

Suppose we wish to measure the temperature of a tank of water. We first carry out a Carnot cycle between two reservoirs at steam-point T_s and ice-point T_i . Let Q_s and Q_i denote the amounts of heat absorbed and rejected. We then carry out a second Carnot cycle between the reservoir at steam-point and tank of water (or between reservoir at ice-point and tank of water). Let, for simplicity, Q_s denote the heat absorbed at steam-point and Q denote the heat rejected at temperature T of the tank. Then

$$\frac{Q_s}{Q_i} = \frac{T_s}{T_i} \quad \text{and} \quad \frac{Q_s}{Q} = \frac{T_s}{T}$$

where $T_s - T_i = 100^\circ\text{C}$.

Knowing Q_s , Q_i and Q experimentally, we can determine the unknown temperature T_s , T_i and T . In actual practice Kelvin scale is established by correcting the readings of a gas temperature.

5.7 ABSOLUTE ZERO OF TEMPERATURE

If the final engine in the series as arrangement shown in Fig.5.15 above is imagined to reject no heat at a certain temperature, the temperature in question is termed as absolute zero. Thus, absolute zero is the temperature of a reservoir to which no heat will be rejected by a Carnot engine operating between this reservoir and a reservoir at higher temperature. Note that under this condition, all the heat absorbed is converted into work. The absolute zero, therefore, represents an absolute zero of energy.

5.8 CLAUSIUS THEOREM

From the description of the second law of thermodynamics and Kelvin temperature scale, we have

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Taking heat Q_2 rejected by the system, a negative quantity, we can write

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad \dots (5.19)$$

or
$$\sum \frac{Q}{T} = 0$$

for the Carnot cycle. The generalized form of Eq.(5.19) is called Clausius Theorem. It states that

"If a system undergoing a cyclic process (reversible or irreversible) exchanges quantities of heat $Q_1, Q_2, Q_3, \dots, Q_n$ with a set of reservoir at temperatures $T_1, T_2, T_3, \dots, T_n$ respectively, the algebraic sum of the ratios Q/T is either less than or equal to zero".

This is mathematically expressed by the relation

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \dots \leq 0$$

or

$$\boxed{\sum \frac{Q}{T} \leq 0}$$

... (5.20)

and is known as Clausius Inequality.

If the number of reservoirs $N \rightarrow \infty$ and the system exchanges only infinitesimal quantities of heat with each reservoir, the sigma notation can be replaced by integral notation. That is

$$\oint \frac{dQ}{T} \leq 0 \quad \dots (5.21)$$

where the symbol \oint implies integration over a closed path. It should be noted that temperatures involved are only those of reservoirs but not of system. The equality sign holds for reversible cyclic processes while the inequality sign holds for the irreversible processes.

Let us divide a reversible cycle into a number of Carnot cycles by drawing a set of adiabatics and isothermals as shown in Fig.(5.6).

Let us consider one such Carnot cycle $KLMNK$. It consists of two isothermals KL and MN and two adiabatics LM and NK . There

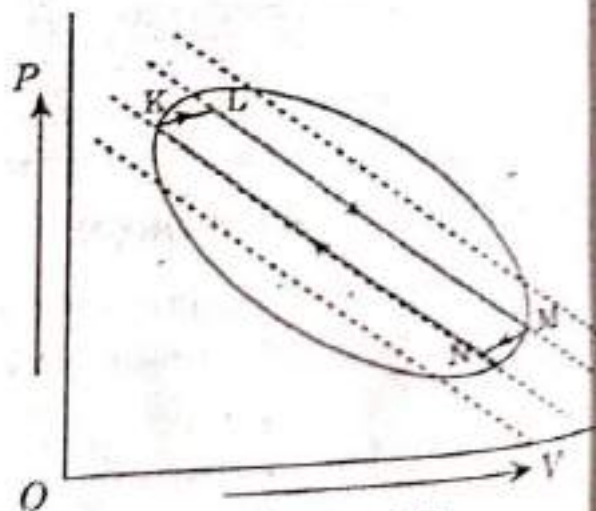


Fig. 5.6

no absorption or rejection of heat along adiabatics. However, a small amount of heat dQ_1 is absorbed along the isothermal KL at temperature T_1 of the source and a small amount of heat dQ_2 rejected at temperature T_2 of sink (it is taken negative) along the isothermal MN . We have for the given Carnot cycle

$$\frac{dQ_1}{T_1} = -\frac{dQ_2}{T_2} \quad \text{or} \quad \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

Taking into account the main cycle comprising a number of isothermals, we can write

$$\sum \left(\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} \right) = 0 \quad \text{or} \quad \sum \frac{dQ}{T} = 0$$

If the Carnot cycles comprising the main cycle is infinitely large, we replace the summation by integration. That is

$$\oint \frac{dQ}{T} = 0 \quad \text{Clausius theorem for reversible cycle.}$$

This is known as Clausius theorem for reversible cycles.

However, for irreversible cycles, we have $\oint \frac{dQ}{T} < 0$

ENTROPY AND MATHEMATICAL FORMULATION OF SECOND LAW

In the formulation and application of the second law of thermodynamics, Clausius was the first to introduce a physical

quantity, called entropy which has proved to be of great importance not only in the further development of thermodynamics but also in the recognition of a fundamental law of nature. Entropy is a Greek term referring to a "Change". Clausius developed the idea of entropy as follows :

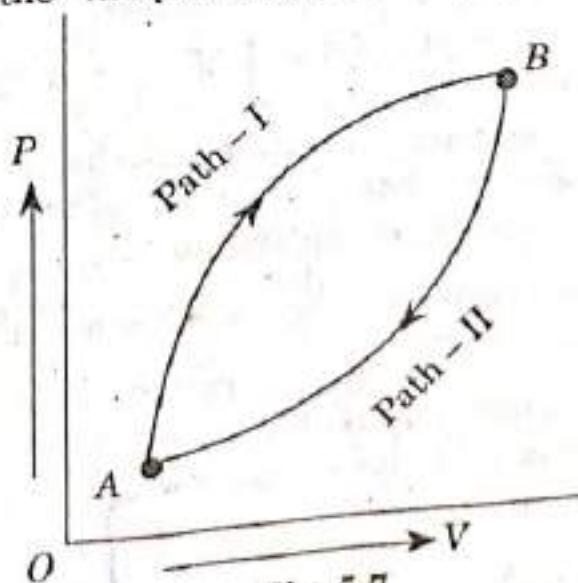


Fig. 5.7

Thermodynamics, specifically to express it in particular differential form. SECOND LAW OF THERMODYNAMICS (Chap 5) Path is not exact differential represented by the given curve. Fig. (5.7). Select arbitrary points A and B on the closed curve. For a reversible cycle, Clausius inequality reduces to

$$\oint \frac{dQ}{T} = 0 \quad \dots (5.22)$$

is independent of path. They are initial and final state.

It is equivalent to the sum of two integrals along the paths I and II.

$$\oint \frac{dQ}{T} = \int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ}{T}$$

$$\int_A^B \frac{dQ}{T} = - \int_B^A \frac{dQ}{T}$$

$$\text{or } (I) \int_A^B \frac{dQ}{T} = (II) \int_A^B \frac{dQ}{T} \quad \dots (5.23)$$



i.e., the integrals along the two reversible paths are the same. Since, the original cycle was entirely arbitrary, it follows that the

integral $\int_A^B \frac{dQ}{T}$ is the same along all the reversible paths from A

to B. In the language of mathematics, the integrand $\frac{dQ}{T}$ is an exact or perfect differential of some function S represented by dS. That is

$$\int_A^B \frac{dQ}{T} = \int_A^B dS = S_B - S_A$$

in complete agreement with the properties of definite integral, whose value depends on the limits of integration. The quantity S is termed as entropy of the system. Note that dQ is an inexact or imperfect

★ differential but $\frac{dQ}{T} = dS$ is an exact differential independent of path. It follows that

behaves as an integrating factor which is used to transform an inexact differential into an exact differential in mathematics. Hence, the change in entropy of a system is given by

$$dS = \frac{dQ}{T} \quad \dots (5.25)$$

which is also the mathematical formulation of the Second Law of Thermodynamics. The MKS unit of entropy is joule/K.

* Probability means chance
of substance, a d
colorful
(all)

10. ENTROPY FUNCTION

Entropy is a Greek term referring to a "change". It refers to that thermal property of a system which remains constant so long as no heat enters or leaves the system. It is a real physical quantity defined for equilibrium states only leading to the formulation of second law of thermodynamics. (The entropy of a system increases if heat flows into the system at its constant temperature and decreases if heat leaves the system without changing its temperature.) Like internal energy, entropy of a system is a function of state and hence it depends on the initial and final states of the system. Like internal energy we cannot determine absolute value of entropy. However, a change in entropy of the system is measured by the relation:

$$dS = \frac{dQ}{T}$$

* available of
entropy
ex p d c

where dQ is the quantity of heat flowing into or out of the system at the temperature of the system. Entropy function is a thermodynamic coordinate like pressure, volume, temperature and internal energy. We cannot form a tangible concept of entropy as it cannot be felt like pressure and temperature. In the language of statistical mechanics it is taken as a measure of disorder or randomness in the molecular arrangement of the system. Addition of heat to a system produces violent agitation of its molecules, resulting in an increase of entropy. Similarly abstraction of heat from a system produces a state of greater order, resulting in a decrease of entropy. We therefore, infer that increase of entropy implies a transition from a more ordered to a less ordered state of the system, or a transition from a more available energy, or a transition from a less probable to a more probable state of the system. Entropy like internal energy is a function of thermodynamic coordinates defining the state of the system. It is an extensive property of a system proportional to its mass in Kg or in moles. It is expressed in joules/K or K Cal/K.

depending upon
initial and final
points

5.11 CALCULATION OF ENTROPY FOR A REVERSIBLE CYCLIC PROCESS

The Carnot cycle depicted in Fig. 5.3 provides the best example of a reversible-cyclic process. It comprises two isothermals AB and CD and two adiabatics BC and DA . For the cyclic process

$$\begin{aligned}\sum \Delta S &= \oint dS = \Delta S_{ABCD} \int \frac{dQ}{T} \\ &= \int_A^B \frac{dQ}{T} + \int_B^C \frac{dQ}{T} + \int_C^D \frac{dQ}{T} + \int_D^A \frac{dQ}{T} \quad \dots (5.26)\end{aligned}$$

Since no heat enters or leaves the system during adiabatic process, we have

$$\Delta S_{BC} = \int_B^C \frac{dQ}{T} = 0 \quad \text{and} \quad \Delta S_{DA} = \int_D^A \frac{dQ}{T} = 0$$

A reversible adiabatic process is, therefore, called an *isentropic process* as it proceeds at constant entropy. However, this is not the case with irreversible adiabatic processes.

The entropy change along the isothermals AB and CD is given by

$$\Delta S_{AB} = \int_A^B \frac{dQ}{T} = \frac{Q_1}{T_1} \quad \text{and} \quad \Delta S_{CD} = \int_D^A \frac{dQ}{T} = -\frac{Q_2}{T_2}$$

since during the isothermal expansion heat Q_1 enters the system and during isothermal compression heat ' $-Q_2$ ' leaves the system.

Using these equations in Eq.(5.26) we get the net change of entropy of the system

$$\begin{aligned}\sum \Delta S &= \oint dS = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA} \\ &= \frac{Q_1}{T_1} + (-\frac{Q_2}{T_2}) = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \quad \dots (5.27)\end{aligned}$$

From the relation

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

we have
$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \dots (5.28)$$

Combining Eqs. (5.27, 5.28) we get

$$\sum \Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = \sum \frac{Q}{T} = 0 \quad \dots (5.29)$$

i.e., the net change in entropy of a reversible cyclic process is zero and the same holds for all reversible processes. "When such processes are performed, the entropy of the universe remains unchanged." Conversely, if $\sum \Delta S = 0$ for a process, it must certainly be a reversible cyclic process. The Eq. (5.29) expresses Clausius theorem for reversible processes.

5.12 ^{Ex 11} CALCULATION OF ENTROPY CHANGE DURING FREE EXPANSION OF AN IDEAL GAS

The ideal gas rushing into vacuum constitutes free expansion. That is so because the gas has to do no work against molecular attractions and its temperature and internal energy do not change.

Setting $dU = 0$ in the 1st law of thermodynamics

$$dQ = dU + PdV$$

we get
$$dQ = PdV$$

$$\therefore dS = \frac{dQ}{T} = \frac{P dV}{T} = nR \frac{dV}{V} \quad (\text{from } PV = nRT)$$

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

$$\Delta S = \int_{V_1}^{V_2} dS = \int_{V_1}^{V_2} nR \frac{dV}{V} = nR \ln \frac{V_2}{V_1} \quad \dots (5.30)$$

where V_1 and V_2 stand for the initial and final volumes. Since $V_2 > V_1$, the entropy change is positive i.e. entropy of the system increases.

5.13 CALCULATION OF ENTROPY CHANGE WHEN AN IDEAL GAS IS HEATED

(a) at constant volume (b) at constant pressure.

(a) From 1st of thermodynamic we have

$$dQ = dU + P dV$$

At constant volume $dV = 0$

$$\therefore dQ = dU = \left(\frac{\partial U}{\partial T} \right)_V dT = C_v dT$$

$$\text{and } dS = \frac{dQ}{T} = C_v \frac{dT}{T}$$

$$\Delta S = \int dS = \int_{T_1}^{T_2} C_v \frac{dT}{T} = C_v \ln \frac{T_2}{T_1} \quad \dots (5.31)$$

Since $T_2 > T_1$ as the gas is heated at constant volume, the entropy change is positive.

(b) When the gas is heated at constant pressure

$$C_p = \left(\frac{dQ}{dT} \right)_P \quad \text{or} \quad dQ = C_p dT$$

$$\text{and } dS = \frac{dQ}{T} = C_p \frac{dT}{T}$$

$$\therefore \Delta S = \int dS = \int_{T_1}^{T_2} C_p \frac{dT}{T} = C_p \ln \frac{T_2}{T_1} \quad \dots (5.32)$$

Since $T_2 > T_1$, the entropy change is positive.

Problem 5.1. Calculate the gain in entropy when m kg of ice at T_1 K change into steam at T_2 K.

Solution. When m kg. of ice at T_1 change into water at the same temperature, amount of heat absorbed $Q_1 = m L_1$ where L_1 is the heat of fusion of ice. The entropy change in this process is

$$\Delta S_1 = \frac{Q_1}{T_1} = \frac{mL_1}{T_1}$$

When m kg of water at T_1 are heated to T_2 , the entropy change is

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C dT}{T} = C \ln \frac{T_2}{T_1} = mc \ln \frac{T_2}{T_1}$$

where $C = \frac{dQ}{dT}$ = Heat capacity of water = mc and c = Sp. heat.

When m kg. of water at T_2 are converted into steam at T_2 , the entropy charge is

$$\Delta S_3 = \frac{Q_2}{T_2} = \frac{mL_2}{T_2}$$

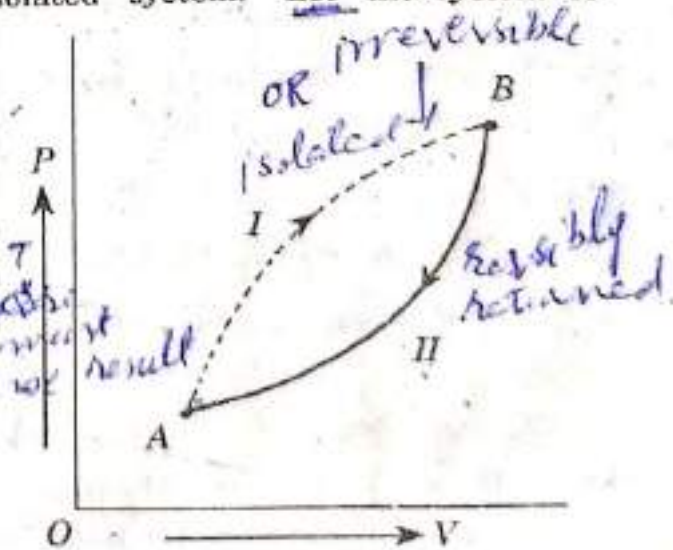
where L_2 is the heat of vaporisation of water.

Net gain in entropy is

$$\begin{aligned} \sum \Delta S &= \Delta S_1 + \Delta S_2 + \Delta S_3 = \frac{mL_1}{T_1} + C \ln \frac{T_2}{T_1} + \frac{mL_2}{T_2} \\ &= \frac{mL_1}{T_1} + mc \ln \frac{T_2}{T_1} + \frac{mL_2}{T_2} \end{aligned}$$

5.14. **PRINCIPLE OF INCREASE OF ENTROPY**

Consider a natural process taking place in an isolated system represented by the broken line taking the system from the equilibrium state A to B along it. Note that a system and its surroundings constitute an isolated system. Let the system be reversibly returned to the initial state A along the path II represented by the continuous line. Processes I and II taken together constitute a cycle which is irreversible on the whole and hence Clausius inequality must hold. That is



$\oint \frac{dQ}{T} < 0$

(I) $\int_A^B \frac{dQ}{T}$ + (II) $\int_B^A \frac{dQ}{T} < 0$

isolated system
irreversible

Fig. 5.8

$S_A = 10.5$
 $S_B = 10.0$
 $diff = 0.5 < 0 - (10.0 - 10.5) < 0$
 $-0.5 < 0$

The first integral is zero, since the system was isolated in the irreversible process and hence could not gain or lose heat. The second integral is simply $S_A - S_B$ as the process along path II is reversible and $\frac{dQ}{T} = dS$ holds only for reversible processes. Thus

$S_A - S_B < 0$ or $-(S_B - S_A) < 0$ or $S_B - S_A > 0$
according to Maths
Multiplying on both by minus

* about log

i.e., entropy of the system in state B (new state) is greater than in state A (initial state). Since the original process was arbitrary, we conclude that net entropy of an isolated system increases in all natural processes which are irreversible. This statement is restricted to isolated systems and the entropy we talk about refers to the total entropy of the system. In natural (arbitrary) processes taking place in isolated systems, entropy of the parts of the system may decrease and that of other parts may increase. On the whole, the entropy of the system either remains constant or increases. This fact is known as law of increase of entropy. Just as first law of thermodynamic embodies law of conservation of energy, the second law embodies the law of increase of entropy. The 1st law states that energy can neither be created nor destroyed but 2nd law states that entropy can be created but it cannot be destroyed. Since the universe is replete with irreversible processes which are spontaneous, we conclude that entropy of the universe either remains constant or increases. That is

$\Delta S_{universe} \geq 0$

System and surroundings

where universe means a system and its surroundings in thermodynamic sense. That is

$\Delta S_{system} + \Delta S_{surrounding} \geq 0$

5.15 DEGRADATION OF ENERGY AND ENTROPY

From the discussion on Carnot engine we have the relation

$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$... (5.33)

where $Q_1 =$ Heat absorbed by the system from hot body at temp. T_1
 $Q_2 =$ Heat rejected by the system to the cold body at temp. T_2

10-0-10.5 → Q
 10.5 → Q

This means only the balance $Q_1 - Q_2$ is available for conversion into mechanical work W while Q_2 is the unavailable portion of energy rejected to the cold body. Now

available energy

$$W = Q_1 - Q_2 = \left(\frac{Q_1 - Q_2}{Q_1} \right) Q_1 \quad \dots (5.34) \quad \text{--- (2)}$$

Using the relation (6.33) we get

available energy

$$W = \left(1 - \frac{T_2}{T_1} \right) Q_1 = \left(\frac{T_1 - T_2}{T_1} \right) Q_1 \quad \dots (5.35) \quad \text{--- (3)}$$

This is the relation between the available energy and the total energy. From Eq. (5.33).

$$Q_2 = \frac{T_2}{T_1} Q_1$$

from (1) $\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{20}{30} = 0.66$
 the $Q_2 = 0.66$
 $Q_2 = 0.9$
 $\frac{T_2}{T_1} = \frac{20}{30} = 0.66$
 $\frac{T_2}{T_1} = \frac{20}{30} = 0.66$

This is the relation between the unavailable energy and total energy.

It follows from Eq. (5.35) that heat energy is available in useful form if there is temperature difference. That is, greater the temperature difference, the greater is the availability of energy. It follows from Eq. (5.36) that smaller the temperature difference, the greater the unavailability of energy. When the heat in physical universe is at the same temperature, none of it will be converted into mechanical work. There will be as much energy present as there is now but it will be of no practical use and the universe will be stagnant. Since different factors at work in the physical universe are equalising temperature difference, the energy is assuming a form less useful to us. This is referred to as the degradation of energy. In other words, the universe is destined to face "heat death". Since unavailability of energy for conversion into useful work implies an increase in entropy, we conclude that law of increase of entropy must be intimately connected with the law of degradation of energy.

Probable :- likely but not
 certain to be
 probability means
 chance.

Throttling Process is defined

as a process in which there is no change in enthalpy from one state to another, $h_1 = h_2$; no work is done, $W = 0$ and the process is adiabatic, $Q = 0$.

6

APPLICATIONS OF THE LAWS OF THERMODYNAMICS

6.1 COMBINED FIRST AND SECOND LAWS

According to first law of thermodynamics, we have

$$dQ = dU + dW = dU + P dV \quad \text{--- (6.1)}$$

From the mathematical formulation of second law we have

$$dS = \frac{dQ}{T} \quad \text{or} \quad dQ = T dS \quad \text{--- (6.2)}$$

Combining these two equations, we get

$$\begin{aligned} T dS &= dU + P dV \\ \text{or } dU &= T dS - P dV \end{aligned} \quad \text{--- (6.3)}$$

Although Eqs.(6.1) and (6.2) are true only for a reversible process but equations (6.3) are true for any process between the pair of equilibrium states and not peculiar only to a reversible process. That is so because P, V, T, S and U are state functions of a system and change by the same amount in all processes between two given equilibrium states. Eqs. (6.3) is the fundamental equation of thermodynamics and whole of the science grows out of its consequences just as whole science of mechanics is based on Newton's laws of motion.

For reversible $S_f = S_i$
and for irreversible $S_f > S_i$

ENTHALPY FUNCTION

calorific P

The first and second laws of thermodynamics have established the existence of the functions U and S , each of which depends on the state of a given system defined by thermodynamic coordinates P , V and T . Various combinations of P , V , T , U and S define additional functions.

Enthalpy implies the total heat content of a system defined by the relation

$$H = U + PV \quad \dots (6.4)$$

For an infinitesimal reversible process

$$dH = dU + P dV + V dP = dQ + V dP \quad \dots (6.5)$$

on using first law of thermodynamics.

For an isobaric process, $P = \text{constant}$, so $dP = 0$ and we get

$$dH = dQ \quad \text{differentiating w.r.t } T$$

$$\text{or} \quad \left(\frac{dH}{dT}\right)_P = \left(\frac{dQ}{dT}\right)_P = C_p$$

$$\therefore dH = C_p dT \quad \dots (6.6)$$

Integrating we get

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

$$\therefore H_2 - H_1 = Q = \int_{T_1}^{T_2} C_p dT \quad \dots (6.7)$$

For an ideal gas passing through a throttling process, we can have

$$U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$$\text{or} \quad H_1 = H_2 \quad \dots (6.8)$$

i.e., enthalpy remains constant when an ideal gas undergoes a throttling process.

HELMHOLTZ FUNCTION

Free energy
of a physical system
can be converted into
work at a constant temp and volume

It was interpreted by Helmholtz as free energy of a system defined by

$$F = U - TS \quad \text{Differentiating} \quad \dots (6.9)$$

For an infinitesimal reversible process

$$dF = dU - T dS - S dT$$

Using Eq.(6.3) we get

$$dF = T dS - P dV - T dS - S dT$$

$$dF = -S dT - P dV \quad \dots (6.10)$$

For a reversible isothermal process, $T = \text{constant}$, so $dT = 0$ and we get

$$dF = -P dV$$

Integrating $F_f - F_i = - \int P dV \quad \dots (6.11)$

i.e., change in Helmholtz function is equal to the work done on the system.

For a reversible isothermal and isochoric process,

$dT = 0$, $dV = 0$ and so we get

$$dF = 0 \quad \dots (6.12)$$

at const P and T

or $F = \text{constant}$

GIBBS FUNCTION or Gibbs energy :- the energy associated with a chemical reaction that can be used to do work.

It was also interpreted by Gibb as free energy defined by

$$G = H - TS \quad \text{Differentiating} \quad \dots (6.13)$$

For an infinitesimal reversible process

$$dG = dH - T dS - S dT$$

Using Eq.(6.5) and noting that $dQ = T dS$, we get

$$dG = dQ + V dP - T dS - S dT$$

$$= T dS + V dP - T dS - S dT$$

$$= -S dT + V dP \quad \dots (6.14)$$

For a reversible isothermal and isobaric process, $dT = 0$, $dP = 0$, and we get

$$\left. \begin{aligned} dG &= 0 \\ \text{or } G &= \text{constant} \end{aligned} \right\} \dots (6.15)$$

This result finds application in the processes involving a change of phase such as sublimation, fusion and vaporisation which take place isothermally and isobarically.

6.2 MAXWELL'S RELATIONS

*same temp. of
same volume
pressure*

We have in all eight thermodynamic functions P , V , T , U , S , H , F and G . Any two of these are sufficient to completely determine state of a system. Moreover, any one of them may be expressed as a function of any two others. Their differentials are exact in the sense that they are integrable between the limits of integration. The properties of a pure substance are represented in terms of the four functions.

Internal energy	U	—	(1)
Enthalpy	$H = U + PV$	—	(2)
Helmholtz function	$F = U - TS$	—	(3)
Gibb's Function	$G = H - TS$	—	(4)

For an infinitesimal reversible process we can write from combined first and second law

$$dQ = dU + PdV \quad \text{First law}$$

$$dQ = TdS \quad \text{Second law}$$

$$TdS = dU + PdV$$

$$\text{or } dU = TdS - PdV \quad \dots (6.16)$$

The enthalpy change by an amount

$$dH = dU + PdV + VdP$$

Using Eq.(6.16), we get

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP \quad \dots (6.17)$$

The Helmholtz function changes by an amount

$$dF = dU - T dS - S dT$$

Using Eq.(6.16), we get

$$dF = T dS - P dV - T dS - S dT$$

$$dF = -S dT - P dV$$

$$\rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \dots (6.18)$$

The Gibb's function changes by an amount

$$dG = dH - T dS - S dT$$

Using Eq.(6.17) we get

$$dG = T dS + V dP - T dS - S dT$$

$$dG = -S dT + V dP$$

$$\rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \dots (6.19)$$

Since, dU , dH , dF and dG are all exact differentials of the type

$$dZ = M dx + N dy$$

$$Z = Z(M, N)$$

we have

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \dots (6.20)$$

Applying this condition to the above exact differentials dU , dH , dF and dG , we get

Mistakes
These are not off-diagonal but outside brackets are not same.
Cross multiply
From Gibbs

$$\left. \begin{aligned} (a) \quad \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ \text{or} \quad \left(\frac{\partial S}{\partial P}\right)_V &= -\left(\frac{\partial V}{\partial T}\right)_S \\ (b) \quad \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ \text{or} \quad \left(\frac{\partial S}{\partial V}\right)_P &= \left(\frac{\partial P}{\partial T}\right)_S \\ (c) \quad \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ (d) \quad \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P \end{aligned} \right\} \dots (6.21)$$

if reciprocal are outside no. 1 will

By the word property is any physical property which changes measurably with temperature. e.g. length of a column of liquid e.g. mercury

Phase transitions, chemical reactions ~~and all other~~ ^{melts.} These are known as Maxwell's relations. They equate a calorimetric property of a system to its thermometric property. Since calorimetric properties are very difficult to measure experimentally, while thermometric properties can be measured directly, the Maxwell's relations provide relationship between measurable quantities and those which are difficult to measure. ^{of a therm couple}

6.9 FIRST T dS EQUATION

We know that enthalpy of a system is a function of the variables V and T. We can derive T dS equations by treating S as a function of (V, T) and (P, T). Let

then $S = S(T, V)$
 $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

Multiplying both sides by T

$$T dS = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV \quad (6.22)$$

Since $T dS = dQ$ for a reversible process, we have at constant volume \rightarrow ~~Divide both T at constant V~~ ^{all the terms of T at constant V}

$$T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{dQ}{dT}\right)_V = C_v$$

Also from Maxwell's third relation

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

Using these values in Eq. (6.22) gives

$$T dS = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

This is called 1st T dS Equation.

Using mathematical theorem

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

we have

~~of partial is due to eq~~ ^{is due to eq} ~~is not only~~ ^{is not only} ~~upon V but also upon T.~~ ^{upon V but also upon T.}

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

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

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

$$= - V \left(\frac{\partial P}{\partial V}\right)_T \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \kappa \beta = \kappa \gamma_p$$

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

where $\kappa = \frac{1}{K} = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

Using this value in 1st TdS equation we get

$$T dS = C_v dT + \frac{\beta T dV}{\kappa}$$

6.4 SECOND TdS EQUATION

Let, $S = S(T, P)$

then $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

Multiplying both sides by T

$$T dS = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{--- (1) ... (6.24)}$$

Since $T dS = dQ$ for a reversible process, we have at constant pressure

$$T \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{dQ}{dT}\right)_P = C_p$$

differentiating w.r.t T at constant P

Also from Maxwell's fourth relation

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

Using these values in Eq.(6.24) gives

$$\left[\begin{aligned} T dS &= C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP \\ \text{or } T dS &= C_p dT - T V \gamma_p dP \end{aligned} \right] \quad \text{... (6.25)}$$

where $\gamma_p =$ isobaric volume coefficient.

This is called 2nd TdS Equation.

6.6 ENERGY EQUATION

From the combined 1st and 2nd laws of thermodynamics

$$Tds = dU + PdV$$

or $\Rightarrow dU = Tds - PdV$ — (1) ... (6.25)

or $\frac{dU}{dV} = T \frac{dS}{dV} - P$

At constant T

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \quad \text{--- (2)}$$

Using Maxwell's 3rd relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{put in (2)}$$

we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{--- (6.2)}$$

This is called 1st Energy Equation. It shows that the internal energy depends on volume. The energy equation can also be obtained in the following form. We have

$$dU = Tds - PdV$$

so $\frac{dU}{dP} = T \frac{dS}{dP} - P \frac{dV}{dP}$

At constant T

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

Using Maxwell's 4th relation

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

we get

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T \quad \text{--- (6.3)}$$

$$= -TV \left[\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \right] - PV \left[\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \right]$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -TV\beta + PV\kappa \quad \text{--- (6.4)}$$

For an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = 0$

✓ CLAUSIUS - CLAPEYRON EQUATION

Matter exists in three phases; namely solid, liquid and gas. Clausius - Clapeyron equation connects the slope $\frac{dP}{dT}$ of equilibrium curve between any pair of phases with temperature and latent heat of transition.

By definition,

$$G = \textcircled{H} - TS = \underbrace{U + PV}_1 - TS$$

$$\therefore dG = \underbrace{dU + P dV}_1 + V dP - T dS - S dT \quad \dots (6.1)$$

From combined first and second laws

$$T dS = dU + P dV \quad \dots (6.2)$$

Combining the two relations

$$dG = \cancel{T dS} + V dP - \cancel{T dS} - S dT$$

$$dG = -S dT + V dP \quad \text{--- } \textcircled{A} \quad \dots (6.3)$$

Since change of phase from liquid to vapour occurs at constant temperature and pressure, we get an isothermal and isobaric process. That is, $dT = 0$ and $dP = 0$. Hence

$$dG = 0 \Rightarrow \boxed{G = \text{constant.}}$$

Suppose a substance exists in two phases in an equilibrium at pressure P and temperature T . Then

$$\boxed{G_1 = G_2} \quad \dots (6.4)$$

If the temperature is increased to $T + dT$, the pressure increases to $P + dP$ and the equilibrium under new conditions gives

$$G_1 + dG_1 = G_2 + dG_2 \quad \dots (6.38)$$

Subtracting Eq.(6.37) from Eq.(6.38)

$$dG_1 = dG_2 \quad \dots (6.39)$$

Using Eq.(6.36) we get

$$-S_1 dT + V_1 dP = -S_2 dT + V_2 dP$$

arranging

$$dP (V_2 - V_1) = dT (S_2 - S_1)$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1}$$

$$\frac{dP}{dT} \stackrel{\text{by } T}{=} \frac{T(S_2 - S_1)}{T(V_2 - V_1)} = \frac{TdS}{T(V_2 - V_1)} = \frac{dQ}{T(V_2 - V_1)} \quad \dots \beta$$

Now $dQ = mL$ and $V_2 - V_1 = m(v_2 - v_1)$, where v_1 and v_2 denote the specific volumes of liquid and vapour and L is the latent heat of vaporisation.

$$\frac{dP}{dT} = \frac{mL}{T(v_2 - v_1)m} = \frac{L}{T(v_2 - v_1)} \quad \dots (6.40)$$

which is the required Clausius - Clapeyron equation. It has many applications both in Physics and Chemistry. Two immediate conclusions of this equation are :

1. The vapour pressure of a liquid increases with rise in temperature.
2. The melting point of the substances which expand on melting is raised by increase of pressure, while that of substance which contract on melting is lowered by increase of pressure.

End

For an ideal gas : $v_1 - v_2 = v$, say and Eq.(6.40) reduces to cooling

$$\frac{dP}{dT} = \frac{L}{Tv} = \frac{L}{T \left(\frac{RT}{P} \right)} = \frac{PL}{RT^2}$$

$$\frac{dP}{P} = \frac{L}{R} \frac{dT}{T^2}$$

Negative temperature

Integrating, we have

$$\ln P = -\frac{L}{RT} + \ln C = \ln e^{-\frac{L}{RT}} + \ln C = \ln C e^{-\frac{L}{RT}}$$

$$P = C e^{-\frac{L}{RT}} \quad \dots (6.41)$$

which is an important physical problem in Chemistry.

10 JOULE-THOMSON EFFECT (POROUS PLUG EXPERIMENT)

Joule was of opinion from his experimental study that internal energy of real gases like an ideal gas is independent of volume and pressure. This fact is called Joule's law. In 1852, Joule in collaboration with Thomson (Lord Kelvin), performed a more sensitive experiment known as *Porous Plug experiment*. In this experiment a gas at constant high pressure seeps through a porous wall (cotton plug) into a region of constant lower pressure under adiabatic conditions. The escaping gas then suffers a change in temperature. This type of expansion is called *Joule-Thomson expansion* or *throttling process*. The change of temperature during throttling process (cooling or heating) is called *Joule-Kelvin Effect*. In the original experiments conducted by Joule and Kelvin, a cotton plug was used and the gas flowed through the fine pores parallel to the axis of the pipe. In the modern measurements, a cup of a strong porous material capable of withstanding great force allows the gas to seep through in a radial direction. Rigid precautions are adopted to provide adequate thermal insulation for the plug and portion of pipe near the plug. Temperatures and pressures on both sides of the plug are measured by sensitive thermometers and manometers.

A continuous stream of gas at pressure P_1 and temperature T_1 is forced through the porous plug and it emerges from the plug at a lower pressure P_2 and a temperature T_2 . The insulation conditions