

Work done in reversible isothermal expansion

$$W = \cancel{nRT} - nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

work done in compression $V_2 - V_1$

$$W = -nRT \ln \frac{V_1}{V_2} = -nRT \ln \frac{P_2}{P_1}$$

In adiabatic expansion

$$\Delta U = 0 + W$$

$$W = \Delta U = C_V \Delta T$$

Zeroth law of thermodynamics

$$A \rightleftharpoons C$$

$$B \rightleftharpoons C$$

then $A \rightleftharpoons B$

If A is in equilibrium with C and B is also in equilibrium with C then A is in equilibrium with B. Application of thermometer

Second law of thermodynamics

Heat can not be completely transformed into work is maximum in reversible process. expansion in vacuum, work done is zero.

Cyclic process - $\Delta U = 0$

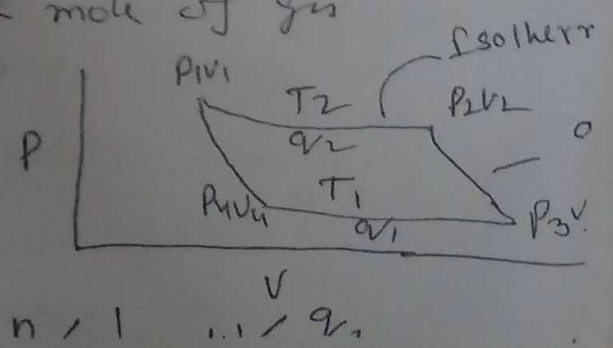
$q = -w \Rightarrow$ Carnot cycle

Reversible cyclic process - Carnot employed reversible cycle to demonstrate maximum convertibility of work. He considered one mole of gas

$$W = q_2 \left(\frac{T_2 - T_1}{T_2} \right)$$

$$\frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$$



(3)

Carnot theorem \rightarrow All periodic machines working reversibly between same two temperatures have the same efficiency.

Second law \rightarrow It is impossible to convert heat into work without compensation.

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \quad \text{or} \quad \frac{q_{rev}}{T} = \text{constant} = \text{entropy change.}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

$q = +ve$ heat absorbed
 $q = -ve$ heat

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

$$\Delta S = \frac{q_{rev}}{T}$$

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

Entropy change in an isothermal expansion of an ideal gas.

$$\Delta U = 0$$

$$\text{So } q_{rev} = -W$$

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

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{sys} + \Delta S_{sur} \geq 0 \quad \text{or} \quad \Delta S$$

equal to 0 \rightarrow reversible

greater than 0 \rightarrow irreversible

Entropy of the system and surroundings taken together remain constant in reversible process and increases in irreversible process. Entropy of the universe is increasing.

Energy of universe remain constant, entropy of the universe tend towards a ~~max~~ maximum.

Entropy change of an ideal gas with change in P, V and T .

(I) T and V changes, $P = \text{constant}$ —

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad \text{--- (I)}$$

(II) T and P changes $V = \text{constant}$

$$\Delta S = nC_P \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} \quad \text{--- (II)}$$

(a) For isothermal process

Eq. (I) becomes $\Delta S_T = nR \ln \frac{V_2}{V_1} = -nR \ln \frac{P_2}{P_1}$

(b) Isobaric process $\Delta S_P = nC_P \ln \frac{T_2}{T_1}$

(c) Isochoric process $\Delta S_V = nC_V \ln \frac{T_2}{T_1}$

Entropy of mixing —

$$\Delta S_{\text{mix}} = -R \sum n_i \ln x_i$$

where $n_i = \text{number of moles}$ of each constituent of the mixture.
 $x_i = \text{mole fraction}$

for a total of 1 mole of gas mixture

or Molar

$$\Delta S_{\text{mix}} = -R \sum x_i \ln x_i$$

molar entropy of mixing.

Work and free energy

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Work function $A = U - TS$
free energy functn. $G = H - TS$

— ΔG gives the maximum work obtainable

Net work = $-\Delta G$ that can be obtained from a system at constant T and P

$$\Delta G = \text{Gibbs free energy.}$$

Variation of free energy with P and T .

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

$$\Delta G \leq 0 \quad \begin{array}{l} 0 - \text{reversible} \\ < 0 - \text{irreversible} \end{array}$$

Gibbs - Helmholtz Equation

$$\Delta G = \Delta H + T \left(\frac{\partial (\Delta G)}{\partial T} \right)_P$$

Applicable to all processes at constant P

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

Thermodynamics of open system, Partial Molar Property

Thermodynamic properties U, H, S, A, G are extensive properties because their values change with change in mass (no. of moles). In derivation of various thermodynamic equations change of T and P only. The system was considered to be closed system. Under consideration was supposed to be closed system there could be no change in mass of the system.

When we consider open system, mass (no. of moles) of components changed. In that case an extensive property X must be function of T, P and no. of moles of w components.

$$X = f(T, P, n_1, n_2, n_3, \dots, n_j) \quad \text{--- (I)}$$

where $n_1, n_2, n_3, \dots, n_j = \text{Total no. of moles} = N$

For small change in T, P and N the change in property

$$dX = \left(\frac{\partial X}{\partial T}\right)_{P, N} dT + \left(\frac{\partial X}{\partial P}\right)_{T, N} dP + \left(\frac{\partial X}{\partial n_1}\right)_{T, P, n_2, n_3, \dots, n_j} dn_1 + \dots + \left(\frac{\partial X}{\partial n_j}\right)_{T, P, n_1, n_2, \dots, n_j} dn_j \quad \text{--- (II)}$$

The quantity $\left(\frac{\partial X}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_j}$ is called partial molar property of the i th component, represented as \bar{X} .

Thus the i th component in a system

$$\begin{aligned} \text{Partial Molar internal energy} &= \left(\frac{\partial U}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_j} = \bar{U}_i \\ \text{" " enthalpy} &= \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_j} = \bar{H}_i \\ \text{entropy} &= \left(\frac{\partial S}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_j} = \bar{S}_i \end{aligned}$$

Chemical Potential

Partial molar free energy is designated as chemical potential and represented as

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_j} = \bar{G}_i = \mu_i = \text{Chemical potential} \quad (I)$$

Chemical potential of a given substance is the change in free energy of the system that results on the addition of one mole of that substance at constant T and P to such a large quantity of the system that there is no appreciable change in the overall composition of the system.

$$G = f(T, P, n_1, n_2, \dots, n_j)$$

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \dots, n_j} dn_1 + \dots \\ &\quad + \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_j} dn_i \\ &= \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N} dP + \mu_1 dn_1 + \dots + \mu_j dn_j \end{aligned} \quad (II)$$

If T and P remains constant

$$(dG)_{T, P} = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j$$

If the system has a definite composition

$$(dG)_{T, P, N} = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_j dn_j \quad (III)$$

Integration of eq. (III) we get

$$(G)_{T, P, N} = n_1 \mu_1 + n_2 \mu_2 + \dots + n_j \mu_j \quad (IV)$$

The total differential of eq. (IV) gives

$$n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_j d\mu_j$$

$$dg = dg + n_1 du_1 + n_2 du_2 + \dots + n_j du_j \quad \text{--- (8)}$$

or

$$n_1 du_1 + n_2 du_2 + \dots + n_j du_j = 0 \quad \text{--- (V)}$$

$$\text{or } \sum n_i du_i = 0$$

This relation (V) is known as Gibbs-Duhem equation

For a system having only two components eq. (V) is writ.

$$n_1 du_1 + n_2 du_2 = 0$$

$$du_1 = -\frac{n_2}{n_1} du_2$$

Thus if μ_1 increases μ_2 must decrease.