DEPARTMENT OF PHYSICS
SUBJECT: THERMODYNAMICS
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Q. (a) Explain what you mean by entropy of a substance?

(b) Derive an expression for entropy of an ideal gas in terms of its pressure, volume and ~~sp. heat~~ molar heat capacity.

Ans: (a) Entropy: — Clausius approach —

Let us consider a reversible cycle consisting of a ~~rep~~ reversible path R_1 between two equilibrium states i and f followed by another reversible path R_2 bringing the system back to i. Fig (a).
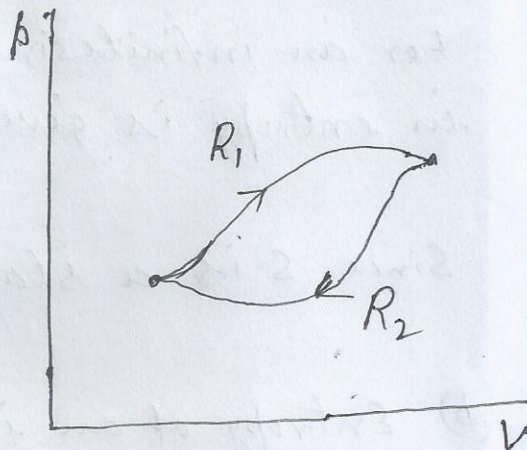

Fig (a)

Applying Clausius theorem

$$\oint_R \frac{dQ}{T} = 0 \quad (\text{for any reversible cycle})$$

to the cycle shown in Fig a., we have

$$\oint_R \frac{dQ}{T} = \int_{i \atop R_1}^{f} \frac{dQ}{T} + \int_{R_2 f}^{i} \frac{dQ}{T} = 0$$

As both the paths are reversible we have

$$\oint_R \frac{dQ}{T} = \int_{R_1 \, i}^{f} \frac{dQ}{T} - \int_{R_2 \, i}^{f} \frac{dQ}{T} = 0$$

or $$\int_{R_1 \, i}^{f} \frac{dQ}{T} = \int_{R_2 \, i}^{f} \frac{dQ}{T} \Rightarrow \text{independent of path}$$

this shows that $\int_{R \, i}^{f} \frac{dQ}{T}$ has the same value for all reversible paths between initial state i and final state f. ~~the~~

The quantity $\int_{R \, i}^{f} \frac{dQ}{T}$ is independent of path and is a fn. of end states i and f only.

Hence it follows that there exists a fn. S of thermodynamic ~~coor~~ co-ordinates whose change is

$$S_f - S_i = \Delta S = \frac{1}{R} \int_i^f \frac{dQ}{T}$$

This fn. is called entropy.

For an infinitesimal reversible process, change in entropy is given by

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

Since S is a state variable, dS is an exact differential.

(b) Entropy of an ideal gas.

Let us consider 1 mole of an ideal gas.
Let p, T and V be the pressure, temperature and volume respectively. When an ~~at~~ amount of heat dQ is given to the gas reversibly, the increase in its entropy will be

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

Let dU = increase in internal energy of gas
   dW = external work done by gas

Then by first law of thermodynamics

$$dQ = dU + dW$$

Let C_v = molar ~~sp.~~ heat capacity a const. volume
   dT = rise in temp. of gas
   dV = change in vol. of gas

then

$$dU = C_v \, dT$$

and $dW = p \, dV = RT \frac{dV}{V}$ $[\because PV = RT]$

Hence

$$dQ = C_v \, dT + RT \frac{dV}{V}$$

and $dS = \frac{dQ}{T} = \frac{C_v \, dT}{T} + R \frac{dV}{V}$

P.3

We want to calculate the change in entropy of the gas when it passes from initial state i (p_i, V_i, T_i) to final state f (p_f, V_f, T_f). This is given by

$$\Delta S = \int_i^f dS = \int_i^f \left(\frac{C_v dT}{T} + R \frac{dV}{V} \right)$$

$$= \int_i^f C_v \frac{dT}{T} + \int_i^f R \frac{dV}{V}$$

$$= C_v \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}$$

This is the expression in terms of temp, volume, and molar heat capacity.

Now

$$R = C_p - C_v$$

$$\therefore \Delta S = C_v \ln \frac{T_f}{T_i} + (C_p - C_v) \ln \frac{V_f}{V_i}$$

But

$$\frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f}$$

or

$$\frac{T_f}{T_i} = \frac{p_f V_f}{p_i V_i}$$

$$\therefore \Delta S = C_v \left(\ln \frac{p_f}{p_i} + \ln \frac{V_f}{V_i} \right) + (C_p - C_v) \ln \frac{V_f}{V_i}$$

or

$$\Delta S = C_v \ln \frac{p_f}{p_i} + C_p \ln \frac{V_f}{V_i}$$

This is the required expression for entropy change which is usually measured from an arbitrary zero when the gas is at $0°C$ and exerts a pressure of 76 cm of Hg.

Some Important Thermodynamical Relations,

For an infinitesimal reversible process

$$dQ = T\,ds$$

and $\dfrac{dQ}{dT} = T\,\dfrac{ds}{dT}$

At constant volume

$$\left(\frac{dQ}{dT}\right)_V = C_V = T\left(\frac{\partial s}{\partial T}\right)_V$$

and at constant pressure

$$\left(\frac{dQ}{dT}\right)_P = C_P = T\left(\frac{\partial s}{\partial T}\right)_P$$

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(1) Enthalpy, H

Enthalpy, H of a system is defined as

$$H = U + pV$$

Change in enthalpy when a system undergoes an infinitesimal process from an ~~equilibrium state~~ ~~into~~ initial state of equilibrium to a final equilibrium state,

$$dH = dU + p\,dV + V\,dp$$

but $dQ = dU + p\,dV$

$$\therefore \boxed{dH = dQ + V\,dp} \quad\quad — (1)$$

Dividing booth sides by dT we ~~oblaan~~ obtain

$$\frac{dH}{dT} = \frac{dQ}{dT} + V\,\frac{dp}{dT}$$

and at constant p,

$$\boxed{\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P} \quad\quad — (2)$$

Since

$$dH = dQ + V\,dp$$

the change in enthalpy during an isobaric process (const. pressure) is equal to heat that is transferred.

P-5   If a pure substance undergoes an infinitesimal reversible process then change in enthalpy

$$dH = Tds + Vdp \quad \underline{\quad\quad} \quad (3)$$

Since in an infinitesimal reversible process, $dQ = Td$

$dQ = Tds$.

Thus

$$\left(\frac{\partial H}{\partial s}\right)_p = T \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_s = V$$

(2) ~~Helmholtz~~ Helmholtz Function

Helmholtz fn. F is defined by

$$\boxed{F = U - TS} - \text{defn. of Helmholtz fn.}$$

For an infinitesimal reversible process the change in F is given by

$$dF = dU - Tds - SdT$$

and $Tds = dU + pdv$

$$\therefore \quad dF = d\cancel{U} - d\cancel{U} - pdv - SdT$$

$$\text{or} \quad \boxed{dF = -pdv - SdT}$$

From this it follows that—

(i) For a reversible isothermal process

$$dF = -pdv$$

$$\text{or} \quad \int_i^f dF = -\int_i^f pdv$$

$$\text{or} \quad F_f - F_i = -\int_i^f pdv$$

i.e. change in Helmholtz fn. during a reversible ~~process~~ isothermal process equals the work done on the system.

(ii) For a reversible isothermal and isochoric process

$$dF = 0 \quad \text{i.e.} \quad F = const.$$

Since $dF = -SdT - pdV$

We have

$$S = \left(\frac{\partial F}{\partial T}\right)_V \text{ and } p = -\left(\frac{\partial F}{\partial V}\right)_T$$

(3) Gibbs Function, G

Gibb's fn. G is defined as

$$\boxed{G = H - TS}$$

For an infinitesimal reversible process the change in G is given by

$$dG = dH - TdS - SdT$$

Now since

$$dH = TdS + Vdp$$

$$\therefore \boxed{dG = -SdT + Vdp}$$

In the case of a reversible isothermal and isobaric process

$$dG = 0 \text{ or } G = \text{const.}$$

Change in phase namely, sublimation, fusion and vapourisation take place isothermally and isobarically and can be thought of occuring reversibly. Hence ~~during~~ during such processes, the Gibbs function of the system remains constant.

Let g', g'' and g''' denote molar Gibbs fns. of a saturated solid, saturated liquid, and saturated vapour respectively. Then the eqn. of the fusion curve is

$$g' = g''$$

the ~~eqn~~ eqn. of vapourisation curve is

$$g'' = g'''$$

and the eqn. of sublimation curve is

$$g' = g'''$$

At the triple point the two eqns hold simultaneously namely

$$g' = g'' = g'''$$

P-7 All the g's can be regarded fns of T and p only and so the two eqns above serve to determine T and p of triple point uniquely.

~~Gibbs Helmholtz~~
Gibbs - Helmholtz Eqn.

For an infinitesimal reversible process

$$dF = -SdT - pdV$$

At constant volume, $dV = 0$

and $dF = -SdT$

$\therefore$ at const. volume

$$-S = \left(\frac{\partial F}{\partial T}\right)_V$$

Substituting this ~~value~~ value in Eq.

$$F = U - TS$$

we obtain

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

or

$$\boxed{U = F - T\left(\frac{\partial F}{\partial T}\right)_V}$$

This is Gibbs - Helmholtz Eqn.

Maxwell's Thermodynamical Relations

We know that properties of a pure substance one are conveniently represented in terms of these four functions :

Internal Energy, U

Enthalpy, $H = U + PV$

Helmholtz function, $F = U - TS$

Gibbs function, $G = H - TS$

Any one of these may be regarded as function of any two of P, V and T. For example let U and S both are expressed as fns. of V and T, thus

$$U = \text{fn. of } (V, T)$$

and $S = \text{fn. of } (V, T)$

The second eqn. may be solved for T in terms of S and V and substituting this value of T in first eqn. we will have

$$U = \text{fn. of } (S, V)$$

In this way it may be shown that any one of the eight quantities, P, V, T, S, U, H, F and G may be expressed as fn. of any two others.

Now let us imagine that a hydrostatic system undergoes an infinitesimal reversible process from one equilibrium state to one another equilibrium state.

1. The internal energy changes by an amount

$$dU = dQ - PdV$$

$$= \cancel{TdS} \; TdS - PdV \qquad —— (1)$$

where U, T and P are all imagined to be fns. of S and V.

2. The enta enthalpy changes by an amount

$$dH = dU + PdV + VdP$$
$$= TdS + VdP \qquad \text{——— (2)}$$

where H, T and V att are all imagined to be fns. of S and P.

3. Helmholtz fn. changes by an amount

$$dF = dU - TdS - SdT$$
$$= -SdT - PdV \qquad \text{——— (3)}$$

where F, S and P are all imagined to be fns. of T and V.

4. Gibbs fn. changes by an amount

$$dG = dH - TdS - SdT$$
$$= -SdT + VdP \qquad \text{——— (4)}$$

where G, S and V are all imagined to be fns of T and P.

Since U, H, F and G are actual fns. their differentials are exact-differentials of the type

$$dz = Mdx + Ndy \qquad \text{——— (5)}$$

where z, M and N as are all fns. of x and y. Therefore

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \qquad \text{——— (condition of exact differential)}$$

Hence applying this result to the foure exact-differentials dU, dH, dF and dG we obtain

$$dU = TdS - PdV; \text{ hence } \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \text{——(A)}$$

$$dH = TdS + VdP; \text{ hence } \boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \text{— (B)}$$

$$dF = -SdT - PdV; \text{ hence } \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \text{— (C)}$$

$$dG = -SdT + VdP; \text{ hence } \boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P} \text{— (D)}$$

These four eqns (A), (B), (C) and (D) are known as Maxwell's thermodynamical ~~equations~~ relations or equations.

———————— X ————————

(Q.) Show that-
$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_P.$$

Ans. From definitions

molar heat-capacity at const. pressure
$$C_p = \left(\frac{dQ}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

and molar heat-capacity at constant volume
$$C_v = \left(\frac{dQ}{dT}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v, \quad \text{since } dQ = Tds$$

$$\therefore \ C_p - C_v = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_v \quad \text{—— (1)}$$

Now if entropy S is considered as a fn. of T and V, then since dS is a perfect differential, we have
$$dS = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial V}\right)_T dv$$

or
$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_v + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

or
$$T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{—— (2)}$$

Hence from Eqns. (1) and (2) we get
$$C_p - C_v = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Now from Maxwell's eqn.
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\therefore \ C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial V}{\partial T}\right)_P$$

Proved