodynamic functions of G and H then derive the relation between ΔG and w(net)

$G = H - TS$ Definition of free energy G

$H = U + PV$ Definition of enthalpy H

Therefore, $G = U + PV - TS$

If the changes are made in the system so that its properties are also changed, we shall have

$$\Delta G = \Delta(U + PV - TS)$$

$$= \Delta U + \Delta(PV) - \Delta(TS)$$

$$= \Delta U + P\Delta V + V\Delta P - T\Delta S - S\,\Delta T$$

For isothermal process $\Delta T = 0$ and for isobaric process $\Delta P = 0$. Therefore, under isothermal and isobaric conditions

$$\Delta G = \Delta U + P\Delta V - T\Delta S \qquad .(i)$$

From the first law of thermodynamics, we have

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

Second law of thermodynamics gives

$$T\,\Delta S = q_{\text{rev}}$$

For a reversible change the combined form of the two laws is written as

$$\Delta U = q + w = T\Delta S + w \qquad (ii)$$

On substituting the expression for ΔU from equation (ii) into equation (i), we get

$$\Delta G = T\Delta S + w + P\Delta V - T\Delta S$$

$$= w + P\Delta V$$

The mechanical work (involving pressure - volume work) is defined as

w (mechanical) $= -P\Delta V$

Therefore, $\Delta G = w - w$ (mechanical) $= w$ (nonmechanical)

$= w$ (net) $= w$ (useful)

This relation is valid for isothermal isobaric reversible process. In reversible process the work obtained from the system is maximum therefore useful work is also written as w (max)

Interpretation of the relation $\Delta G = w$ (net)

In an isothermal isobaric reversible process:

1. The increase in free energy of the system is equal to the work done on the system over and above the mechanical work.
2. The decrease in free energy of the system is equal to the net work that can be obtained from the system

Application of the relation $\Delta G = w$ (net)

In electrochemical processes, the network that can be obtained from the system is equal to the electrical work.

w (net) $= w$ (electrical)

In a galvanic cell

w (electrical) $= -nFE = w$ (net)

where n = moles of electrons involved in a redox reaction

F = faraday constant = 96500 C mol^{-1}

E = potential difference (emf of reversible cell)

Therefore, $\Delta G = w$ (net) $= w$ (electrical) $= -nFE$

(i) The electrical work can be used for different purposes. That is why w(net) is called useful work and ΔG is called free energy change or available energy.

(ii) The relation $\Delta G = -nFE$ implies that decrease of free energy in a chemical reaction is the cause of cell potential and such reactions are source of electricity.

Relation between ΔG_{system} and $\Delta S_{\text{universe}}$

At constant pressure and constant temperature the change of free energy of the system is related to the enthalpy change (ΔH) and entropy change (ΔS) by

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} \qquad \text{(i)}$$

At constant pressure the heat exchanged between the system and surroundings is equal to the enthalpy change of the system.

$$q_{\text{system}} = \Delta H_{\text{system}} \qquad \text{at constant pressure}$$

But heat exchanged between the system and surroundings are related by

$$q_{\text{surroundings}} = -q_{\text{system}} = -\Delta H_{\text{system}}$$

Therefore, entropy change of surroundings is given by

$$.\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} = -\frac{q_{\text{ssystem}}}{T} = -\frac{\Delta H_{\text{ssystem}}}{T}$$

Or, $$\Delta H_{\text{system}} = -T\,\Delta \text{S}_{\text{surroundings}} \qquad \text{(ii)}$$

Substituting equation (ii) into equation (i), we get

$$\Delta G_{\text{system}} = -T\,\Delta \text{S}_{\text{surroundings}} - T\Delta S_{\text{system}}$$

$$= -[T\,\Delta \text{S}_{\text{surroundings}} + T\,\Delta S_{\text{system}}] \qquad \text{(iii)}$$

But $$\Delta \text{S}_{\text{surroundings}} + \Delta S_{\text{system}} = \Delta S_{\text{universe}} \qquad \text{(iv)}$$

Therefore, from equations (iii) and (iv), we get

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

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

Conclusion: The decrease in the free energy of the system is equal to increase in the entropy of the universe multiplied by the kelvin temperature.

Free energy change and spontaneous processes

We have already discussed that for a spontaneous process the total entropy change ($\Delta \text{S}_{\text{universe}}$) must be positive. Therefore, in view of the relation $\Delta G_{\text{system}} = -T\Delta S_{\text{universe}}$, the free energy change of the system must be negative. That is, at constant temperature and constant pressure the free energy of the system must decrease in a spontaneous process and

$$(\Delta G)_{\text{T, P}} < 0 \qquad \text{.for a spontaneous process}$$

A decreasing quantity must attain its minimum value at equilibrium after which there is no net change, therefore.

$$(\Delta G)_{\text{T, P}} = 0 \qquad \text{at equilibrium}$$

If there is increase in the free energy, the process is nonspontaneous (forbidden)

$$(\Delta G)_{\text{T, P}} > 0 \qquad \text{nonspontaneous}$$

These criteria may be summarized as follows

(i) ΔG is negative	Spontneous process
(ii) ΔG is posive	Nonspontneous process
(iii) ΔG is zero	Equilibrium state

Criteria of spontaneous process in terms of ΔH and $T\,\Delta S$

A change is spontaneous only when ΔG is negative. Therefore, it is essential to learn the roles of ΔH and

$T\,\Delta S$ in the relation $\Delta G = \Delta H - T\Delta.S$ and decide the direction of the change under different situations.

(1) When ΔH is negative and ΔS is positive

From the relation $\Delta G = \Delta H - T\Delta.S$, it is clear that under the given situation ΔG is negative and therefore, the change is spontaneous. In other words, we may state that an exothermic reaction with positive entropy change is always spontaneous.

(2) When ΔH is positive and ΔS is negative

From the relation $\Delta G = \Delta H - T\Delta.S$, it is clear that under the given situation ΔG is positive and therefore, the change is nonspontaneous (forbidden) in the desired direction. In other words, we may state that an endothermic reaction with negative entropy change is never spontaneous However, it may be spontaneous in the opposite direction

(3) **When both ΔH and ΔS are positive**

At lower temperature $T\Delta S$ will be small therefore, ΔH will predominate. Thus $\Delta G = \Delta H - T\Delta S$ will be positive and the change will be nonspontaneous. But at higher temperature $T\Delta S$ will be larger than ΔH. Therefore, $\Delta G = \Delta H - T\Delta.S$ will be negative and the change will be spontaneous. In other words, we may state that an endothermic reaction with positive entropy change is spontaneous at high temperature but nonspontaneous at lower temperature.

(4) **When both ΔH and ΔS are negative**

At lower temperature $T\Delta S$ will be small therefore, ΔH will predominate. Thus $\Delta G = \Delta H - T\Delta S$ will be negative and the change will be spontaneous. But at higher temperature $T\Delta S$ will predominate ΔH. Therefore, $\Delta G = \Delta H - T\Delta.S$ will be positive and the change will be nonspontaneous. In other words, we may state that an exothermic reaction with negative entropy change is spontaneous at lower temperature but nonspontaneous at higher temperature.

Summary of the direction of the change in terms of ΔH and $T\Delta S$

S. No.	**Sign of ΔH**	**Sign of ΔS**	**Sign of ΔG**	**Nature of the change**
(1)	– (exothermic)	positive	Always negative	Spontaneous
(2)	+ (endothermic)	negative	Always positive	Nonspontaneous

Important deductions from equation $dG = VdP - S\,dT$

(3)	+ (endothermic)	positive	Positve at lower T	Nonspontaneous
			Negative at higher T	Spontaneous
(4)	– (exothermic)	negative	Negative at lower T	Spontaneous
			Positive at higher T	Nonspontaneous

Example. An exothermic reaction is sometimes thermodynamically not spontaneous. Give reason

Soluion. An exothermic reaction is sometimes thermodynamically not spontaneous under the conditions when the entropy change ΔS is large negative and temperature T is very high

Reason. Under the above conditions $T\Delta S$ is large postive and therefore, $\Delta G = \Delta H - T\Delta S$ is positive

Variation of Gibbs energy (G) with temperature and pressure

$$\mathbf{G = H - TS} \quad \textit{\textbf{and}} \quad \mathbf{H = U + PV}$$

Therefore,
$$G = U + PV - TS \qquad \text{(i)}$$

For small changes

$$dG = dU + PdV + VdP - TdS - SdT \qquad \text{(ii)}$$

From combined form of first and second laws thermodynamics, we have

$$\mathbf{TdS = dU + PdV} \qquad \textit{\textbf{(iii)}}$$

From equations (ii) and (ii), we get

$$\begin{aligned} dG &= TdS + VdP - TdS - SdT \\ &= VdP - S\,dT \qquad \text{(iv)} \end{aligned}$$

From equation (vi) it is observed that Gibbs function depends on pressure and temperature that is, $G = G(P, T)$. Its total differential is written as

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_P \mathrm{d}T \qquad \text{(v)}$$

(i) When T is constant, $dT = 0$, therefore,

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Volume is positive and thus right hand side of the above equation is positive. Therefore, $(\partial G/\partial P)_T$ is also positive. This means that at constant temperature, Gibbs energy increases with increase of pressure and decreases with decrease of pressure.

(ii) When P is constant, $dP = 0$, therefore,

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

Entropy (S) is positive and thus right hand side of the above equation is negative. Therefore, $(\partial G/\partial T)_P$ is also negative. This means that at constant pressure, Gibbs energy decreases with increase of temperature and increases with decrease of temperature.

Note: The entropy depends on the nature of the three states matter as given by

$$S(\text{gas}) > S(\text{liquid}) > S(\text{solid})$$

Therefore, with increase of temperature there is more decrease in Gibbs energy of a gas than that of a liquid and there is more decrease in G of a liquid than that of a solid

Calculation of ΔG for isothermal pressure change of an ideal gas

In an isothermal process, T is constant and $dT = 0$, therefore, equation $dG= VdP - S\,dT$ is written as

$$dG = VdP \qquad \text{(i)}$$

A finite change in G is calculated by integrating equation (i) for the change of state from initial state 1 to final state 2

$$\int_1^2 dG = \int_1^2 VdP \qquad \text{(ii)}$$

Equation (ii) is applicable for all the three states of matter. But right hand side of this equation has different values for different substances. Therefore, variation of G is also different for different type of substances.

(a) For condensed states of matter namely liquids ad solids

The volume of a liquid or solid is almost independent of pressure at constant temperature. Therefore, it can be taken outside the integration sign of equation (ii). Thus

$$\int_1^2 dG = V\int_1^2 dP$$

Or, $G_2 - G_1 = V(P_2 - P_1)$

Or, $\Delta G = V\Delta P$

(b) For an ideal gas

The volume of an ideal gas is given by $V= nRT/P$. Therefore, equation (ii) is rewritten as

$$\int_1^2 dG = nRT\int_1^2 \frac{dP}{P} = nRT\int_1^2 d\ln P$$

Or, $$G_2 - G_1 = \Delta G = nRT\ln\frac{P_2}{P_1} \qquad \text{(iii)}$$

From equation (iii) it is clear that ΔG is negative for isothermal expansion of an ideal gas (Gibbs energy decreases as the gas expands) while it is positive for isothermal compression (Gibbs energy increases as the gas is compressed).

Helmholtz energy

Helmholtz energy function (A) was introduced by German physicist Hermann Ludwig Ferdinand von Helmholtz and is defined by

$$A = U - TS$$

where U is internal energy, T is Kelvin temperature and S is entropy. The symbol A is the first letter of the German word ***Arbeit*** which means work. Therefore, Helmholtz energy (A) is also called ***work function.***

Helmholtz energy as work function

Definition: $$A = U - TS \qquad \text{(i)}$$

For infinitesimally small change

$$dA = dU - TdS - SdT \qquad \text{(ii)}$$

From the combined form of first and second laws of thermodynamics we have

$$dU = dq + dw = TdS + dw_{\text{rev}} \text{ (iii)}$$

From equations (ii) and (iii) we get

$$dA = TdS + dw_{\text{rev}} - TdS - SdT$$

$$= dw_{\text{rev}} - SdT \qquad \text{(iv)}$$

For isothermal process, T is constant and $dT = 0$, therefore, equation (iv) reduces to

$$(dA)_T = dw_{\text{rev}}$$

For finite changes

$$(\Delta A)_T = w_{\text{rev}}$$

Or, $$-(\Delta A)_T = -w_{\text{rev}} = w_{\text{rev}}(\text{by})$$

The work done by a system under isothermal reversible condition is the maximum work Therefore, decrease in Helmholtz energy is equal to the isothermal reversible maximum work which can be obtained from a system It is because of this relation that A is called ***work function***.

Relation between ΔA_{system} and $\Delta S_{\text{universe}}$

At constant volume and constant temperature the change of Helmholtz energy of the system is related to the internal energy change *(ΔU)* and entropy change (Δ*S)* by

$$\Delta A_{\text{system}} = \Delta U_{\text{system}} - T\Delta S_{\text{system}} \qquad \text{(i)}$$

At constant volume the heat exchanged between the system and surroundings is equal to the internal energy change of the system.

$$q_{\text{system}} = \Delta U_{\text{system}} \qquad \text{at constant volume}$$

But heat gained by the system is equal to heat lost by the surroundings and vice versa. That is,

$$q_{\text{surroundings}} = -q_{\text{system}} = -\Delta U_{\text{system}}$$

Entropy change of surroundings is given by

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} = -\frac{q_{\text{ssystem}}}{T} = -\frac{\Delta U_{\text{ssystem}}}{T}$$

Or, $$\Delta U_{\text{system}} = -T\Delta \mathrm{S}_{\text{surroundings}} \qquad \text{(ii)}$$

Substituting equation (ii) into equation (i), we get

$$\Delta A_{\text{system}} = -T\Delta \mathrm{S}_{\text{surroundings}} - T\Delta S_{\text{system}}$$

$$= -[T\Delta \mathrm{S}_{\text{surroundings}} + T\Delta S_{\text{system}}] \qquad \text{(iii)}$$

But $$\Delta \mathrm{S}_{\text{surroundings}} + \Delta S_{\text{system}} = \Delta S_{\text{universe}} \qquad \text{(iv)}$$

From equations (iii) and (iv), we get

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

Or, $$-\Delta A_{\text{system}} = T\Delta S_{\text{universe}}$$

Conclusion: The decrease in the Helmholtz energy of the system is equal to increase in the entropy of the universe multiplied by the kelvin temperature.

Helmholtz energy change and spontaneous processes

We have already discussed that for a spontaneous process the total entropy change ($\Delta \mathrm{S}_{\text{universe}}$) must be positive. Therefore, in view of the relation $\Delta A_{\text{system}} = -T\Delta S_{\text{universe}}$, the Helmholtz energy change of the system must be negative. That is, at constant temperature and constant volume in a spontaneous process the Helmholtz energy of the system must decrease and

$$(\Delta A)_{\mathrm{T,V}} < 0 \qquad \text{for a spontaneous process}$$

A decreasing quantity must attain its minimum value at equilibrium after which there is no change, therefore,

$(\Delta A)_{T,V} = 0$ at equilibrium

If there is increase in the Helmholtz energy, the process is nonspontaneous (forbidden)

$(\Delta A)_{T,V} > 0$ nonspontaneous

These criteria may be summarized as follows

(i) ΔA is negative	Spontneous process
(ii) ΔA is posive	Nonspontneous process
(iii) ΔA is zero	Equilibrium state

Summary of the direction of the change at constant *T* and *V* in terms of ΔU and $T\Delta S$

S. No.	Sign of ΔU	Sign of ΔS	Sign of ΔA	Nature of the change
(1)	– (exothermic)	positive	Always negative	Spontaneous
(2)	+ (endothermic)	negative	Always positive	Nonspontaneous
(3)	+ (endothermic)	positive	Positve at lower *T*	Nonspontaneous
			Negative at higher *T*	Spontaneous
(4)	– (exothermic)	negative	Negative at lower *T*	Spontaneous
			Positive at higher *T*	Nonspontaneous

ADVANTAGES OF USING ΔA AND ΔG OVER ΔS

(i) Use of entropy change to predict the nature of a process requires the knowledge of the entropy changes for both the system and surroundings. But the change of Helmholtz energy or change of Gibbs energy of the system alone is sufficient to predict the direction of a process.

(ii) While using the entropy change it is required that energy and volume are constant $(\Delta S)_{U,V.} > 0$. But it is not very convenient to maintain a constant energy condition in the laboratory. On the other hand, while using free energy change ΔA or ΔG only the state variables (*T, V,* or *T, P*) are to be kept constant, which are easy to maintain in the laboratory. Therefore, the use of ΔA_s or ΔG is preferred over ΔS as a driving force to predict the direction of a process

Advantages of using ΔG over ΔA

When ΔG is used to predict the direction of a process it is required to maintain constant temperature and constant pressure as $(\Delta G)_{T,\,P} < 0$ for a spontaneous process.. On the

Important deductions from equation $dA = -PdV - S\,dT$

other hand, if ΔA is used to decide the direction of a process the temperature and volume are to be kept constant as $(\Delta A)_{T,\,V} < 0$ for spontaneous process. Since in the chemistry laboratory usually the experiments are performed at constant temperature and constant pressure, therefore, the use of ΔG as driving force is preferred over the use of ΔA which requires the condition of constant T and constant V.

Variation of Helmholtz energy (A) with volume and temperature

$$A = U - TS \qquad \text{(i)}$$

$$dA = dU - TdS - SdT \qquad \text{(ii)}$$

From combined form of first and second laws thermodynamics, we have

$$\mathbf{dU = TdS - PdV} \qquad \textit{(iii)}$$

From equations (ii) and (iii), we get

$$dA = TdS - PdV - TdS - SdT$$

$$= -PdV - S\,dT \qquad \text{(iv)}$$

From equation (iv) it is observed that $A = A(V, T)$ and its total differential is written as

$$\mathrm{d}A = \left(\frac{\partial A}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial A}{\partial T}\right)_V \mathrm{d}T \qquad \text{(v)}$$

(i) When T is constant, $dT = 0$, therefore,

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Pressure (P) is positive and thus right hand side of the above equation is negative. Therefore, $(\partial A/\partial V)_T$ is also negative. This means that at constant temperature, Helmholtz energy decreases with increase of volume and increases with decrease of volume

(ii) When V is constant, $dV = 0$, therefore,

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Entropy (S) is positive and thus right and side of the above equation is negative. Therefore, $(\partial A/\partial T)_V$ is also negative. This means that at constant volume, Helmholtz energy decreases with increase of temperature and increases with decrease of temperature.

Calculation of ΔA for isothermal volume change of an ideal gas

For isothermal process

$$dA = -PdV \qquad \text{(i)}$$

A finite change in *A* is calculated by integrating equation (i) for the change of state from initial state 1 to final state 2

$$\int_1^2 dA = -\int_1^2 PdV \qquad \text{(ii)}$$

For an an ideal gas we have *PV = nRT and P= nRT/V*. Therefore, equation (ii) is rewritten as

$$\int_1^2 dA = -nRT\int_1^2 \frac{dV}{V} = -nRT\int_1^2 d\ln V$$

Or, $$A_2 - A_1 = \Delta A = -nRT\ln\frac{V_2}{V} \qquad \text{(iii)}$$

From equation (iii) it is clear that ΔA is negative for isothermal expansion of an ideal gas (Gibbs energy decreases as the gas expands) while it is positive for isothermal compression (Gibbs energy increases as the gas is compressed).

Relation between *G* and *A*

$$G = H - TS = U + PV - TS \qquad \text{(i)}$$

$$A = U - TS \qquad \text{(ii)}$$

From equations (i) and (ii) we get

$$G = A + PV$$

Or, $$G - A = PV$$

For a finite change in the state of the system

$$\Delta G - \Delta A = \Delta(PV) = P_2V_2 - P_1V_1$$

At constant temperature, $P_2V_2 = P_1V_1$ for an ideal gas

Therefore, $\Delta G - \Delta A = 0$

and $\Delta G = \Delta A$ for an ideal gas at constant temperature

In terms of change of pressure and volume

$$nRT\ln\frac{P_2}{P_1} = -nRT\ln\frac{V_2}{V} \qquad \text{for an ideal gas at constant temperature}$$

VARIATION OF *G* AND *A* WITH *T*

Variation of free energy functions with *T* is called ***Gibbs Helmholtz equation***. Such variation is studied for *G* and *A* separately.

(1) Variation of *G* with *T* at constant *P*

The change of Gibbs energy is given by

$$dG = VdP - S\,dT \qquad \text{(i)}$$

At constant pressure, dP = 0 and thus

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

From equations (ii) and (i) we get

$$\mathbf{G = H + T}\left(\frac{\partial G}{\partial T}\right)_P$$

Or,
$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P \qquad \text{(iii)}$$

Equation (iii) is called ***Gibbs Helmholtz***

Second form of Gibbs Helmholz equation: For finite changes in H and G Gibbs Helmholtz equation is written as

$$\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad \text{(iv)}$$

On dividing both sides of equation (iv) by T^2, we get

$$\frac{\Delta H}{T^2} = \frac{\Delta G - T\partial(\Delta G/\partial T)_P}{T^2} \qquad \text{(v)}$$

Now right hand side of equation (v) is the differential of $-\Delta G/T$ with respect to T. Therefore,

$$\frac{\Delta H}{T^2} = -\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P$$

Or,
$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \qquad \text{(vi)}$$

Third form of *Gibbs Helmholtz equation:* We know that d$T = -T^2$ d$(1/T)$.*How?*

$$d\left(\frac{1}{T}\right)_P = -\frac{1}{T^2}dT$$

Or,
$$dT = -T^2\,d\left(\frac{1}{T}\right)_P$$

Therefore, equation (xi) is rewritten as

$$\left(\frac{\partial(\Delta G/T)}{\partial(1/T)}\right)_P = \Delta H$$

Integrated form of *Gibbs Helmholtz equation:* Equation (ix) is written as

$$\int \mathrm{d}\left(\frac{\Delta G}{T}\right) = -\int \frac{\Delta H}{T^2}\,\mathrm{d}T + \mathrm{I}$$

If we suppose that ΔH is independent of temperature, then integration of the above equation gives

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} + \mathrm{I}$$

Here , I is the integration constant and its value can be evaluated if the values of ΔG and ΔH are known

Gibbs Helmholtz equation for work function (*A*)

Starting with the definition of Helmholtz energy (A) we can derive the following equations.

$$\mathbf{A - T}\left(\frac{\partial A}{\partial T}\right)_V \mathbf{= U} \qquad \textbf{\textit{(i)}}$$

$$\left(\frac{\partial(\Delta A/T)}{\partial T}\right)_V = -\frac{\Delta U}{T^2} \qquad \text{(ii)}$$

$$\left(\frac{\partial(\Delta A/T)}{\partial(1/T)}\right)_V = \Delta U \qquad \text{(iii)}$$

$$\frac{\Delta A}{T} = \frac{\Delta U}{T} + \text{Integration constant} \qquad \text{(iv)}$$

MASTER EQUATIONS OF THERMODYNAMICS

Thermodynamics is an exact science. It is very systematic and interesting. Therefore, to become a master of the subject one needs to remember the following fundamental thermodynamic relations

$$\mathrm{d}U = dq - PdV \qquad \text{(i)}$$

$$dq = TdS \qquad \text{(ii)}$$

$$H = U + PV \qquad \text{(iii)}$$

$$A = U - TS \qquad \text{(iv)}$$

$$G = H + TS \qquad \text{(v)}$$

Using these equations any other desired relation can be derived keeping in mind the fact that *U, H, S, A* and *G* etc.*,* are state functions and obey Euler's reciprocity relation.

Maxwell relations

There are four main Maxwell relations which provide the expressions for partial derivatives and thus the rate of change of one thermodynamic property with another.

(i) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(ii) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(iii) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(iv) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

(1) Derivation of Maxwell relation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

We shall start with the combined form of first and second laws of thermodynamics and give the most convenient and accurate method of derivation of Maxwell relation.

$$\mathrm{d}U = TdS - PdV \qquad \text{(i)}$$

Remembering that for a state function (□)

$$\mathrm{d}□ = M\,\mathrm{d}x + N\,dy \qquad \text{(ii)}$$

and Euler's reciprocity relation states that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \qquad \text{(iii)}$$

Now, U is a state function and dU is exact differential. Therefore, in view of equations (iii) and (i) we can state that differential of T with respect to V at constant S is equal to the differential of $-P$ with respect to S at constant T. That is,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \text{… Maxwell relation}$$

(2) Derivation of Maxwell relation $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

The combined form of first and second laws of thermodynamics in terms of enthalpy change is given by

$$dH = TdS + VdP$$

Now, H is a state function and dH is exact differential. Therefore, in view of Euler's reciprocity relation it can be stated that differential of T with respect to P at constant S is equal to the differential of V with respect to S at constant T. That is,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \text{Maxwell relation}$$

(3) Derivation of Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

The change in Helmholtz energy is given by

$$dA = -SdT - PdV$$

Now, A is a state function and dA is exact differential. Therefore, in view of Euler's reciprocity relation it can be stated that differential of $-S$ with respect to V at constant T is equal to the differential of $-P$ with respect to T at constant V. That is,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{Maxwell relation}$$

(4) Derivation of Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

The change in Gibbs energy is given by

$$dG = -SdT + VdP$$

Now, G is a state function and dG is exact differential. Therefore, in view of Euler's reciprocity relation it can be stated that differential of $-S$ with respect to P at constant T is equal to the differential of V with respect to T at constant P. That is,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{Maxwell relation}$$

Significance of Maxwell relations

(i) Maxwell relations provide us methods of evaluation of even those properties which are otherwise very difficult to measure directly in the laboratory. For example

(a) Variation of entropy with volume at constant temperature cannot be studied directly by experimental method.

Reason: We do not have an apparatus called entropymeter as we have barometer for pressure or. thermometer for temperature

Remedy: Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ provides a method to estimate the value of $\left(\frac{\partial S}{\partial V}\right)_T$ in terms of the change of pressure with temperature at constant volume $\left(\frac{\partial P}{\partial T}\right)_V$ which is also equal to the ratio of coefficient of thermal expnsion and isothermal compressibity coefficient ($\tilde{\alpha}\tilde{\square}$)

(b) Variation of entropy with pressure at constant temperature cannot be studied directly by experimental method.

But Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ provides a method to estimate the value of $\left(\frac{\partial S}{\partial P}\right)_T$ in terms of $\left(\frac{\partial V}{\partial T}\right)_P = -\,\alpha V$

(ii) Maxwell relations are useful to derive other important thermodynamic relations in a simple way. For example,

(a) Thermodynamic equation of state in terms of change in internal energy

Combined form of first and second laws of thermodynamics states that

$$TdS = dU + PdV \qquad \text{(i)}$$

On dividing equation (i) by dV at constant temperature we gave

$$T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P \qquad \text{(ii)}$$

Or, $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \qquad \text{(iii)}$$

But Maxwell relation states that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{(iv)}$$

From equations (iii) and (iv) we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{(v)}$$

Equation (v) is called ***thermodynamic equation of state***. It provides a method to study the variation of internal energy with volume at constant temperature in terms of PVT data for any substance.

(b) Thermodynamic equation of state in terms of change in enthalpy

Entropy change and enthalpy change are related by

$$TdS = dH - VdP \qquad \text{(i)}$$

On dividing equation (i) by dP at constant temperature we gave

$$T\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - V \qquad \text{(ii)}$$

Or, $$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \qquad \text{(iii)}$$

But Maxwell relation states that

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{(iv)}$$

From equations (iii) and (iv) we get

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{(v)}$$

Equation (v) provides a method to study the variation of enthalpy with pressure at constant temperature in terms of PVT data for any substance.

Calculation of standard reaction free energy ($\Delta_r G^{\upsilon}$)

The standard free energy of a reaction is calculated by the following methods.

(i) Using the relation $\Delta_r G^{\upsilon} = \Delta_r H^{\upsilon} - T\Delta_r S^{\upsilon}$

where

$\Delta_r H^{\upsilon}$ = standard reaction enthalpy.

and $\Delta_r S^{\upsilon}$ = standard reaction etropy

(a).The value of $\Delta_r H^{\upsilon}$ is estimated calorimetrically or by the use of standard enthalpy of formation values of the reactants and products as

$$\Delta_r H^{\upsilon} = \Sigma \nu_P \, \Delta_f H^{\upsilon} \text{ (products)} - \Sigma \nu_R \, \Delta_f H^{\upsilon} \text{ (reactants)}$$

(b) The value of $\Delta_r S^{\upsilon}$ is calculated by the use of standard entropy (S^{υ}) values of the reactants and products as

$$\Delta_r S^{\upsilon} = \Sigma \nu_P \, S^{\upsilon} \text{ (products)} - \Sigma \nu_R \, S^{\upsilon} \text{ (reactants)}$$

Here ν_P = stoichiometric coefficient of the product

and ν_R = stoichiometric coefficient of the reactant

(ii) Using the relation $\Delta_r G^{\upsilon} = \Sigma \nu_P \, \Delta_f G^{\upsilon} \text{ (products)} - \Sigma \nu_R \, \Delta_f G^{\upsilon} \text{ (reactants)}$

Where $\Delta_f G^{\upsilon}$ = standard free energy of formation.

(a) For compounds the values $\Delta_f G^{\upsilon}$ are taken from the table of thermodynamic properties.

(b) The standard free energy of formation of an element is assumed to be zero by convention

$$\Delta_f G^{\upsilon} \text{ (element)} = 0$$

(c) Entropy of an element is not zero at temperatures higher than 0 K

$$S^{\upsilon} \text{ (element)} \neq 0$$

Example: Calculate $\Delta_r G^{\upsilon}$ at 25 °C for the reaction $2NH_3 (g) \longrightarrow N_2(g) + 3 H_2(g)$ using the following data

Substance	**NH_3**	**N_2**	**H_2**
$\Delta_f H^{\upsilon}$/ kJ mol^{-1}	**– 46**	**–**	**–**
S^{υ}/ J K^{-1} mol^{-1}	**193**	**192**	**131**

Solution. Formula used $\Delta_r G^{\upsilon} = \Delta_r H^{\upsilon} - T\Delta_r S^{\upsilon}$

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

$$\Delta_r H^{\upsilon} = \Sigma \nu_P \, \Delta_f H^{\upsilon} \text{ (products)} - \Sigma \nu_R \, \Delta_f H^{\upsilon} \text{ (reactants)}$$

$$= \Delta_f H^{\upsilon} (N_2, g) + 3\Delta_f H^{\upsilon} (H_2, g) - 2\Delta_f H^{\upsilon} (NH_3, g)$$

Since $\Delta_f H^{\upsilon}$ (element) = 0, therefore $\Delta_f H^{\upsilon} (N_2, g) = 0$ and $\Delta_f H^{\upsilon} (H_2, g) = 0$

Therefore, $\Delta_r H^{\upsilon} = 0 + 3\times 0 - 2\times (- 46 \text{ kJ mol}^{-1}$

$$= 92 \text{ kJ mol}^{-1}$$

$$\Delta_r S^{\upsilon} = \Sigma \nu_P \, S^{\upsilon} \text{ (products)} - \Sigma \nu_R \, S^{\upsilon} \text{ (reactants)}$$

$$= S^{\upsilon} (N_2, g) + 3 S^{\upsilon} (H_2, g) - 2 S^{\upsilon} (NH_3, g)$$

$$= 192 \text{ J K}^{-1} \text{ mol}^{-1} + 3\times 131 \text{ J K}^{-1} \text{ mol}^{-1} - 2\times 193 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 199 \text{ J K}^{-1} \text{ mol}^{-1} = 0.199 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Therefore, $\Delta_r G^{\upsilon} = \Delta_r H^{\upsilon} - T\Delta_r S^{\upsilon}$

$$= 92 \text{ kJ mol}^{-1} - 298 \text{ K}\times 0.199 \text{ kJ K}^{-1} \text{ mol}^{-1} = 32.698 \text{ kJ mol}^{-1}$$

Example. Calculate the change of entropy at 298 K for the formation of urea from ammonia and carbon dioxide as per equation $2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)$ using the following data.

Substance	**NH_3**	**CO_2**	**H_2O**	**NH_2CONH_2**
S^{υ} / JK^{-1} mol^{-1}	**192.3**	**213.7**	**69.8**	**174.0**

Solution. For the reaction $2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)$

$$\Delta_r S^{\upsilon} = [S^{\upsilon}(NH_2CONH_2) + S^{\upsilon}(H_2O) — [2\ S^{\upsilon}(NH_3 + S\upsilon\ (CO_2)]$$

$$=174.0 + 69.8]\ JK^{-1} — [2\times192.3 + 213.7]$$

$$= 243.8\ JK^{-1} — 598.3\ JK^{-1}\ mol^{-1} = -\ 354.5\ JK^{-1}\ mol^{-1}$$

Example. Using the $\Delta_f G^{\upsilon}$ values calculate $\Delta_r G^{\upsilon}$ for the following reactions and state the spontaneous and nonspontaneous reactions.

(a) $Ca\ (s) + Cl_2\ (g) \rightarrow CaCl_2\ (s)$

(b) $HgO\ (s) \rightarrow Hg\ (1) + 1/2\ O_2\ (g)$

(c) $NH_3\ (g) + 2\ O_2\ (g) \rightarrow HNO_3\ (1) + H_2O\ (1)$

Data given:

Compound	**$CaCl_2$**	**HgO**	**NH_3**	**HNO_3**	**H_2O**
$\Delta_f G^{\upsilon}$ /kJ mol^{-1}	**–748.1**	**– 58.54**	**– 16.45**	**– 80.71**	**– 237.13**

Solution.

(a) For the reaction $Ca\ (s) + Cl_2\ (g) \rightarrow CaCl_2\ (s)$

$$\Delta_r G^{\upsilon} = \Delta_f G^{\upsilon}\ (CaCl_2, s) — [\Delta_f G^{\upsilon}\ (Ca,s) + \Delta_f G^{\upsilon}\ (Cl_2, g)$$

$$= -748.1 kJ\ mol^{-1} - [0 + 0] = \mathbf{-748.1kJ\ mol^{-1}}$$

$\Delta_r G^{\upsilon}$ is negative, therefore the given reaction is ***spontaneous***.

(b) For the reaction $HgO\ (s) \rightarrow Hg\ (1) + 1/2\ O_2\ (g)$

$$\Delta_r G^{\upsilon} = [\Delta_f G^{\upsilon}\ (Hg, l) + 1/2\ \Delta_f G^{\upsilon}\ (O_2, g)\ ] — \Delta_f G^{\upsilon}\ (HgO, s)$$

$$=[0 + 0] — [-\ 58.54\ \ kJ\ mol^{-1}] = \mathbf{58.54\ \ kJ\ mol^{-1}}$$

$\Delta_r G^{\upsilon}$ is positive, therefore the given reaction is ***nonspontaneous***.

(c) For the reaction $NH_3\ (g) + 2\ O_2\ (g) \rightarrow HNO_3\ (1) + H_2O\ (1)$

$$\Delta_r G^{\upsilon} = [\Delta_f G^{\upsilon}\ (HNO_3, l) + \Delta_f G^{\upsilon}\ (H_2O.l)\ ] — [\Delta_f G^{\upsilon}\ (NH_3, g) + 2\ \Delta_f G^{\upsilon}\ (O_2, g)\ ]$$

$= [-80.71 - 237.13]\ \text{kJ mol}^{-1} — [-16.45 + 2\times0]\ \text{kJ mol}^{-1}$

$= \mathbf{-301.39\ kJ\ mol^{-1}}$

$\Delta_r G^{\upsilon}$ is negative, therefore the given reaction is ***spontaneous***.

Example. Calculate Gibbs energy change ($\Delta_r G^{\upsilon}$) for the reaction $CaCO_3$ (s) →CaO (s) + CO_2 (g) at 1273 K and at 1 bar using the following data

Substance	**$CaCO_3$ (s)**	**CaO (s)**	**CO_2 (g)**
$\Delta_f H^{\upsilon}$/ kJ mol^{-1}	**–1207**	**–633.2**	**–393.5**
S^{υ}/ JK^{-1} mol^{-1}	**92.9**	**39.75**	**213.74**

Is this reaction spontaneous at this temperature and pressure ?

Solution. For the reaction $CaCO_3$ (s) →CaO (s) + CO_2 (g) first we shall calculate the values of $\Delta_r H^{\upsilon}$ and $\Delta_r S^{\upsilon}$ then the value of $\Delta_r G^{\upsilon}$

Calculation of $\Delta_r H^{\upsilon}$

$\Delta_r H^{\upsilon} = [\ \Delta_f H^{\upsilon}\ (CO_2) + \Delta_f H^{\upsilon}\ (CaO)\ ] — \Delta_f H^{\upsilon}\ (CaCO_3)]$

$= [-393.5 + (-633.2)]\ \text{kJ mol}^{-1} — (-1207\ \text{kJ mol}^{-1})$

$= -1026.7\ \text{kJ mol}^{-1} + 1207\ \text{kJ mol}^{-1} = +180.3\ \text{kJ mol}^{-1}$

Calculation of $\Delta_r S^{\upsilon}$

$\Delta_r S^{\upsilon} = [\ S^{\upsilon}\ (CO_2) + S^{\upsilon}\ (CaO)\ ] — S^{\upsilon}\ (CaCO_3)]$

$= [213.74 + 39.75]\ \text{JK}^{-1}\ \text{mol}^{-1} — 92.9\ \text{JK}^{-1}\ \text{mol}^{-1}$

$= 253.49\ \text{JK}^{-1}\ \text{mol}^{-1} — 92.9\ \text{JK}^{-1}\ \text{mol}^{-1} = 160.59\ \text{JK}^{-1}\ \text{mol}^{-1}$

Calculation of $\Delta_r G^{\upsilon}$

$\Delta_r G^{\upsilon} = \Delta_r H^{\upsilon} — T\times\Delta_r S^{\upsilon}$

$= 180.3\ \text{kJ mol}^{-1} — 1273\ \text{K} \times 160.59\ \text{JK}^{-1}\ \text{mol}^{-1}$

$= 180.3\ \text{kJ mol}^{-1} — 204.4 = -24.1\ \text{kJ mol}^{-1}$

The negative value of $\Delta_r G^{\upsilon}$ suggests that the given reaction is spontaneous

Example. Use the following $\Delta_r G$ values at 1073 K to calculate the change in Gibbs energy and show that the roasting of zinc sulphide in to zinc oxide is a spontaneous process

(i) $S_2(s) + 2\ O_2(g) \longrightarrow 2\ SO_2(g)$ $\quad$ $\Delta_r G(i) = -544\ \text{kJ mol}^{-1}$

(ii) 2 Zn(s) + $O_2(g) \longrightarrow 2\,ZnO(s)$ $\quad \Delta_r G(ii) = -480$ kJ mol^{-1}

(iii) 2 Zn(s) + $S_2(g) \longrightarrow 2\,ZnS(s)$ $\quad \Delta_r G$ (iii) = -293 kJ mol^{-1}

Solution. Roasting of zinc sulphide in to zinc oxide is spontaneous if $\Delta_r G$ is negative for reaction (A) $\quad 2\,ZnS(s) + 3\,O_2(g) \longrightarrow 2\,ZnO(s) + 2\,SO_2(g)$ $\quad$ (A)

Operations: Equation (i) + equation (ii) – equation (iii) = Equation (A)

That is,

$S_2(s) + 2\,O_2(g) + 2\,Zn(s) + O_2(g) - [2\,Zn(s) + S_2(g)] \longrightarrow 2\,SO_2(g) + 2\,ZnO(s) - 2\,ZnS(s)$

On cancelling the common terms and rearranging the above equation we get

$$2\,ZnS(s) + 3\,O_2(g) \rightarrow 2\,ZnO(s) + 2\,SO_2(g)$$

Therefore, $\quad \Delta_r G(A) = \Delta_r G(i) + \Delta_r G(ii) - \Delta_r G(iii) = -544 - 480 + 293 = -\ 731$ kJ mol^{-1}

The value of is negative. Therefore, ***roasting of zinc sulphide is spontaneous.***

Example. For the reaction $Ag_2O(s) \longrightarrow 2Ag\ (s) + 1/2\ O_2(g)$, $\Delta_r H^\ominus = 30.56$ kJ mol^{-1} and $\Delta_r S^\ominus = 6.6$ JK^{-1} mol^{-1} at 1 bar. Calculate the temperature at which $\Delta_r G^\ominus$ will be zero. What will be the direction of the reaction at this temperature and above and below this temperature and why?

Solution. When $\Delta_r G^\ominus = \Delta_r H^\ominus - T\times\Delta_r S^\ominus = 0$

$$T\times\Delta_r S^\ominus = \Delta_r H^\ominus$$

or, $$T = \frac{\Delta_r H^\Theta}{\Delta_r S^\Theta} = \frac{30.56\ \text{kJ mol}^{-1}}{0.0066\ \text{kJ mol}^{-1}} = \mathbf{4630\ K}$$

(i) The reaction will be at equilibrium when $T = 4630$ K

(ii) The reaction will proceed in the forward direction when $T > 4630$ K

(iii) The reaction will proceed in the reverse direction when $T < 4630$ K

Example. The standard free energy change for a reaction is – 212.3 kJ mol^{-1} . If the standard enthalpy change is – 216.7 kJ mol^{-1}, calculate the standard entropy change for the reaction at 298 K.

Solution. From the relation $\Delta_r G^\ominus = \Delta_r H^\ominus - T\times\Delta_r S^\ominus$ we have

$$\Delta_r S^\ominus = \frac{\Delta_r H^\Theta - \Delta_r G^\Theta}{T}$$

$$= \frac{-216.7\ \text{kJ mol}^{-1} - (-212.3\ \text{kJ mol}^{-1}}{298\ \text{K}}$$

$= -\ 0.01476\ \text{kJ K}^{-1}\ \text{mol}^{-1} = \mathbf{-14.76\ J\ K^{-1}\ mol^{-1}}$

Example. Calculate the standard Gibbs energy change $\Delta_r G^{\upsilon}$ for the reaction $CaCO_3$ (s) + $2H^+$ (aq) → Ca^{2+} (aq) + H_2O (l) + CO_2 (g) at 298 K using standard Gibbs energy of formation:

Data given:

Species	**CO_2 (g)**	**H_2O(l)**	**$CaCO_3$ (s)**	**Ca^{2+} (aq)**
$\Delta_f G^{\upsilon}$/kJ mol^{-1}	**–394.36**	**–237.13**	**–1128.8**	**–553.58**

Solution. For the reaction $CaCO_3$ (s) + $2H^+$ (aq) → Ca^{2+} (aq) + H_2O (l) + CO_2 (g)

$$\Delta_r G^{\upsilon} = [[\Delta_f G^{\upsilon}(Ca^{2+}) + \Delta_f G^{\upsilon}(CO_2) + \Delta_f G^{\upsilon}(H_2O)] — [\Delta_f G^{\upsilon}(CaCO_3) + 2\Delta_f G^{\upsilon}(H^+)]$$

$$= [-553.58\ - 394.36 - 237.13]\ \text{kJ mol}^{-1} — [\ -1128.8 + 2\times 0]\ \text{kJ mol}^{-1}$$

$$= —\ 1185.07\ \text{kJ mol}^{-1}\ +\ 1128.8\ \text{kJ mol}^{-1} = \mathbf{-\ 56.27\ kJ\ mol^{-1}}$$

Example. Calculate the standard Gibbs free energy change ($\Delta_r G^{\upsilon}$)for the formation of propane at 298 K 3 C(graphite) +$4H_2$ (g) → C_3H_8(g) using the following data:

Data given:

Substance	**C_3H_8(g)**	**C(graphite)**	**H_2 (g)**
$\Delta_f H^{\upsilon}$/kJ mol^{-1}	**–103.8**	**0**	**0**
S^{υ} /JK^{-1} mol^{-1}	**270.2**	**5.70**	**130.7**

Solution. For the reaction 3 C(graphite) + 4 H_2 (g) → C_3H_8(g) fisrt we shall calculate $\Delta_r H^{\upsilon}$ and $\Delta_r S^{\upsilon}$ then $\Delta_r G^{\upsilon}$

Calculation of $\Delta_r H^{\upsilon}$

$$\Delta_r H^{\upsilon} = \Delta_f H^{\upsilon}(C_3H_8, g)\ — [3\Delta_f H^{\upsilon}(C, \text{graphite})) + 4\Delta_f H^{\upsilon}(H_2, g)]$$

$$= -\ 103.8\ \text{kJ mol}^{-1}\ — 3\times 0 + 4\times 0]\ \mathbf{= -\ 103.8\ kJ\ mol^{-1}}$$

Calculation of $\Delta_r S^{\upsilon}$

$$\Delta_r S^{\upsilon} = S^{\upsilon}(C_3H_8, g)\ — [3S^{\upsilon}(C, \text{graphite})) + 4\ S^{\upsilon}(H_2, g)]$$

$$= 270.2\ \text{JK}^{-1}\ \text{mol}^{-1}\ — [\ 3\times 5.70\ + 4\times 130.7]\ \text{JK}^{-1}\ \text{mol}^{-1}$$

$$= -\ 269.7\ \text{JK}^{-1}\ \text{mol}^{-1} = \mathbf{-\ 269.7 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}}$$

Calculation of $\Delta_r G^{\upsilon}$

$$\Delta_r G^{\upsilon} = \Delta_r H^{\upsilon}\ — T\ \Delta_r S^{\upsilon}$$

$= -\ 103.8\ \text{kJ mol}^{-1} - 298\ \text{K}\times(-\ 269.7\times10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})$

$= -\ 103.8\ \text{kJ mol}^{-1}\ +\ 80.37\ \text{kJ mol}^{-1} = \mathbf{-\ 23.43\ kJ\ mol^{-1}}$

CONFIDENCE BUILDING QUESTIONS ON ENTROPY AND GIBBS ENERGY

(A) Complete the following statements using a correct word/term from the list:

[decrease, lower, more, greater, increase, perfectly crystalline, positive, entropy, $\Delta S_{\text{universe}}$, $H + TS$, ΔG, negative, lower, third, zero, lower, JK^{-1}

1. Higher randomness of a molecular system means --------------- entropy.

2. For a spontaneous change the Gibbs energy must -------------

3. Entropy of 1 mole of ice is ---------------- than that of steam.

4. Net work done on the system would -------------- its free energy.

5. In a spontaneous process $\Delta S_{\text{universe}}$ is ---------------- than zero.

6. The Gibbs energy is expressed by the equation G =

7. The entropy of a ------------- substance is zero at 0 K.

8. For a spontaneous change ---------------- is greater than zero.

9. In an isothermal isobaric reversible process ----------- is equal to $w($ net).

10.For the process Normal egg $\longrightarrow$ Hard boiled egg the sign of ΔS is --------------

11. When ΔH is negative and ΔS is positive then ΔG is -----------------

12.The ------------ is a measure of randomness of the molecular system.

13.The entropy of diamond is ---------------- than the entropy of graphite.

14. The entropy of a substance is expressed in the units of ------------

15 The ------------- law of thermodynamics provides a method to evaluate the absolute entropy of a substance.

16.The entropy of helium is ------------ than the entropy of dihydrogen

17. For an ideal gas the entropy change in an adiabatic reversible process is ---------------

(B) Give a very brief answer of the following questions

1. Write a limitation of the first law of thermodynamics.
2. Write the symbol of entropy.
3. Mention the condition when the thermodynamic relation $dS = dq/T$ is applicable.
4. State the third law of thermodynamics.
5. Write the meaning of each term and symbol of the equation $G = H - TS$

6. Write a relation between the free energy change and net work done.
7. Mention the conditions under which the relation $\Delta G = w$ (net) is valid.
8. Write a relation between Gibbs energy (G) and Helmholtz energy (A).
9. Write the condition or conditions when $\Delta G = \Delta A$
10. Write the signs of ΔH and ΔS when a reaction is always spontaneous.
11. Write the signs of ΔH and ΔS when a reaction is never spontaneous.
12. Give an example of a reaction driven by entropy change.
13. Give an example of a reaction driven by enthalpy change.
14. Deduce the sign of ΔG when ΔH is positive and ΔS is negative.
15. Derive the relation $(\partial G/\partial T)_P = -S$.
16. Prove that $(\partial G/\partial P)_T = V$
17. Using equation $dG = -SdT + VdP$ derive Maxwell equation.
18. Calculate the value of $\left(\frac{\partial U}{\partial V}\right)_T$ for ideal gas when $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$
19. Prove that the internal pressure is zero for an ideal gas.
20. Write the thermodynamic relation which you will use to derive Maxwell equation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
21. Derive the following equations:

    (i) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ (ii) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (iii) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

(C) Slect True and False Statements

1. The free energy is defined by $G = H - TS$.
2. The total energy of the universe is constant and its entropy is increasing.
3. The entropy of the universe is constant and its energy *(U)* is decreasing.
4. For spontaneous process free energy decreases.
5. The entropy change in an adiabatic reversible process is zero.
6. The standard entropy of an element is zero.

7. In a spontaneous reaction there is always an increase in the entropy of the system.

8. Entropy is a measure of randomness in a molecular system.

9. $\Delta G = w_{\text{net}}$ is valid under all conditions.

Answers

True statements: 1, 2, 4, 5, 8 **False statements:** 3, 6, 7, 9

(D) Numerical Questions

1. Calculate the standard Gibbs energy change $\Delta_r G^{\upsilon}$ for the reaction SiH_4 (g) + $2O_2$ (g) → SiO_2 (s) + $2H_2O$ (g) at 298 K using standard Gibbs energy of formation:

Data given:

Species	SiH_4 (g)	SiO_2(s)	H_2O(g)
$\Delta_f G^{\upsilon}$/kJ mol^{-1}	52.3	– 805	–228.6

[Ans: $\Delta_r G^{\upsilon}$ = – 1314.5 kJ mol^{-1}]

2. For the reaction MgO(s) + C(s) → Mg(s) + CO(g) it is given that ΔH^{υ}= +491.18 kJ mol^{-1} and ΔS^{υ} =197.17 JK^{-1} mol^{-1}. Find out whether it is possible to reduce MgO using carbon at 298 K. If not, at what temperature it becomes spontaneous

[Ans: Nonspontaneous at 298 K because $\Delta_r G^{\upsilon}$ =+433.148 kJ mol^{-1}, but spontaneous when $T > 2491$ K]

3. Error! Bookmark not defined. Calculate the standard Gibbs energy change for the reaction CH_3OH (1) + 3/2O_2 (g) → CO_2(g) + $2H_2O$ (1) that can be converted into electrical work in a fuel cell. What is the efficiency of conversion of Gibbs energy into useful work if standard enthalpy of combustion for methanol is –726 kJ mol^{-1}? Data give:

Compound	CH_3OH (l)	CO_2 (g)	H_2O (l)
$\Delta_f G^{\upsilon}$ / kJ mol^{-1}	– 166.27	– 394.36	– 237.13

[$\Delta_r G^{\upsilon}$ = – 702.35 kJ mol^{-1} , Efficiency = $\Delta_r G^{\upsilon} / \Delta_r H^{\upsilon}$ = = 0.9674 = 96.7%

4. Predict whether the reaction 2NO (g) + O_2 (g) → $2NO_2$ (g) is spontaneous or not. It is given that $\Delta_f G^{\upsilon}$ (NO) = 86.55 kJ mol^{-1} and $\Delta_f G^{\upsilon}$ (NO_2) =51.31 kJ mol^{-1}

[Ans: $\Delta_r G^{\upsilon}$= – 70.48 kJ mol^{-1}. A negative value of $\Delta_r G^{\upsilon}$ suggests that the given reaction is spontaneous]

5. Calculate the standard Gibbs energy change $\Delta_r G^{\upsilon}$ for the formation of methane at 298 K using the following data:

Data given:

Substance	CH_4	C(graphite)	H_2 (g)
$\Delta_f H^{\upsilon}$/kJ mol^{-1}	−74.81	0	0
S^{υ} /JK^{-1} mol^{-1}	186.3	5.70	130.7

[Ans: $\Delta_r H^{\upsilon} = -74.81$ kJ mol^{-1}, $\Delta_r S^{\upsilon} = = -80.8 \times 10^{-3}$ kJ K^{-1} mol^{-1}, $\Delta_r G^{\upsilon} = -50.7$ kJ mol^{-1}]

6. Two moles of an ideal gas is compressed isothermally at 300 K from 2.0×10^5 Pa to 4.0×10^5 Pa Calculate the Gibbs energy change for this process. **[Ans:** $\Delta G = 2.303 nRT \log \frac{P_2}{P_1}$ = **3458.3 J]**

7. One mole of ideal gas is allowed to expand isothermally at 300 K into an evacuated vessel so that its pressure drops from 1.01×10^6 Pa to 1.01×10^5 Pa. Calculate the values of *w,q,* ΔU, ΔH, ΔS. ΔA, *anf* ΔG for the process.

[Ans: $w = 0$, $q = 0$, $\Delta U = 0$, $\Delta H = 0$, $\Delta A = \Delta G = -5744$ J, $\Delta S_{\text{system}} = 19.15$ J]

8. The enthalpy of vaporization of a liquid is 30.76 kJ mol^{-1}. What is the boiling point of the liquid if it obeys Trouton's rule. **[Ans: $T_b = \Delta_{vap}H/85$ JK^{-1} mol^{-1} =30760 J mol^{-1} / 85 JK^{-1} mol^{-1} = 361.88 K]**

9. The enthalpy of vaporistaion of liquid diethyl ether ($C_2H_5 - O - C_2H_5$) is 26.0 kJ mol^{-1} at its boiling point of 35.0 °C. Calculate ΔS^{υ} for conversion of liquid to vapour

[Ans; $\Delta_{vap}S$ = 84.4 J K^{-1} mol^{-1}]

10. Calculate the entropy change when 0.02 mole of an ideal gas ($C_{V,m}$ = 12.6 JK^{-1} mol^{-1}) is heated from 298 K to 373 K so that its volume is also doubled.

[**Ans:** $\Delta S = nC_{V,m} \times 2.303 \log\frac{T_2}{T_1} + nR \times 2.303 \log\frac{V_2}{V_1}$ **=0.175 JK^{-1}**