THERMOCHEMISTRY

Objectives

- Heat of Reaction
- Laws of Thermochemistry
- Types of Heat of Reaction
- Kirchhoff's Relation
- Born Haber Process

5.1 Introduction

Thermo chemistry deals with the study of heats of chemical reactions. When a chemical reaction takes place, energy in various forms may either be emitted or absorbed. During many reactions the temperature rises indicating that heat is being evolved. In others, when temperature falls, absorption of heat is indicated. Thus, the study of the heat produced or required by chemical reaction forms the basis of **thermochemistry.**

The reactions in which heat escapes from the system to the surroundings are termed as **exothermic process** that means the surrounding ultimately becomes hotter. The release of heat leads to decrease in the enthalpy of a system when the pressure remains constant, thus the enthalpy change is negative i.e.

$$\Delta H \langle 0$$

For such reaction Q is (-) ve.

The chemical processes in which heat is absorbed by the system from the surroundings are **endothermic process** that means the surrounding ultimately become colder. Here the absorption of heat leads to increase in the enthalpy of a system at constant pressure, thus the enthalpy change is positive i.e. $\Delta H \rangle 0$. For such reaction Q is (+) ve.

Let us suppose that in a reaction, A reacts with B to give C and Q amount of heat are evolved (exothermic). Therefore,

$$\mathrm{A} + \mathrm{B} = \mathrm{C} + \mathrm{Q}$$

Similarly if the reaction is endothermic it can be represented as

$$\mathrm{A} + \mathrm{B} = \mathrm{C} - \mathrm{Q}$$

If the chemical reaction takes place at constant pressure, the heat change is denoted by $q_p$and when the chemical reaction occurs at constant volume, the heat change is denoted byq_v. But the magnitude of $q_p$and $q_v$may not be equal for the same chemical process.

For example

$$C_7H_8 + 9O_2 = 7CO_2 + 4H_2O; \qquad q_p = -930kcal$$
$$q_v = -928.8kcal$$

Since q_p= Δ H and q_v= Δu , so it is our usual custom, to express the heat changes on the right hand side of the chemical equation in terms of Δ H and Δu .

Exothermic reaction: $C + O_2 = CO_2$ Δ H = - 94050 cal

Endothermic reaction: $N_2 + O_2 = 2NO$ Δ H= + 42000 cal.

SKILL TEST

1. What is exothermic process? What is the magnitude of change in enthalpy in an exothermic reaction?
2. What is endothermic process? What is the magnitude of change in enthalpy in an endothermic reaction?
3. Draw the energy profile diagram in an exothermic reaction.
4. Draw the energy profile diagram in an endothermic reaction.

5.2 Heat of Reaction

The heat of reaction is defined as the amount of heat liberated or absorbed at a given temperature when the reactants are converted into products as represented by the balanced chemical equation. If $q$is the heat of reaction, W is the work done by the reactants during reaction, then according to the first law of thermodynamics, one can write

$$q = \Delta U - W$$

ΔU is the energy difference between the internal energy of products and that of reactants as given below

$$\Delta U = \sum U_{(products)} - \sum U_{(reac\tan ts)}$$

If the chemical reaction occurs at constant volume in a bomb calorimeter then W = 0 and in that case

$$q_v = \Delta U$$

Therefore, the heat of reaction at constant volume q_v is the change in internal energy of the system during a chemical reaction. However, if the chemical reaction occurs at constant pressure in an open calorimeter then $W = -P\Delta V$and in that case

$$\begin{aligned} q_v &= \Delta U - (-P\Delta V) \\ &= \Delta U + P\Delta V = \Delta H \end{aligned}$$

The amount of heat evolved, or absorbed during a chemical reaction occurring at a constant pressure and at a particular temperature, is referred to as *enthalpy of reaction*. Let us consider a general chemical reaction where a moles of A react with b moles of B to produce c moles of C and d moles of D, which may be represented as:

$$aA + bB \rightarrow cC + dD$$

The change in enthalpy of the system when the reactants are transferred into products is given by the difference between the total enthalpy of the products and that of the reactants at constant temperature and pressure. This quantity is called the heat of reaction.

$$\Delta H = \sum H_{(products)} - \sum H_{(reac\tan ts)}$$

$$\Delta H = (cH_C + dH_D) - (aH_A + bH_B)$$

where H_A, H_B, H_C and H_D are enthalpies of A, B, C and D.

The change in volume $\Delta V$is very small for the reactions involving solids and liquids. Thus, $P\Delta V$is very small and can be neglected, therefore $\Delta H$is equal toΔU. However, if the reactants and products are gases then volume changes cannot be neglected and one must specify the manner in which the reaction is performed. Mostly gaseous reactions are performed at constant pressure in which change in enthalpy $(\Delta H)$is measured.

Conditions for which $q_p = q_v$ **or** $\Delta H = \Delta U$

1. When the reaction takes place in a closed vessel the volume remains constant i.e.
$$\Delta V = 0.,$$
2. When only solids, liquids or solutions are involved in the reaction (no gaseous reactant or product), the volume changes are negligible during a chemical reaction.
3. When the number of moles of gaseous reactants and products are equal in a reaction, i.e. $\Delta n = 0$
For example,
$$\mathrm{H_2\,(g) + Cl_2\,(g) \rightarrow 2\,HCl\,(g)}$$

5.3 The Laws of Thermochemistry

The principle of conservation of energy provides a basis for two very important laws of thermochemistry:

5.3.1 Law of Lavoisier and Laplace

The first law of thermochemistry is due to the experimental observations of A.L. Lavoisier and P.S. Laplace (1780). This law can be stated as “The heat change accompanying a chemical process in one direction is equal in magnitude but opposite in sign, to that accompanying the same reaction in the reverse direction.”

Example

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l) \qquad \Delta H = -68300cal$$
$$H_2O(l) = H_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H = +68300cal$$

Suppose two reactants A and B change first into C and D with heat evolution (q) and subsequently C and D react to produce back A and B in the initial state with heat absorbed (q′). According to the law, heat content (H) or energy content (U) of the initial A and B would again return to the same magnitude. Therefore the net heat content change or energy content change would be zero.

$$\mathrm{q} + \mathrm{q}` = 0 \quad \text{or} \quad \mathrm{q} = -\mathrm{q}`$$

5.3.2 Hess's law of constant heat summation

G.H. Hess (1840) experimentally gave the second law of the thermochemistry which has important applications and is known as the law of constant heat summation. This law may be stated as "The net heat change ($q_p \text{or} q_v$) for a given chemical process, will be the same whether the process occurs in one or in several stages.

Example

$$\begin{array}{rcll}
C+O_2 & = & CO_2 & q_p = -94.05kcal \\
C+\frac{1}{2}O_2 & = & CO & q_p^{'} = -26.42kcal \\
C+\frac{1}{2}O_2 & = & CO_2 & q^{''}{}_p = -67.63kcal \\
\hline
C+O & = & CO_2 & q_p = q_p^{'} + q_p^{''}
\end{array}$$

5.4 Different types of heat of reactions

Depending upon the nature of the reaction various types of heat or enthalpy changes occur in the chemical reactions.

5.4.1 Heat of formation

The enthalpy change occurring when a gm-molecule of a substance is formed from its constituent elements is called its 'heat of formation'. When 1gm-

mole of HCl is produced from hydrogen and chlorine 22.06 kcal of heat are evolved. Hence heat of formation of $HCl$is - 22.06 kcal.
Suppose the elements A and B unite to form a compound C

$$A + B \rightarrow C$$

The heat of formation of C

$$\Delta H_{f(C)} = H_C - H_A - H_B$$

The enthalpy of a substance depends upon pressure and temperature. The standard temperature for a thermochemical measurement has been chosen as 298°K and pressure 1 atom. The standard enthalpy is H^0; superscript '0' indicating standard state.

$$\Delta H^0_{f(C)} = H^0_C - H^0_A - H^0_B$$

It is not possible to determine the absolute value of the standard enthalpy (H^0) of a substance. Therefore to measure the change in enthalpy it is therefore necessary to assume some arbitrary value at a given state. It has been decided to assign the value **zero** for the enthalpy of every element at 1 atom and 298°K.

$$\Delta H^0_{f(C)} = H^0_C - H^0_A - H^0_B = H^0_C(\because H^0_A = H^0_B = 0)$$

$$\therefore H^0_C = \Delta H^0_{f(C)}$$

Thus, the standard enthalpy of a compound = its standard heat of formation.

5.4.2 Heat of combustion

The heat change accompanying the complete combustion of a gm-mole of the substance at a given temperature under normal pressure is called its heat of combustion.
In case of organic compounds, complete combustion is regarded to have taken place when they are transformed finally into CO_2 and H_2O.

The example of combustion reactions is

$$\mathrm{CH_4\ (g)} + \mathrm{2O_2\ (g)} \ = \ \mathrm{CO_2\ (g)} + \mathrm{2H_2O\ (l)}; \Delta H_C^0 = 890.3 kJmol^{-1}$$

5.4.3 Heat of neutralization

Neutralization of an acid or a base is always an exothermic process. The amount of heat liberated when one gm-eqv of an acid is neutralized by a gm-eqv of base is called the heat of neutralization.

If q calories of heat be evolved when one gm-eqv of acid HA reacts with a gm-eqv of base BOH.

Then

$$HA + BOH = BA + H_2O \qquad \Delta H = -q$$

If the acid and the base are both strong, both of them be assumed to be completely dissociated; hence

$$H^+ + A^- + B^+ + OH^- = B^+ + A^- + H_2O \qquad \Delta H = -q$$

$$H^+ + OH^- = H_2O$$

Therefore the heat of neutralization is really the heat of formation of gm-mole of water from gm-ion of hydrogen and a gm-ion of hydroxyl ion. Therefore the heat of neutralization of any strong acid by any strong base in dilute solutions is always the same and is equal to 13.7 kcal.

But when a weak acid or a weak base is neutralized, the heat of neutralization deviates considerably from the value 13.7 kcal. This is because of the fact that a weak acid or a base is very slightly dissociated and a portion of energy is utilized in the process of dissociation.

5.4.4 Heat of Solution or Heat of Dilution

The net thermal change which occurs when a gm-mole of solute is completely dissolved in a solvent is called the heat of solution or more appropriately the integral heat of solution.

The value of the heat of solution, obtained graphically by extrapolating $\Delta H$to infinite dilution is called the integral heat of solution at infinite dilution. In fact, when the solution becomes very dilute the heat change assumes a constant value.

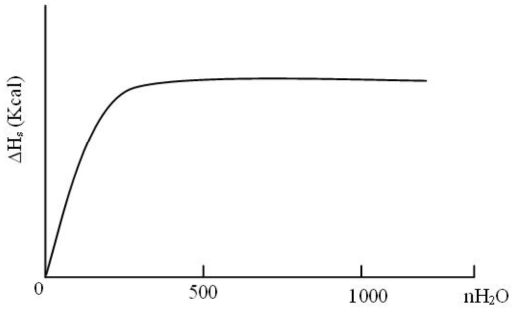

Figure 5.1: Heat of solution graph

Thus during the process of dissolution of a gm-mole of solute, the concentration continuously changes and hence the magnitude of heat changes would also vary. Thus the heat of solution at any instant, $^{\Delta H}/_{\Delta n}$is called the differential heat of solution.

Since the heat of solution varies with concentration, the addition of a quantity of solvent to a given solution of fairly high concentration would involve a thermal change. The net heat change associated with the dilution of a solution containing 1 mole of solute from a concentration C^1 to a concentration C^2 is called the **integral heat of dilution.**

If a spontaneous process takes place suddenly and heat produced during the chemical process has no opportunity to be dissipated to the surroundings, obviously the heat will increase the temperature of the resultant system, which is equivalent to an adiabatic one. Then formation of flame takes place.

5.4.5 Differential heats of solution and dilution

The differential heat of solution may be defined as the change in enthalpy, or heat content when one mole of a substance (solute) is added (dissolved) to a large amount of a solution in such a way that the concentration of the solution remains unchanged. Whereas, the differential heat of dilution is defined as the heat change when one mole of a solvent is added to a large volume of the solution of known concentration in such a way that the concentration of the solution is not altered. The heat change associated with this process is called the differential heat of dilution.

SKILL TEST

1. State Hess's law of constant heat summation. How does it follow from the first law of thermodynamics?
2. What is heat of solution? In an experiment how it can be determined?
3. What is integral heat of dilution?
4. What do you mean by differential heats of solution and dilution?

5.5 Change in internal energy with temperature:

The Kirchhoff's relation

It is possible to calculate the heat of reaction at standard temperature (298 K) and pressure (1 atm) by using the data of standard heats of formation from table. But several times, the heats of reaction at other temperature and pressures are also necessary. The variation of heat of reaction with temperature at constant pressure was given by Kirchhoff who derived an expression which explains the temperature dependence of the heat of reaction. This expression can be derived in the following manner:

When a system undergoes a change from one step to another then the internal energy of the system would alter. Hence we can write,

$\Delta u = u_f - u_i$ [where suffix f and i denote the final and initial state respectively]

Differentiating both sides with respect to temperature at constant volume we get

$$\left[\frac{d\,(\Delta u)}{dT}\right]_v = \left[\frac{du_f}{dT}\right]_v - \left[\frac{du_i}{dT}\right]_v$$

$$= C_{v_f} - C_{v_i}$$

$$\Rightarrow \qquad \partial(\Delta u) = \Delta C_v dT$$

Integrating both side between the limit T°K and 0°K we get

$$\int_0^T d(\Delta u) = \int_0^T \Delta C_v dT$$

$$\Delta u_T = \Delta u_0 + \int_0^T \Delta C_v dT$$

For process occurring at T_1°K we can write

$$\begin{aligned}
\Delta u_{T_1} &= \Delta u_0 + \int_0^{T_1} \Delta C_v dT \\
&= \Delta u_0 + \int_0^{T_1} \left(C_{v_f} - C_{v_i}\right) dT \\
\Delta u_{T_1} &= \Delta u_0 + \int_0^{T_1} \left[\left(a_f + b_f T + c_f T^2 + \cdots\cdots\right) - \left(a_i + b_i T + c_i T^2 + \cdots\cdots\right)\right]
\end{aligned}$$

C_v increases with temperature and the influence of temperature empirically given by a power series of T.

$$\therefore \qquad C_v = a + bT + cT^2 + \cdots\cdots \qquad [a,\ b,\ c \text{ are constant}]$$

$$\therefore \qquad \Delta u_{T_1} = \Delta u_0 + \int_0^{T_1} \left[(a_f - a_i) + (b_f - b_i)T + (c_f - c_i)T^2 + \cdots\cdots\right] dT$$

$$= \Delta u_0 + \int_0^{T_1} \left[\alpha + \beta T + \gamma T^2 + \cdots\cdots\right] dT \qquad \begin{bmatrix} \alpha = a_f - a_i \\ \beta = b_f - b_i \\ \gamma = c_f - c_i \end{bmatrix}$$

$$= \Delta u_0 + \alpha T_1 + \frac{\beta}{2} T_1^2 + \frac{\gamma}{3} T_1^3 + \cdots\cdots$$

Similarly for the process at T_2°K

$$\Delta u_{T_2} = \Delta u_0 + \alpha T_2 + \frac{\beta}{2} T_2^2 + \frac{\gamma}{3} T_2^3 + \cdots\cdots$$

Therefore,

$$\left(\Delta u_{T_2} - \Delta u_{T_1}\right) = \alpha\left(T_2 - T_1\right) + \frac{\beta}{2}\left(T_2^2 - T_1^2\right) + \frac{\gamma}{3}\left(T_2^3 - T_1^3\right) + \cdots\cdots$$

If C_v values of the final and initial state are assumed to be constant i.e. independent of temperature then ΔC_v is also constant.

$$(\Delta u_{T_2} - \Delta u_{T_1}) = \Delta C_v \int_{T_1}^{T_2} dT \quad = \Delta C_v (T_2 - T_1). \tag{5.1}$$

Variation of enthalpy change with change of temperature

If a system undergoes a change from one given state to another given state then enthalpy of the system would alter. Hence we can write

$\Delta H = H_f - H_i$ [where suffix f and i denote final and initial state of the system]

Differentiating both sides with respect to temperature at constant pressure we get

$$\begin{aligned} \left[\frac{d(\Delta H)}{dT}\right]_P &= \left[\frac{dH_f}{dT}\right]_P - \left[\frac{dH_i}{dT}\right]_P \\ &= C_{P_f} - C_{P_i} \\ \Rightarrow \qquad \partial(\Delta H) &= \Delta C_P dT \end{aligned}$$

Integrating both side between limit T°K and 0° K we get

$$\int_0^T d(\Delta H) = \int_0^T \Delta C_P dT$$

or, $(\Delta H_T - \Delta H_0) = \Delta C_P \int_0^T dT$

or, $\Delta H_T = \Delta H_0 + \int_0^T \Delta C_P dT$

For process occurring at T_1°K we can write

$$\Delta H_{T_1} = \Delta H_0 + \int_0^{T_1} \Delta C_P dT$$

$$= \Delta H_0 + \int_0^{T_1} \left(C_{P_f} - C_{P_i}\right) dT$$

$$= \Delta H_0 + \int_0^{T_1} \left[\left(a'_f + b'_f T + C'_f T^2 + \cdots\cdots\right) - \left(a'_i + b'_i T + c'_i T^2 + \cdots\cdots\right)\right] dT$$

C_P increases with temperature and the influence of temperature empirically given by a power series of T

$$C_P = a' + b'T + c'T^2 + \cdots\cdots \qquad [a',\, b',\, c' \text{ are constant}]$$

$$\therefore \qquad \Delta H_{T_1} = \Delta H_0 + \int_0^{T_1} \left[\left(a'_f - a'_i\right) + \left(b'_f - b'_i\right)T + \left(c'_f - c'_i\right)T^2 + \cdots\cdots\right] dT$$

$$= \Delta H_0 + \int_0^{T_1} \left[\alpha' + \beta' T + \gamma' T^2 + \cdots\cdots\cdots\right] dT$$

[where $\alpha' = \left(a'_f - a'_i\right);\ \beta' = \left(b'_f - b'_i\right);\ \gamma' = \left(c'_f - c'_i\right)$]

$$= \Delta H_0 + \alpha' T_1 + \frac{\beta'}{2} T_1^2 + \frac{\gamma'}{3} T_1^3 + \cdots\cdots\cdots$$

Similarly for the process at T_2°K

$$\Delta H_{T_2} = \Delta H_0 + \alpha' T_2 + \frac{\beta'}{2} T_2^2 + \frac{\gamma'}{3} T_2^3 + \cdots\cdots$$

Thus,

$$\left(\Delta H_{T_2} - \Delta H_{T_1}\right) = \alpha' (T_2 - T_1) + \frac{\beta'}{2}\left(T_2^2 - T_1^2\right) + \frac{\gamma'}{3}\left(T_2^3 - T_1^3\right) + \cdots\cdots$$

If C_P values of the final and initial state are assumed to be constant i.e. independent of temperature the ΔC_P is also constant

$$\left(\Delta H_{T_2} - \Delta H_{T_1}\right) = \Delta C_P \int_{T_1}^{T_2} dT \ = \Delta C_P \left(T_2 - T_1\right) \qquad (5.2)$$

Equation 5.1 and 5.2 are the different forms of **Kirchhoff's Equation**.

5.6 Born Haber Cycle

Based on Hess's law Born and Haber in 1919 developed a simplified and cyclic method to correlate lattice energies of ionic crystals to other thermodynamic data. For example, the net energy changes during the formation of sodium chloride from metallic sodium and chlorine gas can be represented by$\Delta \mathrm{H_f}$.

$$\mathrm{Na(s)} + 1/2\,\mathrm{Cl_2(g)} \rightarrow \mathrm{NaCl}$$

The overall process is thought to take place in following intermediate steps:

Intermediate Steps

1. **Metallic sodium into gaseous sodium atom**

   The energy required per mole of sodium is "enthalpy of sublimation" which is represented by$(\Delta \mathrm{H_s})$. This step is energy consuming process.

   $$Na(s) + \Delta H \rightarrow Na(g) \tag{5.3}$$

2. **Dissociation of chlorine molecule into chlorine atom**

   The energy required per mole of chlorine is "enthalpy of dissociation" represented by $(\Delta \mathrm{H_d})$.

   $$\mathrm{Cl_2\,(g)} + \Delta \mathrm{H_d} \longrightarrow \mathrm{2Cl\,(g)}$$

   $$\text{or, } \frac{1}{2}\mathrm{Cl_2\,(g)} + \frac{1}{2}\Delta \mathrm{H_d} \longrightarrow \mathrm{Cl\,(g)} \tag{5.4}$$

3. **Gaseous sodium atom into gaseous cation**

   The energy required in this process is called Ionization Energy (IE).

   $$\mathrm{Na\,(g)} + \mathrm{IE} \longrightarrow \mathrm{Na^+\,(g)} + \mathrm{e^-} \tag{5.5}$$

4. **Gaseous chlorine atom into gaseous anion**

   This step involves the release of energy referred as Electron Affinity (EA).

   $$\mathrm{Cl\,(g)} + \mathrm{e^-} \longrightarrow \mathrm{Cl^-\,(g)} + \mathrm{EA} \tag{5.6}$$

5. **Combination of oppositely charged gaseous ions to form solid**

crystal

This involves the release of energy referred as lattice energy (U).

$$Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl(s) + U$$

The various energy changes in different steps are as follows:

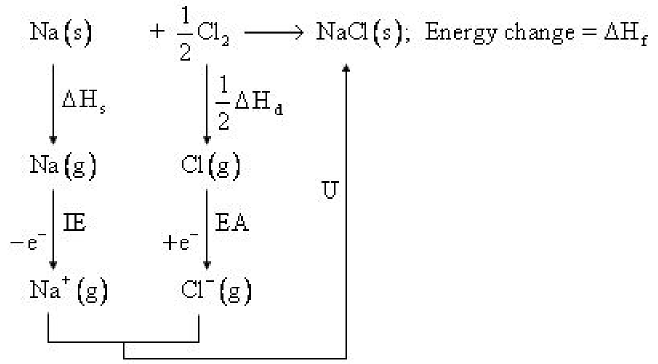

Figure 5.2: Born Haber Cycle for NaCl

The sum of the energy changes taking place during various steps is equal to ΔH_f i.e, heat of formation of NaCl(s) according to Hess's law.

$$\Delta H_f = \Delta H_s + \frac{1}{2}\Delta H_d + IE + EA + U \qquad (5.7)$$

Various values for NaCl are as follows:

Heat of sublimation of sodium $(\Delta H_s) = 108.5$ K J mole^{-1}

Dissociation energy of chlorine $(\Delta H_d) = 243.0$ K J mole^{-1}

IE of sodium (IE) = 495.8 K J mole^{-1}

EA of chlorine (EA) = -349 K J mole^{-1}

Lattice energy of NaCl (U) = -769.8 K J mole^{-1}

Substituting these values in equation 5.7 we get

$$\begin{aligned}\Delta H_f &= \Delta H_s + \frac{1}{2}\Delta H_d + IE + EA + U \\ &= 108.5 + \frac{1}{2}(243.0) + 495.8 + (-349) + (-769.8) \\ &= -393 K\,J\ mole^{-1}\end{aligned}$$

Applications of Born Haber Cycle

Lattice energy of ionic solids

Born Haber cycle helps us to calculate the lattice energy of ionic solid, provided other thermodynamic data is known. For example, the lattice energy of magnesium fluoride (MgF_2) can be calculated when the sublimation energy (ΔH_s) of Mg = 146.4 K J mole^{-1} ; IE_1 and IE_2 values of Mg = 737 and 1449 K J mole^{-1}respectively; dissociation energy (ΔH_d) of fluorine = 158.8 K J mole^{-1}; EA of fluorine = -328 K J mole^{-1}and $\Delta H_f$of MgF_2 = -1096.5 K J mole^{-1}.

Born Haber Cycle of MgF_2 can be represented as follows:

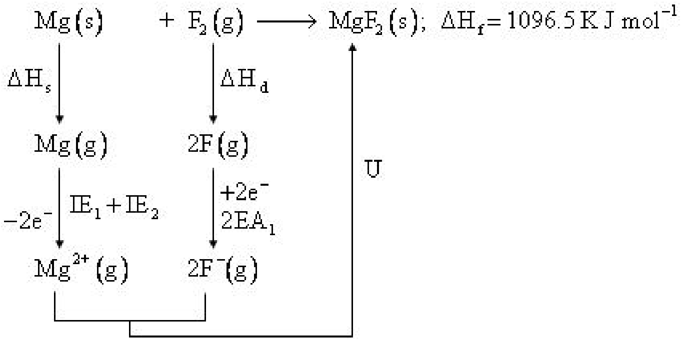

Figure 5.3: Born Haber Cycle for MgF2

$$\begin{aligned} \Delta H_f &= \Delta H_s + \Delta H_d + (IE_1 + IE_2) + 2EA_1 + U \\ \therefore \quad U &= \Delta H_f - \Delta H_s - \Delta H_d - (IE_1 + IE_2) - 2EA_1 \\ &= -1096.5 - 146.4 - 158.8 - (737 + 1449) - 2(-328) \\ &= -2931.7 \text{K J mole}^{-1} \end{aligned}$$

ΔH_f ***Values***

Born Haber cycle can help us to calculate the values of ΔH_f for unknown compounds. From the calculated values of ΔH_f one can predict whether the compound is stable or not. If ΔH_f value is negative, the compound is stable. If ΔH_f is positive, the formation of compound is highly unfavorable. For example, to calculate the value of ΔH_f for hypothetical compound ArCl the data given is: IE1 for Ar = 1526.3 K J mole^{-1}, dissociation energy of chlorine $(\Delta H_d) = 243$ K J mole^{-1}, EA of chlorine is -349 K J mole^{-1}, lattice energy (U) of ArCl (s) is -703 K J mole^{-1}.

Born Haber cycle of ArCl (s) can be represented as follows:

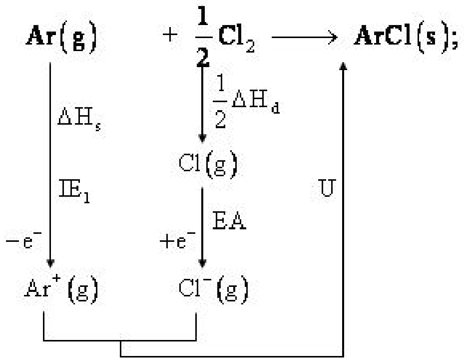

Figure 5.4: Born Haber Cycle for ArCl (s)

$$\begin{aligned} \Delta H_f &= IE_1 + \frac{1}{2}\Delta H_d + EA + U \\ &= 1526.3 + \frac{1}{2}(243) - 349 - 703 \\ &= 595.8 \text{K J mole}^{-1} \end{aligned}$$

The (+) ve value of ΔH_f indicates that net energy is required for this process. Hence formation of ArCl is energetically unfavorable.

Electron affinities

The Born Haber Cycle can be used for the calculation of electron affinities of some elements that are otherwise very difficult to measure.

Heat of formation of a compound may be expressed as:

$$\Delta H_f = \Delta H_s + \frac{1}{2}\Delta H_d + IE + EA + U$$

or, $EA = \Delta H_f - \Delta H_s - \frac{1}{2}\Delta H_d - IE - U$

ΔH_s, ΔH_f, ΔH_d and IE are determined experimentally and lattice energy (U) may be calculated by using other equation such as Born Lande equation. Using the above equation electron affinity may be calculated.

Proton affinities:

The Born Haber Cycle can also be used to calculate the proton affinities (PA) of some bases. The proton affinity of a species X is defined as the energy released in the reaction:

$$X(g) + H^+(g) \rightarrow HX^+(g) + \text{Energy}\,(PA)$$

To calculate the proton affinity of NH3 using Born Haber Cycle for the process,

$$NH_3(g) + HCl(g) \rightarrow NH_4^+ + Cl^-(s)$$

According to Born Haber Cycle

$$\Delta H_f = \Delta H_d + IE + EA + PA + U$$

$$PA = \Delta H_f - \Delta H_d - IE - EA - U \tag{5.8}$$

Various values of NH_4Cl are as follows:

Heat of formation (ΔH_f) of NH_4Cl (s) = -144.5 K J mole^{-1}

Dissociation energy (ΔH_d) of HCl (g) = 433.0 K J mole^{-1}

IE of hydrogen = 1312.0 K J mole^{-1}

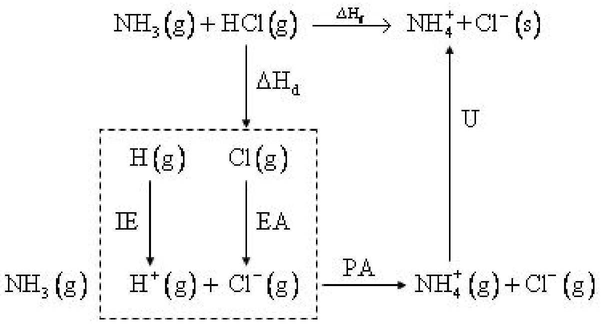

Figure 5.5: Calculating PA

EA of chlorine = -349.0 K J mole^{-1}
Lattice energy (U) of NH_4Cl = - 649.0 K J mole^{-1}
Substituting the values in equation 5.8 we get,

$$PA = -144.5 - 433.0 - 1312.0 - (-349.0) - (-649.0)$$

$$= -891.5 \text{K J mole}^{-1}.$$

Review Questions

1. **What is the relation between heat of reaction at constant pressure and heat of reaction at constant volume.**

Answer:

In case of gaseous reactants and products and assuming them to be ideal, it can be written at constant temperature and pressure

$$PV_1 = n_1RT$$

and $PV_2 = n_2RT$

where $n_1$and $n_2$are the number of moles of the reactants and products respectively. V_1 and $V_2$are the volume of reactants and products respectively. The change in volumeΔV, is therefore given by

$$\Delta V = V_2 - V_1 = \frac{n_2RT}{P} - \frac{n_1RT}{P}$$

$$= (n_2 - n_1)\frac{RT}{P}$$

Thus, $\Delta V = \Delta n\frac{RT}{P}$ [where $\Delta n$is the change in number of moles.]

The relation between the change in enthalpy and change in internal energy at constant pressure are expressed as:

$$\Delta H = \Delta U + P\Delta V$$

On substituting the value of $P\Delta V$the expression becomes

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

This relation is used to calculate the enthalpy of reaction from the energy of reaction at a given temperature. The value of gas constant R is considered in calories or joules (R = 1.987 calories, or 8.314 joules).

Further, since $\Delta H = q_p \text{and} \Delta U = q_v$, therefore,

$$q_p = q_v + \Delta nRT$$

where ‘q’ denotes the heat of reaction.

2. **“Heat of neutralization of any strong acid by any strong base in dilute solution is always the same, but the value deviates in case of a weak acid or a weak base” - justify the statement**

   Answer:
   Strong acid and strong base are both strong electrolyte, therefore they are completely dissociated into their ions in dilute solution. So the heat of neutralization of any strong acid by any strong base in dilute solutions is always the same and is equal to 13.7 kcal. But weak acid or weak base are weak electrolytes so they are partially dissociated into their ions in solution and some amount of heat is utilized for the dissociation of either weak acid or weak base, therefore the heat of neutralization value deviates.

3. **The molar heat of sublimation of a solid is always greater than the molar heat of vaporization of the corresponding liquid. Explain.**

   Answer:
   Since the molar heat of sublimation is the summation of heat of melting and heat of vaporization so it is always greater than the heat of vaporization of the corresponding liquid.

4. **State Hess’s law of constant heat summation. How does it follow from the first law of thermodynamics?**

   Answer:
   The Hess’s law may be stated as “The net heat change ($q_p \text{or} q_v$) for a given chemical process, will be the same whether the process occurs in one or in several stages.

Example

$$\begin{array}{rcll}
C+O_2 & = & CO_2 & q_p=-94.05kcal \\
C+\frac{1}{2}O_2 & = & CO & q_p^{'}=-26.42kcal \\
C+\frac{1}{2}O_2 & = & CO_2 & q^{"}_{\ p}=-67.63kcal \\
\hline
C+O & = & CO_2 & q_p=q_p^{'}+q_p^{"}
\end{array}$$

From 1st law of thermodynamics, $\Delta U=q-W$

$$=q-P\Delta V$$

ΔU is a state function. Its value depends only on the initial and final states of the system but not on the path of the transformation. However, the values of q and W depend on the path by which the change is carried out.

At constant volume $\Delta V=0$, thus $W=0$.

Therefore, $\Delta U=q$

Since, ΔU is a definite quantity, therefore at constant volume, q is also a definite quantity. Moreover, at constant pressure, the work done W becomes a definite quantity. Thus, at constant pressure, $q\,(=\Delta U+P\Delta V)$, becomes a definite quantity.

Since at constant volume or pressure, the heat evolved or absorbed in the reaction must be independent of the path of the transformation, therefore, Hess's law is only a special case of 1st law of thermodynamics.

5. What is the significance of Hess's law?

Answer:
Hess's law is used to calculate:

(a) Enthalpy changes of formation from enthalpy changes of combustion.

(b) Enthalpy changes of reaction from enthalpy changes of formation.

(c) Lattice energies in the Born-Haber cycle.

6. **Why does a (-) ve value of ΔHmean an exothermic reaction and (+) ve value of ΔHmean an endothermic reaction?**

Answer:

The reactions in which heat escapes from the system to the surroundings are termed as **exothermic process** that means the surrounding ultimately becomes hotter. The release of heat leads to decrease in the enthalpy of a system when the pressure remains constant, thus the enthalpy change is negative i.e. $\Delta H \langle 0$.

The chemical processes in which heat is absorbed by the system from the surroundings are **endothermic process** that means the surrounding ultimately become colder. Here the absorption of heat leads to increase in the enthalpy of a system at constant pressure, thus the enthalpy change is positive i.e. $\Delta H \rangle 0$.

Worked -Out Examples

1. **The molar heat of vaporization of** $H_2O\,(l) \rightarrow H_2O\,(g)$**is 9,700 cal. At 100° C molar volumes of liquid and vapour are 18 c.c. and 30.2 litres at 100° C and 1 atm. Evaluate** ΔU**per mole at 1000 C and 1 atm.**

   Answer:
   Given molar heat of vaporization ΔH= 9700 cal

   Now $\Delta H = \Delta U + P\,(V_2 - V_1)$

   Here $P\,(V_2 - V_1)$ = 1(30.2 - 0.018) litre-atm

   = 730.40 cal

   So 9700 = ΔU + 730.40

   Or ΔU= 8969.6 cal.

2. **Heat of neutralization between** HCl**and** NaOH**is 13.7 K. cal. and between** HCN **and** NaOH**is 3000 cal. at 25° C. What is the heat of ionization of**HCN**?**

   Answer:
   Neutralization between HCl and NaOHoccurs in one step as

   $H^+ + OH^- = H_2O$ ΔH= -13.7 K. Cal.

   But neutralization between HCN and NaOH occurs in two steps, which are

   $HCN = H^+ + CN^-$ ΔH= let x K. Cal.

   $H^+ + OH^- = H_2O$ ΔH= -13.7 K. Cal.

   xK. Cal. is heat of ionization. So here

   $$x - 13.7 = -3$$

   or x = 10.7 K. Cal.

3. **Given the following heats of reaction at 25°C**

$C_2H_4\,(g) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 2H_2O\,(l)$
$\Delta H = -337.3 K.Cal$

$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$
ΔH= -136.6 K. Cal

$2C_6H_6\,(g) + 7O_2\,(g) \rightarrow 4CO_2\,(g) + 6H_2O\,(l)$
ΔH= -745.6 K. Cal.
Calculate ΔH for the reaction

$C_2H_4\,(g) + H_2\,(g) \rightarrow C_2H_6\,(g)$**at 25° C.**

Answer:
Given

(a) $C_2H_4\,(g) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 2H_2O\,(l)$ ΔH= -337.3 K. Cal
(b) $2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$ ΔH= -136.6 K. Cal
(c) $2C_6H_6\,(g) + 7O_2\,(g) \rightarrow 4CO_2\,(g) + 6H_2O\,(l)$ ΔH= -745.6 K. Cal

We multiply equation (a) by b and add the product with equation (b) to get

$$2C_2H_4 + 7O_2 + 2H_2 = 4CO_2\,(g) + 6H_2O\,(l)$$

and ΔH= 2(-337.3) + (-136.6)

= -811.2 K. cal.

If from this equation we subtract equation (c) then we get

$$2C_2H_4\,(g) + 2\,H_2\,(g)\text{®}2C_2H_6\,(g)$$

$$\Delta H = -811.2 - (-745.6)$$

= - 65.6 K. Cal.

So for $C_2H_4\,(g) + H_2\,(g) \rightarrow C_2H_6\,(g)$ ΔH= $-\frac{65.6}{2}$ = - 32.8 K. Cal.

---

4. **Calculate the heat of formation of ammonia, given the heats of combustion of ammonia and hydrogen is - 90.6 and - 68.3 K. Cal mole respectively.**

Answer:

Given

$$\mathrm{NH_3} + \frac{3}{4}\mathrm{O_2} = \frac{1}{2}\mathrm{N_2} + \frac{3}{2}\mathrm{H_2O}\Delta H = -90.6 K.Cal \tag{5.9}$$

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} = \mathrm{H_2O}\Delta H = -68.3 K.Cal \tag{5.10}$$

Multiplying equation 5.10 by $\frac{3}{2}$and subtracting the product from equation 5.9 we get

$$\mathrm{NH_3} - \frac{3}{2}\mathrm{H_2} = \frac{1}{2}\mathrm{N_2}, \Delta H = -90.6 - \frac{3}{2}(-68.3)$$

$$= 11.85$$

Thus the reaction becomes

$\frac{1}{2}\mathrm{N_2} + \frac{3}{2}\mathrm{H_2} = \mathrm{NH_3}$ ΔH= - 11.85 K. Cal.

Multiple Choice Questions

1. **In exothermic process**
   - **(a)** $\Delta H \langle 0$
   - **(b)** $\Delta H \rangle 0$
   - **(c)** $\Delta H = 0$
   - **(d)** **none of these**

   Answer:
   (a)

2. **In endothermic process**
   - **(a)** $\Delta H \langle 0$
   - **(b)** $\Delta H \rangle 0$
   - **(c)** $\Delta H = 0$
   - **(d)** **none of these**

   Answer:
   (b)

3. **Heat of neutralization of a strong acid with a strong base is constant since**
   - **(a)** **salts are formed**
   - **(b)** **only H^+ and OH^-ions react in each case**
   - **(c)** **strong acid and strong base react completely**
   - **(d)** **none of these**

   Answer:
   (c)

4. **When the change in number of moles of gaseous products and reactants is zero, then**

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

(b) $\Delta H \rangle \Delta U$

(c) $\Delta H \langle \Delta U$

(d) none of these

Answer:
(a)

5. **Heat of neutralization of any strong acid by any strong base in dilute solution is always the same and the value is**

   (a) 14.5 K. Cal.

   (b) - 13.7 K. Cal

   (c) 13.7 K. Cal.

   (d) 15.5 K. Cal.

   Answer:
   (c)

6. **Heat of combustion of a substance can have**

   (a) only (-) ve value i.e ΔH**is (-) ve**

   (b) only (+) ve value i.e ΔH**is (+) ve**

   (c) some times (+) ve, some times (-) ve value

   (d) none of these

   Answer:
   (a)

7. **If enthalpy of product is greater than that of reactants**

   (a) the reaction is endothermic

   (b) the reaction is exothermic

   (c) either exothermic or endothermic

(d) none of these

Answer:
(a)

8. **Hess's law is an application of**
   - **(a) second law of thermodynamics**
   - **(b) first law of thermodynamics**
   - **(c) third law of thermodynamics**
   - **(d) zeroth law of thermodynamics**

Answer:
(b)

9. **The enthalpy change occurring when a gm-molecule of a substance is formed from its constituent elements is called its**
   - **(a) heat of combustion**
   - **(b) heat of neutralization**
   - **(c) heat of formation**
   - **(d) none of these**

Answer:
(c)

10. **The net thermal change which occurs when a gm-mole of solute is completely dissolved in a solvent is called**
    - **(a) heat of dilution**
    - **(b) heat of neutralization**
    - **(c) heat of solution**
    - **(d) none**

Answer:

(c)

Exercise

1. **What is exothermic and endothermic process? Discuss with example.**

2. **What is the relation between heat of reaction at constant pressure and heat of reaction at constant volume?**

3. **State Hess's law of constant heat summation? Explain how it can be used to calculate the heats of formation.**

4. **What is heat of neutralization? "Heat of neutralization of any strong acid by any strong base in dilute solution is always the same, but the value deviates in case of a weak acid or a weak base" - justify the statement.**

5. **Write notes on**
   (a) **Heat of formation**
   (b) **heat of combustion.**

6. **Write note on Kirchhoff's Equation.**

7. **State the law of Lavoisier and Laplace.**

Problems

1. **The enthalpy of formation of gaseous** H_2O **at 298K and 1 atm pressure is -241.82 kJ/mole. Calculate the** ΔH_f **of** H_2O **gas at 373K. The heat capacity of** H_2 **(g) ,** O_2 **(g) and** H_2O **(g) is** $33.58 JK^{-1} mole^{-1}$**, 28.84** $JK^{-1} mole^{-1}$**, and 29.37** $JK^{-1} mole^{-1}$ **respectively. Assuming that heat capacity is independent of temperature.**

2. **The enthalpy change (ΔH) for a reaction**

$$A_2\,(g) + 3\,B_2\,(g) \rightarrow 2AB_3\,(g)$$

Is -100 KJ at 298K. What is ΔU at 298K?

3. **Calculate the standard enthalpy change(ΔH^o) for the reaction**

   CH_4 (g) + $2O_2$ (g) → CO_2 (g) + **2** H_2O **(l)**

   The standard enthalpies of formation of $CH_4(g)$, $CO_2(g)$ andH_2O **(l) are -75.2** KJmole^{-1}**, -390.5** KJmole^{-1}**, and -285.7** KJmole^{-1} **respectively.**

4. **From the following data, calculate the enthalpy of the formation of** C_2H_5OH **at 298K.**

   (a) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ **ΔH1 = -1380.7** KJmole^{-1}

   (b) $C + O_2 \rightarrow CO_2$ **ΔH2 = -394.5** KJmole^{-1} **(3)** $H_2 + O_2 \rightarrow H_2O$ **ΔH3 = -286.6** KJmole^{-1}

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THERMODYNAMICS

Objectives

- First Law of Thermodynamics
- Second Law of Thermodynamics
- Entropy
- Free Energy
- Clausius Clapeyron Equation
- Gibbs Duhem Equation

6.1 Simple mathematical expressions

Some simple formulae are often used in thermodynamic discussions.

6.1.1 Maximum minimum:

$$y = f(x)$$

1. First of all we have to calculate $\frac{dy}{dx}$ of the function.
2. Put $\frac{dy}{dx} = 0$, solve for x(obtained one/more values of x)
3. Note for what value of$x$, $\frac{dy}{dx}$ changes its sign from positive to negative. This is the condition for maximum value of the function.
4. For what value of x, $\frac{dy}{dx}$ changes its sign from negative to positive. This is the condition for minimum value of the function.
5. For some value of x it will be seen that $\frac{dy}{dx}$ does not changes its sign. This is the condition for neither maximum nor minimum of the function. This is known as the particular point of the function.

$$\begin{aligned}
& y = x^5 - 5x^4 + 5x^3 \\
& \frac{dy}{dx} = 5x^4 - 20x^3 + 15x^2 \\
or, \quad & 0 = 5x^4 - 20x^3 + 15x^2 (but\ \frac{dy}{dx} = 0) \\
or, \quad & 5x^2(x^2 - 4x + 3) = 0 \\
or, \quad & 5x^2 \left\{x^2 - 3x - x + 3\right\} = 0 \\
or, \quad & 5x^2 \{x(x-3) - 1(x-3)\} = 0 \\
or, \quad & 5x^2(x-3)(x-1) = 0
\end{aligned}$$

$$\therefore x = 0,\ x = 3, x = 1$$

If $1 < x < 3$ $\quad \therefore \frac{dy}{dx} = \Theta ve$

If $x > 3$ $\quad \therefore \frac{dy}{dx} = \oplus ve$

So the minimum value will be

$$\begin{aligned} Y &= 3^5 - 5\times 3^4 + 5\times 3^3 \\ &= 243 - 405 + 135 \\ &= 378 - 405 \\ &= -27 \end{aligned}$$

If $0 < x < 1 \qquad \therefore \frac{dy}{dx} = \oplus ve$

$x > 1 \qquad \therefore \frac{dy}{dx} = \Theta ve$

So the maximum value will be

$$\begin{aligned} Y &= 1^5 - 5\times 1^4 + 5\times 1^3 \\ &= 1 - 5 + 5 = 1 \end{aligned}$$

When $0 < x < 1 \qquad \therefore \frac{dy}{dx} = \oplus ve$

$x < 0 \qquad \therefore \frac{dy}{dx} = \oplus ve$

6.1.2 Partial Derivative:

Suppose a quantity $Z$is a function of two independent variables x and yi.e.

$$Z = f(x,y)$$

If the co-ordinates(x, y)change by the amount dxanddy, then the change in the value of Zwill be given by

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$$

Where $\left(\frac{\partial Z}{\partial x}\right)_y$ is the rate of change in the magnitude of $Z$when $y$remains constant. Like wise $\left(\frac{\partial Z}{\partial y}\right)_x$ is the rate of change in the magnitude of $Z$when $x$remain constant.

Suppose

$$x = f(y,z) \tag{6.1}$$

$$y = f(x,z) \tag{6.2}$$

From (6.1) we get,

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \tag{6.3}$$

From (6.2) we get,

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{6.4}$$

From equation (6.3) we get,

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

or, $dx - \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial x}{\partial z}\right)_y dz$

1. (a) Suppose $dz = 0$, $dx \neq 0$

   1- $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 0$

   $$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

   or,

   $$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \tag{6.5}$$

   Let, $PV = RT$, $x = P$, $y = V$ and $Z = T$

   $$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{6.6}$$

(b) Suppose $dx = 0$ *and* $dz \neq 0$

$$\left(\frac{\partial x}{\partial y}\right)_Z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0$$

$$\text{or, } \left(\frac{\partial x}{\partial y}\right)_Z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

$$\text{or, } \left(\frac{\partial x}{\partial y}\right)_Z \left(\frac{\partial y}{\partial z}\right)_x = -\frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

or,

$$\left(\frac{\partial x}{\partial y}\right)_Z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{6.7}$$

Let, $PV = RT$, $x = P$, $y = v$ *and* $z = T$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \tag{6.8}$$

2. Let us consider 1 mole of an ideal gas

$$\begin{aligned} PV &= RT \\ P &= \frac{RT}{V} \\ or, \left(\frac{\partial P}{\partial V}\right)_T &= RT\left[\frac{\partial}{\partial V}\left(\frac{1}{V}\right)\right] \end{aligned}$$

$$= RT\left[-\frac{1}{V^2}\right] = -\frac{RT}{V^2} \tag{6.9}$$

again $V = \dfrac{RT}{P}$

$$\left(\frac{\partial V}{\partial P}\right)_T = RT\left[\frac{\partial}{\partial P}\left(\frac{1}{P}\right)\right]$$

$$= RT\left[-\frac{1}{P^2}\right] = -\frac{RT}{P^2} \tag{6.10}$$

$$\begin{aligned}
\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T &= \left(-\frac{RT}{V^2}\right)\times\left(-\frac{RT}{P^2}\right)\\
&= \frac{R^2T^2}{P^2v^2}=\left(\frac{RT}{PV}\right)^2 [We\, know\, PV=RT]\\
&= 1^2=1\\
\left(\frac{\partial P}{\partial V}\right)_T &= \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}\ (Proved)
\end{aligned}$$

3. $PV=RT\ or\ P=\frac{RT}{V}$

$$\left(\frac{\partial P}{\partial V}\right)_T=-\frac{RT}{V^2} \tag{6.11}$$

$$V=\frac{RT}{P}\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{P} \tag{6.12}$$

$$T=\frac{PV}{R}\left(\frac{\partial T}{\partial P}\right)_V=\frac{V}{R} \tag{6.13}$$

$$\begin{aligned}
&(6.11)\times(6.12)\times(6.13)\Rightarrow\\
\left(\frac{\partial P}{\partial V}\right)_T\times\left(\frac{\partial V}{\partial T}\right)_P\times\left(\frac{\partial T}{\partial P}\right)_V &= -\frac{RT}{V^2}\times\frac{R}{P}\times\frac{V}{R}\\
&= -\frac{RT}{PV}(We\, know\, PV=RT)\\
&= -1(Proved)
\end{aligned}$$

6.1.3 Perfect Differential:

Let P and Q in the figure 6.1 have co-ordinates $(x,y)$and $(x+\Delta x, y+\Delta y)$ respectively. Suppose the transition from P to Q can be effected in two ways along PRQ or PSQ.

In the path PRQ, we first change the variable $x\, to\, x+\Delta x$, y remaining constant to reach the point R. Then x being kept constant as $x+\Delta x$ the variable $y$is altered to

$y+\Delta y$, till Q is reached. Then at R, the value of Zwould be $Z_2=Z_1+$

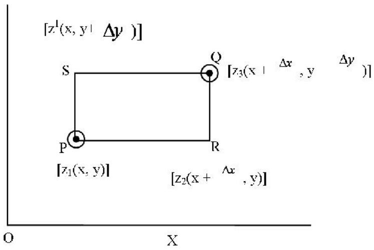


Figure 6.1: Perfect Differential

$\left(\frac{\partial Z_1}{\partial x}\right)_y \Delta x$

So at Q,

$$\begin{aligned}
Z_3 &= Z_2 + \left(\frac{\partial Z_2}{\partial y}\right)_x \Delta y \\
&= Z_2 + \frac{\partial}{\partial y}\left[Z_1 + \left(\frac{\partial Z_1}{\partial x}\right)_y \Delta x\right]\Delta y \\
&= Z_1 + \left(\frac{\partial Z_1}{\partial x}\right)_y \Delta x + \frac{\partial}{\partial y}\left[Z_1 + \left(\frac{\partial Z_1}{\partial x}\right)\Delta x\right]\Delta y
\end{aligned}$$

$$= Z_1 + \left(\frac{\partial Z_1}{\partial x}\right)_y \Delta x + \left(\frac{\partial Z_1}{\partial y}\right)\Delta y + \left(\frac{\partial^2 Z_1}{\partial y . \partial x}\right)\Delta x . \Delta y \quad ... \qquad (6.14)$$

Similarly if we follow the path PSQ, the co-ordinate at the point S, would be $x, y + \Delta y$and the value of Zat the point S would be

$$Z^1 = Z_1 + \left(\frac{\partial Z_1}{\partial y}\right)_x . \Delta y$$

So when the point Q is reached

$$Z_3 = Z^1 + \left(\frac{\partial Z^1}{\partial x}\right)_y . \Delta x$$

$$= Z_1 + \left(\frac{\partial Z_1}{\partial y}\right)_x \Delta y + \left(\frac{\partial}{\partial x}\left[Z_1 + \left(\frac{\partial Z_1}{\partial y}\right)\Delta y\right]\Delta x\right)$$

$$= Z_1 + \left(\frac{\partial Z_1}{\partial y}\right)_x \Delta y + \left(\frac{\partial Z_1}{\partial x}\right)\Delta x + \left(\frac{\partial^2 Z_1}{\partial x . \partial y}\right)\Delta y . \Delta x \quad ... \qquad (6.15)$$

From (6.14) and (6.15) we get

$$\frac{\partial^2 Z_1}{\partial y\, \partial x}\Delta x\, \Delta y = \frac{\partial^2 Z_1}{\partial x\, \partial y}\Delta y\, .\, \Delta x$$

or, $\frac{\partial^2 Z_1}{\partial y\, .\, \partial x} = \frac{\partial^2 Z_1}{\partial x\, .\, \partial y}$

That is, if dZ_1 is a perfect differential, then $\frac{\partial^2 Z_1}{\partial y.\, \partial x} = \frac{\partial^2 Z_1}{\partial x\, .\, \partial y}$

Conversely, we can conclude that dzwill be a perfect differential when it is found that

1. Z is a single valued function depending entirely on the instantaneous values of x and$y$, (i.e. its magnitude at any moment or in any given state is solely determined by the instantaneous values of x and $y$at that moment in the given state).

2. dzbetween any two specified points or states is independent of the path of transition.

3. $\oint dz$ for complete cyclic process is equal to zero.

4. $\frac{\partial^2 Z_1}{\partial y.\, \partial x} = \frac{\partial^2 Z_1}{\partial x.\, \partial y}$, i.e. the second differential of $Z$with respect to $x$and yy carried out in either order become equal to one another.

Let us consider 1 gm mole of an ideal gas.

$$\begin{aligned} PV &= RT \\ T &= \frac{PV}{R} \\ \left(\frac{\partial T}{\partial P}\right)_V &= \frac{V}{R} \\ or, \frac{\partial}{\partial V}\left[\left(\frac{\partial T}{\partial P}\right)\right] &= \frac{\partial}{\partial V}\left(\frac{V}{R}\right) \end{aligned}$$

or,

$$\frac{\partial^2 T}{\partial V.\, \partial P} = \frac{1}{R} \tag{6.16}$$

$$
\begin{aligned}
T &= \frac{PV}{R} \\
\left(\frac{\partial T}{\partial V}\right)_P &= \frac{P}{R} \\
\frac{\partial}{\partial P}\left(\frac{\partial T}{\partial V}\right)_P &= \frac{\partial}{\partial P}\left[\frac{P}{R}\right]
\end{aligned}
$$

or,

$$\frac{\partial^2 T}{\partial P.\partial V} = \frac{1}{R} \tag{6.17}$$

From (6.16) and (6.17) we get

$$\frac{\partial^2 T}{\partial V.\partial P} = \frac{\partial^2 T}{\partial P.\partial V} \; (Proved)$$

6.1.4 Heat and Work:

If the piston of a cylinder containing a gas is quickly pushed, then the temperature increases. If the temperature is not allowed to increase, the pressure increases. If we increase the temperature at constant volume, the pressure will increase. And if the pressure is increased at constant volume, the temperature will increase. These suggest that there is a relationship between temperature and pressure.

But a thermodynamic approach is to develop a relationship between pressure and temperature through observations without assuming anything about molecules.

6.2 Thermodynamic System

A system is defined as an object or a quantity of matter, i.e. a part of the universe.

The system is enclosed by a boundary which separates it from the rest of the universe.

All other parts of the universe, out side the boundary of the system, are called the surroundings.

The **boundary walls** of a system may be of two types;

1. **The diathermal walls:** permit the transmission of heat through them, **example :-** a liquid contained in a glass vessel.
2. **The adiabatic walls:** do not allow any heat to enter into or to come out of the system. Example**:** a liquid contained in silver mirrored double walled Dewar flask.

   - When a system undergoes a change, one or more of its thermodynamic variables would also change. If as a result of series of changes, the system returns to its initial state, its thermodynamic parameter would also return to their original values. Such a process is called a **cyclic process.**
   - If a change takes place in such a way that the temperature remains constant through out, it is called an **isothermal process.**
   - On the other hand, if the change occurring in a thermally insulated system which does not permit heat exchange with the surroundings, is called an **adiabatic process.**

Thermodynamic Systems

1. Isolated system
2. Closed system
3. Open system

1. **Isolated System:** Isolated system means a system when it is incapable of exchanging either matter or energy with the surroundings.
2. **Closed system:** Closed system means a system where exchange of energy with the surrounding is possible but no matter exchange is possible.
3. **Open system:** Open system means a system which is capable of exchanging both energy and matter with the surrounding.

6.3 Extensive and intensive property

By extensive property we mean that energy of system will change with the quantity of material present.

Example: Volume, surface area, energy.

By intensive property we mean that this is independent of the quantity of material present.

Example: Temperature, pressure, density etc.

6.4 First Law of thermodynamics

The relation between heat and work is the origin of first law of thermodynamics. This law may be stated as – Whenever heat is obtained from work the amount of heat obtained is proportional to the work done, or conversely if heat is transferred to work, there is a proportionality between work obtained and heat disappeared. However, this law is derived from experiment. Different scientists gave different statements on the basis of experiments.

1. Helmholtz's statement:

   The different forms of energy are interchangeable, but whenever energy of one kind disappears an equivalent amount of another kind or kinds makes it appearance.

2. Clausius statement:

   Various changes and transformation may occur but the total energy of the universe must remain constant.

3. Ostwald's statement:

   A machine which does work without any supply of energy from outside is known as perpetual motion of the 1st kind. Ostwald enunciated that perpetual motion of the 1st kind is impossible.

All the statements are identical in significance. All signify basically that – "Energy can neither be created nor destroyed, but can be converted from one form to another". Thus 1st law is actually the law of conservation of energy.

6.4.1 Algebraic formulation of 1 st law:

Let a closed system is state 'A' having internal energy $U_i$change to state B. Let us assume that during transformation 'q' cal of heat was absorbed from

surroundings and 'W' amount of work is done. Now heat absorbed by the system is positive and heat given out from the system is negative.
If U_f= internal energy is state B.
Then net energy before transformation = $U_i + q$
Net energy after transformation = $U_f + W$.
By the principle of conservation of energy

$$\begin{aligned} \Rightarrow U_i + q &= U_f + W \\ q &= (U_f - U_i) + W \\ q &= \Delta U + W \;\; [\Delta U = U_f - U_i] \end{aligned}$$

Thus differential form is

$$dq = dU + dW$$

Heat absorbed is equal to change in internal energy plus work done.

Skill Test

1. What is thermodynamic system?
2. What are the different types of thermodynamic system?
3. What is open system? Give an example.
4. What is extensive and intensive property? Give example in each case.
5. State 1^{st} law of thermodynamics. Derive the mathematical form of 1^{st} law of thermodynamics.

6.5 Internal Energy (U)

A thermodynamic system by virtue of its very existence must possess a store of energy.

Example:

1. zinc and Copper sulphate in a Daniel Cell react producing electrical energy.
2. a liquid freezes into solid yielding heat energy.

3. Steam expands from higher to lower pressure yielding work of mechanical energy.
4. Carbon monoxide unites with oxygen to produce CO_2 and heat energy.

Definition: Internal energy of a thermodynamic system is the inherent energy possessed by the system within itself and it is denoted by the symbol$U$. Origin of internal energy comes from the molecular movement of the working substances of the system. Thus in a gas, the kinetic energy of the random moving molecules are responsible for the internal energy of the whole gas.

6.5.1 Characteristics:

There are some special characteristics of the internal energy.

1. **Extensive property**

   The internal energy is an extensive property [open system =$f(n)$]

2. When a system changes from a thermodynamic state A to a thermodynamic state B, its internal energy will also change. If U_A *and* U_B indicate the internal energy of the two states then the change in internal energy

   $$\Delta U = U_B - U_A$$

3. **State function**

   Magnitude of the internal energy is dependent only on the state of the system. Again, in case of a gas of constant composition the state is defined by three parameters P, V and T. For those being related by an equation of state and any two parameters are regarded as independent quantity;

   $$U = f(State)$$

   $$U = f(P,V)\ ;\ U = f(V,T)\ ;\ U = f(P,T)$$

   Perfect Differential

   Internal energy U of a given system depends only on the state of the system and hence is dependent on any two (say P, T or V, T or P, V) of the three common variables (P, V, T). $dU$is then the perfect differential

$$\frac{\partial^2 U}{\partial P\,.\,\partial T} = \frac{\partial^2 U}{\partial T\,.\partial P}$$

(a) $U$is a single valued function depending on the instantaneous values of P and T.

(b) dUbetween any two specified points or state is independent of the path of transformation.

(c) dU for complete cyclic process is equal to zero.

(d) $\frac{\partial^2 U}{\partial P.\partial T} = \frac{\partial^2 U}{\partial T\,.\partial P}$ i.e. second differential of U with respect to T and P carried out in either order become equal to one another.

(e) U is a function of two independent variables P and T i.e.

$$\Delta U = \left(\frac{\partial U}{\partial P}\right)_T \Delta P + \left(\frac{\partial U}{\partial T}\right)_P \Delta T$$

4. (a) Absorption of heat usually increases the internal energy of the system.

   (b) Rejection of heat by the system decreases the internal energy of the system.

   (c) But changes in internal energy in a cyclic process are zero.

6.5.2 Physical significance

If a system absorbs heat at constant volume $(dV = 0)$
Then $W = \int PdV = 0$
So from first law of thermodynamics

$$dq = dU + dW$$

or, $dq = dU + PdV$
At constant volume $dV= 0$

$$(dq)_V = (dU)_V + 0$$

or, $(dq)_V = (dU)_V$

Thus the function of internal energy is such that its change is equal to the heat absorbed by the system at constant volume.

6.5.3 Mathematical expression for change in internal energy

$$U = f(State)$$

$$= f(T,V)$$

If the temperature and volume of the system changes by dT *and* dV, then the corresponding change in internal energy is expressed by,

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= \left(\frac{\partial q}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= nC_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \left[Here,\ C_V = \frac{1}{n}\left(\frac{\partial q}{\partial T}\right)_V\right] \end{aligned}$$

Since C_V or molar heat capacity of a gas in constant volume is defined as the energy required to raise the temperature.
From first law of thermodynamics

$$dq = dU + dW$$

$$dU = dq - dW$$

$= TdS - PdV$ [Since by definition$dS = \dfrac{dq}{T}$]
Differentiating both sides with respect to volume at constant temperature we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Since from Maxwell's relation $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Thus

$$dU = nC_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

For ideal gas $PV = nRT$

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

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$[for closed system]

$$\begin{aligned}
dU &= nC_V dT + \left[T \times \frac{nR}{V} - P\right] dV \\
&= nC_V dT + [P - P]\, dV \\
&= nC_V dT \\
dU &= nC_V\, dT
\end{aligned}$$

or, $\Delta U = n\, C_V (T_2 - T_1)$

For real gas

For real gas obeying Vander Waals' equation we have

$$\left(P + \frac{n^2 a}{V^2}\right)(v - nb) = nRT$$

or, $P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$

Differentiating both sides with respect to temperature at constant volume we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb} - 0$$

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{nRT}{V - nb} = P + \frac{n^2 a}{V^2}$$

Thus

$$\begin{aligned}
dU &= nC_V\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV \\
&= nC_V dT + \left[P + \frac{n^2a}{V^2} - P\right]dV \\
dU &= nC_V\,dT + \frac{n^2a}{V^2}dV \\
\int_{U_1}^{U_2} dU &= nC_V \int_{T_1}^{T_2} dT + n^2a \int_{V_1}^{V_2} \frac{dV}{V^2}
\end{aligned}$$

or, $(U_2 - U_1) = nC_V\,(T_2 - T_1)\ - n^2a\left[\frac{1}{V}\right]_{V_1}^{V_2}$

or, $\Delta U = nC_V(T_2 - T_1) - n^2a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$

For isothermal process $dT = 0$

For ideal gas the change in internal energy in isothermal process is $(\Delta U)_T = nC_V \times 0 = 0$

For real gas the change in internal energy in isothermal process is

$$(\Delta U)_T = nC_V \times 0 - n^2a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

or, $(\Delta U)_T = n^2a\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$

Skill Test

1. What is internal energy of a system?
2. Whether internal energy is an extensive or intensive property – Explain.
3. What are the characteristics of internal energy?
4. What is the physical significance of internal energy?
5. What is the expression of change in internal energy for $n$mole of ideal gas?

6.6 Enthalpy or Heat Content (H)

Enthalpy of any thermodynamic system is the measure of the total energy of the system.

In case of a gas, the product of pressure (P) and volume (V) is expressed as energy. The sum of these two energy terms associated with the system namely the internal energy (U) and PV energy is known as enthalpy or heat content.

Heat content = Internal energy + (Pressure ×Volume) energy

$$H = U + PV$$

6.6.1 Characteristics :

There are some special characteristics of enthalpy.

1. **State function :** Magnitude of enthalpy is dependent only on the state of the system. As in case of gas, the state is defined by three parameters, P.V and T. So we can write mathematically

$$H = f(State)$$

$$\Rightarrow H = f(P,T)$$

$$\begin{aligned} &= f'(P,V) \\ &= f''(V,T) \end{aligned}$$

2. When a system changes from a thermodynamic state A to B, its enthalpy will also change. If $H_A\, and\, H_B$ denote enthalpies in the two states then the change in enthalpy.

$$\Delta H = H_B - H_A$$

3. **Extensive Property**

   Since the volume (V) and internal energy (U) are dependent on the number of moles present in a gaseous system and their motion. Thus enthalpy must be dependent on mass of the gases.

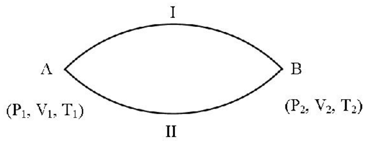
In open system

$H = f(n)$ [n = number of moles present in the system]

4. **Perfect Differential**

Since enthalpy is only dependent on the initial and final state of the system and not on the manner in which the change is carried out, is called the path independent and hence it is a perfect differential.

$$\Delta H_I = \Delta H_{II}$$



Let a change takes place by path I from state A to B. Suppose change of parameter (say V) takes place first followed by the change in the other parameter (say T) to reach state B from A. Again by path II change takes place from state A to B but the change of parameter takes place in the just opposite way to that of I.

In both cases, we shall find the change in enthalpy is identical. So mathematically,

$$\frac{\partial^2 H}{\partial V.\partial T} = \frac{\partial^2 H}{\partial T.\partial V}$$

(a) H is a single valued function depending on the instantaneous values of V and T.

(b) dH between any two specified points or state is independent of the path of transformation.

(c) dH for a complete cyclic process is equal to zero.

(d) $\frac{\partial^2 H}{\partial V.\partial T} = \frac{\partial^2 H}{\partial T.\partial V}$ i.e. second differential of H with respect to T and V carried out in either order become equal to one another.

6.6.2 Physical Significance

If a system absorb heat at constant pressure ($dP = 0$)

So from first law of thermodynamics

$$dq = dU + dW$$

or, $dq = dU + PdV$

at constant pressure

$$(dq)_P = (dU)_P + PdV$$

Again, from the definition of enthalpy

$$H = U + PV$$

or, $dH = dU \; + PdV + VdP$

At constant pressure $dP = 0$

$$(dH)_P = (dU)_P + PdV$$

or, $(dH)_P = (dq)_P$

Thus the function enthalpy is such that its change is equal to the heat absorbed by the system at constant pressure.

6.6.3 Mathematical expression for change in enthalpy

$$H = f(state)$$

$$= f(P,T)$$

If the temperature and pressure of a system changes by dT and dP respectively then the corresponding change in enthalpy be

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \\ &= \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial q}{\partial T}\right)_P dT \\ &= nC_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad \left[Here\, C_P = \frac{1}{n}\left(\frac{\partial q}{\partial T}\right)_P\right] \end{aligned}$$

From definition of enthalpy

$$H = U + PV$$

or, $dH = dU + PdV + VdP$

$$= dq + VdP$$

$= TdS + VdP$ [Since by definition $dS = \frac{dq}{T}$]

Differentiating both sides with respect to pressure at constant temperature, we get

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Since from Maxwell's relation

$$\begin{aligned} \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial H}{\partial P}\right)_T &= -T\left(\frac{\partial V}{\partial T}\right) + V \\ dH &= nC_P dT + \left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] dP \end{aligned}$$

For ideal gas

$$
\begin{aligned}
PV &= nRT \\
V &= \frac{nRT}{P} \\
\left(\frac{\partial V}{\partial T}\right)_P &= \frac{nR}{P} \\
dH &= nC_PdT + \left[-T\times\frac{nR}{P}+V\right]dP \\
\Rightarrow dH &= nC_PdT + [-V+V]\ dP \\
\Rightarrow dH &= nC_PdT
\end{aligned}
$$

Integrating left hand side between $H_1$and H_2 and right hand side between $T_1\ and\ T_2$ we get

$$\int_{H_1}^{H_2} dH = nC_P\int_{T_1}^{T_2} dT$$

or, $(H_2-H_1) = nC_P(T_2-T_1)$

or, $\Delta H = nC_P(T_2-T_1)$

For real gas

For real gas obeying Vander Waals' equation is

$$\left(P+\frac{n^2a}{V^2}\right)\ (v-nb) = nRT$$

or, $PV+\dfrac{n^2a}{V}-Pnb-\dfrac{n^3ab}{V^3} = nRT$

or, $P\left(\dfrac{\partial V}{\partial T}\right)_P + n^2a\left(-\dfrac{1}{V^2}\right)\left(\dfrac{\partial V}{\partial T}\right)_P - 0 - n^2ab\left(-\dfrac{2}{V^3}\right)\left(\dfrac{\partial V}{\partial T}\right)_P = nR$

or, $\left(\dfrac{\partial V}{\partial T}\right)_P\left[P-\dfrac{n^2a}{V^2}+\underset{\substack{\uparrow\\ negligible}}{\dfrac{2n^3ab}{V^3}}\right] = nR$

or, $\left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{nR}{P-\dfrac{n^2a}{V^2}}$

or, $T\left(\frac{\partial V}{\partial T}\right)_P = \dfrac{nRT}{P - \dfrac{n^2a}{V^2}}$

or, $T\left(\frac{\partial V}{\partial T}\right)_P = \dfrac{nRT}{\left(P + \dfrac{n^2a}{V^2}\right) - \dfrac{2n^2a}{V^2}}$

$$= \frac{nRT}{\dfrac{nRT}{V-nb} - \dfrac{2n^2a}{V^2}}$$

$$= \frac{nRT}{nRT\left[\dfrac{1}{V-nb} - \underset{\substack{\uparrow \\ \textit{is quite small and so negligible}}}{\dfrac{2n^2a}{V^2RT}}\right]}$$

or, $T\left(\frac{\partial V}{\partial T}\right)_P = (V - nb)$

$$dH = nC_PdT + \left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]\ dp$$

$= nC_PdT + [-(V - nb) + V]\,dp$

$$= nC_PdT + [-V + nb + V]\ dP$$

$$dH = nC_PdT + nb\ dP$$

Integrating LHS between H_1 *and* H_2 *and RHS between* T_1 *and* T_2 *and* P_1 *to* P_2 we get,

$$\int_{H_1}^{H_2} dH = nC_P \int_{T_1}^{T_2} dT + nb \int_{P_1}^{P_2} dp$$

or, $(H_2 - H_1) = nC_P\,(T_2 - T_1) + nb(P_2 - P_1)$

or, $\Delta H = nC_P(T_2 - T_1) + nb(P_2 - P_1)$

For isothermal process $dT = 0$

For ideal gas the change in enthalpy in isothermal process is $(\Delta H)_T = nC_P \times 0 = 0$

For real gas the change in enthalpy in isothermal process is

$$(\Delta H)_T = nC_P \times 0 + nb(P_2 - P_1)$$

$$(\Delta H)_T = nb(P_2 - P_1)$$

Skill Test

1. What is enthalpy of a system?
2. Whether enthalpy is an extensive or intensive property – Explain.
3. What are the characteristics of enthalpy?
4. What is the physical significance of enthalpy?
5. What is the expression of change in enthalpy for n mole of ideal gas?

6.7 Heat Capacity (C)

Definition: Molar heat capacity (C) is the amount of heat required to raise the temperature of 1 mole of the substance through $1^\circ K$
Mathematically $C = \dfrac{dq}{dT}$
Where $dq$is the amount of heat required to raise the temperature $dT$for 1 mole of the substance.

Unit

$$Cal\ degree^{-1} mole^{-1}$$

There are **two** types of heat capacity

1. Molar heat capacity at constant pressure (C_P)
2. Molar heat capacity at constant volume (C_V)

$$\begin{aligned}
C_P &= \left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P, at\ constant\ pressure dH_P = dq_P \\
C_V &= \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V,\ at\ constant\ volume\ dq_V = dU_V \\
C_P - C_V &= \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V
\end{aligned}$$

By definition

$$\begin{aligned}
H &= U+PV \\
\left(\frac{\partial H}{\partial T}\right)_P &= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \\
C_P - C_V &= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V
\end{aligned}$$

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

$$\begin{aligned}
dU &= \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \\
\left(\frac{\partial U}{\partial T}\right)_P &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \\
C_P - C_V &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \\
&= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P
\end{aligned}$$

Again from 1^{st} law of thermodynamics

$$\begin{aligned}
dq &= dU + dW \\
dU &= dq - dW \\
&= TdS - PdV \\
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - P
\end{aligned}$$

From Maxwell's relation we know that

$$\begin{aligned}
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P \\
C_P - C_V &= \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \\
&= T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \\
C_P - C_V &= T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P
\end{aligned}$$

6.7.1 Discussion

1. $T, \left(\frac{\partial P}{\partial T}\right)_V$ *and* $\left(\frac{\partial V}{\partial T}\right)_P$ are always positive. Thus $C_P - C_V$ is always (+) ve. $C_P > C_V$

2. At absolute zero, i.e. when $T = 0^\circ K$

$$C_P - C_V = 0 \, or \, C_P = C_V$$

   But it is a hypothetical case.

3. Thus for water at $4^\circ C$ under a pressure of 1 atom, density (d) is maximum and volume (V) is minimum

$$d = \frac{m}{V}$$

   But differential of a minimum quantity $= 0$ *or* $\left(\frac{\partial V}{\partial T}\right)_P = 0$

$$C_P - C_V = 0$$

   or, $C_P = C_V$

4. For ideal gas

$$PV = RT \; [for \; 1 \; mole]$$

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

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

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

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$= T \times \frac{R}{V} \times \frac{R}{P}$$

$$= R \times \frac{RT}{PV} = R$$

5. **For real gas**

For real gas obeying Vander Waals' equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \ [for\,1\,mole]$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

$$P\left(\frac{\partial V}{\partial T}\right)_P - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P - 0 - \frac{ab(-2)}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = R$$

or, $P\left(\frac{\partial V}{\partial T}\right)_P - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{2ab}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = R$

or, $\left(\frac{\partial V}{\partial T}\right)_P \left[P - \frac{a}{V^2} + \frac{2ab}{V^3}\right] = R$

$\downarrow$

neglectingthisterm

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

or, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2}} = \frac{R}{\left(P + \frac{a}{V^2}\right) - \frac{2a}{V^2}}$

$$= \frac{R}{\left(\frac{RT}{V-b} - \frac{2a}{V^2}\right)}$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$= T \times \frac{R}{V-b} \times \frac{R}{\left(\frac{RT}{V-b} - \frac{2a}{V^2}\right)}$$

$$= \frac{RT}{(V-b)} \times \frac{R}{\frac{RT}{V-b}\left\{1 - \frac{2a(V-b)}{V^2RT}\right\}}$$

$$= R \times \left\{1 - \frac{2a(V-b)}{V^2RT}\right\}^{-1}$$

Expanding and neglecting the higher power terms

$$C_P - C_V = R \times \left(1 + \frac{2a(V-b)}{V^2RT}\right)$$

$$= R \times \left(1 + \frac{2aV}{V^2RT} - \underset{\substack{\downarrow \\ \textbf{neglectingthisterm}}}{\frac{2ab}{V^2RT}}\right)$$

$$= R\left(1 + \frac{2aV}{V^2RT}\right)$$

$$= R\left(1 + \frac{2a}{RTV}\right)$$

$$= R\left(1 + \frac{2ap}{R^2T^2}\right) \quad \left[PV \approx RT \; or \; V \approx \frac{RT}{P}\right]$$

6. **For real gas without intermolecular force of attraction**

For real gas obeying Vander Waals' equation is

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

Inter molecular force of attraction represented by $\frac{a}{V^2}$being assumed to be absent,

i.e. $\frac{a}{V^2} = 0$

$$P(V-b) = RT$$

or, $P = \frac{RT}{(V-b)}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

Again $PV - Pb = RT$

$$P\left(\frac{\partial V}{\partial T}\right)_P - 0 = R$$

or, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$= T \times \frac{R}{(V-b)} \times \frac{R}{P}$$

$$= \frac{P(V-b)}{(V-b)} \times \frac{R}{P}$$

= R

7. For a gas having molecules like geometrical point, then b = 0.

   Thus Vander Waals' equation is

$$\left(P + \frac{a}{V^2}\right) V = RT$$

$$PV + \frac{a}{V} - RT = 0$$

$$P\left(\frac{\partial V}{\partial T}\right)_P - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P - R = 0$$

or, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left(P - \frac{a}{V^2}\right)}$

$$= \frac{R}{\left(P + \frac{a}{V^2} - \frac{2a}{V^2}\right)}$$

$$= \frac{R}{\left(\frac{RT}{V} - \frac{2a}{V^2}\right)} = \frac{R}{\frac{RT}{V}\left(1 - \frac{2a}{RTV}\right)}$$

Again $P = \frac{RT}{V} - \frac{a}{V^2} \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$= T \times \frac{R}{V} \times \frac{R}{\frac{RT}{V}\left(1 - \frac{2a}{RTV}\right)}$$

$$= R\left(1 - \frac{2a}{RTV}\right)^{-1}$$

$C_P - C_V = R\left(1 + \frac{2a}{RTV}\right)$ (Expanding and neglecting higher power terms.)

Skill Test

1. What is heat capacity?
2. What is the unit of heat capacity?
3. What are the different types of heat capacity?
4. Derive the expression of change in heat capacity.
5. On which condition $C_P = C_V$.

6.8 Change of State

The change that take place in nature are termed as natural or **spontaneous process** e.g. flow of water from upper level to lower level, falling of a body, passing of heat from a body at higher temperature to a body at lower temperature.

This change may take place as a result of some unbalance in intensive properties e.g. P and T

This can be explained with the help of **storms or cyclones.** Normally the pressure is same everywhere. If for some reason the pressure of a particular place is lowered, air will rush in from outside leading to very high rate of air flow and this causes the storm.

Let us suppose that some gas is kept in a cylinder covered by a movable weightless piston. The gas exerts some pressure at the piston and this pressure at the specific volume may or may not be identical with atmospheric pressure. If they are different the piston will move in the direction of lower pressure. Because the properties like volume, gas pressure will change every moment. Then after a certain time the gas pressure will become identical with the external pressure, then the piston will not move. The pressure, volume and temperature of the gas will not change with time that means a state of equilibrium has been reached. This means an **equilibrium state** is one where properties are not changing with time. This definition is sufficient for isolated system.

But this definition is not sufficient for non isolated systems. For non isolated systems, a system is in equilibrium when

1. the properties do not change with time
2. removal of the system from contact with the surroundings causes no change of properties.

If condition

1. is satisfied and condition
2. is not satisfied, then the system is in a **steady state**.

Example

A metal rod in contact at one end with a large body at 180° and in contact with another large body at 160° at the other end is in a steady state.

A state can be at equilibrium or thermodynamic equilibrium if it is at **mechanical, thermal or chemical equilibrium.**

If there is imbalance of force between different parts of a system and between the system and surroundings, then there is no net observable movement and the system is at **mechanical equilibrium.**

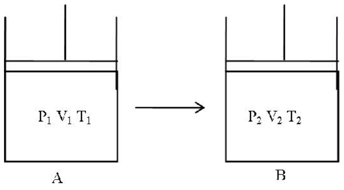
This does not mean that the pressure or force is same everywhere. It means that there is no disbalance e.g. a column of water.

If the temperature is same throughout the system and there is no difference of temperature between the system and the surroundings then the system is at **thermal equilibrium.**

If there is no thermal equilibrium, heat will move form high to low temperature and this may lead to mechanical movement also. Balance of pressure and temperature is sufficient for the equilibrium of non reacting system.

But if there is chemical interaction, there can't be equilibrium even if there is no imbalance in P and T. Thus if the chemical composition is same throughout and unchanging , the system is at **chemical equilibrium.**

Once a system is in equilibrium and the surroundings are kept unchanged, no motion will take place. There will be no change and hence no work. Work can be done if some intensive properties are changed.



Let the initial state of a system (A) be designated by P_1, V_1, T_1 and let the external pressure be made P_2. There will be change until the gas pressure is also P_2.

Let the new state B be designated as P_2, V_2 *and* T_2.

The change may be isothermal $(T_1 = T_2)$, isobaric $(P_1 = P_2)$or isochoric $(V_1 = V_2)$.

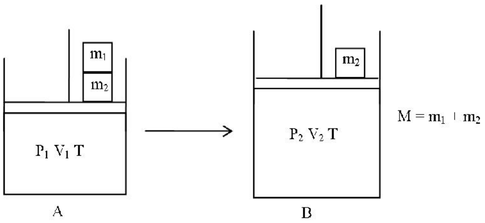
If we go from state A to B, and then again come back to state A, the change is cyclic. A change or a process may be reversible or irreversible.

If the system and surroundings are restored to their initial conditions after a cyclic change, then the change is termed as **reversible.**

A system may undergo a change of state from state A to B by a single step or through a specified sequence of intermediate steps. The state B has again to be changed to A by traversing the same sequence in reverse order for the purpose of checking whether the change is reversible or not.

If after such a cycle the surroundings are not restored to their initial condition, then the change is **irreversible.**

Let us suppose that a certain amount of ideal gas is kept in a vessel



and is covered by a piston. Let the pressure, temperature and volume be $P_1, T\ and\ V_1$. The system is at equilibrium and hence the external pressure is equal to P_1 also.

Let say two boxes of sand of mass M is placed over the piston. Now the external pressure is suddenly reduced toP_2. This is achieved here by raising one box of sand corresponding to massm_1.

As a result of this finite unbalance, the condition of mechanical equilibrium is disturbed. Due to raising one box the piston moves outwards at a high speed and as a result there may be a difference of temperature near the piston and away from it. Due to friction, some heat may be released. Same thing will take place during compression. Even if the piston is frictionless and there is no change of temperature, the universe can not be restored to its original condition after a cyclic change.

Then the work done by the system is, $W_{AB} = P_2(V_2 - V_1)$ and the work is positive.

It cannot be returned to initial state A unless some extra weight is added. Let the sand box of weight m_1 be again placed over the piston so that there is now mass of weight M. The piston is lowered and the initial volume V_1 is reached.

The work done against pressure P_1 is now

$$W_{BA} = P_1(V_1 - V_2)$$

W_{BA} is obviously negative.

Naturally work done in the whole cycle is

$$W_{cy} = W_{AB} + W_{BA} \neq 0$$

That means it is proved that, in irreversible change

$$W_{cy} \neq 0$$

6.8.1 Work done in isothermal reversible process

Suppose n moles of a perfect gas are enclosed in a cylinder by a frictionless piston. The whole cylinder is kept in a large constant temperature bath at$T^{\circ}K$. Any change that would occur to the system is isothermal. There is a latch at the top B, and the piston can not move beyond that. The volume of the gas when the piston is at B isV_2. When the piston is at the point A, the volume of the gas isV_1. The aim is to expand the gas from volumeV_1 to V_2.

But we can carryout the process in the following way. Let the pressure P_1 be reduced by an infinitesimal amountdP. Let the new pressure be $P_1^{/} = P_1 - dp$.

The work would be $dW = (P_1 - dP)dV$.

The change in volume would be small and equal todV.

The new pressure be again reduced slightly so that it changes to $P^{//} = P_1^{/} - dP$

Then the work would be $dW = (P_1^{/} - dP)dV$

The process may be repeated by such infinite number of successive steps that the gas may be expanded from volumeV_1 to V_2.

The net work for all the minute stages would be

$$\int dW = \sum (P - dP)dV = \int_{V_1}^{V_2} PdV - \int_{V_1}^{V_2} dPdV$$

Since $dp and\ dV$ are infinitesimal quantity, $dPdV$ is negligible

$$\int dW = \int_{V_1}^{V_2} PdV$$

or, $W = \int_{V_1}^{V_2} pdv = \int_{V_1}^{V_2} \frac{nRT}{V} dv = nRT \ln \frac{V_2}{V_1} \quad \left[PV = nRT\ or, P = \frac{nRT}{V} \right]$

$$W = nRT\ \ln \frac{V_2}{V_1}$$

$$= nRT\ \ln \frac{P_1}{P_2}$$

Since $\frac{V_2}{V_1} = \frac{P_1}{P_2}$ there is an isothermal expansion of perfect gas.

Relation between $\Delta H\ and\ \Delta U$

At constant pressure

$$\Delta H_P = \Delta U_P + P\Delta V$$

For gaseous system

$$P\Delta V = P(V_f - V_i)$$

$$= n_f RT - n_i RT$$

$$= (n_f - n_i)RT$$

$$\Rightarrow\ P\Delta V = \Delta nRT$$

$$\Delta H_P = \Delta U_P + \Delta nRT$$

Skill Test

1. What is the difference between equilibrium and steady state?
2. What is mechanical equilibrium? Give an example.
3. What is reversible and irreversible process?
4. How will you prove that in irreversible cyclic process $W_{cy} \neq 0$?

6.9 Out come of first law of thermodynamics

1. **Isobaric process**

   Isobaric process i.e. process at constant pressure $(dP = 0)$

   From 1^{st} law of thermodynamics we have

$$\begin{aligned}
dq_P &= dU_P + dW_P [Suffix\, P\, denotes\, constant\, pressure] \\
&= dU_P + (PdV)_P \\
&= dH_P \\
H &= U + PV \\
dH &= dU + PdV + VdP \\
dH_P &= dU_P + (PdV)_P + 0 \\
(dH)_P &= dU_P + (PdV)_P
\end{aligned}$$

   Thus heat absorbed at constant pressure is utilized partly to increase internal energy and rest is used in work done.

2. **Isochoric change**

   Isochoric change i.e. process at constant volume $(dV = 0)$

   From 1^{st} law of thermodynamics we have

   $dq_V = dU_V + (dW)_V$ [Suffix V denotes constant volume]

   or, $dq_V = dU_V + 0$

   or, $dq_V = dU_V$

   Thus heat absorbed at constant volume is fully utilized to increase internal energy.

3. **Isothermal Change**

   Isothermal change i.e. process at constant temperature $(dT = 0)$

   From 1^{st} law of thermodynamics we have

$$dq_T = dU_T + dW_T$$

6.9.1 Ideal gas

$$dq_T = 0 + dW_T$$

$$\Rightarrow \quad dq_T = dW_T$$

Thus total heat is utilized to do work at constant temperature.

Reversible Process

$$(Q_T)_{rev} = (W_T)_{rev}$$

$$= \int_{P_1,V_1}^{P_2,V_2} PdV$$

$$= \int_{V_1}^{V_2} \frac{nRT}{V} dV \quad \left[PV = nRT \ or, P = \frac{nRT}{V} \right]$$

$$= nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

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

$$= nRT \ \ln \frac{P_1}{P_2}$$

Irreversible Process

$$(Q_T)_{irrev} = (W_T)_{irrev}$$

$$= P_{applied} \int_{V_1}^{V_2} dV$$

$$= P_{applied} \ (V_2 - V_1))$$

$= P_2 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$ [Applied pressure = final pressure =P_2]

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

6.9.2 For real gas (obeying Vander Waals' equation)

$$dU_T = \frac{n^2a}{V^2}dV \ , \ dH_T = nb\,dP$$

$$dq_T = dU_T + dW_T$$

$$= \frac{n^2a}{V^2}dV + (PdV)_T$$

Reversible Process

$$(Q_T)_{rev} = n^2a\int\limits_{V_1}^{V_2}\frac{dV}{V^2} + \int\limits_{P_1,V_1}^{P_2,V_2} P\,dV$$

$$= n^2a\int\limits_{V_1}^{V_2}\frac{dV}{V^2} + \int\limits_{V_1}^{V_2}\left(\frac{nRT}{V-nb)} - \frac{n^2a}{V^2}\right)dV$$

For Vander Waals' equation we know that

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

or, $P = \left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right)$

$$(Q_T)_{rev} = n^2a\int\limits_{V_1}^{V_2}\frac{dV}{V^2} + nRT\int\limits_{V_1}^{V_2}\frac{dV}{V-nb} - n^2a\int\limits_{V_1}^{V_2}\frac{dV}{V^2}$$

$$= nRT\int\limits_{V_1}^{V_2}\frac{dV}{V-nb}$$

$$(Q_T)_{rev} = nRT\ \ln\frac{V_2-nb}{V_1-nb}$$

$$dW_T = dq_T - dU_T$$

$$= nRT\int\limits_{V_1}^{V_2}\frac{dV}{V-nb} - n^2a\int\limits_{V_1}^{V_2}\frac{dV}{V^2}$$

$$= nRT\ \ln\frac{V_2 - nb}{V_1 - nb} - n^2a\left[-\frac{1}{V}\right]_{V_1}^{V_2}$$

$$= nRT\ln\frac{V_2 - nb}{V_1 - nb} + n^2a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

Here $(Q_T)_{rev} \neq (W_T)_{rev}$

Irreversible process

$$(Q_T)_{irrev} = n^2a\int_{V_1}^{V_2}\frac{dV}{V^2} + P_2\int_{V_1}^{V_2} dV$$

$$= n^2a\left[-\frac{1}{V}\right]_{V_1}^{V_2} + P_2\left(V_2 - V_1\right)$$

$$= n^2a\left[\frac{1}{V_2} - \frac{1}{V_1}\right] + P_2\left(V_2 - V_1\right)$$

$$= n^2a\left[\frac{1}{V_1} - \frac{1}{V_2}\right] + \left(\frac{nRT}{V_2 - nb} - \frac{n^2a}{V_2^2}\right)\left(V_2 - V_1\right)$$

6.10 Adiabatic Change

Adiabatic change involves no heat transfer $(dq = 0)$

From 1^{st} law of thermodynamics

$$0 = dU_{adia} + dW_{adia}$$

or, $(dU)_{adia} = -(dW)_{adia}$

6.10.1 Adiabatic Work

We know for adiabatic process

$$W_{adia} = -\Delta U_{adia}$$

$$= -nC_V\,dT\,(for\ ideal\ gas)$$

$$= -nC_V(T_2 - T_1)$$

$$= nC_V(T_1 - T_2) \begin{bmatrix} T_1 = Initial\ temperature \\ T_2 = Final\ temperature \end{bmatrix}$$

$$= nC_V\left(\frac{P_1V_1}{nR} - \frac{P_2V_2}{nR}\right) \qquad [R = C_P - C_V]$$

$$= \frac{C_V}{R}(P_1V_1 - P_2V_2) \qquad \left(\frac{R}{C_V} = \frac{C_P}{C_V} - 1\right)$$

$$= \frac{1}{\gamma - 1}(P_1V_1 - P_2V_2) \qquad \left(\frac{R}{C_V} = \gamma - 1\right)$$

$$\left(or, \frac{C_V}{R} = \frac{1}{\gamma - 1}\right)$$

6.10.2 Inter relation between thermodynamic parameters

Reversible Process

In an adiabatic reversible change $q = 0$
So from first law of thermodynamics

$$\Delta U = -W$$

$$\Rightarrow dU = -dW$$

$$\Rightarrow nC_V dT = -PdV$$

[from ideal gas PV = nRT $\Rightarrow nC_V dT = -\frac{nRT}{V}dV \quad P = \frac{nRT}{V}]$

1. Now integrating left hand side between temperature T_1 *and* T_2 and right hand side between volume V_1 *and* V_2 we get,

$$\int_{T_1}^{T_2} nC_V dT = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

or, $nC_V \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V}$

or, $C_V\ \ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1} \quad [C_P - C_V = R$

or, $\ln\frac{T_2}{T_1} = -\frac{R}{C_V}\ln\frac{V_2}{V_1} \quad \frac{C_P}{C_V} - 1 = \frac{R}{C_V}$

or, $\ln\frac{T_2}{T_1} = \frac{R}{C_V}\ln\frac{V_1}{V_2} \quad or\ (\gamma - 1) = \frac{R}{C_V}\Big]$

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

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

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

or,

$$\frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} \tag{6.18}$$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} = T_3V_3^{\gamma-1} = \cdots\cdots = Constant$$

So the general formula is $TV^{\gamma-1} = Constant$

2. We have $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

   From an ideal gas, we know $P_1V_1 = RT_1\ and\ P_2V_2 = RT_2$

$$\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$$

or, $\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$

or, $\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1}$

or, $\frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} = \frac{P_2V_2}{P_1V_1}$

or, $P_1V_1V_1^{\gamma-1} = P_2V_2V_2^{\gamma-1}$

or,

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \tag{6.19}$$

So we can write $P_1V_2^{\gamma} = P_2V_2^{\gamma} = P_3V_3^{\gamma} = \cdots\cdots = Constant$

So the general expression is PV^{γ} =Constant.

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3. From equation (6.18) we get $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

   From equation (6.19) we get $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

   From equation (6.18) we get $\frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} = \frac{T_2}{T_1}$

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

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

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

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

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

   or, $\frac{T_1^{\gamma}}{P_1^{\gamma-1}} = \frac{T_2^{\gamma}}{P_2^{\gamma-1}}$

   So we can write $\frac{T_1^{\gamma}}{P_1^{\gamma-1}} = \frac{T_2^{\gamma}}{P_2^{\gamma-1}} = \frac{T_3^{\gamma}}{P_3^{\gamma-1}} = \cdots\cdots\cdots = Constant$

   So the general expression is $\frac{T^{\gamma}}{P^{\gamma-1}}$ = Constant.

Irreversible process

We have $\Delta U = -W_{irrev}$

$$\Rightarrow nC_V dT = -P(\Delta V)_{irrev}$$

$$\Rightarrow nC_V(T_2 - T_1) = -P_2(V_2 - V_1)\,[P_2 = final\ pressure]$$

$$\Rightarrow nC_V(T_2 - T_1) = -P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

$$\Rightarrow nC_V(T_2 - T_1) = -nR\left(T_2 - T_1 \,.\frac{P_2}{P_1}\right)$$

$$\Rightarrow C_V(T_2 - T_1) = -R\left(T_2 - T_1 \,.\frac{P_2}{P_1}\right)$$

6.10.3 P – V Curve

Now the slope of P – V curve is obtained form $\frac{dP}{dV}$

For adiabatic reversible change

$$P = \frac{K^{/}}{V^{\gamma}}$$

$$\left(\frac{dP}{dV}\right)_{adia} = -(\gamma)\frac{K^{/}}{V^{\gamma+1}}$$

$$= -\gamma\frac{P}{V}$$

For isothermal change

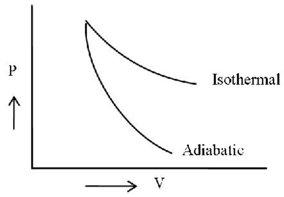
$$P = \frac{K}{V}$$

$$\left(\frac{dP}{dV}\right)_{iso} = -\frac{K}{V^2} = -\frac{P}{V}$$

In both, the change in the slope is negative since γ is greater than 1. The slope of adiabatic P – V curve will be steeper than isothermal curve as follows

$$\left(\frac{dp}{dV}\right)_{adia} = -\gamma\left(\frac{P}{V}\right) = \gamma\left(\frac{dP}{dV}\right)_{isothermal}$$

$$\left(\frac{dp}{dV}\right)_{adia} \Big/ \left(\frac{dp}{dV}\right)_{isothermal} = \gamma > 1$$



6.11 Cyclic Change

Cyclic change i.e. system returns to its original state

$$\oint dq = \oint dU + \oint dW$$

Since in a cyclic process the state does not change, so the change in internal energy is zero.

$$\oint dU = 0$$

$$\oint dq = 0 + \oint dW$$

$$or \oint dq = \oint dW$$

$$\Rightarrow \; q = W$$

Thus net work done is equal to the heat evolved in a cyclic process.

6.11.1 Adiabatic reversible process

We know that work done in adiabatic process

$$W_A = \int_{V_1}^{V_2} PdV \quad \begin{bmatrix} V_1 = Initial\ volume\ of\ the\ system \\ V_2 = Final\ volume\ of\ the\ system \end{bmatrix}$$

For an adiabatic reversible process $PV^\gamma = Constant = K(Say)$

$$P = \frac{K}{V^\gamma}$$

$$W_A = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV$$

$$= K \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2}$$

$$= K\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2}$$

$$= \frac{K}{1-\gamma}\left[V^{1-\gamma}\right]_{V_1}^{V_2}$$

$$= \frac{K}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$= \frac{1}{1-\gamma}\left[KV_2^{1-\gamma} - KV_1^{1-\gamma}\right]$$

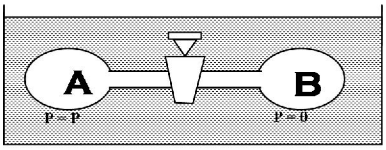
Let the initial pressure and volume of the system be P_1 *and* V_1, and the final pressure and volume of the system be P_2 *and* V_2 respectively.
$P_1V_1^\gamma = P_2V_2^\gamma =$ constant = K (say)

$$W_{(adia)} = \frac{1}{1-\gamma}[P_2V_2^\gamma V_2^{1-\gamma} - P_1V_1^\gamma V_1^{1-\gamma}]$$

$$= \frac{1}{1-\gamma}[P_2V_2 - P_1V_1]$$

This is the expression for work done in adiabatic reversible process.

6.12 Joules Experiment :-



Gay Lussac and, later on, Joule carried out some interesting experiments to find out the internal energy change of a gas. Two bulbs A and B connected by a stop-cock at the middle were kept immersed in the water of a bath. Initially the bulb A was filled with a gas and B was practically evacuated. When thermal equilibrium was established, the stop-cock was opened. The gas was readily passed into B. Since gas expands against a zero pressure.

$$Work\ W = 0$$

Very careful and repeated observations revealed no change in the temperature of the bath or the bulbs : i.e. $dq = 0$

Hence from 1^{st} law

$$dU = dq - W = 0$$

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

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

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

But

$$dV \neq 0 \qquad \left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{6.20}$$

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

But

$$\left(\frac{\partial P}{\partial V}\right)_T \neq 0 \qquad \left(\frac{\partial U}{\partial P}\right)_T = 0 \tag{6.21}$$

It was later found, from Joule and Thomson's experiments, that the above mentioned relations are strictly true for **ideal gases.** For real gases $\left(\frac{\partial U}{\partial V}\right)_T$ is a small positive quantity.

Besides, ideal gases obey Boyle's Law

Hence

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = 0 \tag{6.22}$$

Further, the enthalpy, $H = U + PV$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T$$

But for ideal gases, each term on the right hand side equal to zero, $\left(\frac{\partial H}{\partial P}\right)_T = 0$ and consequently $\left(\frac{\partial H}{\partial V}\right)_T = 0$

The behaviour of ideal gases, may then be summarized as

(a) $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0 \quad b) \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = 0$

(c) $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = 0$

Skill Test

1. Derive the expression of heat absorbed in reversible isothermal process for ideal gas?
2. Derive the expression of heat absorbed in irreversible isothermal process for ideal gas?
3. Show that for Vander Waals' gas $(Q_T)_{rev} \neq (W_T)_{rev}$.
4. Derive the expression of work done in adiabatic reversible process.
5. What is the relation between temperature and pressure in adiabatic reversible process?
6. Discuss about the slope of adiabatic and isothermal P-V curve.
7. Justify the statement – " the net work done is equal to the heat evolved in a cyclic process".

6.13 The Second Law of Thermodynamics

From the first law we know that

1. the different forms of energy are interconvert able

   and

2. when one form of energy disappears an equivalent amount of another kind must appear.

But the first law does not indicate whether a transformation (or transfer) would at all occur and if it occurs to what extent or in which direction the transformation would take place.

The 2nd law of thermodynamics has been stated by different scientists in different forms as:

1. ***Clausius's statement***

It is impossible for a self acting machine (unaided by any external energy or agency) to convey heat from a body at lower temperature to another body at higher temperature.

2. ***Kelvin's statement***

   It is impossible by an engine to derive mechanical work from any portion of matter by cooling it below the temperature of the coldest of the surroundings.

   All these statements differ in language, but signify the same idea.

   "Work can be obtained when heat flows from higher temperature to lower temperature"

3. It is impossible to construct an engine, working in a cycle, which can convert heat completely into (the equal amount of) work without providing change elsewhere.

4. ***Ostwald's statement***

   It is impossible to construct a perpetual motion machine of the second kind, i.e. a machine which will continuously take up heat from a reservoir (there by gradually cooling the reservoir) and convert it fully into work.

Heat can not be completely converted into work i.e. conversion of heat into work without compensation is impossible.

Thus all the statements signify the same idea: "Engine of unit efficiency cannot be developed".

Conclusion

Work can be obtained from heat only when heat is allowed to flow from a body at higher temperature (source) to a body at lower temperature (sink). Under this condition, only a fraction of the supplied heat is converted into work.

6.14 Carnot cycle

According to 1st law of thermodynamics, heat can be converted into work. But it says nothing about –

1. The condition of conversion and
2. The extent of conversion

The brilliant French engineer Sadi Carnot in 1824 developed a cyclic process and explained clearly how and to what extent work is obtained from heat.

Requirement

1. **System:** Perfect gas, enclosed in a cylinder, fitted with weightless, frictionless movable piston.
2. **Surroundings:**
   (a) High temperature thermostat (source) ? supplier of heat
   (b) Low temperature thermostat (sink) ? acceptor of heat
   (c) Thermally insulated jacket
   (d) **Process:** The process is cycle process

What is an Engine?

Engine is an inanimate material agency which works in a reversible process and can convert one form of energy into another

(a) Heat engine which converts heat into work.
(b) Galvanic cell (i.e. Electro chemical cell) which converts chemical energy into electrical energy.

Thermodynamical Engine

Carnot cycle involves 4 stages which can be represented diagrammatically as follows, where the pressures and the volumes are being plotted as ordinate and abscissa respectively.

Indicator Diagram

At the start, the working substance is kept in the source till it attains the temperature of the source. Thus the temperature of the system becomes T.

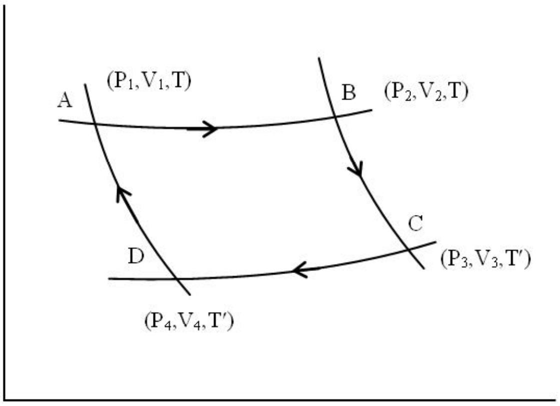


Figure 6.2: Indicator Diagram

Let the corresponding pressure and volume beP_1 and V_1. This condition of the system is represented by the point A in the diagram. Then the system is subjected to the following operations, also represented in the P-V] indicator diagram. The total enclosed area (■ ABCD) represents the work obtained.

Operation - I

The cylinder having 1 mole of gas and the gas is allowed to expand isothermally and reversibly from the volume V_1 to the volume V_2.

The heat absorbed by the gas $= Q$ (say)

The work done by the gas $W = RT\ln\frac{V_2}{V_1}$

Since the gas is ideal, we know, $Q = RT\ln\frac{V_2}{V_1}$

Operation II

The cylinder is next taken out of the thermostat and kept in a thermally insulated enclosure. The gas is allowed to expand further from volume V_2 to volume V_3 adiabatically and reversibly until the temperature falls down to that of the sink T^1

The heat absorbed by the gas =Nil.

The work done by the gas = C_v $(T - T^1)$

(C_v is the heat capacity of the gas).

Operation III

The cylinder is then placed in a thermostat at temperature T^1 (sink); the gas is compressed isothermally and reversibly until the volume changes to V_4 from V_3

The heat given out by gas = Q^1 (say)

The work done by the gas $= RT^1 \ln \frac{V^4}{V^3}$

[Since V_4 is smaller than V_3, the work is negative which means work is done on the gas]

Operation IV

The cylinder is now thermally isolated as in operation II. The gas is then adiabatically and reversibly compressed to its initial volume V_1 and its original temperature T is attained. The gas thus comes back to its initial state.

The heat absorbed by the gas = Nil

The work done by the gas = $C_v (T^1 - T)$

The net work done by the gas in the complete cycle,

$$W = RT \ln \frac{V_2}{V_1} + C_v \left(T - T^1\right) + RT^1 \ln \frac{V_4}{V_3} + C_v \left(T^1 - T\right)$$

$$= RT \ln \frac{V_2}{V_1} + RT^1 \ln \frac{V_4}{V_3}$$

But considering the adiabatic changes in operation II and IV we get

$$TV_2^{\gamma} = T^1 V_3^{\gamma-1} \ldots \qquad (6.23)$$

$$TV_1^{\gamma-1} = T^1 V_4^{\gamma-1} \ldots \qquad (6.24)$$

Dividing $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

$$\begin{aligned} \therefore W &= RT \ln \frac{V_2}{V_1} - RT^1 \ln \frac{V_2}{V_1} \\ &= R\left(T - T^1\right) \ln \frac{V_2}{V_1} \end{aligned}$$

The efficiency of the process is given by the equation

$$\begin{aligned} \eta = \frac{W}{Q} &= \frac{R\left(T - T^1\right) \ln \frac{V_2}{V_1}}{RT \ln \frac{V_2}{V_1}} = \frac{T - T^1}{T} = 1 - \frac{T^1}{T} \\ W &= Q \times \frac{T - T^1}{T} \end{aligned}$$

This relation expresses the maximum amount of work obtained from the heat flowing from T to T^1. This is the mathematical form of the second law.

Corollary I

If the process be completely adiabatic i.e.

(a) No heat is absorbed (taken from the source 0).

$\therefore Q = 0$ then $W_{\max} = 0$

$\therefore$ No work can be obtained.

(b) No heat is rejected to the sink i.e. $Q^{/} = 0$

$$\begin{aligned}
W &= Q - Q^{/} \\
Q - Q^{/} &= Q\frac{T - T^{/}}{T} \\
\textit{or,} \quad 1 - \frac{Q^{/}}{Q} &= 1 - \frac{T^{/}}{T} \\
\textit{or,} \quad \frac{Q^{/}}{Q} &= \frac{T^{/}}{T} \\
\textit{or,} \quad Q &= Q^{/}\frac{T}{T^{/}} \\
\therefore W_{\max} &= Q \times \frac{T - T^{/}}{T} \\
&= \frac{Q^{/}}{T^{/}} \times T \times \frac{T - T^{/}}{T} \\
&= \frac{Q^{/}}{T^{/}}\left(T - T^{/}\right) = 0
\end{aligned}$$

i.e. no work can be obtained.

Hence to have work, heat must be supplied to the system from the source and more over some heat must be rejected to the sink by the system i.e. heat must flow from source to sink.

Corollary II

(a) If the process is carried out under isothermal condition,

i.e. $T = T^1$ then $W_{\max} = Q\frac{T - T^{/}}{T} = 0$

i.e. no work can be obtained by opening the engine under isothermal condition.

(b) If $T^1 > T$ then $W_{\max} = -ve$

i.e. work is done on the system.

(c) But if $T > T^1$ then $W_{\max} = +ve$

i.e. work is done by the system.

Thus heat can be converted into work, provided heat is allowed to flow from high temperature (T) source to low temperature $\left(T^1\right)$ sink.

Corollary III

Since to have to work, some heat (Q) must be rejected to the sink

$\therefore Q - Q^1$ must be $< Q$

$$W < Q$$

$$\frac{Q - Q^1}{Q} < 1$$

$$\therefore \ \eta \langle 1$$

i.e. 100% conversion is not feasible. Thus only a fractional quantity of supplied heat can be converted into work and this fraction is $\frac{T - T^1}{T}$

$W_{\max} = Q.\frac{T - T^1}{T}$, For these reasons, the Carnot cycle is regarded as the mathematical statement of 2nd Law of thermodynamics.

Corollary IV

If $T^1 = 0$ then $W = Q$

or, $\eta = \frac{W}{Q} = 1$

The absolute zero is that temperature of the sink when an engine operating between the sink and the source produces 100 % efficiency. But as absolute zero cannot be achieved in practice; the complete conversion of heat into work is impossible.

*Again net weight involved = Q + 0 – Q^1 + 0

= Q – Q^1

But the process being cycle

Net work = Net heat

$$Q - Q^1 = W_{\max}$$

$$= R\left(T - T^1\right) \ln \frac{V_2}{V_1}$$

SKILL TEST

(a) State second law of thermodynamics.

(b) What is the expression of efficiency of a reversible Carnot cycle?

(c) If the process is carried out under isothermal condition, then how much work is done from reversible Carnot cycle?

(d) At absolute zero what is the efficiency of Carnot cycle?

(e) How will you show that Carnot cycle is the mathematical form of second law of thermodynamics?

6.15 Entropy

The second law leads to a definition of a new thermodynamic property, called entropy. Like internal energy and enthalpy it is a state property and it helps in the understanding of the condition of a system.

dq is not a perfect differential but $\frac{dq}{T}$ is a perfect differential

(a) Suppose one mole of a perfect gas undergoes a reversible expression from volume V1 to volume V2 when the temperature changes from T_1 to T_2.Then from the first law

$$dq = dU + dW$$

or, $dq = dU + PdV$
or, $\int_I^{II} dq = \int_I^{II} dU + \int_I^{II} PdV$

$$= \int_{T_1}^{T_2} C_V dT + \int_{T_1}^{T_2} RT d\ln V$$

$$= C_v (T_2 - T_1) + \int_{V_1}^{V_2} RT d\ln V$$

The integral on the right hand side $\int_{V_1}^{V_2} RT d\ln V$ can not be evaluated unless we know the relation between T and V. If T be constant (i.e. isothermal change) the integral will have one value, and if T changes during the process, the integral will have different values. Thus, the magnitude of $\int_T^{II} dq$ depends on the way the expansion is carried out.

Now dividing the equation by T, we have

$$\int_{I}^{II} \frac{dq}{T} = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} Rd\ln V$$

$$= C_V \ln \frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$

That is, the $\int \frac{dq}{T}$ for a given change from state I to state II can be evaluated without any reference to the path of transformation. Hence $\int \frac{dq}{T}$ is independent of the way the change is carried out though $\int dq$ is not.

(b) We can also arrive at this conclusion in other ways.

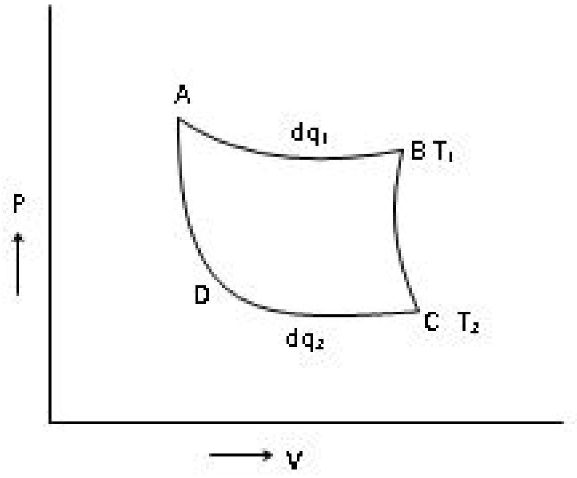


Figure 6.3: P-V diagram

Here AB and CD are isothermal stages at temperature T_1 and T_2 ; BC and DA adiabatic stages. Let dq_1 , be the heat supplied to the working system at T_1 and dq_2 be the heat rejected by it to the sink at T_2. All steps are reversible. We know in a Carnot cycle.

$$\frac{dq_1 - dq_2}{dq_1} = \frac{T_1 - T_2}{T_1}$$

or, $\dfrac{dq_1}{T_1} = \dfrac{dq_2}{T_2}$

(dq_2 is negative as it is rejected by the system)

Now let us confine our attention only to the change of the system from the point A to the point C and attempt to find out the ratio of the heat change to the temperature at which the thermal change occurs.

We can proceed from A to C either along ABC or along ADC

Along the path ABC, we have the isothermal AB, when heat change dq_1, takes place at T_1, followed by adiabatic change BC having no heat change.

Hence, $\dfrac{\text{Heat change}}{\text{Temperature}} = \dfrac{dq_1}{T_1} + 0 = \dfrac{dq_1}{T_1}$

Along the path ADC, the adiabatic AD involves no thermal change; but along the isothermal DC, heat absorbed would be dq_2 at temperature T_2.

Hence, $\dfrac{\text{Heat change}}{\text{Temperature}} = 0 + \dfrac{dq_2}{T_2} = \dfrac{dq_2}{T_2}$

Since from reversible Carnot cycle, we have

$$\frac{dq_1}{T_1} = \frac{dq_2}{T_2}$$

Thus the ratio of heat change to the temperature i.e. $\dfrac{dq}{T}$ is the some whatever path may be followed by the system in its reversible change. Hence $\dfrac{dq_{rev}}{T}$ is regarded as a perfect differential. Moreover, if we consider the four steps of the entire Carnot cycle, the sum of $\dfrac{dq}{T}$ values would be

$$\begin{aligned}\sum \frac{dq}{T} &= \frac{dq_1}{T_1} + 0 + \left(-\frac{dq_2}{T_2}\right) + 0 \\ &= \frac{dq_1}{T_1} - \frac{dq_2}{T_2} \\ &= 0\end{aligned}$$

Hence $\sum \dfrac{dq}{T} = 0$

or, $\oint \dfrac{dq}{T} = 0$

or, $\oint ds = 0$

In any reversible cycle process, the net increase in entropy of the system is zero.

Definition of entropy

The heat change dq and the temperature T are thermodynamic quantities. Therefore, we can say that the system has a thermodynamic function whose change, measured by $\frac{dq}{T}$ is independent of the path of the transformation of the system. This function has been called **entropy by Clausius** and is denoted by the symbol S.

Its change dS is measured by the ratio of the reversible heat change and the temperature at which the heat change occurs i.e.

$$dS = \frac{dq_{rev}}{T}$$

Characteristics:

1. It is a thermodynamic function
2. Its magnitude depends only on the thermodynamic parameters of the system viz. P, V, T etc. i.e. $f\,(\text{state})$ i.e. $f\,(P,V)\,,f'\,(P,T)\,,f''\,(V,T)$
3. The entropy change dS is a perfect differential. Its value depends only on the initial and final states of the system, independent of the path of the change.
4. (a) **Absorption of heat by a system**

   Hence dq is $(+)\,ve$

   $\because T$ is $(+)\,ve$

   $\therefore\ dS$ is always $(+)\,ve$

   Thus with absorption of heat, the entropy of the system increases.

   (b) **Rejection of heat by a system**

   Hence dq is $(-)\,ve$

   $\because T$is $(+)\,ve$

   $\therefore dS$ is $(-)\,ve$

Thus with rejection of heat, entropy of the system decreases.

(c) **Reversible adiabatic process**

Hence $dq = 0$

$\therefore dS = 0$

Thus in adiabetic process, entropy of the system does not change. Hence the reversible adiabatic process is regarded as isoentropic.

Unit of entropy

$$\begin{aligned} \because dS &= \frac{dq_{\text{rev}}}{T} \\ &= \frac{\text{Unit of heat}}{\text{Unit of temperature}} \\ &= \text{cal deg}^{-1} \end{aligned}$$

1 cal $\text{deg}^{-1} = 1$ entropy unit $= 1$ e u

Inter relation with Δu

$$\begin{aligned} dU &= dq - dW \\ &= TdS - PdV \end{aligned}$$

Inter relation with ΔH

$$H = U + PV$$

We have, $dH = dU + PdV + VdP$

$$\begin{aligned} \Rightarrow dH &= dq + VdP \\ &= TdS + VdP \end{aligned}$$

Expression of entropy of n moles of a gas

By definition, we have entropy change

$$\begin{aligned} ds &= \frac{dq_{rev}}{T} \\ &= \frac{dU + dW}{T} \end{aligned}$$

[from 1st law of thermodynamic is $dQ = dU + dW$]

For ideal gas,
$dS = \dfrac{nC_V dT + PdV}{T}$[$\because dU$ = $nCvdT$ and dW = PdV; Here we consider that the gas is ideal.]
$\Rightarrow dS = nC_V\dfrac{dT}{T} + \dfrac{nRT}{V}\dfrac{dV}{T}$ [for n mole of perfect gas PV = nRT]

$$S = nC_V \ln T + nR \ln V + S_0 ... \qquad (6.25)$$

$$= nC_V T + nR \ln \frac{nRT}{P} + S_0$$
$$= n\left(C_V + R\right) \ln\, T + nR \ln nR - nR\, \ln P + S_0$$
$$= nC_P \ln\, T - nR \ln P + S_0^{/} ...(2)\, \left[S_0^{/} = S_0 + nR \ln nR\right] \qquad (6.26)$$
$$= nC_P \ln \frac{PV}{nR} - nR \ln P + S_0^{/}$$
$$= n\left(C_P - R\right) \ln P + nC_P \ln V - nC_P \ln nR + S_0^{//}$$
$$= nC_V \ln P + nC_P \ln v - S_0^{//} ...(3)\, \left[S_0^{//} = S_0^{/} - nC_p \ln nR\right] \qquad (6.27)$$

Thus it is apparent that entropy ”S”can be expressed in terms of the parameters (P, V, T) of the system.
Since the value of the constants S_0, $S_0^{/}$, $S_0^{//}$ can not be obtained from the parameters alone, consequently the absolute value of the entropy $'S'$ can not be ascertained.

SKILL TEST

1. What is the definition of entropy?
2. What is its physical significance?
3. What is the magnitude of entropy change, when a system absorbed heat?
4. What is the magnitude of entropy change, when a system rejected heat?
5. What is the entropy change under reversible adiabatic condition?
6. What is the relation betweenΔU andΔS?

7. What is the relation betweenΔH andΔS?
8. Show that entropy change in irreversible process is appositive quantity.

Entropy change in irreversible process

Since entropy is a function of state only, the entropy change of a system from a given state I to given state II is always the same and is independent of the path. Only if the path is reversible, the change in entropy will be given by

$$\Delta S = S_{II} - S_I = \int_I^{II} \frac{dq_r}{T}$$

Hence in order to compute the entropy change of a system in an irreversible process, we can take the system from state I to state II along any reversible path and then divide the heat absorbed at each point by the temperature and sum up the quotients. That means in any irreversible process there would be a net increase in entropy.

Suppose a heat reservoir at temperature T_1 is brought in contact with a second reservoir at a low temperatureT_2. Let a small quantity of heat q is flowing from T_1 to T_2.

The decrease in entropy of $A = \frac{q}{T_1}$

The increase in entropy of $B = \frac{q}{T_2}$

$\therefore$ Net entropy change $= \frac{q}{T_2} - \frac{q}{T_1}$

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

$= (+)\,ve$ quantity.

Hence irreversible flow of heat leads to an increase in entropy.

Irreversible isothermal expansion of an ideal gas

Suppose n moles of an ideal gas is enclosed in a vessel A of volume V_1.

The vessel is connected through a stop-cock to a completely evacuated vessel B of volume V_2. The temperature is T and the system is insulated. If

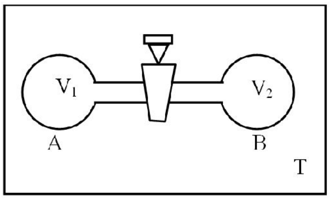


Figure 6.4: The described section

the stop-cock is opened, the gas would spontaneously irreversibly expand to the volume $V_1 + V_2$.The work $W$is zero, and the heat supplied (q) from surroundings is zero. Hence ΔU is zero and temperature remains unaltered.

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

Now if this expansion of the gas were carried out reversibly at T^0k from volume V_1 to volume $(V_1 + V_2)$, the heat absorbed

$$\begin{aligned} q_{rev} &= \Delta U + RT \ln \frac{V_1 + V_2}{V_1} \\ &= 0 + RT \ln \frac{V_1 + V_2}{V_1} \\ \Delta s_{system} &= \frac{q_{rev}}{T} = R \ln \frac{V_1 + V_2}{V_1} \end{aligned}$$

Since dS is a perfect differential, $\Delta S_{irr(system)}$would be the same.
The surroundings has no thermal change, hence $\Delta S_{surr} = 0$.
Hence in the irreversible expansion of the gas,

$$\begin{aligned} \Delta S_{univ} &= \Delta s_{system} + \Delta S_{surroundings} \\ &= R \ln \frac{V_1 + V_2}{V_1} + 0 \\ &= R \ln \frac{V_1 + V_2}{V_1} = (+)\, ve \end{aligned}$$

Irreversible isothermal expansion of an ideal gas increases the entropy of the universe.
$\mathrm{dq}_1^* \mathrm{dq}_1^*$

An irreversible cycle process

Consider a cycle process, similar to that of the Carnot cycle, in which one or

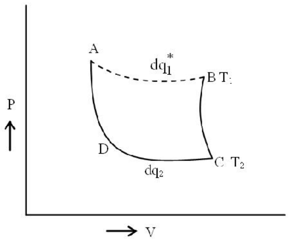


Figure 6.5: Irreversible cycle process

more of its stages are performed irreversibly. Let $ABCD$ denote the cycle in which AB and CD are isothermal stages. Let us further suppose, the absorption of heat $dq_1^*$by the system at temperature T_1 from the source along AB is irreversible. The rest of the stages are carried out reversibly. The asterisk (*) would indicate the irreversibility. Otherwise the transformation is reversible. The heat dq_2 is given up to the sink at temperature T_2along CD.

This is an irreversible cycle and hence the efficiency of the engine is less than that of the Carnot cycle.

$$\frac{dq_1^* - dq_2}{dq_1^*} < \frac{T_1 - T_2}{T_1}$$

or, $1 - \frac{dq_2}{dq_1^*} < 1 - \frac{T_2}{T_1}$

$$or, \frac{dq_2}{T_2} - \frac{dq_1^*}{T_1} > 0 \tag{6.28}$$

When the cycle is completed, the engine has returned to its initial state,

$$\Delta S_{system} = 0$$

It is $-\frac{dq_1^*}{T_1}$for the source and $\frac{dq_2}{T_2}$for the sink.

Hence, for the surroundings, $\sum \frac{Q}{T} = \frac{dq_2}{T_2} - \frac{dq_1^*}{T_1}$which is from 6.28 greater than zero i.e. positive.

The heat change of the sink is reversible. The heat dq_1^* from the source was taken by the system irreversibly. The source has lost dq_1^* and its entropy has decreased. The entropy change of the source from $A \rightarrow B$ would be

$$\Delta S_{source} = -\frac{dq_1^*}{T_1}$$

We can say $\Delta S_{surr} = \frac{dq_2}{T_2} - \frac{dq_1^*}{T_1} > 0$

In the irreversible cyclic process therefore

$$\begin{aligned}\Delta S_{universe} &= \Delta S_{system} + \Delta S_{surr} \\ &= 0 + \Delta S_{surr} > 0\end{aligned}$$

In an irreversible cyclic process, there would occur a net increase in entropy.

The physical significance of entropy

The state of equilibrium really means a state of maximum disorder or chaos. For example, if we put a quantity of yellowish green chlorine gas at a corner of the floor of the room, the gas though heavy would spread in all directions until it would be most chaotically distributed in the entire room and the equilibrium would be reached.

Again if we arrange a number of red and black balls on a tray in a particular pattern and then shake the tray the balls would mix up in the most disorderly fashion.

These are all natural processes and the reverse process is not possible in nature. Moreover, these processes which always have a tendency to attain the state of equilibrium are irreversible and thus leads to entropy increase. That means when the system approaches to equilibrium, the greater is the disorder and irreversibility and when equilibrium is reached, it has the maximum disorder. The entropy also goes on increasing and reaches its maximum value at the equilibrium state.

Thus, entropy is a measure of the disorder of the system or it may be called a measure of the mixedupness of the system.

Change in entropy in irreversible process

Reversible process is an ideal one which is rarely attained in practice. The actual processes like chemical reactions are normally far from reversible and are irreversible.

Let us consider a system changing its state reversibly as well as irreversibly. U being a thermodynamic function, dU is independent of path i.e. value of dU will be same whether the process is carried out reversibly or irreversibly. Thus for an infinitesimal change

$$\begin{aligned} dU_{rev} &= dU_{irrev} \\ \Rightarrow dq_{rev} - dW_{rev} &= dq_{irrev} - dW_{irrev} \\ \Rightarrow dq_{rev} - dq_{irrev} &= dW_{rev} - dW_{irrev} = (+)\, ve \\ \therefore dq_{rev} &> dq_{irrev} [since dW_{rev} > dW_{irrev}] \\ \frac{dq_{rev}}{T} &> \frac{dq_{irrev}}{T} \end{aligned}$$

$$\because \frac{dq_{rev}}{T} = dS \qquad \therefore dS > \frac{dq_{irrev}}{T} \ldots \tag{6.29}$$

Thus from this relation 6.29 dS for irreversible process can not be calculated. Only a qualitative idea is possible but not the quantitative value

e.g. $dq_{irrev} = 1500$cal at $300k$

$\Delta S > 5$But actual value is unknown

But dS being a perfect differential, its value is always same, i.e. independent of the way of the process – reversible or irreversible. Hence the value of $dS$of a system for an irreversible process is same as that if the same change of state is carried out in any reversible path.

Expression of ΔS

When a system exists in an initial state, its entropy becomes

$$S_i = nC_V \ln T_i + nR \ln V_i + S_0$$

Now if it goes to final state, then the entropy becomes

$$S_f = nC_V \ln T_f + nR \ln V_f + S_0$$

Thus the change in entropy associated with the process

$$\S_f - S_i = nC_V\left(\ln T_f - \ln T_i\right) + nR\left(\ln V_f - \ln V_i\right)\Delta S = nC_V\ln\frac{T_f}{T_i} + nR\ln\frac{V_f}{V_i} \tag{6.30}$$

$$= n\left(C_P - R\right)\ln\frac{T_f}{T_i} + nR\ln\frac{nRT_f/P_f}{nRT_i/P_i}$$

$$= nC_P\ln\frac{T_f}{T_i} - nR\ln\frac{T_f}{T_i} + nR\ln\frac{P_i}{P_f} + nR\ln\frac{T_f}{T_i}$$

$$= nC_P\ln\frac{T_f}{T_i} + nR\ln\frac{P_i}{P_f} \tag{6.31}$$

$$= nC_P\ln\frac{P_fV_f}{nR}/\frac{PiVi}{nR} - nR\ln\frac{P_f}{P_i}$$

$$= nC_P\ln\frac{P_f}{P_i} + nC_P\ln\frac{V_f}{V_i} - nR\ln\frac{P_f}{P_i}$$

$$= n\left(C_P - R\right)\ln\frac{P_f}{P_i} + nC_P\ln\frac{V_f}{V_i}$$

$$= nC_V\ln\frac{P_f}{P_i} + nC_P\ln\frac{V_f}{V_i} \tag{6.32}$$

ThusΔS is independent of the integration constant but dependent on thermodynamic parameters only. So when system changes from one state to another, the corresponding change in entropy can be ascertained from the parameters only.

Entropy change (ΔS) for reversible process

For ideal gas (n moles)

we have, $dS = \dfrac{dq_{rev}}{T}$ (by definition)

Entropy change in isothermal process

$$\left(\Delta S\right)_T = nR\ln\frac{V_f}{V_i} = nR\ln\frac{P_i}{P_f}$$

Alternatively, $(\Delta S)_T = \int_{S_i}^{S_f} dS_T = \int \dfrac{dq_T}{T} = \int \dfrac{dW}{T} = \int \dfrac{PdV}{T} = \int \dfrac{nRT}{V} \times \dfrac{dV}{T} = nR\int_{V_i}^{V_f} \dfrac{dV}{V} = nR\ln\dfrac{V_f}{V_i} = nR\ln\dfrac{P_i}{P_f}$

Entropy change at constant volume i.e. for isochoric process

$(\Delta S)_V = nC_V \ln \frac{T_f}{T_i} = nC_V \ln \frac{P_f}{P_i}$ (Assuming $C_V$to be independent of temperature)

Alternatively

$$(\Delta S)_V = \int_{S_i}^{S_f} (dS)_V = \int \frac{dq_V}{T} = nC_V \int_{T_i}^{T_f} \frac{dT}{T} = nC_V \ln \frac{T_f}{T_i}$$

$$\therefore (\Delta S)_V = nC_V \ln \frac{T_f}{T_i} = nC_V \ln \frac{P_f}{P_i}$$

Entropy change at constant pressure i.e. isobaric process

$$(\Delta S)_P = nC_P \ln \frac{T_f}{T_i} = nC_P \ln \frac{V_f}{V_i}$$

Alternatively,

$$(dS)_P = \frac{dq_P}{T} = \frac{nC_P dT}{T}$$

Integrating left hand side between the limit S_i and S_f and right hand side between T_i and T_f

$\int_{S_i}^{S_f} (dS)_P = nC_P \int_{T_i}^{T_f} \frac{dT}{T}$ (Assuming $C_P$is independent of temperature)

$$\Rightarrow (\Delta S)_P = nC_P \ln \frac{T_f}{T_i} = nC_P \ln \frac{V_f}{V_i}$$

For *n* moles of a real gas (obeying Vander Waals' equation)

We have by definition

$$\begin{aligned} dS = \frac{dq_{rev}}{T} = \frac{dU + PdV}{T} &= \frac{1}{T}\left[\left(nC_V dT + \frac{n^2a}{V^2}dV\right) + \left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right)dV\right] \\ &= \frac{1}{T}\left[nC_V dT + \frac{n^2a}{V^2}dV + \frac{nRT}{V-nb}dV - \frac{n^2a}{V^2}dV\right] \\ &= nC_V \frac{dT}{T} + nR\frac{dV}{V-nb} \end{aligned}$$

Integrating both sides we get

$$\int dS = nC_V \int \frac{dT}{T} + nR \int \frac{dV}{V-nb}$$

$S = nC_V \ln T + nR \ln (V - nb) + S_0^{//}$ [$S_0^{//}$integration constant]

Hence change in entropy

$$S = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f - nb}{V_i - nb}$$

Entropy change at constant temperature i.e. isothermal process

$$\begin{aligned} \int_{S_i}^{S_f} (dS)_T &= nR \int_{V_i}^{V_f} \frac{dV}{V - nb} \\ \therefore (\Delta S)_T &= nR \ln \frac{V_f - nb}{V_i - nb} \end{aligned}$$

Entropy change at constant volume i.e. isochoric process

We have from definition

$$\begin{aligned} (dS)_V &= \frac{dq_V}{T} = \frac{dU_V}{T} = \frac{nC_V dT}{T} \\ \int_{S_i}^{S_f} (dS)_V &= nC_V \int_{T_i}^{T_f} \frac{dT}{T} \\ (\Delta S)_V &= nC_V \ln \frac{T_f}{T_i} \end{aligned}$$

Entropy change at constant pressure i.e. isobaric process

$$\begin{aligned} (dS)_P &= \frac{dq_P}{T} = \frac{dH_p}{T} = \frac{nC_P dT}{T} \\ \int_{S_i}^{S_f} (dS)_P &= nC_P \int_{T_i}^{T_f} \frac{dT}{T} \\ (\Delta S)_P &= nC_P \ln \frac{T_f}{T_i} \end{aligned}$$

Entropy change of a mixture of gases

Two or more gases when brought in contact would immediately diffuse into one another and mix up irreversibly. Such a spontaneous irreversible process would of course lead to an entropy increase.

Let $n_A$and n_B gm moles of two gases A and B be mixed at a constant temperature T and under pressure P. Before mixing, their entropy are

$$\begin{aligned} S_A &= n_A\left[C_{P_A}\ln T - R\ln P + S_A^0\right] \\ S_B &= n_B\left[C_{P_B}\ln T - R\ln P + S_B^0\right] \end{aligned}$$

After mixing the total pressure remaining constant (P), the partial pressure are P_A and P_B;such that$P = P_A + P_B$. The entropies of the two components in the mixture are:

$$\begin{aligned} S_{A(m)} &= n_A\left[C_{P_A}\ln T - R\ln P_A + S_A^0\right] \\ S_{B(m)} &= n_B\left[C_{P_B}\ln T - R\ln P_B + S_B^0\right] \end{aligned}$$

The entropy change due to mixing

$$\begin{aligned} &\Delta S_m = S_{A(m)} + S_{B(m)} - S_A - S_B \\ &\quad = n_A C_{P_A}\ln T - n_A R\ln P_A + n_A S_A^0 + n_B C_{P_B}\ln T - n_B R\ln P_B \\ &+ n_B S_B^0 - n_A C_{P_A}\ln T + n_A R\ln P - n_A S_A^0 - n_B C_{P_B}\ln T \\ &+ n_B R\ln P - n_B S_B^0 \end{aligned}$$

$$\begin{aligned} \Delta S_m &= -n_A R\ln P_A - n_B R\ln P_B + n_A R\ln P + n_B R\ln P \\ &= -n_A R\ln\frac{P_A}{P} - n_B R\ln\frac{P_B}{P} \end{aligned}$$

The total amount of mixture moles.

Hence the mole fraction $x_A = \frac{n_A}{n}$ and $x_B = \frac{n_B}{n}$

Now $\frac{P_A}{P} = x_A$ and $\frac{P_B}{P} = x_B$

Hence the entropy change $\Delta S = -n_A R\ln x_A - n_B R\ln x_B$

Dividing both side by $(n_A + n_B)$ we get

$$\begin{aligned} \frac{\Delta S}{(n_A+n_B)} &= \bar{\Delta}\bar{S} = -\frac{n_A}{n_A+n_B}R\ln x_A - \frac{n_B}{n_a+n_B}R\ln x_B \\ \therefore Entropychangepermole &= -x_A R\ln x_A - x_B R\ln x_B \\ \therefore \bar{\Delta}\bar{S} &= -x_A R\ln x_A - x_B R\ln x_B - x_C R\ln x_C .... \end{aligned}$$

In general mixing for any number of gases

$$\Delta S_m = -\sum x_i R\ln x_i = -R\sum x_i \ln x_i$$

Entropy of universe (i.e. world) is increasing

In universe there are two types of processes.

1. Thermally reversible process
2. Thermally irreversible process

All natural processes like,

1. The falling of fruit from a tree
2. The flowing of a river down hill
3. The rusting of iron
4. The dissolution of sugar in water etc. are irreversible process

For reversible process there is no net change in entropy but for irreversible process net entropy increases.

$\Delta S_{universe}$(i.e. world) $= (\Delta S_{universe})_{rev} + (\Delta S_{universe})_{irrev}$

$$= 0+ > 0$$
$$=> 0$$

Thus the second law of the thermodynamics is stated as "The net entropy of universe (i.e world) increases and tends to maximum".

SKILL TEST

1. What is the expression of entropy change in isochoric process for ideal gas?
2. What is the expression of entropy change in isobaric process for ideal gas?
3. What is the expression of entropy change in isothermal process for ideal gas?
4. Entropy of universe (i.e. world) is increasing and tends to maximum. – Explain.

6.16 Available work function

Introduction

Every thermodynamic system possesses

1. Internal energy (U)
2. Total energy (also called enthalpy or heat content) i.e. $H = U + PV$ and
3. Entropy (S) – which is the measure of the **unavailable energy** of the system.

The actual value of the unavailable energy is the product of temperature and entropy. Thus, unavailable energy $= T \times S$

Again any kind of energy which can be converted into useful work is termed as **"available energy"** while the other portion of the energy (which can not be transferred into useful work) is termed as **unavailable energy**.

Free energy

When the energy of a system is not in equilibrium with the surroundings, the balance of energy is only available for doing work and this is known as **free energy**.

Holmholtz free energy or work function (A)

The portion of the internal energy which can be utilized to carry out useful work i.e. available internal energy is called Helmholtz free energy or the function (A).

Thus,

Internal energy = Available internal energy +unavailable internal energy

= Helmholtz free energy + (Temperature $\times$entropy)

$$U = A + TS$$
$$\Rightarrow A = U - TS$$

$$A = U - TS \qquad (6.33)$$

Characteristics

1. A being a thermodynamic function and it is a function of state i.e. $A = f(V,T)$, $A = f'(P,V)\, etc$
2. So its magnitude depends on the thermodynamic parameters $(P, V \& T)$
3. Change in work function (dA) is a perfect differential
4. It is an extensive property i.e. its value depends on the quantity of matter involved.
5. In a cyclic process change in work function is zero. This is because it is state function i.e. $\oint dA = 0$

Physical Significance of A

If a system undergoes a reversible isothermal change from one state to another, then

$$\begin{aligned}(\Delta A)_T &= (\Delta U)_T - T\Delta S \\ &= (\Delta U)_T - T \times \frac{q_{rev}}{T} \quad = -(W_{rev})_T \\ &= -(\Delta A)_T = (W_{\max})_T\end{aligned}$$

Thus, work function A is such a thermodynamic function that its decrease for an isothermal reversible process represent maximum amount of available work.

Discussion

1. If the change is not isothermal, the change in work function 'A' will not be equivalent to the maximum work.
2. Whenever a system undergoes an infinitesimal reversible change, the corresponding change in work function.

$$\begin{aligned}dA &= dU - TdS - SdT \\ &= dU - dq - SdT \qquad \left[\because dS = \frac{dq_{rev}}{T}\right] \\ &= -PdV - SdT \qquad \left[\begin{aligned}\because dq &= dU + dW \\ &= dU + PdV\end{aligned}\right]\end{aligned}$$

Thus the value of A changes with change in temperature and volume i.e.

$A = -f(T, V)$

Corollary

1. For isochoric process

$$(dA)_V = -SdT$$

   or, $\left(\frac{\partial A}{\partial T}\right)_V = -S$

   or $S = -\left(\frac{\partial A}{\partial T}\right)_v$

   The entropy of the system represents the rate of decrease of maximum work function with respect to temperature at constant volume

2. For isothermal process

$$(dA)_T = -PdV$$

   or, $\left(\frac{\partial A}{\partial V}\right)_T = -P$

   which gives a relation between thermodynamic parameter $P$and thermodynamic function A.

Expression of A and ΔA

On integrating For n moles of ideal gas

$$\int dA_T = -\int PdV \quad \begin{matrix} PV = nRT \\ P = \dfrac{nRT}{V} \end{matrix}$$

Case – I

For ideal gas

$$\int dA_T = -\int \frac{nRT}{V} dV$$

or, $A_T = -nRT \ \ln V + n\bar{A}_0$ [$\bar{A}_0$ is the integration constant for 1 mole of ideal gas]

Integrating within limits

$$\begin{aligned}
\int_{A_1}^{A_2} dA_T &= -\int_{V_1}^{V_2} \frac{nRT}{V} dV \\
or, (A_2 - A_1)_T &= -nRT \ln \frac{V_2}{V_1} \\
or, (\Delta A)_T &= nRT \ln \frac{V_1}{V_2} \\
&= nRT \ln \frac{P_2}{P_1} = -W_{\max}
\end{aligned}$$

Case II

For real gas obeying Vander walls' equation

$A_T = -nRT \ln (V - nb) + \frac{n^2 a}{V} + n\bar{A}_0$ [$\bar{A}_0$ is the integration constant for 1 mole of real gas]

Integrating within limits

$$\int_{A_1}^{A_2} (dA_T) = -\int_{V_1}^{V_2} \left[\frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \right] dV$$

or, $(A_2 - A_1) = -(\Delta A)_T = -\left[nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) + n^2 a \left[\frac{1}{V_2} - \frac{1}{V_1} \right] \right]$

Case III

For gas obeying the following equation

$$P(V - nb) = nRT$$

On integrating we get,

$A_T = nRT \ln (V - nb) + n\bar{A}_o$ [$\bar{A}_0$ is the integration constant for 1 mole of real gas]

Integrating within limits

$$\begin{aligned}\int_{A_1}^{A_2}(dA)_T &= -\int_{V_1}^{V_2}\frac{nRT}{(V-nb)}dV\\ (A_2-A_1) &= (\Delta A)_T = -nRT\ln\left(\frac{V_2-nb}{V_1-nb}\right)\\ &= nRT\ln\left(\frac{V_1-nb}{V_2-nb}\right)\end{aligned}$$

Case IV

Gas obeying equation $\left(P+\frac{n^2a}{V^2}\right)V = nRT$

On integrating we get

$$A_T = -nRT\ln V + \frac{n^2a}{V} + n\bar{A}_0$$

Integrating within limits

$$\int_{A_1}^{A_2}(dA)_T = -\int_{V_1}^{V_2}\left(\frac{nRT}{V}-\frac{n^2a}{V^2}\right)dV$$

or, $(A_2-A_1) = (\Delta A)_T = -\left[nRT\ln\frac{V_2}{V_1}+n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)\right]$

SKILL TEST

1. What is Helmholtz free energy?
2. Whether Helmholtz free energy is an extensive or intensive property?
3. Prove that $(\Delta A)_T = -W_{\max}$.
4. How will you show that Helmholtz free energy is a state function?

Free Energy

Introduction

Every thermodynamic system possess

1. Internal energy (U)

2. Enthalpy i.e. total energy or heat content (H)

$$H = U + PV$$

   and

3. Entropy (S) which is a measure of the unavailable energy. The actual value of unavailable energy is the product of temperature and entropy.

The unavailable energy $= T \times S$

Gibb's free energy

The portion of a total energy of a thermodynamic system which can be utilized for doing useful work i.e. available total energy is known as **Gibb's free energy** or **thermodynamic potential** of the system symbolically represented by G

Thus,

Enthalpy = Available enthalpy + unavailable enthalpy

= Gibb's free energy + (Temperature $\times$entropy)

$$H = G + TS$$

or $G = H - TS$

Characteristics

1. G is a thermodynamic function hence it is a single valued function of the state of the system or in other words it is a function of state i.e. G =$f(P, T)$.

   Consequently its magnitude depends on thermodynamic parameters. (P, V and T) and can be expressed in terms of these parameters.

2. Change in thermodynamic potential, $dG$is a perfect differential.

3. It is an extensive property i.e. its value depends on the quantity of matter involved.

4. In a cyclic process the net change in Gibbs free energy is zero i.e.; $\oint dG = 0$.

Physical significance of G

If a system undergoes a reversible change under isothermal and isobaric conditions from one state to another state then,

$$(\Delta G)_{T,P} = (\Delta H)_{T,P} - T\Delta S \quad [\because \quad H = U + PV$$
$$\therefore (\Delta H)_{T,P} = \Delta U + P\Delta V]$$

$$\begin{aligned} &= \Delta U + P\Delta V - T\Delta S [\because \Delta S = \frac{q_{rev}}{T} q_{rev} = T\Delta S] \\ &= \Delta U - q_{rev} + P\Delta V \\ &= -W + P\Delta V [\text{From 1st law} q = \Delta U + W \Delta U - q = -W] \end{aligned}$$

or, $-(\Delta G)_{\text{T,P}} = W_{\text{Total}} - W_{\text{mechanical}}$
$= W_{nonmechanical}$ [Where $P\Delta V$ is the mechanical work involved in the system itself during transformation and W denotes maximum total work output]
$W_{\text{nonmechanical}}$ is the work received for any external use exclusive of the mechanical work e.g. electrical work.
The Gibb's free energy (G) is such a thermodynamic function that its decrease for isothermal and isobaric reversible process represents the non mechanical work available during the transformation of the system.
Thus $-(\Delta G)_{\text{T, P}} = W_{\text{electrical}}$

Discussion

1. If the change is carried out under non isothermal and non isobaric conditions, then the change in thermodynamic potential is not equal to non mechanical work.

2. Whenever a system undergoes an infinitesimal change, the corresponding change in Gibbs free energy is given by

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= dU + PdV + VdP - TdS - SdT \\ &= dq + VdP - dq - SdT \\ &= VdP - SdT \end{aligned}$$

   Thus value of '*G*' changes with pressure and temperature. So it is a function of pressure and temperature.

i.e. $G = f(P, T)$

Corollary

1. For isobaric process

$$(dG)_P = -SdT$$

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

The entropy (S) of a system represents the rate of decrease of Gibbs free energy with temperature at constant pressure.

2. For isothermal process

$$(dG)_T = VdP$$

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

which gives a relation between thermodynamic parameter V with thermodynamic function G

Expression for G and ■G

$$\int (dG)_T = \int VdP$$

Case – I

For ideal gas $\int dG_T = \int \frac{nRT}{P} dP$

$$G_T = nRT \ \ln P + n\bar{G}_0$$

Again integrating within limits we get,

$$\int_{G_1}^{G_2} (dG)_T = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

or, $$\begin{aligned}(G_2 - G_1)_T &= nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2} \\ &= -W_{\max} \quad = (\Delta A)_T\end{aligned}$$

Case II

For real gas obeying vander Walls' equation

$$\begin{aligned}\int (dG)_T &= \int V dP \\ &= \int \left[\frac{nRT}{P} + n\left(b - \frac{a}{RT}\right)\right] dP\end{aligned}$$

For n moles of a gas

$$\left(P + \frac{n^2 a}{V^2}\right)(v - nb) = nRT$$

or, $PV + \dfrac{n^2 a}{v} - pnb - \dfrac{n^3 ab}{v^2} = nRT$

or, $V + \dfrac{n^2 a}{PV} - nb - \dfrac{n^3 ab}{pv^2} = \dfrac{nRT}{P}$

or, $V = \dfrac{nRT}{P} + nb - \dfrac{n^2 a}{PV}$

We weight the term $\dfrac{n^3 ab}{PV^2}$ as it is very small and assume that

$$\begin{aligned}PV &\approx nRT \\ \therefore V &= \frac{nRT}{P} + n\left(b - \frac{a}{RT}\right) \\ \therefore G_T &= nRT \ln P + n\left(b - \frac{a}{RT}\right)P + n\bar{G}_0\end{aligned}$$

If $\left(b - \dfrac{a}{RT}\right) = B^1$ we have

$$G_T = nRT \ln P + nB^1 P + n\bar{G}_0$$

Integrating within limits we have

$$\int_{G_1}^{G_2} (dG)_T = \int_{P_1}^{P_2} \left(\frac{nRT}{P} + nB^1\right) dP$$

or, $(G_2 - G_1)_T = nRT \ln \dfrac{P_2}{P_1} + nB^1 (P_2 - P_1)$

or, $(\Delta G)_T = nRT \ln \dfrac{P_2}{P_1} + n\left(b - \dfrac{a}{RT}\right)(P_2 - P_1)$

Case III

Gas obeying the equation

$$P(V-nb)=nRT\left[\begin{array}{l}P(V-nb)=nRT\\ V=\dfrac{nRT}{P}+nb\end{array}\right]$$

$$\int (dG)_T=\int VdP$$

or, $$\begin{aligned}G_T&=\int\left(\frac{nRT}{P}+nb\right)dP\\ &=nRT\ln P+nbP+n\bar{G}_0\end{aligned}$$

Integrating within limits we get

$$\int_{G_1}^{G_2} dG_T=\int_{P_1}^{P_2}\left(\frac{nRT}{P}+nb\right)dp$$

or, $(G_2-G_1)_T=nRT\ln\dfrac{P_2}{P_1}+nb(P_2-P_1)$

or, $(\Delta G)_T=nRT\ln\dfrac{P_2}{P_1}+nb(P_2-P_1)$

Case IV

For gas obeying the equation

$$\left(P+\frac{n^2a}{V_2}\right)V=nRT$$

$$PV+\frac{n^2a}{V}=nRT$$

or, $V+\dfrac{n^2a}{PV}=\dfrac{nRT}{P}$

or, $$\begin{aligned}V&=\frac{nRT}{P}-\frac{n^2a}{PV}\\ &=\frac{nRT}{P}-\frac{n^2a}{nRT}\quad=\frac{nRT}{P}-\frac{na}{RT}\end{aligned}$$

$$\begin{aligned}\int (dG)_T&=\int VdP\\ &=\int\left(\frac{nRT}{P}-\frac{na}{RT}\right)dP\\ &=nRT\ln P-\frac{na}{RT}P+n\bar{G}_0\end{aligned}$$

Integrating with limits.

$$\int_{G_1}^{G_2} (dG)_T = \int_{P_1}^{P_2} \left(\frac{nRT}{P} - \frac{na}{RT} \right) dp$$

or, $(G_2 - G_1)_T = nRT \ln \frac{P_2}{P_1} - \frac{na}{RT} (P_2 - P_1)$

SKILL TEST

1. What is Gibbs free energy?
2. Whether Gibbs free energy is an extensive or intensive property?
3. Prove that $(\Delta G)_{T,P} = -W_{\text{non-mechanical}}$.
4. How will you show that Gibbs free energy is a state function?
5. Prove that $(\Delta G)_T = (\Delta A)_T$.

6.17 Gibbs Helmholtz Equation

Introduction

The equations relating work function (A) with internal energy (U) of a thermodynamic system and Gibb's free energy (G) with total energy (H) of the system as well as respective change for a process are known as Gibbs Helmholtz equation.

Thus internal energy = Available internal energy + unavailable internal energy

= Helmholtz free energy + Temperature × entropy

$$U = A + TS$$

or,

$$A = U - TS \tag{6.34}$$

Whenever a system undergoes an infinitesimal reversible change, the corresponding change in work function

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= dU - dq - SdT \\ &= PdV - SdT \end{aligned}$$

At constant volume i.e. $dV = 0$

$$\therefore (dA)_V = -SdT$$

or, $\left(\frac{\partial A}{\partial T}\right)_V = -S$

or, $S = -\left(\frac{\partial A}{\partial T}\right)_V$

Substituting the value of S in equation 6.34 we get

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

$$A = U + T\left(\frac{\partial A}{\partial T}\right)_V \cdots \qquad (6.35)$$

This equation which co-relates work function (Helmholtz free energy) with internal energy is commonly known as Gibb's Helmholtz equation. Again if the system changes reversibly from one state to another state, the change in work function

$$\Delta A = \Delta U - T\Delta S - S\Delta T$$

At constant temperature

$$\begin{aligned} (\Delta A)_T &= \Delta U - T\left(S_f - S_i\right) \\ &= \Delta U - T\left[-\left(\frac{\partial A_f}{\partial T}\right)_V - \left\{-\left(\frac{\partial A_i}{\partial T}\right)_V\right\}\right] \\ &= \Delta U + T\left[\frac{\partial}{\partial T}\left\{(A_f)_V - (A_i)_V\right\}\right] \end{aligned}$$

$$(\Delta A)_T = \Delta U + T\left[\frac{\partial}{\partial T}(\Delta A)\right]_V \cdots \qquad (6.36)$$

where ∂A_i and $\partial A_f$are the changes in Helmholtz free energy at constant volume for an infinitesimal change in temperature for the initial and final state respectively. $S_f$andS_I are the entropies of the system at final and initial states.

Again we know

$$\begin{aligned}\left[\frac{\partial}{\partial T}\left({}^{A}\!/_{T}\right)\right]_V &= \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V + A\left(-\frac{1}{T^2}\right)\\ &= \frac{1}{T}(-S)+\left(-\frac{A}{T^2}\right)\\ &= -\left(\frac{A+TS}{T^2}\right) = -\frac{U}{T^2}\end{aligned}$$

$$\therefore \left[\frac{\partial}{\partial T}\left({}^{A}\!/_{T}\right)\right]_V = -\frac{U}{T^2}\ldots \tag{6.37}$$

Thus the above equation is another form of Gibbs Helmholtz equation

Again $\left[\frac{\partial}{\partial T}\left({}^{\Delta A}\!/_{T}\right)\right]_V = \left[\frac{\partial}{\partial T}\left(\frac{A_f - A_i}{T}\right)\right]_V$

$$\begin{aligned} &= \left[\frac{\partial}{\partial T}\left(\frac{A_f}{T}\right)\right]_V - \left[\frac{\partial}{\partial T}\left(\frac{A_i}{T}\right)\right]_V\\ &= -\left[\frac{U_f}{T^2}\right] - \left[-\frac{U_i}{T^2}\right]\\ &= -\left[\frac{U_f - U_i}{T^2}\right] = -\frac{\Delta U}{T^2}\end{aligned}$$

$$\therefore \left[\frac{\partial}{\partial T}\left({}^{\Delta A}\!/_{T}\right)\right]_V = -\frac{\Delta U}{T^2}\ldots \tag{6.38}$$

Similarly,

Total energy = available total energy + unavailable total energy

= Gibb's free energy + Temperature × entropy

$$H = G + TS$$

$$\therefore G = H - TS\ldots \tag{6.39}$$

Again

$$G = (U + PV) - TS \tag{6.40}$$

Whenever a system undergoes an infinitesimal change then corresponding change in Gibbs free energy is given by

$$\begin{aligned} dG &= dU + PdV + VdP - TdS - SdT \\ &= dq + VdP - dq - SdT \end{aligned}$$

$$\therefore dG = VdP - SdT$$

For an isobaric process i.e. $dP = 0$

$$(dG)_P = -SdT$$

or, $\left(\dfrac{\partial G}{\partial T}\right)_P = -S$

or, $S = -\left(\dfrac{\partial G}{\partial T}\right)_P$

Substituting this value of S in equation 6.39 we get

$$G = H - T\left[-\left(\frac{\partial G}{\partial T}\right)_P\right]$$

or,

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \tag{6.41}$$

Again if a system changes reversibly from one state to another, the change in Gibbs free energy

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

If changes occur at constant temperature

$$\begin{aligned} (\Delta G)_T &= \Delta H - T\Delta S \\ &= \Delta H - T(S_f - S_i) \\ &= \Delta H - T\left[-\left(\frac{\partial G_f}{\partial T}\right)_P - \left\{-\left(\frac{\partial G_i}{\partial T}\right)_P\right\}\right] \\ &= \Delta H + T\left[\frac{\partial}{\partial T}\left\{(G_f)_P - (G_i)_P\right\}\right] \end{aligned}$$

$$(\Delta G)_T = \Delta H + T\left[\frac{\partial}{\partial T}(\Delta G)\right]_P \cdots \tag{6.42}$$

where $(\partial G_f)_P$ and $(\partial G_i)_P$ are the small changes in Gibbs free energy for an infinitesimal change in temperature ∂T at constant pressure for final and initial state. S_f and $S_i$are the entropies of the system at final and initial states.

Again we know,

$$\begin{aligned}\left[\frac{\partial}{\partial T}\left({}^{G}\!/_{T}\right)\right]_P &= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G\left(-\frac{1}{T^2}\right)\\ &= -\frac{S}{T} - \frac{G}{T^2}\\ &= -\left(\frac{G+TS}{T^2}\right) = -\frac{H}{T^2}\end{aligned}$$

$$\therefore \left[\frac{\partial}{\partial T}\left({}^{G}\!/_{T}\right)\right]_P = -\frac{H}{T^2}\cdots \tag{6.43}$$

Again

$$\begin{aligned}\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_P &= \left[\frac{\partial}{\partial T}\left(\frac{G_f - G_i}{T}\right)\right]_P\\ &= \left[\frac{\partial}{\partial T}\left(\frac{G_f}{T}\right)\right]_P - \left[\frac{\partial}{\partial T}\left(\frac{G_i}{T}\right)\right]_P\\ &= \left(-\frac{H_f}{T^2}\right) - \left(-\frac{H_i}{T^2}\right) = -\left[\frac{H_f - H_i}{T^2}\right] = -\frac{\Delta H}{T^2}\end{aligned}$$

$$\therefore \left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = -\frac{\Delta H}{T^2}\cdots \tag{6.44}$$

Thus the equation 2, 3, 4, 5, 7, 8, 9, 10 are known as Gibb's Helmholtz equation.

Use

1. Gibbs Helmholtz equation has been used to evaluate ΔH from e.m.f of cell.

$$\Delta H = n\Im\left\{T\left(\frac{\partial E}{\partial T}\right) - E\right\}$$

2. The relation $\Delta H = \Delta G - T\frac{\partial}{\partial T}(\Delta G)$ has been used for derivate of Vant

Hoff equation i.e.

$$\frac{d\ln k}{dT} = \frac{\Delta H}{RT^2}$$

3. A knowledge of ΔG would enable us to ascertain $\Delta H$of a process.

6.18 Maxwell's Relation

1. According to 1st law of thermodynamics

$$\begin{aligned} dq &= dU + dW \\ dU &= dq - dW \\ &= TdS - PdV \end{aligned}$$

Assuming the process was reversible one.

Corollary 1

For isoentropic process i.e. $dS = 0$

$$(dU)_s = -PdV$$

or, $\left(\frac{\partial U}{\partial V}\right)_s = -P$

Second differentiation of U with respect to S at constant V gives

$$\frac{\partial^2 U}{\partial S.\delta V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

Corollary 2

For isochoric process i.e. $dV = 0$

$$(dU)_V = TdS$$

$$\therefore \left(\frac{\delta U}{\delta S}\right)_V = T$$

Second differentiation of U with respect to V at constant S gives

$$\frac{\partial^2 U}{\partial V.\delta S} = \left(\frac{\partial T}{\partial V}\right)_S$$

Since du is perfect differential

$$\begin{aligned} \frac{\partial^2 U}{\partial S.\partial V} &= \frac{\partial^2 U}{\partial V.\partial S} \\ \therefore -\left(\frac{\partial P}{\partial S}\right)_V &= \left(\frac{\partial T}{\partial V}\right)_S \\ \therefore \left(\frac{\partial P}{\partial S}\right)_V &= -\left(\frac{\partial T}{\partial V}\right)_S ...(A) \end{aligned}$$

2. According to the definition of entropy

$$H = U + PV$$

If the system undergoes infinitesimal change

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= dq + VdP \\ &= TdS + VdP \end{aligned}$$

Corollary 1

For isoentropic process i.e. $dS = 0$

$$(dH)_S = VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_s = V$$

Second differentiation of H with respect to S at constant P gives

$$\frac{\partial^2 H}{\partial S.\partial P} = \left(\frac{\partial V}{\partial S}\right)_P$$

Corollary 2

For isobaric process i.e. $dP = 0$

$$(dH)_P = TdS$$

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

Second differentiation of H with respect to P at constant S gives

$$\frac{\partial^2 H}{\partial P.\partial S} = \left(\frac{\partial T}{\partial P}\right)_S$$

Since dH is a perfect differential

$$\frac{\partial^2 H}{\partial S.\partial P} = \frac{\partial^2 H}{\partial P.\partial S}$$

$\therefore \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$ ... (B)

3. According to the definition of work function

$$U = A + TS$$
$$A = U - TS$$

If the system undergoes infinitesimal change, then

$$dH = dU - TdS - SdT \quad = dU - dq - SdT \quad = -PdV - SdT$$

Corollary 1

i.e. $dV = 0$

$$(dA)_V = -SdT$$

or, $\left(\frac{\partial A}{\partial T}\right)_V = -S$

Second differentiation of A with respect to V at constant T gives

$$\frac{\partial^2 A}{\partial V.\partial T} = -\left(\frac{\partial S}{\partial V}\right)_T$$

Corollary 2

For isothermal process i.e. $dT = 0$

$$(dA)_T = -PdV$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Second differentiation of A with respect to T at constant V gives

$$\frac{\partial^2 A}{\partial T.\partial V} = -\left(\frac{\partial P}{\partial T}\right)_V$$

Since dA is a perfect differential

$$\frac{\partial^2 A}{\partial V.\partial T} = \frac{\partial^2 A}{\partial T.\partial V}$$

$$\therefore -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

or, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ ... (C)

4. According to the definition of Gibb's free energy

$$G = H - TS$$

whenever the system undergoes a small change, the corresponding change in Gibb's free energy will be,

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= dU + PdV + VdP + TdS + SdT \\ &= dq + VdP - dq - SdT \\ &= VdP - SdT \end{aligned}$$

Corollary 1

For isobaric process i.e. $dP = 0$

$$(dG)_P = -SdT$$

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

Second differentiation of G with respect to P at constant T gives

$$\frac{\partial^2 G}{\partial P.\partial T} = -\left(\frac{\partial S}{\partial P}\right)_T$$

Corollary 2

For isothermal process i.e. $dT = 0$

$$(dG)_T = VdP$$
$$\therefore \left(\frac{\partial G}{\partial P}\right)_T = V$$

Second differentiation of G with respect to T at constant P gives

$$\frac{\partial^2 G}{\partial T.\partial P} = \left(\frac{\partial V}{\partial T}\right)_P$$

Since dG is a perfect differential

$$\frac{\partial^2 G}{\partial P.\partial T} = \frac{\partial^2 G}{\partial T.\partial P}$$

or $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ ... (D)

Equation (A), (B), (C) and (D) are known as Maxwell's relation.

SKILL TEST

1. What are the applications of Gibbs Helmholtz equation?
2. Prove that $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$.
3. Prove that $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

6.19 Joule Thomas Experiment

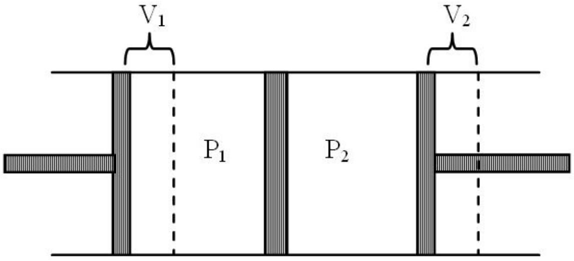


Figure 6.6: Joule Thomas Experiment

Joule's Experiment

Free expansion of a gas into a vacuum revealed that the temperature drop of the system was negligible and would zero if the gas be ideal.

Joule's and Thomson's modified experiment

The passage of a gas from a higher pressure to a lower pressure through fine orifices of a porous plug under adiabatic condition.

Thermodynamic condition

Suppose, the volume $V_1$of a gas under a constant pressure P_1 is allowed to pass through a porous barrier from the region on the left to the region on the right where pressure is P_2.The volume of the gas becomes V_2.The process is carried out with two frictionless pistons attached at the two ends. The whole system is thermodynamically insulated i.e $q = 0$

Work done with the system at the left $= W_L = \int_{V_1}^{0} P_1 dV$

$$= -P_1 V_1$$

Work done with he system at the right

$$\begin{aligned} W_R &= \int_0^{V_2} P_2 dV \\ &= P_2 V_2 \end{aligned}$$

Thus total work done

$$\begin{aligned} W_{total} &= W_L + W_R \\ &= -P_1 V_1 + P_2 V_{2.} \end{aligned}$$

Then from first law of thermodynamics

$$\begin{aligned} Q &= \Delta U + W \\ 0 &= (U_2 - U_1) + (P_2 V_2 - P_1 V_1) \\ &= (U_2 + P_2 V_2) - (U_1 + P_1 V_1) \\ &= H_2 - H_1 = \Delta H \end{aligned}$$

Hence adiabatic expansion of a gas through fine orifice is **isoenthalpic**.

Result

Usually there is a change in temperature of the outcoming gas and this variation of temperature is known as **Joule Thomson effect.**

Joule Thomson co efficient

The rate of change in temperature with pressure when enthalpy remains constant is called **Joule – Thomson co efficient**

i.e. $\mu_{J.T} = \left(\frac{\partial T}{\partial P}\right)_H$

Deduction of the expression of μ_{JT}

H being a thermodynamic function is a single valued function of state. Hence it can be represented as

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

So, if the pressure and temperature of a system are changed by dp and dT

respectively, then the change in entropy

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

The Joule Thomson experiment being isoenthalpic $(dH = 0)$

$$0 = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

or, $-\left(\frac{\partial H}{\partial P}\right)_T dP = \left(\frac{\partial H}{\partial T}\right)_P dT$

or, $\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P$

or, $\mu_{JT} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$

Here $H = U + PV$

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{\partial U}{\partial P}\right)_T - \frac{1}{C_P}\left[\frac{\partial (PV)}{\partial P}\right]_T$$

$$= -\frac{1}{C_p}\left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

Case I (For ideal gas)

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

$$= -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

$$= -\frac{1}{C_P}\left[\left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\}\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

$$
\begin{aligned}
[dU &= dq - d\,W \\
&= TdS - PdV \\
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - P \\
&= T\left(\frac{\partial P}{\partial T}\right)_V - P\Bigg]
\end{aligned}
$$

$$
= -\frac{1}{C_P}\left[(P-P)\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]
$$

$$
= -\frac{1}{C_P}\left\{\frac{\partial (PV)}{\partial P}\right\}_T = -\frac{1}{C_P}\times 0 = 0
$$

Hence $\mu_{JT} = 0 \qquad \therefore dT = 0$

i.e. Neither heating nor cooling

Case II (For real gas)

Obeying Vander Waals' equation

$$
\begin{aligned}
\left(P + \frac{n^2 a}{V^2}\right)(V - nb) &= nRT \\
P &= \frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \\
\left(\frac{\partial P}{\partial T}\right)_v &= \frac{nR}{V-nb} - 0 = \frac{nR}{V-nb}
\end{aligned}
$$

$$
\begin{aligned}
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P \\
&= \frac{nRT}{V-nb} - P \\
&= P + \frac{n^2 a}{V^2} - P = \frac{n^2 a}{V^2}
\end{aligned}
$$

Thus for a real gas, $\left(\frac{\partial U}{\partial V}\right)_T$ is positive while $\left(\frac{\partial V}{\partial P}\right)_T$ for any gas is always negative. As a result the first is always positive. The magnitude of the second term may be negative or positive.

Corollary A

1. At low temperature and low pressure $\left[\frac{\partial (PV)}{\partial P}\right]_T$ is negative. Under such condition, both the terms in the equation being positive, μ_{JT} has

a positive value. That means there would be cooling of the gas. Even at the ordinary temperature except for H_2 and He all other gases show $\left[\frac{\partial(PV)}{\partial P}\right]_T$ negative value at low pressure.

2. At high pressure, $\left[\frac{\partial(PV)}{\partial P}\right]_T$ becomes positive, so that the second terms becomes negative and if its value exceed that of the first term, μ_{JT} becomes negative i.e. heating.

Corollary B

At high temperature all gases have $\left[\frac{\partial(PV)}{\partial P}\right]_T$ positive. So, $\mu_{JT}$is generally negative i.e. heating.

Moreover from the expression of μ_{JT}

$$\begin{aligned}\mu_{JT} &= \left(\frac{\partial T}{\partial P}\right)_H \\ &= -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \\ &= -\frac{1}{C_P}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] \\ &= \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\end{aligned}$$

Case I

For ideal gas

$$PV = nRT$$

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

$$\begin{aligned}\therefore \left(\frac{\partial V}{\partial T}\right)_P &= \frac{nR}{P} \\ \therefore T\left(\frac{\partial V}{\partial T}\right)_P &= \frac{nRT}{P} = V \\ \therefore T\left(\frac{\partial V}{\partial T}\right)_P &- V = V - V = 0 \\ \therefore \mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H &= \frac{1}{C_P}\times 0 = 0\end{aligned}$$

J.T experiment $dP$is $(-)\,ve$. So, $dT = 0$i.e. neither heating nor cooling.

Case II

For a gas obeying the following equation

$$P(V-nb)=nRT$$

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

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{nR}{P}+0=\frac{nR}{P}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P=\frac{nRT}{P}=(V-nb)$$

$$\therefore \mu_{JT}=\frac{1}{C_P}[-nb]=-\frac{1}{C_P}\times nb=(-)\,ve$$

As $dP=(-)\,ve$, so dT must be positive in JT experiment.

$\therefore$There is heating

Case III

For real gas obeying Vander Waals' equation, we have for 1 mole of real gas

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

or, $PV+\frac{a}{V}-Pb-\frac{ab}{V^2}=RT$

or,$PV=RT-\frac{a}{V}+Pb+\frac{ab}{V^2}$ (assuming $PV=RT$)

or, $V=\frac{RT}{P}-\frac{a}{PV}+b+\frac{ab}{PV^2}$

$$=\frac{RT}{P}-\frac{a}{RT}+b+\frac{abP}{R^2T^2}$$

$$\therefore\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{P}-\frac{2abP}{R^2T^3}+\frac{a}{RT^2}$$

or, $T\left(\frac{\partial V}{\partial T}\right)_P=\frac{RT}{P}-\frac{2abP}{R^2T^2}+\frac{a}{RT}$

$$=V-b-\frac{abP}{R^2T^2}+\frac{a}{RT}-\frac{2abP}{R^2T^2}+\frac{a}{RT}$$

$$= V - b + \frac{2a}{RT} - \frac{3abP}{R^2T^2}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b - \frac{3abP}{R^2T^2}$$

$$\therefore \mu_{JT} = \frac{1}{C_p}\left[\frac{2a}{RT} - b - \frac{3abP}{R^2T^2}\right] \qquad \left[\frac{3abP}{R^2T^2}\text{term is negligible}\right]$$

$$\approx \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

So from the knowledge of heat capacity (C_P) and Vander Waals' constant $(a \text{ and } b)$, we can calculate μ_{JT}

Special Case

1. **Inversion temperature** (T_i)

   For every real gas there is a characteristic temperature at which neither heating nor cooling would occur due to passage through fine orifices of process plug under adiabatic condition. This temperature is called inversion temperature. Thus at inversion temperature (T_i) real gas behaves ideally.

   If the working temperature is inversion temperature i.e. if $T = T_i$ then $\mu_{JT} = 0$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = 0$$

$$\therefore 0 = \frac{1}{C_p}\left[\frac{2a}{RT_i} - b\right] \left[\because \frac{1}{C_P} \neq 0\right]$$

$$\frac{2a}{RT_i} - b = 0$$

or, $b = \frac{2a}{RT_i} \therefore T_i = \frac{2a}{Rb}$

The value of T_i can be calculated from the knowledge of Vander Waals' constant *a, b* and the value of T_i depends on the nature of the gas (i.e. it depends on a and b which are different for different gases).

---

2. If $T \langle T_i$, then

$$T < \frac{2a}{Rb}$$

or, $b < \dfrac{2a}{RT}$

or, $b - \dfrac{2a}{RT} < 0 \left(\dfrac{2a}{RT} - b\right)$ is positive

$\therefore \mu_{JT} = \left(\dfrac{\partial T}{\partial P}\right)_H$ is$(+)$ve $\quad \therefore dT$ is $(-)$ ve i.e cooling.

$\therefore$ Since in J.T experiment dP is $(-)$ve, dT should be negative to satisfy the condition. Thus CO_2, NH_3 at room temperature exhibit cooling.

3. If $T > T_i$, then $T > \dfrac{2a}{Rb}$

$$b > \frac{2a}{RT}$$

or $\left(\dfrac{2a}{RT} - b\right)$ is $(-)$ ve

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = (-)\text{ ve}$$

$\therefore$ Since in JT experiment dP is (–) ve

$\therefore dT$ is $(+)\,ve$ i.e. heating.

Thus H_2 and Heat room temperature exhibits heating.

4. When $T = T_i$ then, $\mu_{JT} = 0$

Hence from the equation

$$0 = \frac{1}{C_p}\left(\frac{2a}{RT_i} - b - \frac{3abP}{R^2T_i^2}\right)$$

$$\therefore \frac{2a}{RT_i} - b - \frac{3abP}{R^2T_i^2} = 0 \qquad \left[\because \frac{1}{C_p} \neq 0\right]$$

Multiplying both sides by $\left(-\dfrac{T^2}{b}\right)$ we get

$$-\frac{2aT_i}{Rb}+T_i^2+\frac{3aP}{R^2}=0$$

or, $T_i^2-\frac{2aT_i}{Rb}+\frac{3aP}{R^2}=0$

This is a quadratic equation of T_i and T_i can have values given by

$$T_i=\frac{\frac{2a}{Rb}\pm\sqrt{\frac{4a^2}{R^2b^2}-\frac{12aP}{R^2}}}{2}$$

Thus there can exist two inversion temperatures at a particular time.

SKILL TEST

1. What is Joule-Thomson coefficient?
2. What is the expression of Joule-Thomson coefficient?
3. What is the magnitude of μ_{JT}during heating of a gas?
4. What is the magnitude of μ_{JT}during cooling of a gas?

6.20 Gibbs – Duhem Relation

For an open system, the free energy (G), being a state function, depends upon the variable thermodynamic parameters pressure, volume, temperature and the amount of the component (n).

Thus for a system heating n_1 moles of a component A_1, n_2 moles of another component A_2etc the free energy.

$$G=f\left(P,T,n_1,n_2\cdots\cdots\cdots etc.\right)$$

If all the variables undergo change, then the corresponding change in free energy (dG)will be given by.

$$dG=\left(\frac{\partial G}{\partial P}\right)_{T,n_i}dP+\left(\frac{\partial G}{\partial T}\right)_{P_i n_i}dT+\left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2\cdots}dn_1$$

$$+\left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1,n_3\cdots} dn_2+..........=VdP-SdT+\mu_1 dn_1+\mu_2 dn_2+................$$

$$\left[\because \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}=\mu_i \text{ chemical potential}\right]$$

$$\left[\left(\frac{\partial G}{\partial P}\right)_{T,n_i}=V \text{ and } \left(\frac{\partial G}{\partial T}\right)_{P,n_i}=-S\right]$$

At constant pressure and temperature

$$(dG)_{P,T}=\mu_1 dn_1+\mu_2 dn_2+...............$$

$$=\sum \mu_i dn_i... \tag{6.45}$$

If at constant pressure and temperature, all the components are increased in the same proportion (Δx) i.e. A_1 is increased by an amount $n_1\Delta x$ moles, $A_2$is increased by an amount $n_2\Delta x$ moles ....,A_i is increased by an amount $n_i\Delta x$ etc., then $dn_1=n_1\Delta x,\ dn_2=n_2\Delta x,\ dn_i=n_i\Delta x$ etc.

As G is an extensive property, then will also increases by an amount $G\Delta x$. Thus

$$dG=G\Delta x$$

$\therefore$ Equation 6.45 becomes

$$G\Delta x=\mu_1 n_1\Delta x+\mu_2 n_2\Delta x+...............+\mu_i n_i\Delta x$$

or, $G=\mu_1 n_1+\mu_2 n_2+......................+\mu_i n_i$

$$=\sum \mu_i n_i... \tag{6.46}$$

Now complete differentiation of the equation 6.46 gives

$$dG=(\mu_1 dn_1+\mu_2 dn_2+\cdots+\mu_i d\mu_i)+(n_1 d\mu_1+n_2 d\mu_2+\cdots+n_i d\mu_i)... \tag{6.47}$$

Subtracting 6.45 from 6.47

$$0 = n_1 d\mu_1 + n_2 d\mu_2 + ... + n_i d\mu_i$$

or

$$\sum n_i d\mu_i = 0 \tag{6.48}$$

Equation 6.45, 6.46 and 6.48 are different forms of Gibbs –Duhem relations.

6.21 Clausius Clapeyron Equation

Introduction

Thermodynamic relation have been applied to the study of phase change such as

1. melting or freezing
2. Vaporization or Liquifaction
3. Sublimation or Solidification
4. Allotropic transformation

Definition: The equation representing the variation of vapour pressure with temperature for systems existing in different phases in equilibrium is known as _**Clapeyron equation**.

Its modified form which deals with only liquid/vapour or Solid/vapour equilibrium is known as **Clausius Clapeyron equation**

Derivation:

Let us consider a substance existing in two different phases 1 and 2 (e.g. solid/liquid or liquid/vapour) at equilibrium at a particular temperature (T) and pressure (P). Let *dn* **moles** of the substance be transferred from phases 1 to phase 2 without altering temperature and pressure. Then the corresponding change in Gibbs potential is given by Gibbs Duhem equation

$dG_{T,P} = \sum \mu dn$ (from Gibbs Duhem equation)

or, $dG_{T,P} = -\mu_1 dn + \mu_2 dn$

But the system being at equilibrium at constant temperature and pressure

$$dG_{T,P} = 0$$

$$\therefore 0 = -\mu_1 dn + \mu_2 dn$$

$$\Rightarrow \mu_1 = \mu_2 ... \tag{6.49}$$

Thus the chemical potential (μ) of a component will be same in the two phases at equilibrium.
If the temperature and pressure change infinitesimally by dT and dP respectively, then the system will remain at equilibrium. Under this new condition the temperature is $T + dT$ and pressure $P + dP$.
Then

$$\mu_1 + d\mu_1 = \mu_2 + d\mu_2 \tag{6.50}$$

where $d\mu_1$ and $d\mu_2$ are the changes in chemical potential in the phase 1 and 2 respectively.
Substituting equation 6.49 in equation 6.50 we have

$$d\mu_1 = d\mu_2$$

$$\begin{aligned} or, (\bar{V}_2 - \bar{V}_1) dP &= \left(\bar{S}_2 - \bar{S}_1\right) dT \\ or, \frac{dP}{dT} &= \frac{\overline{\Delta S}}{\bar{V}_2 - \bar{V}_1} \\ or, \frac{dP}{dT} &= \frac{L}{T\,(\bar{V}_2 - \bar{V})_1} \end{aligned}$$

[The small change in Gibbs potencial
dG=dU+PdV+VdP+SdT-TdS
=dq+VdP-SdT-dq
=VdP-Sdt
$\therefore d\mu = \bar{V} dp - \bar{S} d\, T$]
This is known as Clapeyron equation.
Slope of Clapeyron equation
Clausius Clapeyron equation is applicable for all types of phase changes.

1. **Change in state like**
   (a) Solid →Liquid $\frac{dP}{dT} = \frac{L_f}{T_f(\bar{V}_L - \bar{V}_S)}$ [L_f= molar latent heat of fusion]
   (b) Liquid→ Vapour $\frac{dP}{dT} = \frac{L_V}{T_V(\bar{V}_g - \bar{V}_L)}$ [L_v = molar latent heat of vaporization]
   (c) Solid→Vapour $\frac{dP}{dT} = \frac{L_s}{T_i(\bar{V}_g - \bar{V}_S)}$ [$L_s = L_f + L_v$ = molar latent heat of sublimation]
2. **Allotropic transformation**

$$S_\alpha \rightarrow S_\beta$$

$\frac{dP}{dT} = \frac{L_E}{T_E\left(\bar{V}_\beta - \bar{V}_\alpha\right)}$ [L_E= molar latent heat transformation]

for fusion

(a) For paraffin $\bar{V}_L > \bar{V}_S$

$$\therefore \bar{V}_L - \bar{V}_S \text{ is } (+)\text{ve}$$

and L_f and T are always $(+)ve$

$\therefore \frac{dP}{dT}$ is $(+)ve$ i.e with rise of temperature, vapour pressure increases or with increase of pressure, m.pt. increases. Slope of P Vs T curve is $(+)ve$.

(b) $\bar{V}_L < \bar{V}_S \quad \therefore \bar{V}_L - \bar{V}_S$ is $(-)ve$

But L_f and T are positive. $\therefore \frac{dP}{dT}$ is $(-)$ ve

Slope of P vs T is $(-)$ ve i.e. with rise of temperature, vapour pressure decreases or with increase of pressure melting point decreases.

Simplified form of the equation

The Clapeyron equation was simplified by Clausius on the basis of the following considerations.

1. $\bar{V}_L$ or $\bar{V}_S <<< \bar{V}_g \qquad \therefore \frac{dP}{dT} = \frac{L}{T\bar{V}_g}$
2. The vapour was assumed to behave like ideal gas.

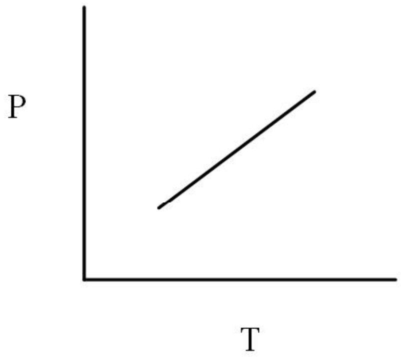


Figure 6.7: P Vs T graph

$$\therefore \frac{dP}{dT} = \frac{L}{T.\frac{RT}{P}}$$

$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

$\Rightarrow \frac{dP}{P} = \frac{L}{R}\frac{dT}{T^2}$?This is differential form of Clausius Clapeyron equation.

3. Moreover the latent heat was supposed to be independent of temperature.

Now integrating within limits

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{L}{R}\int_{T_1}^{T_2} \frac{dT}{T}$$

or, $[\ln P]_{P_1}^{P_2} = \frac{L}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$

or, $\ln\frac{P_2}{P_1} = \frac{L}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

This is the integrated form of Clausius Clapeyron equation.

But if the equation is integrated without limits, then

$$\ln P = \frac{L}{R}\left(-\frac{1}{T}\right) + C$$

Thus the plot of ln P vs $\frac{1}{T}$ is a straight line

If $T = Tb$, $P = 1$

$\therefore$ we have $0 = \frac{L}{R}\left(-\frac{1}{T_b}\right) + C$

or $C = \frac{L}{RT_b}$

or $\boxed{\frac{L}{T_b} = RC = \text{Constant}}$ →Trouton's equation.

6.22 Thermodynamic criteria for reactions

We have

$$\begin{aligned} dS_{universe} &= dS_{system} + dS_{surroundings} \\ &= dS_{system} - \frac{dQ}{T} \end{aligned}$$

[If the surrounding supplies dQamount of heat to the system at temperature T reversibly.]

$$\begin{aligned} &= dS_{system} - \frac{du + dw}{T} \\ &= dS_{system} - \frac{du}{T} - \frac{dw}{T} \end{aligned}$$

$$= dS_{system} - \frac{du}{T} - \frac{PdV}{T} \ldots \tag{6.51}$$

[If only mechanical work is involved]

We have

$$\begin{aligned} A &= U - TS \\ dA &= dU - TdS - SdT \\ or, TdS - dU &= -dA - SdT \\ \Rightarrow dS - \frac{dU}{T} &= -\frac{dA}{T} - S\frac{dT}{T} \end{aligned}$$

$$\Rightarrow dS_{universe} = -\frac{dA}{T} - \frac{SdT}{T} - \frac{PdV}{T} \ldots \tag{6.52}$$

Again we know

$G = H - TS$

$= U + PV – TS$

$$= A + PV$$

$$\begin{aligned}
&\therefore dG = dA + PdV + VdP \\
&\Rightarrow -dA - PdV = VdP - dG \\
&\Rightarrow -\frac{dA}{T} - \frac{PdV}{T} = \frac{VdP}{T} - \frac{dG}{T} \\
&\Rightarrow dS_{\text{universe}} + \frac{SdT}{T} = \frac{VdP}{T} - \frac{dG}{T} \\
&\Rightarrow dS_{\text{universe}} = -\frac{dG}{T} + \frac{VdP}{T} - \frac{SdT}{T} \qquad (6.53)
\end{aligned}$$

Hence

$$dS_{\text{universe}} = \left[(dS)_{\text{system}}\right]_{U,V} \qquad (6.54)$$

$$= -\left(\frac{\partial A}{T}\right)_{T,V} \qquad (6.55)$$

$$= -\left(\frac{\partial G}{T}\right)_{P,T} \qquad (6.56)$$

But for a real process to occur, the change must be irreversible (i.e. spontaneous) since for irreversible process $dS_{universe} > 0$

From 6.51

$(ds_{systrem})_{U,V} > 0$ i.e. entropy increases and from 6.55

$-\left(\frac{dA}{T}\right)_{T,V} \rangle 0$ or $\left(\frac{dA}{T}\right)_{T,V} \langle 0$ i.e. maximum work function or Helmholtz's free energy diminshes.

Similarly from equation 6.56, $\left(\frac{dG}{T}\right)_{P,T} < 0$ i.e. Gibbs free energy diminishes.

When a system attains equilibrium, its state does not change in any way with time (i.e. the system becomes a stable one). So any imagined infinitesimal change would be reversible. Consequently

$$dS_{universe} = 0$$

$(dS_{system})_{U,\,V} = 0$; entropy does not change

$\left(\dfrac{dA}{T}\right)_{T,V} = 0$; Helmholtz free energy does not change

$\left(\dfrac{dG}{T}\right)_{P,\,T} = 0$; Gibb's free energy does not change

	Spontaneous process	**Equilibrium process**
$(dS_{system})_{U,V}$	> 0	$= 0$
$(dA)_{T,V}$	< 0	$= 0$
$(dG)_{T,P}$	< 0	$= 0$

SKILL TEST

1. Write the different forms of Gibbs-Duhem equation.
2. What is the expression of Clapeyron equation for
    (a) Solid – liquid
    (b) Liquid – vapour and
    (c) Solid – vapour system.
3. Derive Trouton's expression.
4. What are the thermodynamic criteria for
    (a) spontaneous and
    (b) equilibrium reaction.

Review Questions

1. **The relation between heat absorbed at constant pressure with that at constant volume.**

Answer:
The heat absorbed at constant pressure is $(dq)_p$ and the heat absorbed at constant volume is $(dq)_V$

From first law of thermodynamics we know that

$$dq = dU + dW$$

Where, dq =heat absorbed by the system.

dU = internal energy of the system.

dW =work done by the system.

$$dq = dU + PdV$$

When pressure remains constant then we get

$$dq_P = dU_P + PdV \tag{6.57}$$

When volume remains constant then we get

$$dq_V = dU_V \tag{6.58}$$

Subtracting (6.57) from (6.58) we get

$$dq_P - dq_V = dU_P + PdV - dU_V$$

$$= (dU_P - dU_V) + PdV \tag{6.59}$$

From an ideal system, we have $dU_P = dU_V \; or \; dU_P - dU_v = 0$

Then from equation (6.59) we get

$$dq_P - dq_V = PdV$$

$$dq_P = dq_V + PdV \tag{6.60}$$

In a gaseous reaction if n_1 *and* n_2 denote the number of reactant molecules and resultant molecules then we have

$$\begin{aligned} PdV &= P(V_2 - V_1) \\ &= P(n_2 - n_1)\frac{RT}{P} \\ &= dnRT \end{aligned}$$

[we know for *n* moles of an ideal gas PV = nRT]

Then from equation (6.60) we get

$$dq_P = dq_V + dn\,RT \tag{6.61}$$

$dn =$ Increase in the number of moles in the reaction.

Therefore (6.60) and (6.61) are the required equations.

2. **Show that when$\gamma \to 1$, the work done in the adiabatic reversible expansion is equal to that of isothermal reversible expansion**

Answer:

Work done in reversible process $W_{rev} = \int\limits_{V_1}^{V_2} PdV$

For an adiabatic reversible process PV^{γ} =constant = (K) say

$$P = \frac{K}{V^{\gamma}}$$

Work done in an adiabatic reversible process

$$W_{rev(adia)} = \int_{V_1}^{V_2} Constant \, . \, \frac{dV}{V^{\gamma}}$$

When $\gamma \rightarrow 1$, the work done in an adiabatic reversible process

$$\begin{aligned}
W_{rev(adia)} &= \int_{V_1}^{V_2} Constant \, . \frac{dV}{V} \\
&= Constant \int_{V_1}^{V_2} \frac{dV}{V} \\
&= Constant \; ln \frac{V_2}{V_1} \quad [Constant = nRT] \\
&= nRT \; ln \frac{V_2}{V_1} \\
&= W_{rev(isothermal)}
\end{aligned}$$

3. **Derive the expression of work done in isothermal reversible process.**

Answer:

Suppose n moles of a perfect gas are enclosed in a cylinder by a frictionless piston. The whole cylinder is kept in a large constant temperature bath at$T^{\circ}K$. Any change that would occur to the system is isothermal. There is a latch at the top B, and the piston can not move beyond that. The volume of the gas when the piston is at B isV_2. When the piston is at the point A, the volume of the gas isV_1. The aim is to expand the gas from volume$V_1 \; to \; V_2$.

But we can carryout the process in the following way. Let the pressure P_1 be reduced by an infinitesimal amountdP. Let the new pressure be $P_1^{/} = P_1 - dp$.

The work would be $dW = (P_1 - dP)dV$.

The change in volume would be small and equal todV.

The new pressure be again reduced slightly so that it changes to $P^{//} = P_1^{/} - dP$

Then the work would be $dW = (P_1^{/} - dP)dV$

The process may be repeated by such infinite number of successive steps that the gas may be expanded from volume$V_1\, to\, V_2$.

The net work for all the minute stages would be

$$\int dW = \sum (P - dP)dV = \int_{V_1}^{V_2} PdV - \int_{V_1}^{V_2} dPdV$$

Since $dp and\ dV$are infinitesimal quantities, $dPdV$ is negligible.

$$\int dW = \int_{V_1}^{V_2} PdV$$

or, $W = \int_{V_1}^{V_2} pdv = \int_{V_1}^{V_2} \frac{nRT}{V} dv = nRT \ln \frac{V_2}{V_1} \quad \left[PV = nRT\ or, P = \frac{nRT}{V} \right]$

$$W = nRT\ \ln \frac{V_2}{V_1}$$

$$= nRT\ \ln \frac{P_1}{P_2}$$

Since $\frac{V_2}{V_1} = \frac{P_1}{P_2}$ there is an isothermal expansion of perfect gas.

4. **Prove that work done in a reversible process is greater than irreversible process.**

Answer:
Work done in reversible process$(W_{rev}) = RT\ ln\ \frac{V_2}{V_1} = RT\ ln \frac{P_1}{P_2}$. Suppose we carry out a small expansion of the same gas in two ways. We

change the volume until the pressure isP_2. The process is reversible.

Secondly, we reduce the pressure over the piston at once to P_2, which would be the equilibrium pressure of the gas when the volume is V_2, then the gas would expand immediately against a constant pressure P_2. The process is irreversible and irreversible work.

$$\begin{aligned}
W_{irrev} &= P_2(V_2 - V_1) \\
&= P_2\left(\frac{RT}{P_2} - \frac{RT}{P_1}\right) = RT\left(1 - \frac{P_2}{P_1}\right) \\
W_{rev} - W_{irrev} &= RT\ ln\frac{P_1}{P_2}\ -\ RT\left(1 - \frac{P_2}{P_1}\right) \\
&= RT\,ln\left(1 + \frac{P_1 - P_2}{P_2}\right) - RT\frac{P_1 - P_2}{P_1}
\end{aligned}$$

If we assume $\frac{P_1 - P_2}{P_2}$ to be small we can write

$$ln\,1 + \frac{P_1 - P_2}{P_2}$$

Since $ln\,(1+X) = X\ when\ X\ is\ small$

$$W_{rev} - W_{irrev} = RT\frac{P_1 - P_2}{P_2} - RT\frac{P_1 - P_2}{P_1}$$

$$= RT\left(\frac{P_1^2 - 2P_1P_2 + P_2^2}{P_1P_2}\right)$$

$$= \frac{RT}{P_1P_2}(P_1 - P_2)^2$$

This is always positive irrespective of the magnitude of $P_1\ and\ P_2$. Thus the work in a reversible process is greater than that in an irreversible process.

5. **For a Vander Waals' gas, show that** $\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V - nb}$

Answer:

For a real gas obeying Vander Waals' equation we have

$$\begin{aligned}\left(P+\frac{n^2a}{V^2}\right)(V-nb) &= nRT \\ P &= \frac{nRT}{V-nb}-\frac{n^2a}{V^2}\end{aligned}$$

Differentiating the equation with respect to temperature at constant volume, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} \tag{6.62}$$

By Maxwell's' relation we know

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Hence from equation (6.62) we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{(V-nb)}$$

6. **Explain why heat energy can not be converted to work in an isothermal cyclic process for ideal gas.**

Answer:

The gas is expanding from volume V_1toV_2, isothermally and reversibly through infinite number of successive steps. Hence work done,

$$\int dW = \sum (P-dP)dV$$

$$\int dW = \int_{V_1}^{V_2} PdV - \int_{V_1}^{V_2} dP\,dV$$

Since $dP\,and\;dV$ are infinitesimal quantities so $dP\;dV$ is negligible.

$$\int dW = \int_{V_1}^{V_2} PdV$$

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT\;ln\frac{V_2}{V_1}$$

The system has now expanded to volumeV_2. Let us now attempt to return the system to its original state reversibly. It is seen that if we increase the pressure in successive stages of infinitesimal amount until the volume becomes V_1 and pressure P_1 the work would be

$$\int dW = \sum (P+dP)dV = \int_{V_2}^{V_1} PdV + \int_{V_2}^{V_1} dP\;dV$$

Since $dP\,and\;dV$ are infinitesimal quantities so $dP\;dV$ is negligible.

$$W = \int_{V_2}^{V_1} PdV = nRT\;ln\frac{V_1}{V_2}$$

In the complete cyclic process then,

$$\oint dW = nRT\;ln\frac{V_2}{V_1} \;+ nRT\;ln\frac{V_1}{V_2} \quad = \quad 0$$

In a reversible isothermal cyclic process $\oint dW = 0$.

We also know for cyclic process $\oint dU = 0$

From 1^{st} law of thermodynamics we know that

$$\oint dq = \oint dU + \oint dW$$

$$\oint dq = \oint dW = 0$$

So heat energy can not be converted into work in an isothermal reversible cyclic process for ideal gas.

7. **What are the differences between reversible and irreversible process?**

Answer:

Reversible Process	Irreversible Process
(i) If the systems and surroundings are restored to their initial conditions after a cyclic change, then the change is termed as reversible. (ii) Work done is maximum in reversible process. (iii) The process occurs through infinite number of successive stages and hence infinite time is required for its completion. (iv) This process takes place very slowly and involves a series of equilibrium states.	(i) If the systems and surroundings are not restored to their initial conditions after a cyclic change, then the change is termed as irreversible. (ii) Work done in an irreversible process is less than reversible process. (iii) This process occurs through one step and hence gets completed in a short time. (iv) This process takes place very rapidly and does not involve any equilibrium state.

8. **Write down which process is reversible and which process is irreversible.**
   (a) **in one step under constant pressure.**
   (b) **in multi steps such that opposing pressure is always less than the gas pressure.**

Answer:

(a) The process occurs in one step against a constant external pressure. Thus the process is irreversible one.

(b) The process occurs through infinite number of successive stages. Thus the process is reversible one.

9. Justify the statement – "First law of thermodynamics is nothing but the law of conservation of energy"

Answer:

The relation between heat and work which is the origin of first law of thermodynamics. However, this law is derived from experiment. Different scientists gave different statements on the basis of experiments.

(a) Helmholtz's statement:

The different forms of energy are interchangeable, but whenever energy of one kind disappears an equivalent amount of another kind or kinds makes it appearance.

(b) Clausius statement:

Various changes and transformation may occur but the total energy of the universe must remain constant.

(c) Ostwald's statement:

A machine which does work without any supply of energy from outside is known as perpetual motion of the 1^{st} kind. Ostwald enunciated that perpetual motion of the 1^{st} kind is impossible.

All the statements are identical in significance. All signify basically that – "Energy can neither be created nor destroyed, but can be converted from one form to another". Thus 1^{st} law is actually the law of conservation of energy.

10. What is the relation between internal energy change and heat absorbed at constant volume?

Answer:
Isochoric change i.e. process at constant volume ($dV = 0$)

From 1^{st} law of thermodynamics we have

$dq_V = dU_V + (dW)_V$[Suffix Vdenotes constant volume]

or, $dq_V = dU_V + 0$

or, $dq_V = dU_V$

Thus heat absorbed at constant volume is fully utilized to increase internal energy.

11. **Justify the statement – "Heat absorbed at constant pressure is utilized partly to increase internal energy and rest is used up in work done."**

Answer:
Isobaric process i.e. process at constant pressure ($dP = 0$)

From 1^{st} law of thermodynamics we have

$dq_P = dU_P + dW_P$[Suffix Pdenotes constant pressure]

$$= dU_P + (PdV)_P$$

Thus heat absorbed at constant pressure is utilized partly to increase internal energy and rest is used in work done.

12. **Justify the statement – "Total heat is utilized to do work at constant temperature for ideal gas."**

Answer:
Isothermal change i.e. process at constant temperature ($dT = 0$)

From 1^{st} law of thermodynamics we have

$$dq_T = dU_T + dW_T$$

Ideal gas

$$dq_T = 0 + dW_T$$

$$\Rightarrow \quad dq_T = dW_T$$

Thus total heat is utilized to do work at constant temperature for ideal gas.

13. **Justify the statement – "The function enthalpy is such that its change is equal to the heat absorbed by the system at constant pressure."**

Answer:

Isobaric process i.e. process at constant pressure ($dP = 0$)

From 1^{st} law of thermodynamics we have

$dq_P = dU_P + dW_P$[Suffix Pdenotes constant pressure]

$$= dU_P + (PdV)_P$$

$$= dH_P$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$
$$dH_P = dU_P + (PdV)_P + 0$$
$$(dH)_P = dU_P + (PdV)_P$$

Thus the function enthalpy is such that its change is equal to the heat absorbed by the system at constant pressure.

14. **Write down which one is extensive and which one is intensive property. (i) volume (ii) temperature (iii) density (iv) internal energy (v) enthalpy (vi) Viscosity.**

Answer:

.

(a) Volume ⟶ Extensive property

(b) Temperature ⟶ Intensive Property

(c) Density ⟶ Intensive Property

(d) Internal Energy ⟶ Extensive Property

(e) Enthalpy ⟶ Extensive Property

(f) Viscosity ⟶Extensive Property

15. Is C_P always greater than C_V? – Explain.

Answer:

No, C_P is not always greater thanC_V.There are some condition where$C_P \rangle C_V$.

The expression for change in heat capacity is:

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$T, \left(\frac{\partial P}{\partial T}\right)_V$ *and* $\left(\frac{\partial V}{\partial T}\right)_P$ are always positive. Thus $C_P - C_V$ is always (+) ve. $C_P > C_V$

There are some conditions where $C_P = C_V$.

(a) At absolute zero, i.e. when $T = 0^\circ K$

$$C_P - C_V = 0\, or\, C_P = C_V$$

But it is a hypothetical case.

(b) Thus for water at $4^\circ C$ under a pressure of 1 atom, density (d) is maximum and volume (V) is minimum

$$d = \frac{m}{V}$$

But differential of a minimum quantity $= 0\ or\ \left(\frac{\partial V}{\partial T}\right)_P = 0$

$$C_P - C_V = 0$$

or, $C_P = C_V$

16. **Why is the enthalpy considered more useful than internal energy in chemical reaction?**

Answer:
Internal energy $(U)$and enthalpy $(H)$are measured by maintaining constant volume and pressure respectively. Since most of the reactions take place under atmospheric pressure, so enthalpy is more useful than internal energy in chemical reaction.

17. **What is the difference between adiabatic and isothermal changes?**

Answer:

Adiabatic Change	Isothermal Change
(i) Heat exchange between the system and the surrounding does not occur. (ii) Internal energy of the system changes. (iii) $PV^\gamma =$ Constant for such process.	(i) Temperature of the system remains constant. (ii) Change in internal energy does not take place for ideal gas. (iii) $PV =$ Constant for such process.

18. **Prove that for ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$.**

Answer:

From 1^{st} law of thermodynamics we have

$$\begin{aligned} & dq = dU + dW \\ \Rightarrow \quad & dU = dq - dW \\ \Rightarrow \quad & dU = TdS - PdV \end{aligned}$$

[From the definition of entropy $dS = \frac{dq}{T}$]

Differentiating both sides with respect to volume at constant temperature, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Since from Maxwell's relation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Therefore,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{6.63}$$

For ideal gas, $PV = nRT$

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

Thus, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$

Therefore, from equation (6.63) $\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - P$

$$= P - P \ = 0$$

19. If the process is completely adiabatic then how much work is obtained from a reversible Carnot engine

Answer:

If the process be completely adiabatic i.e. no heat is absorbed.

$\therefore Q = 0$ then $W_{\max} = 0$

$\therefore$ No work can be obtained.

20. If no heat is rejected to the sink then how much amount of work is obtained from a reversible Carnot engine?

Answer:

No heat is rejected to the sink i.e. $Q^{/}=0$

$$W=Q-Q^{/}$$

$$Q-Q^{/}=Q\frac{T-T^{/}}{T}$$

or, $1-\frac{Q^{/}}{Q}=1-\frac{T^{/}}{T}$

or, $\frac{Q^{/}}{Q}=\frac{T^{/}}{T}$

or, $Q=Q^{/}\frac{T}{T^{/}}$

$$\begin{aligned}\therefore W_{\max} &= Q\times\frac{T-T^{/}}{T}\\ &= \frac{Q^{/}}{T^{/}}\times T\times\frac{T-T^{/}}{T}\\ &= \frac{Q^{/}}{T^{/}}\left(T-T^{/}\right)\\ &= 0\end{aligned}$$

i.e. no work can be obtained.

21. Show that dq is not a perfect differential but $\frac{dq}{T}$ is a perfect differential.

Answer:

Suppose one mole of a perfect gas undergoes a reversible expression from volume V1 to volume V2 when the temperature changes from T_1 to T_2.Then from the first law

$$dq=dU+dW$$

or, $dq=dU+PdV$

or, $\int_I^{II} dq = \int_I^{II} dU + \int_I^{II} PdV$

$$= \int_{T_1}^{T_2} C_V dT + \int_{T_1}^{T_2} RT d\ln V$$

$$= C_v (T_2 - T_1) + \int_{V_1}^{V_2} RT d\ln V$$

The integral on the right hand side $\int_{V_1}^{V_2} RT d\ln V$ can not be evaluated unless we know the relation between T and V. If T be constant (i.e. isothermal change) the integral will have one value, and if T changes during the process, the integral will have different values. Thus, the magnitude of $\int_T^{II} dq$ depends on the way the expansion is carried out. Hence, dq is not a perfect differential.

Now dividing the equation by T, we have

$$\int_I^{II} \frac{dq}{T} = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} Rd\ln V$$

$$= C_V \ln \frac{T_2}{T_1} + R\ln \frac{V_2}{V_1}$$

That is, the $\int \frac{dq}{T}$ for a given change from state I to state II can be evaluated without any reference to the path of transformation. Thus, $\int \frac{dq}{T}$ is independent of the way the change is carried out. Hence, $\frac{dq}{T}$ is a perfect differential.

22. Prove that entropy change (dS) is independent of the path of the transformation.

Answer:

Here AB and CD are isothermal stages at temperature T_1 and T_2 ; BC and DA adiabatic stages. Let dq_1 , be the heat supplied to the working system at T_1 and dq_2 be the heat rejected by it to the sink at T_2. All

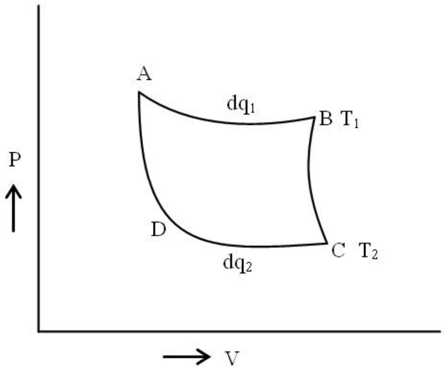


Figure 6.8: P Vs T graph

steps are reversible. We know in a Carnot cycle.

$$\frac{dq_1 - dq_2}{dq_1} = \frac{T_1 - T_2}{T_1}$$

or, $\frac{dq_1}{T_1} = \frac{dq_2}{T_2}$

(dq_2 is negative as it is rejected by the system)

Now let us confine our attention only to the change of the system from the point A to the point C and attempt to find out the ratio of the heat change to the temperature at which the thermal change occurs.

We can proceed from A to C either along ABC or along ADC

Along the path ABC, we have the isothermal AB, when heat change dq_1, takes place at T_1, followed by adiabatic change BC having no heat change.

Hence, $\frac{\text{Heat change}}{\text{Temperature}} = \frac{dq_1}{T_1} + 0 = \frac{dq_1}{T_1}$

Along the path ADC, the adiabatic AD involves no thermal change; but along the isothermal DC, heat absorbed would be dq_2 at temperature T_2.

Hence, $\frac{\text{Heat change}}{\text{Temperature}} = 0 + \frac{dq_2}{T_2} = \frac{dq_2}{T_2}$

Since from reversible Carnot cycle, we have

$$\frac{dq_1}{T_1} = \frac{dq_2}{T_2}$$

Thus the ratio of heat change to the temperature i.e. $\frac{dq}{T}$ is the some whatever path may be followed by the system in its reversible change. Hence $\frac{dq_{rev}}{T}$ is regarded as a perfect differential.

The entropy change (dS) is measured by the ratio of the reversible heat change and the temperature at which the heat change occurs i.e.

$$dS = \frac{dq_{rev}}{T}$$

Since, $\frac{dq}{T}$is independent of the path of the transformation, thus, entropy change (dS) is also independent of the path of the transformation.

23. What is the physical significance of decrease in Gibb's free energy?

Answer:

If a system undergoes a reversible change under isothermal and isobaric conditions from one state to another state then,

$$(\Delta G)_{T,P} = (\Delta H)_{T,P} - T\Delta S \quad [\because \quad H = U + PV \quad \therefore (\Delta H)_{T,P} = \Delta U + P\Delta V]$$

$$\begin{aligned} &= \Delta U + P\Delta V - T\Delta S \quad [\because \Delta S = \frac{q_{rev}}{T}, \; q_{rev} = T\Delta S] \\ &= \Delta U - q_{rev} + P\Delta V \\ &= -W + P\Delta V \quad [\text{From 1st law } q = \Delta U + W\,;\; \Delta U - q = -W] \end{aligned}$$

or,

$$-(\Delta G)_{\mathrm{T,P}} = W_{\mathrm{Total}} - W_{\mathrm{mechanical}}$$

$= W_{nonmechanical}$ [Where $P\Delta V$ is the mechanical work involved in the system itself during transformation and W denotes maximum total work output]

$W_{\text{nonmechanical}}$ is the work received for any external use exclusive of the mechanical work e.g. electrical work.

The Gibb's free energy (G) is such a thermodynamic function that its decrease for isothermal and isobaric reversible process represents the non mechanical work available during the transformation of the system.

Thus $-(\Delta G)_{\text{T, P}} = W_{\text{electrical}}$

24. Prove that $(\Delta G)_T = (\Delta A)_T$.

Answer:

For ideal gas $\int dG_T = \int \frac{nRT}{P} dP$

$$G_T = nRT \ \ln P + n\bar{G}_0$$

Again integrating within limits we get,

$$\int_{G_1}^{G_2} (dG)_T = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

or, $$(G_2 - G_1)_T = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$
$$= -W_{\text{max}} \quad = (\Delta A)_T$$

Hence, $(\Delta G)_T = (\Delta A)_T$

25. What is inversion temperature?

Answer:

For every real gas there is a characteristic temperature at which neither heating nor cooling would occur due to passage through fine orifices of process plug under adiabatic condition. This temperature is called

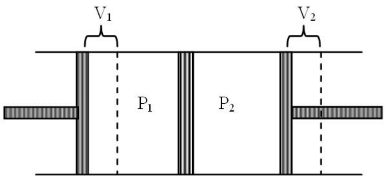


Figure 6.9: Joule Thompson

inversion temperature. Thus at inversion temperature (T_i) real gas behaves ideally.

26. Show that Joule Thomson expansion is an isoenthalpic process.

Answer:

Suppose, the volume $V_1$of a gas under a constant pressure P_1 is allowed to pass through a porous barrier from the region on the left to the region on the right where pressure is P_2.The volume of the gas becomes V_2.The process is carried out with two frictionless pistons attached at the two ends. The whole system is thermodynamically insulated i.e $q = 0$

Work done with the system at the left $= W_L = \int_{V_1}^{0} P_1 dV$

$$= -P_1 V_1$$

Work done with he system at the right

$$\begin{aligned} W_R &= \int_{0}^{V_2} P_2 dV \\ &= P_2 V_2 \end{aligned}$$

Thus total work done

$$\begin{aligned} W_{total} &= W_L + W_R \\ &= -P_1 V_1 + P_2 V_2. \end{aligned}$$

Then from first law of thermodynamics

$$\begin{aligned}Q &= \Delta U + W\\ 0 &= (U_2 - U_1) + (P_2V_2 - P_1V_1)\\ &= (U_2 + P_2V_2) - (U_1 + P_1V_1)\\ &= H_2 - H_1 = \Delta H\end{aligned}$$

Hence adiabatic expansion of a gas through fine orifice is **isoenthalpic**.

27. How will you show that μ_{JT} of an ideal gas is equal to zero?

Answer:

For ideal gas, $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$

$$= -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

$$= -\frac{1}{C_P}\left[\left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\}\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

$$\left[\begin{aligned} du &= dq - d\,W\\ &= TdS - PdV\\ \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - P\\ &= T\left(\frac{\partial P}{\partial T}\right)_V - P\end{aligned}\right]$$

$$= -\frac{1}{C_P}\left[(P-P)\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

$$= -\frac{1}{C_P}\left\{\frac{\partial (PV)}{\partial P}\right\}_T = -\frac{1}{C_P}\times 0 = 0,$$

$$\left[\text{Since from Boyle's law, } \left[\frac{\partial (PV)}{\partial P}\right]_T = 0\right]$$

Hence $\mu_{JT} = 0 \qquad \therefore dT = 0$

i.e. Neither heating nor cooling.

28. What is the significance of (+) ve and (-) ve sign of Joule-Thomson coefficient (μ_{JT})?

Answer:

Positive sign of μ_{JT} indicates that cooling occurs under adiabatic condition and negative sign of μ_{JT} indicates that heating occurs under adiabatic condition.

29. What is the physical significance of Helmholtz free energy?

Answer:

If a system undergoes a reversible isothermal change from one state to another, then

$$\begin{aligned}(\Delta A)_T &= (\Delta U)_T - T\Delta S \\ &= (\Delta U)_T - T \times \frac{q_{rev}}{T} \\ &= -(W_{rev})_T \\ &= -(\Delta A)_T = (W_{\max})_T\end{aligned}$$

Thus, work function A is such a thermodynamic function that its decrease for an isothermal reversible process represent maximum amount of available work.

Worked –Out Examples

1. **A gas is expanding against a constant pressure of 2 atm from 10 to 20 liters absorbs 300 cal of heat. What is the change in internal energy?**

   Answer:

   Work done during expansion W = 2(20 – 10) = 20 Litre atm

   1 litre atm = 24.2 cal So W = 484 cal.

   From 1^{st} law

   $$dq = dU + W$$

   $$300 = dU + 484$$

   So $dU = -184\, cal$

   Hence internal energy is decreased by 184 cal.

2. **A weight of 1000 gm falls freely to a platform from a height of 10 metres. What amount of heat will be evolved when the weight strikes the platform?**

   Answer:

   Work done during fall = mgh

   Here m = 1000 gm; g = 980 cm/Sec^2 ; $h = 10\, metre \equiv\ 10^3\, cm$

   So $W = 10^3 \times 980 \times 10^3 = 9.8 \times 10^8\, ergs =\ 98\, Joule$

   Now W = J H

   So $H = \frac{W}{J} = \frac{98}{4.2}\, cal = 23.3\, cal.$

3. **One mole of an ideal gas expands against a confining pressure that is at all times infinitesimally less than the gas pressure from an initial 10 atm to a final of 0.4 atm ; the temperature being kept**

constant at $0^{\circ}C$.(a) How much work is done by the gas? (b) What is the change in U and H? (c) How much heat is absorbed?

Answer:

The process described is an isothermal reversible process for which

$$W = nRT\ ln\frac{P_1}{P_2}$$

Or, $W = 1.987 \times 273\ ln\frac{10}{0.4} = 1746.08\,Cal$

In isothermal expansion of ideal gas $\Delta U = \Delta H = 0$

Also here $dq = W$

So 1746.08 cal. Heat is absorbed.

4. **A gas expands against a variable external pressure given by $P = \frac{10}{V}$ atm. where V is the volume of the gas at each stage of expansion. Further in expanding from 10 to 100 litres, the gas undergoes a change in internal energy $\Delta U = 100\,Cal$. How much heat has been absorbed?**

Answer:

Work done against a variable pressure $= \int_{V_1}^{V_2} PdV$

Here $P = \frac{10}{V}\,atm.\,So\,W = 10\int_{V_1}^{V_2}\frac{dV}{V}\ litre\ atm$

$W = 10\ ln\frac{V_2}{V_1} = 10ln\frac{100}{10} = 23.03$ litre atm.

Or, $W = 557.3\,Cal$ [1 litre atm ≡24.2 Cal]

As, $dq = dU + W$

So $dq = 100 + 557.3 = 657.3\ cal\ is\ absorbed.$

---

5. **What is the change in U and H suffered by 3 moles of $C0_2$ if the temperature is raised from $100^{\circ}C\,to\,500^{\circ}C$; the pressure remaining constant at 0.1 atm? The heat capacity of $C0_2$is given by $C_P = 44.2 + 8.79\times10^{-3}T - 8.62\times10^{+5}T^{-2}\,mole^{-1}K^{-1}$.**

Answer:

For ideal gas $C_P - C_V = R = 8.31\;Joule$

So

$$\begin{aligned}
C_V &= C_P - R \\
&= 44.2 + 8.79\times10^{-3}T - 8.62\times10^{+5}T^{-2} - 8.31 \\
&= 35.89 + 8.79\times10^{-3}T - 8.62\times10^{+5}T^{-2} \\
\Delta u &= \int_{t_1}^{t_2} nC_V dT \\
&= 3\left[35.89\int_{373}^{773} dT + 8.79\times10^{-3}\int_{373}^{773} TdT - 8.62\times10^{+5}\int_{373}^{773} T^{-2}dT\right] \\
Or, \Delta U &= 3\left[14356 + 2014.66 - 1195.85\right] = 45524.43\;Joule \\
\Delta H &= \int_{T_1}^{T_2} nC_P dT \\
&= 3\left[44.2\int_{373}^{773} dT + 8.79\times10^{-3}\int_{373}^{773} TdT - 8.62\times10^{5}\int_{373}^{773} T^{-2}dT\right] \\
&= 3\left[17680 + 2014.66 - 1195.85\right] \;=\; 55496.43\;Joule.
\end{aligned}$$

6. **Calculate the work done by 5 moles of an ideal gas during expansion from 5 atm. at $25^{\circ}C$ to 2 atm at $50^{\circ}c$against a constant pressure of 0.5 atm. If for the gas $C_P = 5\,Cal.\,mole^{-1}\ \deg^{-1}$ calculate $\Delta U, \Delta H\;and\;q$.**

Answer:

Work $= P_{ext.}[V_2 - V_1]$

Here $P_{ext.} = 0.5\, atm. V_2 = \frac{nRT_2}{P_2} = \frac{5 \times 0.082 \times 323}{2} = 66.22\, litre$

and $V_1 = \frac{nRT_1}{P_1} = \frac{5 \times 0.082 \times 298}{5} = 24.44\, litre$

So

$$\begin{aligned} W = 0.5(66.22 - 24.44) &= 20.89\, litre\ atm \equiv 505.54\, Cal \\ C_P = 5\,Cal.\ So\ C_V &= 3\,Cal\ (Ideal\ gas) \\ \Delta U &= 5 \times 3(323 - 298) = 375\, Cal\ and \\ \Delta H &= 5 \times 5(323 - 298) = 625\, Cal. \\ q &= \Delta U + W = 880.54 Cal. \end{aligned}$$

7. **N_2 gas is expanded reversibly and adiabatically from a volume of one litre at $0^{\circ}C$ and 1 atm to a volume of 2 litre. $C_V\ and\ C_P$ values are 20.8 and 29.1 J $mole^{-1}K^{-1}$. Assuming ideal behaviour calculate the final temperature and pressure. What are $q, W, \Delta U\ and\ \Delta H$?**

Answer:

Poisson's Ratio $\gamma = \frac{C_P}{C_V} = \frac{29.1}{20.8} = 1.40$

From adiabatic reversible relation –

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}\ So\ 1 \times 1 = P_2 \times 2^{1.4}$$

$$or,\ P_2 = 0.38\, atm$$

Again $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}\ or\ 273 \times 1\ =\ T_2 \times 2^{0.4}$

$$or,\ T_2 = 206.9^{\circ}A$$

In adiabatic process $q = 0$

$$\begin{aligned} W = C_V(T_1 - T_2)/mole &= 20.9(273 - 206.9) \\ &= 1381.5\, Joule \\ \Delta U = C_V(T_2 - T_1) &= -1381.5\, Joule \\ \Delta H = C_P(T_2 - T_1) &= -1923.5\, Joule \end{aligned}$$

8. **One mole of an ideal monatomic gas initially at STP experiences a reversible process by which P is doubled. The nature of the process is unspecified but** $\Delta U\ is\ 900\, Cal.\ and\ q\ is\ 400\, Cal.$
   (a) **Calculate final T and V and** $\Delta H\ and\ W.$
   (b) **Suppose that the gas was taken to some final state, but by a two step process consisting first an isobaric change and then an isothermal one, both reversible. Calculate overall** $\Delta H, \Delta U, q\ and\ W$ **for this sequence.**

Answer:

(a) From first law $q = \Delta U + W$

Here 400 = 900 + W

So, W = - 500 Cal.

So 500 Cal work was done on the system.

$$\Delta U = 900 = C_V(T_2 - T_1)$$

For ideal mono-atomic gas $C_V = \frac{3}{2}R \cong 3\, Cal.$

So, $900 = 3(T_2 - 273) \quad or,\ T_2 = 573^\circ K$

$$C_P = 3 + 2 = 5\, Cal.$$

$$\Delta H = nC_P dT = 1 \times 5(573 - 273) = 1500\, Cal$$

Now $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

$$V_2 = \frac{T_2}{T_1}\frac{P_1V_1}{P_2} = \frac{573 \times 1 \times 22.4}{273 \times 2}$$

$$or, V_2 = 23.5\ litres$$

(b) In this case the change is done in the following way

$$\text{1 Mole gas} \begin{bmatrix} P = 1\,atm \\ V = 22.4\,litre \\ T = 273^\circ A \end{bmatrix} \xrightarrow{Isobaric} \begin{bmatrix} P = 1\ atm \\ V = V' \\ T = 573^\circ A \end{bmatrix}$$

$$\xrightarrow{Isothermal} \begin{bmatrix} P = 2\ atm \\ V = 23.5\ litre \\ T = 573^\circ A \end{bmatrix}$$

Since initial and final states are same as step $'a'$ and as U and H are state functions so $\Delta U\ and\ \Delta H$ are same as before i.e. $\Delta U = 900\,Cal\ and \Delta H = 1500\,Cal$. Work done in isobaric step $W_1 = P(V^/ - V)$

Here $V^/ = 2 \times 23.5 = 47\ litre$

So $W_1 = 1(47 - 22.4) Litre\ atm \equiv 595.3\ Cal.$

In the second isothermal step $W_2 = RT\ ln \dfrac{P_1}{P_2}$

$$= 1.987 \times 573\ ln\frac{1}{2} = -789\,Cal.$$

So total work = 595.3 – 789 = - 193.7 Cal.

$$q = \Delta U + W = 900 - 193.7 = 706.3\ Cal.$$

9. Ten litres of a mono-atomic gas expands adiabatically from 5 atm. to 1 atm. Final volume is 23.6 litre. Calculate the adiabatic work.

Answer:

$$\begin{aligned}
Adiabatic\ work &= nC_V(T_1-T_2) = nC_V\left[\frac{P_1V_1}{nR}-\frac{P_2V_2}{nR}\right] \\
&= C_V\left[\frac{P_1V_1-P_2V_2}{R}\right] = \frac{P_1V_1-P_2V_2}{\gamma-1} \\
&\quad [As\ R = C_P - C_V] \\
So\ here\ W_{ad} &= \frac{5\times 10 - 1\times 23.6}{1.66-1}[gas\ is\ mono-atomic] \\
&= 40\ litre-atm \equiv 968\ Cal.
\end{aligned}$$

10. **A given mass of an ideal gas** $(C_P = 5\,Cal.\mathrm{deg}^{-1}.mole^{-1})at\ 27°C$**is compressed adiabatically reversibly to one-quarter of its volume. Calculate the temperature after compression.**

Answer:

$$C_V = C_P - R = 5-2 = 3$$

So, $\gamma = \frac{C_P}{C_V} = 1.66$

Now $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$T_1 = 300°A;\ V_2 = \frac{V_1}{4}\ T_2 = ?$$

So, 300 $V_1^{+0.66} = T_2\left(\frac{V_1}{4}\right)^{+0.66}$

Or, $T_2 = 300\times 4^{+0.66} = 748.99°A$

11. **One mole of an ideal mono-atomic gas at** $27°C$ **is allowed to expand into vacuum from 10 litre to 20 litre; and one mole of the same gas expands isothermally and reversibly from the same initial to the same final volume. Calculate** $q\ and\ W$**in both cases.**

Answer:

In case 1 external pressure is 0. So the external work = 0 (20 – 10) = 0. Internal work is also zero, as the gas is ideal. So total work = 0, heat change = 0.

In case 2 work $= nRT\ \ell n\frac{V_2}{V_1} = 1\times 1.987\times 300\ \ell n\frac{20}{10}$

$$= 413.18\,Cal$$

As the process is isothermal; so heat absorbed = work done

So $q = 413.18\,Cal.$

12. **One mole of an ideal gas at $27^{\circ}C$ and 2 atom. Expands (i) isothermally and reversibly till the final pressure is 1 atm. (ii) isothermally against a constant external pressure of a 1 atm. till the final pressure equals to external pressure. Calcutta $dq, \Delta U\ and\ \Delta H$in each case.**

Answer:

Both the steps are isothermal so as the gas is ideal $\Delta U = 0\ and\ \Delta H =$ 0in both cases.

For isothermal process $dq = W$

In case 1 $W = nRT\ ln\frac{P_1}{P_2} = 1\times 1.987\times 300\ ln\frac{2}{1}$

$$= 413.18\,Cal.$$

In case 2 $W = RT\frac{P_1 - P_2}{P_1} = 1.987\times 300\times\frac{2-1}{2}$

= 298.05 Cal.

13. **One mole of an ideal mono-atomic gas initially at $27^{\circ}C$ and occupying a volume of 10 litres undergo adiabatic expansion in two different way, till the final volume in each case increases to 20 litres. (i) Adiabatic expansion against a constant external pressure of 1 atm and (ii) Adiabatic expansion against zero pressure.**

Calcutta the work done and final temperature in each case.

Answer:

Both the expansions are adiabatic and at the same time irreversible. So in case (i)

$$W = P_{ext}(V_2 - V_1) = 1(20 - 10) = 10\, litre\ atm$$

= 242 Cal.

In case (ii) $W = 0 \times Vol.\, Change = 0$

Now $W = C_V(T_1 - T_2) = \frac{3}{2} \times 1.987(300 - T_2)$

For mono-atomic gas $C_V = \frac{3}{2}R$.

In case (i)

$$242 = \frac{3}{2} \times 1.987(300 - T_2)$$

Or, $242 = 894.15 - 2.9805\ T_2$

Or, $T_2 = 218.8°A$

In case (ii) As $W = 0 \quad T_1 = T_2 = 300°A$

14. 100 gms of $N_2\ at\ 25°C$ are held by a piston under 30 atm. pressure. The pressure is suddenly released to 10 atm. under adiabatic conditions. If the molar heat capacity of N_2at constant value be $4.95\, Cal/°$, calculate the final temperature and $\Delta U$of the gas.

Answer:

This is an adiabatic and at the same time irreversible expansion.

Now

$$\begin{aligned} W_{irrev} &= P_2(V_2 - V_1) = P_2\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right] \\ &= nR\left[T_2 - T_1\frac{P_2}{P_1}\right] \end{aligned}$$

And $W_{ad} = nC_V(T_1 - T_2)$

So here $nC_V(T_1 - T_2) = nR(T_2 - T_1.\frac{P_2}{P_1})$

So, $4.95[298 - T_2] = 1.987\left[T_2 - 298.\frac{10}{30}\right]$

$$or,\ T_2 = 241.09^{\circ}A$$

Here number of moles $n = \frac{100}{28}$

So, $\Delta U = nC_V(T_2 - T_1) = \frac{100}{28} \times 4.95(241.09 - 298) = -1006\,Cal.$

15. A system undergoes a certain change in state by path 1 and the corresponding heat absorbed and the work term are 10K cal and 0 erg. respectively. For the same change in state by path II the respective quantities are 11 K.Cal and 0.5 $W_{\max}$, where $W_{\max}$represents the work if the specified change is reversibly carried out. Find $W_{\max}$in ergs.

Answer:

From 1^{st} law $dq = dU + W$

$dq\ and\ W$are path dependent; but dU is path independent.

In path I $dq = 10\ K.Cal \qquad W = 0$

$$So\ dU = 10K.Cal$$

In path II $dq = 11\,K.Cal \qquad W = 0.5\,W_{\max}$

So $11 = 10 + 0.5W_{\max}$

$$or W_{\max} = 2K.Cal = 2 \times 4.2 \times 10^{10} ergs$$

16. 0.1 mole of a mono-atomic perfect gas with C_V independent of temperature is made to undergo a reversible cyclic process consisting of the following steps:

State 1 (1 lit. 1 atom.) ⟶ State 2 (1 litre, 3 atm.)

State 2 ⟶ State 3 (2 litre, 3 atm.)

State 3 ⟶ State 4 (2 litre, 1 atom.)

State 4 ⟶ State 1

Calculate q ,W and ΔU for each step and for the complete cycle. Comment on thermodynamic nature of these functions on the basis of the evaluated values.

Answer:

$$\text{Temp at state 1 is} = \frac{1 \times 1}{0.1 \times 0.082} = 121.95^{\circ}A$$
$$\text{Temp at state 2 is} = \frac{3 \times 1}{0.1 \times 0.082} = 365.85^{\circ}A$$
$$\text{Temp at state 3 is} = \frac{3 \times 2}{0.1 \times 0.082} = 731.70^{\circ}A$$
$$\text{Temp at state 4 is} = \frac{1 \times 2}{0.1 \times 0.082} = 243.90^{\circ}A$$

$$T = \frac{PV}{nR}$$

Now $dq = dU + W = nC_V dT + PdV$

In Step 1

$$W_1 = PdV = 0$$
$$dU_1 = 0.1 \times \frac{3}{2} \times 1.987(365.85 - 121.95) = 72.69\, Cal$$

$$So\,q_1 = 72.69\,Cal$$

In Step 2

$$W_2 = \int_{V_1}^{V_2} PdV = P\int_{V_1}^{V_2} dV = P(V_2 - V_1) = 3(2-1) = 3\ litre\ atm.$$

$$= 72.6\,Cal.$$

$$\begin{aligned} dU_2 &= 0.1 \times 1.987(731.70 - 365.85) = 109.04\,Cal \\ q_2 &= 109.04 + 72.6 = 181.64\,Cal. \end{aligned}$$

In step 3

$$\begin{aligned} W_3 &= 0\ [dV = 0] \\ dU_3 &= 0.1 \times \frac{3}{2} \times 1.987 \times (243.9 - 731.70) = -145.38\,Cal \\ q_3 &= -145.38 + 0 = -145.38\,Cal \end{aligned}$$

In step 4

$$\begin{aligned} W_4 &= P\int_{V_2}^{V_1} dV = P(V_1 - V_2) = 1(1-2) = -1\ litre\ atm. \\ &\equiv -24.2\,Cal. \\ dU_4 &= 0.1 \times \frac{3}{2} \times 1.987 \times (121.95 - 243.9) \\ &= -36.35\,Cal \\ q_4 &= -36.35 - 24.2 = -60.54\,Cal. \end{aligned}$$

So total

$$\begin{aligned}
W &= W_1+W_2+W_3+W_4 \\
&= 0+72.6+0-24.2 = 48.4\,Cal \\
q &= q_1+q_2+q_3+q_4 \\
&= 72.69+181.64-145.38-60.54 \\
&= 48.41\,Cal \\
dU &= dU_1+dU_2+dU_3+dU_4 \\
&= 72.69+109.04-145.38-36.35 = 0
\end{aligned}$$

The process is cyclic so state functions will not change. As $dU = 0\, but\ q \neq 0\ and\ W \neq 0$ so only U is state function.

17. One mole of an ideal mono-atomic gas initially at STP experience a reversible process in which the pressure is trebled. The nature of the process is unspecified, but it is given that $\Delta U = 4KJ\ and\ q = 1.8KJ.$ Calculate the final temperature and volume and $\Delta H\ and\ W$for the process. Let the gas be taken the same final state, but by an isobaric reversible change, followed by isothermal reversible change. Calculate $\Delta H; \Delta U; q\ and\ W$for this sequence.

Answer:

For ideal mono-atomic gas $C_V = \frac{3}{2}R$
Now $\Delta U = C_V(T_2 - T_1)$ for 1 mole
So $4\times10^3 = \frac{3}{2}\times 8.313(T_2-273)$
So $T_2 = 593.78^\circ A$

$$Now\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ so\ \frac{1\times22.4}{273} = \frac{3\times V_2}{593.78}$$

So $V_2 = 16.24\, litre$

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

Here $P_2V_2 - P_1V_1 = 3 \times 16.24 - 1 \times 22.4 = 26.32\, litre - atm.$

$$\equiv 26.32 \times 101.38\, Joule$$

$$\equiv 2668.27\, Joule$$

So $\Delta H = 4000 + 2668.27 = 6668.27\, Joule = 6.66827\, K.J.$

Again $q = \Delta U + W$

So 1.8 = 4 + W

Or, W = -2.2 k.J.

If the same change is done by an isobaric followed by isothermal process ΔU *and* ΔHwould be same as they are state functions. But as the change is

$$\begin{array}{ccccc} 1\, atm & & 1\, atm & & 3\, atm \\ 22.4 & \xrightarrow{I} & V & \xrightarrow{II} & 16.24\, litre \\ 273^\circ A & & 593.78^\circ A & & 593.73^\circ A \end{array}$$

So $V = 48.72\, litre \qquad [P_1V_1 = P_2V_2]$

Isothermal change

As internal energy has not change in Step II

So ΔU_2 in Step I = 4 K. J.

$$W_1 = P(V_2 - V_1) = 1(48.69 - 22.4)\, litre\ atm \equiv 2665.28\, Joule$$

So $q_1 = 4000 + W_1 = 6665.28\, Joule$

In Step II $W_2 = RT\, ln\frac{V_2}{V_1} = 8.313 \times 593.78\, ln\frac{16.24}{48.72} = -5422.85\, Joule$

So $q_2 = -5422.85\, Joule$

So total $W = 2665.28 - 5422.85 = -2757.57\ Joule$

$$q = 6665.28 - 5422.85 = \ 1242.43\ Joule$$

18. One mole of an ideal gas expands from 10 litres to 50 litres at $27°C$ in the following two ways (i) isothermally reversibly and (ii) against a constant pressure of 1 atmosphere. Show by calculation in which case more heat will be absorbed during expansion.

Answer:

In isothermal processes heat absorbed = work done

In case (i) work = $RT\ ln\dfrac{V_2}{V_1}$

$$= 8.313 \times 300\, ln\frac{50}{10}$$

= 4013.77 Joule

In case (ii) work = $P_{ext}(V_2 - V_1)$

$$= 1(50-10) = 40\ litre - atm$$

= 4055.12 Joule

In case (ii) more work is done, so more heat is absorbed.

19. Find the motor increase in U, H, S, F and G in expanding one litre of an ideal gas at $25°C$ to 100 litresat the same temperature.

Answer:

The process is isothermal. So $\Delta U = \Delta H = 0$ as $\Delta U = C_V dT$ and

per mole.

In an isothermal expansion $\Delta S = R \ln\dfrac{V_2}{V_1}$ per mole

So here $\Delta S = 8.313\ \ln\dfrac{100}{1} = 38.28$ Joules/degree

Also in isothermal expansion $\Delta F_T = \Delta G_T = RT\ \ln\dfrac{V_1}{V_2}$ mole

---

20. Compare the thermodynamic efficiencies to be expected (a) When an engine operates between $1000^{\circ}K$ and $300^{\circ}K$,**(b) When an engine operates between** $1000^{\circ}K$ and $600^{\circ}K$ **and waste heat is passed to another engine working between**$600^{\circ}K$ *and* $300^{\circ}K$**.**

Answer:
Case (a) Efficiency $\eta_1 = \frac{1000-300}{1000} = 0.7$
Case (b) $\frac{W_1}{Q_1} = \frac{1000-600}{1000} = 0.4 \;\; W_1 = 0.4Q_1$
So waste heat $Q_2 = Q_1 - 0.4Q_1 = 0.6Q_1$ then the heat is passed to another which does work W_2 and

$$\frac{W_2}{0.6Q_1} = \frac{600-300}{600} = 0.5$$

$$So, \;\; W_2 = 0.3Q_1$$

Total work = $W_1 + W_2 = 0.4Q_1 + 0.3Q_1 = 0.7Q_1$
So total efficiency = $\frac{0.7Q_1}{Q_1} = 0.7$ *i.e.* same with the efficiency of the engine working between $1000^{\circ}C$ *and* $800^{\circ}K$.

21. Calculate ΔS **per litre of solution when pure** N_2, H_2 and NH_3 **gases are mixed to form a solution having the final composition**
$15\%\ N_2$; $55\%\ H_2$ *and* $30\% NH_3$**(all at S.T.P.).**

Answer:
This is a case of free mixing and we know that for free mixing

$\Delta S = -\sum X_i R \ln X_i/\text{mole}$. *Here* X_i =Mole fraction.

In the given problem $X_{N_2} = 0.15$; $X_{H_2} = 0.55$ *and* $X_{NH_3} = 0.30$

So

$$\begin{aligned} \Delta S &= -0.15 \times 1.987 \ln 0.15 - 0.55 \times 1.987 \ln 0.55 - 0.30 \times 1.987 \ln 0.30 \\ or, \Delta S &= (0.565 + 0.653 + 0.718) \text{ Cal/mole} \\ or, \Delta S &= 1.936 \text{ cal/mole} \end{aligned}$$

As they are S.T.P. 1 mole $\equiv$ 22.4 litre

So, $\Delta S/\text{litre} = 0.086$ Cal/deg/litre.

22. **A mole of steam is condensed at $100°C$, the water is cooled to $0°C$and frozen to ice. What is the difference in entropies of the steam and ice? The heats of vaporization and fusion are 540 cal. gm^{-1} and 80 cal. gm^{-1} respectively. Use the average heat capacity of liquid water as 1 cal .**

Answer:

Entropy change during condensation of steam

$$\Delta S_1 = -\frac{18 \times 540}{373}\,\text{Cal}/^{\circ} = -26.06\,\text{Cal}/^{\circ}$$

Entropy change during cooling of water from $100°C$ to $0°C$

$$\Delta S_2 = 18 \times 1\ \ln\frac{273}{373}\ \text{Cal}/^{\circ} = -5.62\ \text{Cal}/^{\circ}$$

Entropy change during freezing of water at $0°C$

$$\Delta S_3 = -\frac{18 \times 80}{273}\ cal/^{\circ} = -5.27\ cal/^{\circ}$$

So that entropy change = - 26.06 – 5.62 – 5.27 = -36.95 Cal $/°C$

Hence difference in entropy between steam and ice = 36.95 cal$/°$.

23. **An ideal heat engine operates between T_2 *and* T_1. Per cycle, q_1 is -4.5×10^6cal and ΔS_1 *is* $-15{,}000 Cal\ K^{-1}$; T_2 *is* $300°C$. Calculate (a) efficiency of the engine and (b) work done per cycle.**

Answer:

$$\begin{aligned}
\Delta S_1 &= \frac{q_1}{T_1}\ so, -15,000 = \frac{4.5\times 10^6}{T_1} \\
or,\ T_1 &= 3\times 10^2 = 300^\circ A \\
T_2 &= 573^\circ A \\
So\ efficiency\ \eta &= \frac{T_2 - T_1}{T_2} = \frac{573-300}{573} = 0.48\ i.e.\ 48\%
\end{aligned}$$

Now $\frac{q_2}{q_1} = \frac{T_2}{T_1}$

$$or,\ q_2 = -4.5\times 10^6\frac{573}{273} = -9.45\times 10^6\ Cal$$

So work done $W = q_2\frac{T_2 - T_1}{T_2} = -9.45\times 10^6 \times 0.48$

$$= -4.54\times 10^6\,\text{Cal.}$$

24. μ **for a Van-der-Waals gas is given by**

$$\mu = \left[\left(\frac{2a}{RT} - b\right)\right] / C_P$$

Calculate the value of ΔH**in calories for the isothermal** $(300^\circ K)$ **compression of 1 mole of nitrogen from 1 to 500 atm.**

$$(a = 1.34\,litre^2\ atm\ mole^{-2};\ b = 0.039\ litre/mole)$$

Answer:

$$\mu = -\frac{1}{C_P}\left(\frac{dH}{dP}\right)_T$$

So $-\frac{1}{C_P}\left(\frac{dH}{dP}\right)_T = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)$

$$or,\ \left(\frac{dH}{dP}\right)_T = -\left[\frac{2a}{RT} - b\right]$$

$$or,\ \int_{H_1}^{H_2} dH = -\left[\frac{2a}{RT} - b\right] \int_{P_1}^{P_2} dP$$

$or,\ \Delta H = (H_2 - H_1) = -\left[\frac{2a}{RT} - b\right]\ (P_2 - P_1)$ for isothermal compression.

$$or,\ \Delta H = -\left[\frac{2 \times 1.34}{0.082 \times 300} - 0.039\right]\ (500 - 1)$$

$$= -34.90 \text{ litre atm} \equiv -844.62\,\text{Cal}.$$

25. For $C0_2(g)$ at $300^\circ A$ and 1 atm. pressure $\left(\frac{\partial H}{\partial P}\right)_T = -10.2$ Cal mole^{-1}

atm^{-1} and $C_P = 8.919$ Cal mole^{-1}deg^{-1}. **Calculate the joule – Thomson co-efficient of the gas for the given temperature and pressure condition.**

Answer:

Joule – Thomson co-efficient $\mu_{J-T} = -\frac{1}{C_P}\left(\frac{dH}{dP}\right)_T$

So $\mu_{J-T} = -\frac{1}{8.919}\{-10.2\} = 1.1436\ \text{deg}.atm^{-1}$

26. An ideal mono-atomic gas undergoes a reversible process by which its volume and absolute temperature are each doubled. Calculate (a) $\Delta S$and (b) ΔG for this change if the gas is initially at S.T.P. Given there is one mole gas and its entropy at S.T.P. is 36.55 Cal K^{-1}.

Answer:

For the given change

$$\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$

The gas is ideal mono-atomic, so $C_V = \frac{3}{2} R$ also here

$$\frac{T_2}{T_1} = 2 \text{ and } \frac{V_2}{V_1} = 2$$

So $\Delta S = \frac{3}{2} R \ln 2 + R \ln 2 = \frac{5}{2} R \ln 2 = 3.44 \text{ Cal K}^{-1}$
To find ΔG,we write

$$G_2 = H_2 - T_2 S_2$$
$$G_1 = H_1 - T_1 S_1$$

So $(G_2 - G_1) = \Delta G = (H_2 - H_1) - T_2 S_2 + T_1 S_1$

Again $(H_2 - H_1) = \Delta H = C_P (T_2 - T_1) = \frac{5}{2} R (546 - 273)$

= 1356.13 Cal

$$S_2 = S_1 + \Delta S = 36.55 + 3.44 = 39.99$$

So $\Delta G = 1356.13 - 546 \times 39.99 + 273 \times 36.55$

$$= -10500.26\, Cal.$$

27. Calculate the freezing temperature of water under a pressure of 2 atm, given $\ell_f = 80 Cal/gm$; density of ice = 0.92 gms/c.c.

Answer:
Clapeyron equation is $\frac{dP}{dT} = \frac{L_f}{T(V_2 - V_1)}$

Here if $\frac{dP}{dT}$ is atm/deg then L_f should be litre-atm V should be in litre.

Now we know if P = 1 atm fr.pt. $T = 273^\circ C$

If P is made 2 atm $dP = (2 - 1) = 1$ then $dT = ?$

L_f =latent heat of fusion/mole = $18 \times 80 \text{Cal} \equiv 59.50 \text{ litre} - \text{atm}$

V_1 = Molar volume of ice = $\frac{18}{0.92} = 19.6 \text{ c.c} \equiv 0.0196 \text{ litre}$

So, $\frac{1}{dT} = \frac{59.50}{273\,(0.018-0.0196)}$

$$or,\ dT = -0.0073$$

So freezing point at 2 atm will be $-0.0073°C$.

28. **What is the boiling point of water at a place where the atmospheric pressure is 600 m.m.? $(\ell_V = 640 Cal/gm)$.**

Answer:
Clausius – Clapeyron equation is

$$\ln\frac{P_2}{P_1} = \frac{L_V}{R}\cdot\frac{T_2-T_1}{T_1T_2}$$

For water, if $P_1 = 1$ atm $\equiv 760$ m.m. then b.pt $T_1 = 373°A$

$$L_V = 540\times 18 = 9720\,\text{Cal mole}^{-1} \text{ if } P_2 = 600 \text{ m.m. } T_2 = ?$$

So,

$$\begin{aligned}\ln\frac{600}{760} &= \frac{9720}{1.987}\cdot\frac{T_2-373}{373\,T_2}\\ \frac{T_2-373}{373\,T_2} &= -4.83\times 10^{-5}\\ or,\ T_2 &= 366.4° \text{ i.e. } 93.4°C\end{aligned}$$

29. **What is the latent heat of fusion of tin $(m.pt\ 504°K)$ if its m.pt is raised by $0.328°C$ when pressure is increased by 10 atm? The volume change is 0.03894 c.c/gm.**

Answer:
$\frac{dP}{dT} = \frac{\ell_f}{T(V_2-V_1)}$ ℓ_f =latent heat of fusion / gm

$$V = \text{Volume/gm}$$

Here $\frac{10}{0.328} = \frac{\ell_f}{504 \times 0.03894}$

So $\ell_f = 598.35\,\text{c.c. atm} \equiv 14.480$ Cal gm^{-1}

30. **5 gm – moles of water initially at $27^\circ C$ are converted to a final state of vapour at $227^\circ C$, the conversion being effected under 1 atmospheric pressure. Assuming the vapour to behave ideally, compute the total change in entropy.**

[heat capacity of water = 1 cal/gm; heat capacity of water vapour = 0.40 cal/gm, latent heat of vaporization of water = 540 Cal/gm].

Answer:

Entropy change during heating 5 gm moles (i.e. 90 gm) water from $27^\circ C\ (i.e. 300^\circ A)$ to $100^\circ C (i.e.\ 373^\circ A)$ is

$$\Delta S_1 = 90 \times 1\ \ln \frac{373}{300} = 19.60\ \text{Cal}/^\circ$$

Entropy change during vaporization of 5 moles water at $373^\circ A$ is

$$\Delta S_2 = \frac{90 \times 540}{373} = 130.29\ \text{Cal}/^\circ$$

And entropy change during heating 5 moles vapour from $100^\circ C\ (i.e.\ 373^\circ A)$ to $227^\circ C (i.e.\ 500^\circ A)$ is

$$\Delta S_3 = 90 \times 0.40\ \ln \frac{500}{373} = 10.55\,\text{Cal}/^\circ$$

So total change $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$= (19.6 + 130.29 + 10.55)\ \text{e.u.}$$

$$= 160.44\,\text{Cal}/^\circ$$

Multiple Choice Questions

1. **Ideal gas rushing into vacuum is**
   - **(a) Reversible Process**
   - **(b) Irreversible Process**
   - **(c) Sometimes reversible and sometimes irreversible**
   - **(d) None of the above.**

   Answer:
   b

2. **The total change in internal energy in a cyclic process is**
   - **(a) Zero**
   - **(b) infinity**
   - **(c) Negative**
   - **(d) can not be said**

   Answer:
   a

3. **Work**
   - **(a) Depends on path**
   - **(b) does not depend on the path**
   - **(c) sometimes depend on the path**
   - **(d) None of these**

   Answer:
   a

4. **Which is an extensive property?**
   - **(a) Temperature**

(b) **volume**

(c) **density**

(d) **pressure**

Answer:
b

5. **Which is an intensive property?**

   (a) **Pressure**

   (b) **volume**

   (c) **viscosity**

   (d) **internal energy**

Answer:
a

6. **The expression of 1^{st} law of thermodynamics**

   (a) $q = \Delta H - W$

   (b) $\Delta U = \Delta H + P\Delta V$

   (c) $\Delta U = q + W$

   (d) $\Delta U = q - W$

Answer:
d

7. **The process in which temperature remains constant is called**

   (a) **isothermal process**

   (b) **isochoric process**

   (c) **isobaric process**

   (d) **adiabatic process.**

Answer:

a

8. **The process in which pressure remains constant is called**

   (a) isothermal process

   (b) isochoric process

   (c) isobaric process

   (d) adiabatic process.

Answer:

c

9. **The process in which volume remains constant is called**

   (a) isothermal process

   (b) isochoric process

   (c) isobaric process

   (d) adiabatic process.

Answer:

b

10. **When a system is incapable of exchanging either matter or energy with the surroundings then it is called**

    (a) open system

    (b) closed system

    (c) isolated system

    (d) none of these

Answer:

c

11. **When a system is capable of exchanging both matter and energy with the surroundings then it is called**
    - **(a)** **open system**
    - **(b)** **closed system**
    - **(c)** **isolated system**
    - **(d)** **none of these**

Answer:

a

12. **Which is a state function?**
    - **(a)** W
    - **(b)** q
    - **(c)** $\frac{q}{W}$
    - **(d)** $q-W$

Answer:

d

13. **The sum of internal energy and pressure volume energy is called**
    - **(a)** **entropy**
    - **(b)** **enthalpy**
    - **(c)** **heat capacity**
    - **(d)** **free energy**

Answer:

b

14. **The characteristic equation of gas is given by**
    - **(a)** $PV = RT$
    - **(b)** $PV = mRT$

(c) $mPV = RT$

(d) none of these

Answer:
b

15. The change in internal energy of a system depends upon

(a) initial and final states of the system

(b) the reversible path

(c) the irreversibility of the process

(d) the initial state of the system only.

Answer:
a

16. The expression of work done in isothermal reversible process for ideal gas is

(a) $W = nRT \ln \frac{V_2}{V_1}$

(b) $W = nRT \ln \frac{V_1}{V_2}$

(c) $W = nRT \ln \frac{P_2}{P_1}$

(d) none of these

Answer:
a

17. For ideal gas

(a) $\left(\frac{\partial H}{\partial T}\right)_P = 0$

(b) $\left(\frac{\partial H}{\partial T}\right)_V = 0$

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

(d) $\left(\frac{\partial U}{\partial P}\right)_T = 0$

Answer:
c

18. **The process in which heat is not allowed to enter into or to come out of the system, then the process is called**

(a) **isothermal process**

(b) **isochoric process**

(c) **isobaric process**

(d) **adiabatic process.**

Answer:
d

19. **Water at 4^0C, under pressure of 1 atm., $C_P - C_V$ is equal to**

(a) **positive**

(b) **negative**

(c) **zero**

(d) **none of these**

Answer:
c

20. **The change in internal energy for ideal gas in isothermal process is**

(a) **Zero**

(b) **infinity**

(c) **Negative**

(d) can not be said

Answer:
a

21. **The change in enthalpy for ideal gas in isothermal process is**

    (a) negative

    (b) infinity

    (c) zero

    (d) can not be said

Answer:
c

22. **In acyclic process $\oint dS$has value**

    (a) one

    (b) two

    (c) three

    (d) zero

Answer:
d

23. **Available internal energy is called**

    (a) enthalpy

    (b) entropy

    (c) Helmholtz free energy

    (d) Gibbs free energy

Answer:
c

24. **Free energy change for a reversible process is**

   (a) equal to zero

   (b) greater than zero

   (c) less than zero

   (d) none of these

Answer:

a

25. **In irreversible isothermal process, entropy of the universe**

   (a) increases

   (b) decreases

   (c) remains constant

   (d) none of these

Answer:

a

26. **In irreversible cyclic process, entropy of the universe is**

   (a) negative

   (b) positive

   (c) zero

   (d) none of these

Answer:

b

27. **If no heat is rejected to the sink then, $W_{\max}$ for reversible Carnot cycle is**

   (a) infinity

   (b) one

(c) zero

(d) none of these

Answer:
c

28. Joule-Thomson expansion is

(a) isoentropic

(b) isobaric

(c) isothermal

(d) isoenthalpic

Answer:
d

29. In Joule-Thomson effect, heating of a gas

(a) μ **is positive**

(b) μ **is negative**

(c) μ **is zero**

(d) none of these

Answer:
b

30. In Joule-Thomson effect, cooling of a gas

(a) μ **is positive**

(b) μ **is negative**

(c) μ **is zero**

(d) none of these

Answer:

a

31. **Entropy change is**

- **(a) dependent on the path of the transformation**
- **(b) independent of the path of the transformation**
- **(c) sometimes dependent, sometimes independent of the path of the transformation**
- **(d) none of these**

Answer:

b

32. **Reversible adiabatic process is regarded as**

- **(a) isothermal**
- **(b) isochoric**
- **(c) isobaric**
- **(d) isoentropic**

Answer:

d

33. $G = H - TS$ **is the expression for**

- **(a) Gibbs free energy**
- **(b) Helmholtz free energy**
- **(c) Clausius Clapeyron Equation**
- **(d) Gibbs Duhem equation**

Answer:

a

34. **Thermodynamic equilibrium means**

   (a) **only mechanical equilibrium**

   (b) **only thermal equilibrium**

   (c) **only chemical equilibrium**

   (d) **all of these**

Answer:
d

35. **In natural processes, the entropy**

   (a) **increases**

   (b) **decreases**

   (c) **remains constant**

   (d) **none of these**

Answer:
a

36. **By leaving the door of an electric refrigerator open, the temperature of the kitchen**

   (a) **increases**

   (b) **decreases**

   (c) **remains same**

   (d) **none of these**

Answer:
a

37. **We can devise an engine whose efficiency is always**

   (a) **greater than**

   (b) **less than**

- **(c) equal to**
- **(d) some times greater and some times less than the efficiency of Carnot engine**

Answer:

b

38. Which of the following is true always for spontaneous change at all temperature?

- **(a)** $\Delta H \rangle 0 \,\text{and}\, \Delta S \langle 0$
- **(b)** $\Delta H \langle 0 \,\text{and}\, \Delta S \langle 0$
- **(c)** $\Delta H \langle 0 \,\text{and}\, \Delta S \rangle 0$
- **(d)** $\Delta H \rangle 0 \,\text{and}\, \Delta S \rangle 0$

Answer:

c

39. The term chemical potential was first introduced by

- **(a) Maxwell**
- **(b) Duhem**
- **(c) Gibbs**
- **(d) Einstein**

Answer:

c

40. The efficiency of a heat engine is always

- **(a)** $<$**1**
- **(b)** $>$ **1**
- **(c) zero**
- **(d) 1**

Answer:

a

41. **In a solution, the activity of the solvent is**

    (a) equal to unity

    (b) equal to fugacity

    (c) always less than unity

    (d) always greater than unity

Answer:

a

Exercise

1. **Justify the Statement: "First law of thermodynamics is nothing but the law of conservation of energy."**
2. **Show that for $n$mole of ideal gas change in internal energy, $\Delta u = nC_v(T_2 - T_1)$.**
3. **Prove that more work can be obtained from reversible process than that from irreversible process.**
4. **Prove that $C_p - C_v = T\left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P$**
5. **Is C$_P$ always greater than C$_V$? Explain.**
6. **How will you prove that adiabatic P-V curve will be steeper than the isothermal P-V curve?**
7. **What is the relation between heat absorbed at constant pressure with that at constant volume?**
8. **Derive the expression of work done in isothermal reversible process for $n$mole of ideal gas?**
9. **Show that when $\gamma \rightarrow 1$, the work done in the adiabatic reversible expansion is equal to that of the isothermal reversible expansion for ideal gas.**
10. **Show that for $n$mole of ideal gas change in internal energy, $\Delta H = nC_P(T_2 - T_1)$.**
11. **Prove that work done in adiabatic reversible process is** $W_{rev(adia)} = \frac{1}{1-\gamma}[P_2V_2 - P_1V_1]$.
12. **For Vander Waals' gas show that $\left(\frac{\delta S}{\delta V}\right)_T = \frac{nR}{V - nb}$.**
13. **Show that for $n$mole of ideal gas in adiabatic reversible process**
    - **(a)** $TV^{\gamma-1}$ =**Constant**
    - **(b)** PV^{γ} =**Constant**

(c) $T^{\gamma}P^{1-\gamma}$ =Constant

14. Write down the definition of
    (a) Isolated system
    (b) Closed system
    (c) Open system.

15. What is entropy? What is the physical significance of entropy?

16. Show that $dq$is not a perfect differential but $\frac{dq}{T}$ is a perfect differential.

17. Prove that irreversible isothermal expansion of an ideal gas increases the entropy of the universe.

18. What are the thermodynamic criteria for :
    (a) a spontaneous reaction
    (b) an equilibrium reaction

19. Show that
    (a) $\left(\frac{\delta P}{\delta S}\right)_V = -\left(\frac{\delta T}{\delta V}\right)_S$
    (b) $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$

20. Define Joule-Thomson co-efficient (μ) for a gas. Show that Joule Thomson

    expansion is an isoenthalpic process.

21. What is the expression of Joule-Thomson Co-efficient? Show that expansion μ for a Vander Waals' gas is $\frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$.

22. What is inversion temperature of real gas?

23. Derive Gibbs Duhem equation for *n* mole of ideal gas.

24. Derive Clausius Clapeyron equation.

25. If the process is completely adiabatic then how much work is obtained from a reversible Carnot engine?

26. **If no heat is rejected to the sink then how much amount of work is obtained**

    from a reversible Carnot engine?

27. **Derive different expressions of Gibbs Helmholtz Equation.**

28. **Prove that entropy of the universe increases in irreversible cyclic process.**

Problems

1. **One mole of an ideal mono-atomic gas initially at $27°C$ and 10 atm. adiabatically expands against a constant pressure of 1 atm. till the volume is doubled. Calculate W; dU; $dH$and final temperature.**

2. **0.5 mole of an ideal mono-atomic gas initially at 5 atm. pressure and $0°C$is allowed to expand against a constant external pressure of 0.5 atm. Conditions are such that the final volume is 10 times the initial volume; the final gas pressure equals to the external pressure. Calculate $q, W, \Delta U; \Delta H; \Delta S\ and\ \Delta G$ for the process.**

3. **A cylinder is fitted with a frictionless piston and is kept in a thermostat. It contains 2 moles of an ideal gas at $27°C$ and 2 atm. pressure. Following are three separate experiments carried out independently with the above:**

    (a) **The piston is all on a sudden withdrawn to a position where pressure is reduced to 1 atm. and equilibrium restored.**
    (b) **Pressure is reduced at a single step from 2 to 1 atmosphere.**
    (c) **Pressure is reduced slowly to 1 atm. in such a way that the position of the piston remains unaltered if left to itself any moment during the operation.**

    Calculate in each case ΔE; ΔH; $q\ and\ W.$

4. **One mole of an ideal mono-atomic gas at $25°C$ and 5 atm is expanded to a final pressure of 1 atm (a) isothermally against a**

constant pressure of 1 atm and (b) adiabatically and reversible. Calculate for each expansion, final temperature, heat absorbed; $\Delta U \; and \; \Delta H.$

5. **The standard Gibb's free energy** (ΔG°) **for a certain reaction at different temperatures** $(T^\circ K)$ **is given by**

$$\Delta G^\circ (Cals) = -126400 - 5.44T \ln T + 104.7T$$

   Calculate the standard entropy change (ΔS°) **for the reaction at** $2000^\circ K.$

6. **Calculate the thermodynamic potential of a gm-mole of** $SO_2 \; at \; 25^\circ C$ **and 10 atm pressure.**

   (Given $G^\circ \text{ for} S0_2 = -71.8 \text{ K.Cal/mole})$

7. **Calculate the entropy of mixing 2 moles of** N_2 **and 3 moles of** H_2 **behaving as ideal gases.**

8. **One mole of benzene at normal boiling point of** $352.2^\circ K$ **vaporizes into gaseous state at a pressure of 0.1 atm. Calculate**$\Delta S \text{ and} \Delta G$**. [Enthalpy of vaporization is 7364** Cal mole^{-1}**].**

9. **The latest heat of fusion of deuterium is** $18.56^\circ A$ **is 47.0 Cal/g. mole. The slope** $\dfrac{dP}{dT}$ **is 40.5 Kg/**$\text{cm}^2 \text{ deg.}$ **Calculate the difference between molar volumes of solid and liquid deuterium at this temperature.**

10. **One mole of** $H_2 \; gas \; at \; 100^\circ C$ **is compressed adiabatically and reversibly from 1 atm to 10 atm. Assume ideal behaviour and calculate** $\Delta E, \Delta H$**,** $\Delta S \;\; and \; \Delta G$

    Given $C_P = 6.9 \, Cal \;\; \text{deg}^{-1} \;\; mole$

    Standard motor entropy at $25^\circ C$

$$S^\circ_{298} = 49 \; cal \;\; \text{deg}^{-1}$$

11. An ideal heat engine operating between a source having temperature $0^{\circ}C$and sink (T_2) produces 1000 Cal of work per cycle rejecting 6400 cal heat. Calculate the efficiency of the engine and temperature of the sink.

PHASE RULE

Objectives

- Definition
- Components
- Water System
- Cd-Bi System
- Fe-C system

The phase rule is an important rate for the quantitative treatment of the system in equilibrium. It enables to predict the conditions that must be specified for a system to exhibit equilibrium.

J.W. Gibbs enunciated the phase rule in 1876 while investigating heterogeneous equilibrium.

The phase rule states that "If the equilibrium in heterogeneous system is not influenced by electrical, magnetic or gravitational force, the number of degrees of freedom (F) of the system. The number of components (C) and the number of phases of the system are related by the equation

$$F + P = C + 2$$
$$F = C - P + 2$$

2.1 PHASE

A phase is defined as any homogeneous and physically distinct part of a system which is bounded by a surface and is mechanically separable from other part of the system.

1. A gas mixture constitutes a single phase only since gases are completely miscible.

   Example: A mixture of $N_2 \text{ and } H_2$ forms one phase only.

2. Immiscible liquids constitute different phases.

   Example: $CCl_4 \text{ and } H_2O$ which do not mix with each other constitute two phases.

3. Completely miscible liquids such as water and alcohol or benzene and $CHCl_3$ form one phase.

4. A solution of a substance in a solvent consists of one phase only.

   Example: Glucose solution in water

5. Each solid makes up a separate phase except in case of solid solutions.

   Example: $CaCO_{3(s)} \leftrightharpoons CaO_{(s)} + CO_{2(g)}$. It consists of three phases in equilibrium (two solid phase and one gaseous phase).

Similarly in the equilibrium reaction $Fe_{(s)} + H_2O_{(g)} \leftrightharpoons FeO_{(s)} + H_2(g)$. It consists of three phases in equilibrium (two solid phases and one gaseous phase).

6. A system consisting of a liquid in equilibrium with its vapor constitutes two phase viz. liquid phase and vapor phase each phase being separated from each other by a distinct boundary.
7. At freezing point, water constitutes three phases.
$Ice(s) \leftrightharpoons Water(l) \leftrightharpoons WaterVapor$

2.1.1 COMPONENTS

The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase can be expressed directly or in terms of chemical equations.
Example:

1. Water exists in three phases i.e are solid ⇔ liquid ⇔ vapor. However the composition of each phase can be expressed in terms of H_2O . Hence it is one component system.
2. The Sulphur system consists of four phases, rhombic, monoclinic, liquid and vapor but the chemical composition of all phase is “S”. Hence it is one component system.
3. Dissociation of NH_4Cl

$$NH_4Cl(s) \leftrightharpoons NH_3(g) + HCl(g)$$

If the dissociation is carried out in vacuum, then the number of component of the system is one because in gaseous phase both HCl and NH_3 are always present in equal amount.

However if the dissociation is carried in presence of arbitrary amount of NH_3 or/and HCl, then the number of components will be two and the composition of two phases can be represented as follow:

Phase	Composition
Solid	$NH_3(g)+HCl(g)$
Gaseous phase	$xHCl+yNH_3$

4. A system of saturated solution of NaCl consists solid salt, salt solution and water vapor. The chemical composition of all the three phases can be expresses as in terms of NaCl and H_2O . Hence it is a two component system.

5. In the decomposition of $CaCO_3$

   $CaCO_3(s) \Leftrightarrow CaO(s)+CO_2(g))$

   All these components ($CaCO_3$, CaO , CO_2) are not independent of one another. Any two of the three substances can be chosen independently variable constituents to express the composition of each phase by means of equation.

   CASE-I: When CaO and CO_2 are taken as two components

PHASE	COMPOSITION
$CaCO_3$	CaO + CO_2
CaO	CaO + OCO_2
CO_2	OCaO + CO_2

CASE-II: If CaCO $_3$ and CO $_2$ are chosen as two components

PHASE	COMPOSITION
$CaCO_3$	$CaCO_3$ + $O.CO_2$
CaO	$CaCO_3-CO_2$
CO_2	$OCaCO_3$ + CO_2

CASE-III: If $CaCO_3$ and CaO are chosen as two components

PHASE	COMPOSITION
$CaCO_3$	$CaCO_3$ +OCaO
CaO	$OCaCO_3$ +CaO
CO_2	$CaCO_3$ -CaO

6. In the dissociation reaction $CuSO_4.5H_2O \leftrightharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$. The composition of each phase can be represented by the components $CuSO_4$ and H_2O . Hence it is a two component system.

7. The decomposition of PCL_5

$$PCL_5(s) \Leftrightarrow PCl_3(s) + Cl_2(g)$$

   At low temperature, the no. of components is two because the third component is automatically fixed at low temperature. /but at high temperature all the compounds remain in gaseous state and thus it can be explained by only one component.

Degree of freedom of variance: "Degree of freedom" is the minimum number of independently variable factors such as temperature, pressure and composition of the phases which must be arbitrary specified in order to represent the condition of the system perfectly.
Example: For water system

$$Ice \Leftrightarrow Water \Leftrightarrow Vapors$$
$$Solid \quad Liquid \quad Gas$$

The three phases ice, water and vapor may be at equilibrium only for a definite temperature, and definite pressure. If the temperature or pressure is allowed to change, the three phases will not be in equilibrium and one of the phases will disappear. Thus the system would have no degrees of freedom. Consider the system

$$Water(l) \leftrightharpoons Water(vapor)$$

The state of vapor phase depends upon temperature and pressure but not on the concentration. For such a system, there is a fixed value of vapor pressure at a particular temperature. The system is said to be monovariant or univariant.
For a system consisting of water vapors only, we must mention the value of both temperature and pressure in order to describe the system. Hence the

system is bivariant or has two degrees of freedom.

ILLUSTRATION:

1. **Calculate the degree of freedom of the following systems**
   - **(a)** $I_2(s) \leftrightharpoons I_2(v)$
   - **(b) An aqueous solution of** $NaCl\ and\ Na_2SO_4$ **.**
   - **(c) Unsaturated solution of NaCl in equilibrium with its vapor.**
   - **(d)** Na_2SO_4 **in water in a closed container at 32.4** ^{0} **C.**
   - **(e)** $NaCl(s) \leftrightharpoons NaCl - water(aq) \rightleftharpoons Watervapour$

Answer:

(a) No. of phases = 2

Component = 1

So F = C – P + 2 = 1 -2 + 2 = 1

(b) No. of phase = 1

No. of component = 3 ($NaCl$, Na_2SO_4 , H_2O)

Degree of freedom = C – P + 2

= 3- 1 + 2 = 4

(c) Phase = 2 (liquid and vapor)

C = 2 ($NaCl$ and H_2O)

F = C – P + 2 = 2

(d) P = 2 (solution and vapor)

C = 2 (Na_2SO_4 and H_2O)

Since the temperature is fixed, so the phase rule will get reduced to

F = C – P + 1

= 1.2 + 2

= 1

(e) P = 3

C = 2 ($NaCl$ and H_2O)

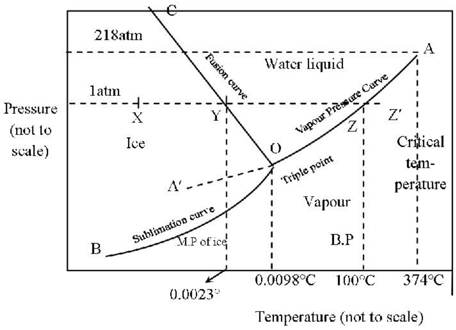
F = C – P + 2 = 2 – 3 + 2 = 1

2.2 Water System

$$Ice \leftrightharpoons Water \leftrightharpoons Vapour$$

In water system, there can be three forms of equilibrium,

1. $Liquid \leftrightharpoons Vapour$
2. $Solid \leftrightharpoons Vapour$
3. $Solid \leftrightharpoons liquid$



Curve OA

It represents the equilibrium between liquid water and vapour at different temperature. Therefore it is called Vapour Pressure Curve or Vapourization Curve of water.

- With rise in temperature, the vapour pressure increases.
- It can be seen that for any given temperature, there exists one and one vapour pressure and vice versa.
- Thus the degree of the system is one.
- At $100°C$, the vapour pressure of water equals the pressure of the atmosphere (760 mm). This is known as boiling point of water.
- The curve OA extends up to the critical point of water beyond which the two phases merge into each other.

The variation of vapour pressure with temperature is quantitatively given by Clapeyron-Clausius equation

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_e)}$$

or $\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

Curve OB - This curve represents the equilibrium between solid ice and water vapour. This is known as sublimation curve.

* It begins from O, the freezing point of ice, and ends at B, the absolute zero (– 273°C) at which no water vapor can exist and only ice phage left.

The variation of vapour pressure of ice with temperature is quantitatively given by Clapeyron-Clausius equation

$$\frac{dP}{dT} = \frac{\Delta H_s}{T(V_g - V_s)}$$

or, $\log \frac{P_2}{P_1} = \frac{\Delta H_s}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

Curve OC - It represents the equilibrium between ice and water. It is called fusion curve of ice.

- This curve shows the effect of on melting point of ice.

- The curve inclined towards the vertical axis, which indicates that melting point of ice is lowered by increase of pressure. The reason for this uncommon behaviour is linked to the decrease in volume that occurs when ice melts into water. Ice has a very open crystal structure in which the water molecules are held apart by the hydrogen bond between them which disintegrates on melting.

The Point “O”- The point ”O” is called the triple point because at this point an the three phases ice, water (l) and water vapour (v) coexists in equilibrium. The system is invariant at point “O”. If either the temperature or the pressure or both are changed, the three phases would no longer coexist and at least one of them would disappear.

This can be predicted from Claperyon-Clausius equation

$$\frac{dT}{dP} = \frac{\Delta H_f}{T(V_l - V_s)}$$

or, $\frac{dT}{dP} = \frac{T(V_l - V_s)}{\Delta H_f}$

Since density of ice is less than water, V_s is greater than V_l . In other words the expression on the right hand side of the above equation is negative. Hence $\frac{dT}{dP}$ also have a negative sign. That means increase of pressure must lower and decrease of pressure must raise the freezing point of water.

True Equilibrium – If the equilibrium can be attained from either direction by following any possible procedure than the system is said to be in a state of true equilibrium.

$Ice \Leftrightarrow Water$ at 1 atm and $273^\circ K$ the equilibrium can be attained by partially melting of ice or partially freezing of water.

Meta Stable Equilibrium: A system is said to be in a state of meta stable equilibrium under a given set of condition if the system can be attained or realized from only one direction by carefully changing the condition.

Ex. It is possible to cool water slowly and carefully to $271^\circ K\ or(-2^\circ C)$ without formation of ice but it is not possible to have water at – $271^\circ K$ by melting of ice.

Curve OA' . The curve AO can be further extended to A' by carefully super cooling the liquid and indicates a metastable state. Curve OA' is called vapor pressure curve of metastable water.

The liquid vapour system along the curve is said to be in metastable equilibrium because of the fact that as soon as a small piece of ice is brought in contact with super cooled liquid, the latter at once changes into solid ice and curve merges in OB.

Areas AOB, BOC, COA

AOB – water vapour

BOC – Ice Solid

COA – Liquid water.

ILLUSTRATION:

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1. **At $100^\circ C$, the specific volume of water and steam are 1 c.c. and 1673 c.c. Calculate the change in vapour pressure of the system by $1^\circ C$ change in temperature. The molar heat of vaporization of water in this range maybe taken as 9.7 Kcal.**

Answer:
Molar heat of liquid water

$$\begin{aligned} V_l &= 1\,cm^3 \times 10^{-3} mol^{-1} \\ &= 18 \times 10^{-6} m^3 mol^{-1} \end{aligned}$$

Molar volume of steam $V_g = 18 \times 1673\ cm^3 mole^{-1}$

$$= 30114 \times 10^{-6} m^3 mole^{-1}$$

Heat of vapourisation

$$\begin{aligned} \Delta H_v &= 9700\, cal\, mol^{-1} \\ &= 9700 \times 4.184 J\,cal^{-1} = 40584.8\ J\,mole^{-1} \\ \frac{dP}{dT} &= \frac{\Delta H_v}{T(V_g - V_l)} \end{aligned}$$

In this case

$$\begin{aligned} dT &= 1\,K \qquad T = 273 + 100 = 373\ K \\ dP &= \frac{\Delta H_v \times dT}{T(V_g - V_l)} = \frac{40584.8\ J\,mole^{-1} \times 1\,K}{373K(30114 - 18) \times 10^{-6}\, m^3 mole^{-1}} \\ &= 0.00361 \times 10^6 Nm^{-2} \\ &= 0.03561\ atm(1\ atm = 101325 Nm^{-2}) \\ &= 27.08 mm\ of\ Hg \end{aligned}$$

2. **The vapor pressure of water at $95^\circ C$ is found to be 634 mm . What would be the vapour pressure at a temperature of $100^\circ C$? The heat of vaporization in this range of temperature maybe taken**

as $40593\,J\,mole^{-1}$ **.**

Answer:

The integrated form of Claperyon – Clausius equation for liquid vapour equilibrium is

$$\ln\frac{P_2}{P_1}=\frac{\Delta H_v}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

In this case $T_1 = 273+95$

= 368 K

$$\begin{aligned} P_1 &= 634\,mm \\ T_2 &= 273+100 \\ &= 373K \\ P_2 &= ? \\ \ln\frac{P_2}{634} &= \frac{40593\,J\,mole^{-1}}{8.314\,JK^{-1}mole^{-1}}\left[\frac{5K}{368K\times 373K}\right] \\ P_2 &= 759.8\,mm \end{aligned}$$

3. **The specific vacuums of ice and water at** $0°C$ **are 1.0907** cm^3 *and* $1.0001\,cm^3$ **respectively. What would be the change in melting point of ice per atm increase of pressure? Heat of fusion of ice = 79.8** $cal g^{-1}$

Answer:

Molar volume of ice $V_s = 18\times 1.0907\times 10^{-6}m^3$

$$V_l = 18\times 1.001\times 10^{-6}m^3$$

T = 273 K

Molar heat of fusion of ice

$$\Delta H_f = 18\,gmol^{-1}\times 79.8\,cal\,g^{-1}\times 4.184\,J\,cal^{-1}$$

$$= 6009.9 Jmole^{-1}$$

Increase of pressure $dP = 1\,atm = 10132.5\,Nm^{-2}$

$$\frac{dT}{dP} = \frac{T(V_l - V_s)}{\Delta H_f} = \frac{273K \times (-0.0906) \times 18 \times 10^{-6}\,m^3}{6009.9\,Jmole^{-1}}$$

$$dT = \frac{273K \times 18 \times 10^{-6}(-0.0906)\,m^3 \times 101325 Nm^{-2}}{6009.9\ Jmole^{-1}}$$

= – 0.0075 K

Effect of change of temperature and pressure

* suppose it is desired to know the effect of heating the ice when it is under a pressure of 1 atm and at a certain temperature represented by point “X” in the figure. As the system is bivariant to the temperature can have any value at the same pressure.

As super cooled liquid water freezes spontaneously, it’s temperature rises to $0°C$. What is the service of heat for the process?

$$H_2O(l)(-10°C) \longrightarrow H_2O(s)\ (0°C)$$

In this case $\Delta H = 0$. No energy is transferred to or from the system. The energy liberated in the freezing process warms the system to $0°C$

4. **Distinguish between triple point and freezing point of a pure substance. b) For most pure substances which is appears to be higher? Triple point or freezing point.**

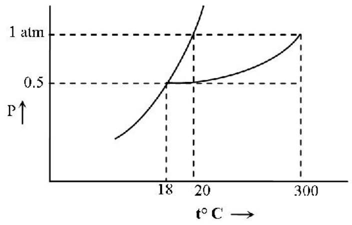
Answer:

(a) The triple point is the point where solid, liquid and vapour are in equilibrium with one another, with no other substance present. The freezing point is the point at which solid and liquid are in equilibrium under 1 atm total pressure. There must be some other substance present to achieve 1 atm pressure.

(b) The freezing point is higher for most substances which have a positive slope of the solid-liquid equilibrium in the phase diagram.

5. **A substance Z has it's triple point at $18^{\circ}C \, and \, 0.5 atm$, it's normal melting point is $20^{\circ}C$ and it's normal b.p is $300^{\circ}C$. Sketch the schematic phase diagram for Z.**

Answer:



6. **Using the following data for the iodine system, draw the phase diagram for the system:**

Triple point - $113^{\circ}C$, $0.12 atm$

Critical point - $512^{\circ}C$, $116\, atm$

Normal melting point $114^{\circ}C$

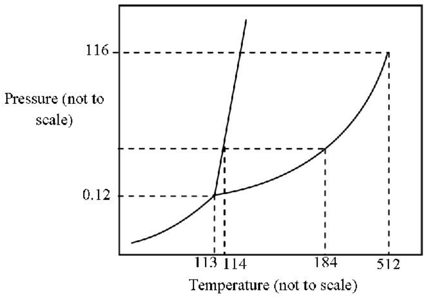
Normal boiling point $184^{\circ}C$

P (Solid) $>$ **P (liquid).**

Answer:

2.3 Sulphur System

- Sulphur exists in two crystalline forms rhombic and monoclinic with $95.6^{\circ}C$ as the transition temperature at one atmosphere pressure at which they can be transferred into one another.

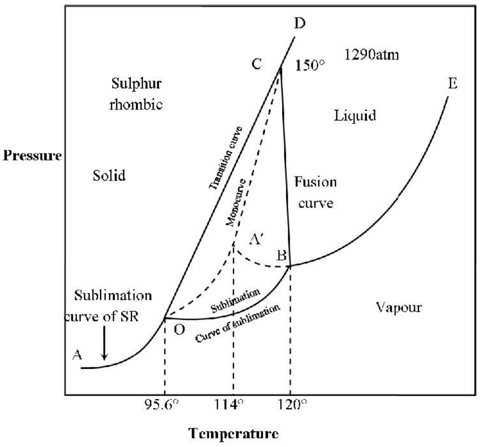


- Below 95.6°C , rhombic is stable while above it monoclinic is stable.
- The liquid form of Sulphur (S_L) undergoes changes in colour and viscosity when heated until it boils at 444°C .
- A system with all four phases can not coexist in equilibrium as F = C – P + 2 = 1– 4 + 2= –1 Degree of freedom becomes negative which has no meaning.
- There are four possibilities of three phases out of four coexisting at equilibrium which are

1. $S_R \leftrightharpoons S_M \leftrightharpoons S_L$
2. $S_R \leftrightharpoons S_M \rightleftharpoons S_V$
3. $S_R \leftrightharpoons S_L \leftrightharpoons S_V$
4. $S_M \rightleftharpoons S_L \leftrightharpoons S_V$

* Six possible system of two phases are

1. $S_R \rightleftharpoons S_M$
2. $S_R \rightleftharpoons S_L$
3. $S_R \rightleftharpoons S_V$
4. $S_M \rightleftharpoons S_L$
5. $S_M \rightleftharpoons S_V$
6. $S_L \leftrightharpoons S_V$



Curve OA - is the sublimation curve and gives the vapor pressure of rhombic sulphur at different temperature. It represents two phase equilibrium $(S_R S_V)$

Curve OB - is the sublimation curve of monoclinic sulphur. It gives vapor pressure of monoclinic sulphur at different temperature.

Curve OC - is the transition curve which gives effect of pressure on the transition temperature of rhombic sulphur into monoclinic sulphur. The equilibrium involved along the curve is $S_R S_M$.

Since the transformation of rhombic into monoclinic sulphur is accompanied by increase of volume, the increase of pressure causes a rise in transition temperature. This can be applied by Clausius – Claperyon equations which when applied to $S_R \leftrightharpoons S_M$ equilibrium may be put as $\frac{dP}{DT} = \frac{\Delta H_t}{T(V_B - V_A)}$

Since density of monoclinic sulphur is less than rhombic sulphur , V_B is larger than V_A . So the R.H.S of the above equation is therefore positive. Therefore increase of pressure raises the transition temperature.

Curve BC is the fusion curve of monoclinic sulphur. As the melting of monoclinic sulphur is accompanied by a slight increase of volume, it follows from Clausius- Claperyon equation that the melting point will rise slightly by increase of pressure. As the slope of this curve is much less than that of the curve OC, the curves meet at the point “C”.

Curve BE is the vapour pressure curve for liquid sulphur.

Curve CD is the fusion curve for rhombic sulphur $(S_R \leftrightharpoons S_L)$.

Meta Stable Equilibrium –

Since the conversion of one solid into another solid, as that of rhombic sulphur into monoclinic sulphur at the point “O” (95.6°) involves molecular rearrangements necessary for bringing about the change in the crystalline form, the process is naturally slow. Therefore unless heating is done extremely slowly, there is a possibility that the first solid may not change into the second solid at the normal transition point.

OA' – If the temperature of rhombic sulphur is allowed to rise rather quickly at about $95.6^{\circ}C$, it will persist in equilibrium with its vapour phase without changing into monoclinic sulphur for several degrees above the normal transition temperature. This along the curve OA' , the meta stable equilibrium $S_R \leftrightharpoons S_V$ exists.

BA' – Similarly if liquid sulphur is allowed to cool along the curve EB, the second phase may not separate out at B unless cooling is extremely slow. Thus the curve BA' represents the meta stable equilibrium $S_L S_V$.

Curve $A'C$ Fusion curve of metastable rhombic sulphur along much rhombic sulphur in metastable equilibrium with the liquid.

Triple Points

O : $S_R \leftrightharpoons S_M \leftrightharpoons S_V$
B : $S_M \leftrightharpoons S_L \leftrightharpoons S_V$
C : $S_R \leftrightharpoons S_M \leftrightharpoons S_L$
A' : $S_R \leftrightharpoons S_L \leftrightharpoons S_V$

Co-exist in meta stable equilibrium

These points cannot be shown on the plain of paper.

Condensed Phase Rule

If one of the variables like pressure or temperature of a system is kept constant, then the system is not known as condensed system and it will reduce the degrees of freedom of the system by one.

For such system the phase rule becomes

This is known as reduced or condensed phase rule.

Q. Define the following terms.

Triple Pont - A point (condition) at which gaseous liquid and solid phases of the system co-exist in equilibrium.

For water system at $0.0098°C\ and\ 4.58mmofHg$

$$H_2O(s) \leftrightharpoons H_2O(l) \leftrightharpoons H_2O(v)$$

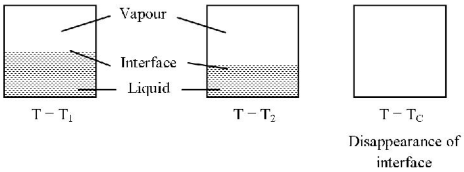
At triple point F = C – P + 2= 1–3+2 = 0

Melting Point – It is the temperature at which the vapour pressure of a liquid is equal to the external pressure.

Normal boiling point It is the temperature at which the vapour pressure of a liquid is equal to the 1 atom.

Critical temperature and Critical Pressure

The temperature above which liquid phase and vapour phase cannot be distinguished and the interface between two phase disappears.



The vapour pressure at critical temperature (T $_C$) is called critical pressure.

Critical Pont – The critical temperature and critical pressure together identifies the critical point of the substance. The liquid and vapour boundary in a phase diagram terminated the critical point.

Freezing Point – The temperature at which vapour pressure of the liquid is equal to vapour pressure of solid or both liquid and solid phase co-exists.

Melting Point –The temperature at which the liquid and solid phase of a substance co-exists in equilibrium at a specified pressure.

Normal Melting Point – It is the temperature at which the liquid and solid phase of a substance eo-exists in equilibrium at 1 atm total pressure.

Transition Temperature The temperature at which one form changes reversible into another at a given pressure is known as transition temperature $S_R \leftrightharpoons S_M$ at 1 atm.

At transition temperature, Gibbs energies of two phase are identical

$$G_{SR} = G_{SM}$$

i.e. $\Delta G = 0$

Eutectic Point - Two or more solid substances capable of forming solid solutions with each other have the property of lowering each other is freezing point and the minimum freezing point attainable corresponding to the eutectic mixture is termed as eutectic point. At eutectic point F = 0. One direction by carefully changing the condition.

Ex. It is possible to cool water slowly and carefully to 271K or (– $2^{\circ}C$) without formation of ice but it is not possible to have water at 271K by melting of ice.

ILLUSTRATION

1. **At $100^{\circ}C$, the specific volume of water and steam are 1cc and 1673 c.c. . Calculate the change in vapour pressure of the system by $1^{\circ}C$ change in temperature. The molar heat of vapourisation of water on this range may be taken as 9.7 kcal.**

   Answer:

   Molar volume of liquid water $V_l = 1cm \times 10 \times 18\, mole^{-1}$

   $$= 18 \times 10^{-6} m^3 mole^{-1}$$

   Molar volume of steam = $18 \times 1673\ cm^3 mole^{-1}$

   = $30114 \times 10^{-6}\, m^3 mole^{-1}$

   Heat of vaporization

   $$\begin{aligned} \Delta H_v &= 9700\, cal\ mole^{-1} \\ &= 9700 \times 4.184\, J mole^{-1} = 40,584.8\, J mole^{-1} \\ \frac{dP}{dT} &= \frac{\Delta H_v}{T(V_g - V_l)} \end{aligned}$$

In the case

$$\begin{aligned}
dT = 1\,K \quad T &= 273 + 100 = 373\,K \\
dP = \frac{\Delta H_v \times dT}{T(V_g - V_l)} &= \frac{40584.8\,J\,mole^{-1} \times 1\,K}{378\,K(30114.18) \times 10^{-63} mole^{-1}} \\
&= 0.00361 \times 10^{6}\,Nm^{-2} \\
&= 0.003561 atm (1 atm = 101375 Nm^{-2}) \\
&= 27.08\,mm\ of\ Hg.
\end{aligned}$$

2. **The vapour pressure of water at 95 ^{o} c is found to be 634mm. What would be the vapour pressure at temperature of 100 ^{o} c The heat of Vapourization in this range of temperature may be taken as 40935 J mole $^{-1}$.**

Answer:

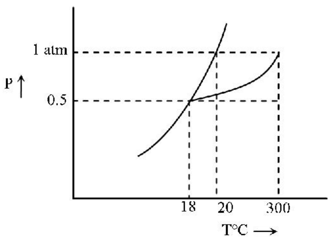
The integrated form of Claperyon - Clausices equation for liquid vapour equilibrium is $\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

In this case

$$\begin{aligned}
T_1 &= 273 + 95 \ = \ 368K \\
P_1 &= 634\,mm \\
T_2 &= 273 + 100 = 373K \\
P_2 &= \ ? \\
\ln \frac{P_2}{P_1} &= \frac{40593\,J\,mole^{-1}}{8.314 JK^{-1} mole^{-1}} \left[\frac{5K}{368K \times 313K} \right] \\
P_2 &= 759.8mm.
\end{aligned}$$

3. **A substance Z has it's triple point at $18^{\circ}C$ and 0.5 atm. Its normal melting point is $20^{\circ}C$ and its normal boiling point is 300˚C . Sketch the schematic phage diagram for Z.**

Answer:



4. **Using the following data, draw the phage diagram for the system**

   Triple point - $118°C$, $0.12\, atm$

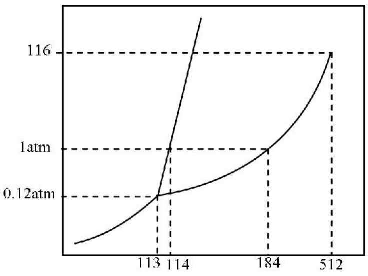
   Critical point - 512˚C , 116 atm

   Normal Melting point - $114°C$

   Normal boiling point - $184°C$

$$\rho_{Solid} > \rho_{liquid}$$

Answer:



Eutectic Reaction

An eutectic reaction is an isothermal reversible reaction in which two metals are completely soluble in the liquid state but completely insoluble in solid phase. Hence below the eutectic point they crystallize as alternate layers of solid structures which is known as eutectic.

$$\text{Liquid} \underset{solid3}{\overset{Cooling}{\rightleftarrows}} \text{Solid 1+ Solid 2}$$

$$Liquid\ Iron \underset{solid3}{\overset{Cooling}{\rightleftarrows}} \text{Cementite +Austenite}$$

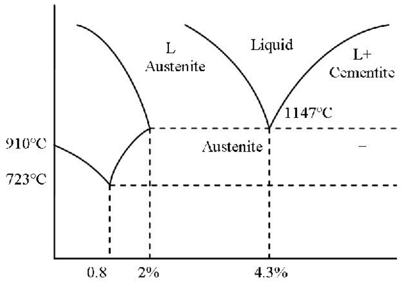


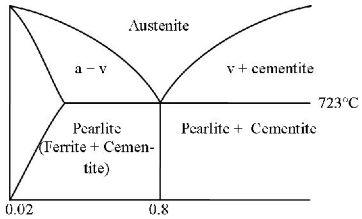
Figure 2.1: In iron-carbon alloy system, the eutectic temperature is 1147^o C below which austenite and cementite crystalizes

Eutectoid Reaction:

An eutectoid reaction is an isothermal and reversible reaction in which a solid phase forms two new solid.

$$Solid_1 \overset{Cooling}{\longrightarrow} Solid2 + Solid\ 3$$

$$Austenite\ (V - Iron) \underset{solid3}{\overset{Cooling}{\rightleftarrows}} \text{Ferrite + cementite (Pearite)}$$



In this reaction the crystalline austenite (Veron) on cooling below the eutectoid point ($723°C$)(0.8) solidifies as Pearite which is an alternate layer of two solid structures namely ferrite & cementite. At the eutectoid temperature $723°C$, ferrite & cementite are in equilibrium with austenite.

Peritactic Reaction:

Peritactic transformation occurs when a liquid and a solid phase of fixed proportions react at a fixed temperature to yield a single solid phase. The solid products form at the interface between the two reactants and can form a diffusion barrier. This causes such reactions to generally proceed much more slowly than eutectoid **transformation**.

OR

It is an isothermal reversible reaction in which a liquid and a solid phase react to form another solid phase on cooling.

$$Liquid + Solid \overset{Cooling}{\longrightarrow} Solid2$$

Ex. $Liquid + \delta - Iron \overset{Cooling}{\longrightarrow} Austenite\,(V - iron)$

On cooling below $1539°C$, the liquid transformation gradually to $\delta - Iron$ up to $1400°C$ when the carbon content is up to 0.5%, when liquid iron having 0.1%, carbon content is cooled to a temperature of $1493°C$, $\delta - Iron$ gradually changes to r-Iron. This temperature $1493°C$, is known as the peritectic point in which δ , liquid and r-Iron coexist.

Peritectoid : Solid 1+ Solid 2 $\underset{solid3}{\overset{Cooling}{\rightleftarrows}}$ Solid 3

2.4 Bi-Cd Eutectic System

1. **Curve AO -** It shows the effect on freezing point of Bi on addition of Cd in small quantities. The curve indicates that the melting or freezing point of Bi falls gradually on adding Cd, along AO, till the lowest point O ($140°C$) is reached. At O, no more Cd can go in solution and hence m.p does not fall any further and if Cd is added, it separates as the solid phase.

2. **Curve BO** – It shows the effect of freezing point of Cd on gradual addition of small amounts of Bi to it. Point “B” is the melting point of pure Cd. Along BO, the m.p. gradually falls on addition of Bi, the lowest point “O” is reached, when the solution get **saturated** w.r.t. Bi and m.p. of Cd does not fall any more.

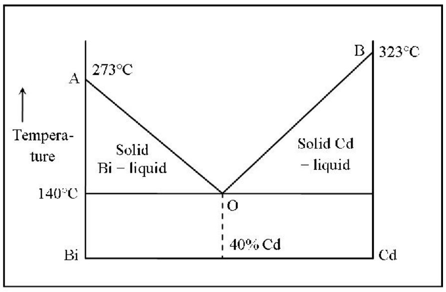


Fig: Mass% Cd

Eutectic Point "O" The two curves AO and BO meet at O, where three phases (Solid Bi, solid Cd and their solution) coexist and hence the system is invariant. The point "O" represents a fixed composition (of 40% Cd and 60% Bi) and is called eutectic point.

Area AOB represents solution of Bi, Cd. It is called liquids curve i.e. above it only liquid exists.

2.5 Iron – Carbon Alloy System

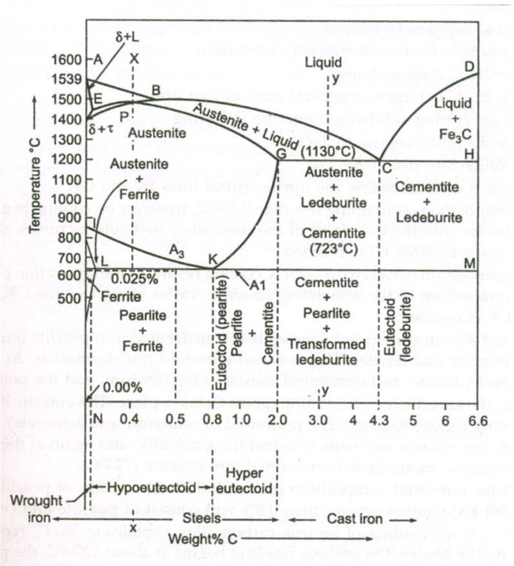
Iron is in molten form above $1539°C$. On cooling below $1539°C$, solidifies to δ –Iron which has BCC structure. On further cooling below $1400°C$, δ - form rearranges to r-form which is fcc structure. In the r-form at loses its the magnetic property and becomes non-magnetic. On further cooling at about $910°C$, the F.C.C., non-magnetic r-form of Iron changes to B.C.C. non-magnetic α– form of iron. At about $769°C$, α– Iron (BCC) becomes magnetic without change in structure. This temperature $(769°C)$ is known curie temperature.

α -Fe magnetic B.C.C	α -Fe non-magnetic B.C.C	r-Fe F.C.C non-magnetic	δ -ferrite B.C.C magnetic	Liquid
-768 ^{o} C	769-910 ^{o} C	910-1404 ^{o} C	1404-1539 ^{o} C	1539- ^{o} C

In Iron Carbon system, the point of interest is up to 6.7% C &within this region the Fe-C alloy system can be classified into

1. up to 0.0008% C → Wrought Iron (Commercially Pure Iron)
2. up to 0.8% C → Hypo eutectoid steel
3. up to 2% C → Hyper eutectoid steel
4. above 2% → 6.7% → Cast Iron

Phase diagram of Iron Carbon alloy system



A eutectic reactor occurs at $1150°C$ with eutectic composition of 4.3% to a mixture of r- ferrite (austenite) and cementite. This mixture is known as Ledburite.

An eutectoid reaction occur at $723°C$ at composition 0.8% carbon to form $\alpha-$ ferrie & cementite. This mixture is known as Pearlite.

1. The curve ABCD represents the liquidus line of the mixture of iron and dissolved carbon. Above this curve only liquid Phase exists.
2. The curves AEPGCH is the solidus line below which only solid phase exists.

3. On the solid line, when carbon is progressively added to iron, the melting point of alloy decreases up to ‘C” where the carbon content is 4.3 at 1147$^\circ C$. On further addition of carbon it matches the point ‘H’ where the carbon content is 6.7%.
4. Within the area AEB, the alloy exist as δ - Iron & liquid. The region DCH consists of cementite and liquid.
5. The transformation of r-Iron (Austenite) to ferrite is represented by curve IJ and transformation of Austenite to cementite is represented by curves GJ. The line LJ at 723$^\circ C$ depicts the eutectoid point “J” when austenite transforms to Pearlite.
6. At 1147$^\circ C$, eutectic transformation of Austenite, cementite to Ledburite and cementite takes place. The eutectic liquid containing 4.3% C, on cooling freezes to Ledburite and on further cooling austenite is converted to cementite.
7. At 723$^\circ C$, austenite transformed to Pearlite. So up to 0.8% C, steel consists of mainly ferrite and Pearlite composition and from 0.8C to 2% C, steel consists of Pearlite and cementite. Above 2% C composition, the cast Iron will be cementite and Ledburite.