03/11/2021

Entropy & arrow of Time

The concept of entropy has importance in flow of time. The increase of entropy (disorderness) of a system and its surroundings occurs in all aging processes, whether it is living organism or inanimate system. There is no doubt which condition is prior in time: youth or maturity, green mango & ripe mango, structure or erosion. One condition always precedes the other, order precedes disorder. Entropy always increases during an aging process. So in a metaphorical sense entropy is the arrow of time. Furthermore, the arrow has only one direction, it points forward into the future.

Increase in entropy due to diffusion of gases

$$S = C_v \ln T + R \ln V + S_0 = C_v \ln T + R \ln \frac{RT}{P} + S_0 = C_v \ln T + R \ln \frac{T}{P} + C$$

If a no. of gases at pressure P & temp T get spontaneously mixed up by diffusion then entropy before diffusion will be

$$S_B = S_1 + S_2 + S_3 \cdots$$

$$= n_1 \left[C_{v_1} \ln T + R \ln \frac{T}{P} + C_1 \right] + n_2 \left[C_{v_2} \ln T + R \frac{T}{P} + C_2 \right] + \cdots$$

$$= \sum_j n_j \left[C_{v_j} \ln T + R \ln \frac{T}{P} + C_j \right]$$

Entropy after diffusion

$$S_A = n_1 \left[C_{v_1} \ln T + R \ln \frac{T}{P_1} + C_1 \right] + n_2 \left[C_{v_2} \ln T + R \ln \frac{T}{P_2} + C_2 \right] + \cdots$$

$$= \sum_j n_j \left[C_{v_j} \ln T + R \ln \frac{T}{P_j} + C_j \right]$$

After diffusion total pressure of the gas mixture remains P made up of partial pressure of each gas P_j

given

$$P_j = \frac{n_j}{\sum_j n_j} P = K_j P \qquad K_j = \frac{n_j}{\sum_j n_i}$$

$$= \sum_j n_j \left[C_{v_j} \ln T + R \ln \frac{T}{K_j P} + C_j \right]$$

$$= \sum_j n_j \left[C_{v_j} \ln T + R \ln \frac{T}{P} + C_j - R \ln K_j \right]$$

Increase in entropy $S_A - S_B$

$$= -(R \ln x_j) n_j = n_1 R \ln \frac{n_1+n_2+\cdots}{n_1} + n_2 R \ln \frac{n_1+n_2\cdots}{n_2}$$

$$= n_j \ln\left(\frac{\sum_j n_j}{n_j}\right) > 0 \qquad +ve$$

04/11/2021

Gibbs' paradox

Entropy of ideal gas with 'n' moles in a volume V, temp T is,

$$S(n,V,T) = n\left[C_v \ln T + R \ln V + C\right]$$

$$S(2n,2V,T) = 2n\left[C_v \ln T + R \ln(2V) + C\right]$$

$$\neq 2\,S(n,V,T)$$

but, should be as entropy is extensive variable

So, entropy loses its extensive character & this is called Gibbs' paradox.

Resolution of Gibbs' paradox: The root of the difficulty embodied in the Gibbs paradox is that the gas molecules are treated as distinguished particles as though interchanging the position of two molecules would lead to a physically distinct state, but this is not so. If the molecules are indistinguishable then by quantum statistical mechanics it can be shown that this paradox would never arise.

Legendre Transformation :

It is a mathematical technique by the help of which one can obtain new functions from a given one by the change of variables. If the state of a system is described by a function of two variables $f(x,y)$ which obeys the eqn

$$df = u\,dx + v\,dy \rightarrow ①$$

and we wish to change the description to one involving a new function $g(u,y)$ satisfying a similar eqn in terms of du, dy, then, L. transformed function

$$g(u,y) = f - ux \Rightarrow dg = df - u\,dx - x\,du$$

$$\Rightarrow dg = x\,du + v\,dy$$

Application : For a hydrostatic system

$$dU = -p\,dV + T\,dS \quad \Rightarrow U = f(V,S) = U(V,S)$$

$$dU = \left(\frac{\partial U}{\partial s}\right)_V ds + \left(\frac{\partial U}{\partial v}\right)_S dv$$

$$= -p\,dv + T\,ds$$

$$\Rightarrow \quad T = \left(\frac{\partial U}{\partial s}\right)_V = x \text{ (say)}, \quad -p = \left(\frac{\partial U}{\partial v}\right)_S = y \text{ (say)}$$

$U = U(s,v)$

$Z_1(x, V) = U(s,v) - xS = U - ST = F$ Helmholtz free energy

$Z_2(s, y) = U - Vy = U + PV = H$ enthalpy

$Z_3(x, y) = U - Sx - Vy = U - TS + PV = H - TS = G$

$\Downarrow$

Gibbs free energy

So, all total 4-different thermodynamic functions.

U, H, F, G

$$\left.\begin{aligned} dU &= -p\,dv + T\,ds \\ dH &= v\,dp + T\,ds \\ dF &= -p\,dv - s\,dT \\ dG &= v\,dp - s\,dT \end{aligned}\right\}$$

These differential eqns form a complete set of functions based on successive L.T. of the four variables (p, v, T, s) for hydrostatic system. The characteristic functions U(s,v), H(s,p), F(T,v), G(P,T) are known as thermodynamic potentials because they have the property that if the functions are expressed in terms of proper thermodynamics variables then all the thermodynamic properties of the system can be calculated by differentiation and in the same manner as the components of a force are deduced from a force potential in mechanics.

09/11/21

Maxwell's relation importance lies in the fact that they provide relationship between non-measurable & measurable quantities. We know that, P,V,T are measurable but entropy can not be determined experimentally. By using Maxwell's relation one can find changes of entropy that can be measured i.e

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

We know that for a hydrostatic system the properties can be described with the help of any one of the differentials of the four functions $U(S,V)$, $H(P,S)$, $G(T,P)$, $F(T,V)$

$$\left.\begin{array}{l} dU = -pdV + TdS \\ dH = VdP + TdS \\ dF = -pdV - SdT \\ dG = VdP - SdT \end{array}\right\} \equiv Mdx + Ndy \quad \because \text{they are exact differential}$$

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

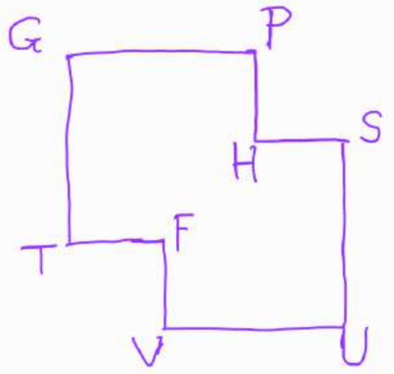
$$\Rightarrow \left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S, \quad \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

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

Mnemonic device to remember

Good Physicist Have Studied Under Very Fine Teachers.

$$\left.\begin{aligned} dG &= Vdp - SdT \\ dH &= vdp + Tds \\ dF &= -sdT - pdv \\ dU &= Tds - pdv \end{aligned}\right\} Mdx + Ndy$$



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

Introduction of free energies in thermodynamics

Let us consider a thermodynamic system undergoing a process from one state to another isothermally at temp T.

From Clausius inequality theorem, for infinitesimal process

$$\frac{\delta Q}{T} \leq \Delta S = S_f - S_i \Rightarrow \delta Q \leq TS_f - TS_i$$

$$\Rightarrow (\Delta U + \Delta W) \leq (TS_f - TS_i) \Rightarrow (U_f - U_i + \Delta W) \leq TS_f - TS_i$$

$$\Rightarrow \Delta W \leq (U_i - TS_i) - (U_f - TS_f)$$

$$\Rightarrow \Delta W \leq F_i - F_f \Rightarrow \delta W \leq -\Delta F \quad (F = U - TS)$$

For isothermal-isochoric $(\delta V = 0)$ process $\delta W = 0$

$$\Rightarrow -\Delta F \geq 0 \Rightarrow F_i \geq F_f \Rightarrow \Delta F \leq 0$$

⇒ State minimum free energy is the eq^{m} condition for const-temp-volume

Let us consider a system undergoing isothermal-isobaric process at, p, T.

$$\text{C.I.T.} \Rightarrow \frac{\delta Q}{T} \leq \Delta S \Rightarrow \delta U + \delta W \leq T \Delta S$$

$$\Rightarrow (U_f - U_i) + p(V_f - V_i) \leq TS_f - TS_i$$

$$\Rightarrow U_f + pV_f - TS_f \leq U_i - TS_i - pV_i \Rightarrow G_f \leq G_i \Rightarrow \delta G \leq 0$$

$$G = U + pV - TS$$

So, the state of minimum Gibbs free energy is the stable eqn condition at cst p, T.

T-ds eqn :

$$S = S(T,V) \Rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

$$\Rightarrow T ds = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dv \quad \left[\because \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V\right]$$

→ 1st T-ds eqn

$$S = S(T,P) \Rightarrow T ds = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial p}\right)_T dp$$

$$= C_p dT - T\left(\frac{\partial v}{\partial T}\right)_P dp \rightarrow \text{2nd T-ds eqn}$$

Internal energy eqn :

$$dU = T ds - p dv \Rightarrow \left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p = T\left(\frac{\partial s}{\partial p}\right)_V - p$$

1st energy eqn

$$\left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial p}\right)_P - p\left(\frac{\partial v}{\partial p}\right)_T \rightarrow \text{2nd energy eqn}$$

20|11|21 **Heat-capacity eqn.**

Using 1st & 2nd Tds eqn we can have

$$c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp = c_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

$$\Rightarrow dT = \frac{1}{c_p - c_v}\left[T\left(\frac{\partial p}{\partial T}\right)_v dv + \underbrace{T\left(\frac{\partial v}{\partial T}\right)_p dp}_{=0}\right]$$

$$\Rightarrow c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$ [differentiate w.r.t. T at const. P]

$$= T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_v$$ [differentiate w.r.t. T at const V]

If $f(P,V,T) = 0 \Rightarrow \left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial v}{\partial p}\right)_T = -1$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial v}\right)_T$$

$$\therefore \Rightarrow c_p - c_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial v}\right)_T = \frac{TV\left[\frac{1}{V}\left(\frac{\partial v}{\partial T}\right)_p\right]^2}{-\frac{1}{V}\left(\frac{\partial v}{\partial p}\right)_T} = \frac{TV\beta^2}{K}$$

$\beta = \frac{1}{V}\left(\frac{\partial v}{\partial T}\right)_p \qquad K = -\frac{1}{V}\left(\frac{\partial v}{\partial p}\right)_T$ → isothermal compressibility

$$= \quad \frac{\partial c_v}{\partial v} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \Rightarrow \left(\frac{\partial^2 s}{\partial T\partial v}\right) = \left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v \Rightarrow \frac{\partial c_v}{\partial v} = T\frac{\partial^2 s}{\partial T\partial v}$$

$$\Rightarrow \frac{\partial c_v}{\partial v} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p \Rightarrow \frac{\partial c_p}{\partial p} = T\frac{\partial^2 s}{\partial p\,\partial T}$$

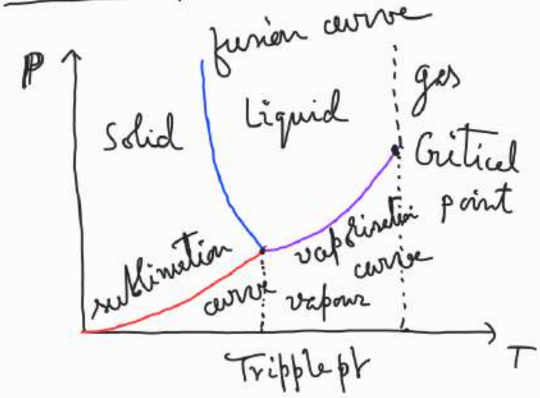
$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \Rightarrow \frac{\partial^2 s}{\partial T\,\partial p} = -\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

$$\Rightarrow \quad \frac{\partial c_p}{\partial p} = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

=

Change of state

Equlibrium between phases : Tripple point



Sublimation curve: When the vapour pressure of a solid is measured at various temperatures until the tripple is reached & the data (P-T) so got when plotted in P-T plane diagram produced is called sublimation curve

P-T data representing coexistence of solid & vapour lie on sublimation curve which is bounded by absolute zero & tripple point.

P-T data representing coexistence of solid & liquid lie on fusion curve, unbounded, starts at tripple pt.

coexistence between liquid & vapour lie on vaporisation curve bounded between tripple pt & Critical point.

Sublimation curve often called Frost line
fusion - - ice line
vaporisation - - steam line

The slopes of frost line & steam line are +ve for all substances. But slope of fusion curve may be +ve or -ve, for most substances it is +ve. Any substance such as water that expands upon freezing has a fusion curve with $\boxed{-ve}$ slope whereas for a substance that contracts upon freezing such as CO_2 has a fusion curve with $\boxed{+ve}$ slope

Tripple point for water ⇒ $T = 273.16K$

$p = 4.58$ mm of Hg

$= 0.000612$ MPa

$\rho = 999.78$ kg/m³

22/11/21 Relation of Gibbs' free energy between two phases

Let us consider one component system (closed) of two phases (liquid-vapour) maintained at const pressure-Temp. Suppose that the masses of liquid & vapour phases are m_l, m_v & their specific Gibbs free energy g_l, g_v

∴ Total Gibbs' free energy for the system

$$G = m_l g_l + m_v g_v$$

obviously $G = G(P, T, m_l, m_v)$

Now, let us take a reversible change in the system consistent with external conditions such that some liquid is converted into vapour. For P, T const. the condition for eq$^{\underline{m}}$ implies that,

$$dG = g_l\, dm_l + g_v\, dm_v = 0 \rightarrow ①$$

Again for a closed system mass is conserved

$$dm_l + dm_v = 0$$

$$\Rightarrow dm_l = -dm_v \rightarrow ②$$

① & ② $\Rightarrow \boxed{g_l = g_v}$

So, for two or more phases of one component system to be in equilibrium the specific Gibbs free energy must have the same value.

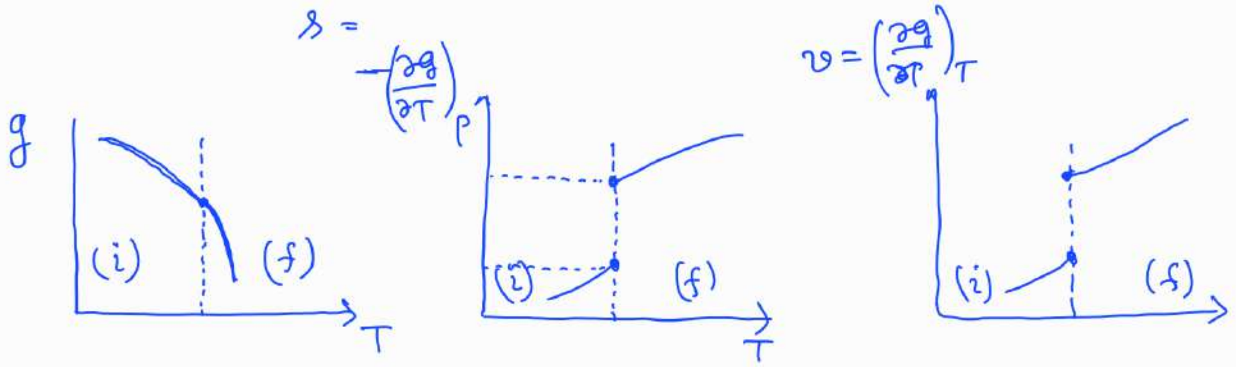
First-Order Phase Transition :

Any phase change that satisfies the following two requirements is known as phase change of 1st order.

i) Molar volume & Molar entropy change occurs

ii) First derivative of molar Gibbs function change discontinuously

Melting, vaporisation, sublimation are example of 1st order P.T.



The characteristics eqn to describe 1st-order phase transition is Clausius-Clapeyron eqn.

When one mole of substance is converted reversibly & isothermally, isobarically from initial phase 'i' to final phase 'f'

from 1st Tds eqn we have

$$T ds = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dv$$

We can have, $\left(\frac{\partial p}{\partial T}\right)_V = \frac{dp}{dT}$ if $p = f(T)$ only, independent of V.

&

$$T(s_f - s_i) = T\frac{dp}{dT}(v_f - v_i)$$

$$\Rightarrow \frac{dp}{dT} = \frac{s_f - s_i}{v_f - v_i} = \frac{\Delta s}{\Delta v} = \frac{L}{T\Delta v} \quad [L = T\Delta s]$$

Alternative: Consider a closed vessel containing liquid with vapour in eqm. The pressure is called saturated vapour pressure that depends on temp only, independent of amount of liquid & vapour present. If we allow the system to expand at const temp. the vapour pressure will remain cont but some liquid will evaporate to fill the extra space with vapour

$$\delta Q = L\,dm\,,\quad L \text{ sp. latent heat of vaporisation}$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

$$T\left(\frac{\partial s}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v \Rightarrow \left(\frac{\delta Q}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v$$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = \frac{L}{T(v_2-v_1)}$$

If we hold volume cont & increase temp some liquid will evaporate till the mixture attains a new eqn for saturated vapour pressure, then we can write

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{sat}$$

$$\therefore \frac{dp}{dT} = \frac{L}{T(v_2-v_1)} \rightarrow \text{C-C eqn}$$

27/11/21

Expression for vapour pressure in eqm with liquid

Consider a liquid-vapour phase transition where the vapour follows ideal gas law. The C-C eqn is

$$\frac{dp}{dT} = \frac{L}{T\Delta V} = \frac{L}{T(v_2-v_1)}$$

$$\Rightarrow dp = \frac{L}{Tv_2}dT$$

as vapour density is very small compared to liquid $v_2 \gg v_1$

$$pv_2 = RT \Rightarrow v_2 = \frac{RT}{p}$$

$$\frac{1}{p}\frac{dp}{dT} = \frac{L}{T^2 R} \Rightarrow p = A e^{-L/RT}$$

$\downarrow$

Young's eqⁿ

Second Latent heat eqⁿ

Let s_i, s_f be the entropies of unit mass of the substance in the initial & final state of an component system (saturated vapor in contact with its liquid). During phase transition the temp remain const & heat absorbed or evolved during the process is wholly latent heat.

$$s_f - s_i = \frac{L}{T} \Rightarrow \frac{d}{dT}\left(\frac{L}{T}\right) = \frac{ds_f}{dT} - \frac{ds_i}{dT}$$

$$\Rightarrow \frac{dL}{dT} - \frac{L}{T} = T\frac{ds_f}{dT} - T\frac{ds_i}{dT} \Rightarrow \frac{dL}{dT} = \frac{L}{T} + (c_f)_s - (c_i)_s$$

$\Downarrow$

second Latent heat eqⁿ

Negative Specific heat of saturated vapour

Latent heat of water decreases with rise in temp. Near the boiling point

$$\frac{dL}{dT} = -0.64 \text{ cal/g/°C}$$

Sp. heat of water at 100°c = 1.01

$$L\big|_{t=100^\circ c} = 540 \text{ cal/g.}$$

$$(c_f)_s = (c_i)_s - \frac{L}{T} + \frac{dL}{dT} = 1.01 - 0.64 - \frac{540}{373}$$

$$= -1.07 \text{ cal}$$

Saturated vapour pressure (SVP) of steam at 100°c is 780 mm of Hg & at 101° it is 787 mm of Hg. Thus the steam which is saturated at 100°c becomes unsaturated at 101°c & thus it is to be compressed for restoration of saturation condition. This compression generates so much heat that is in excess to raise the temp by one degree & this excess heat is rejected by the system.

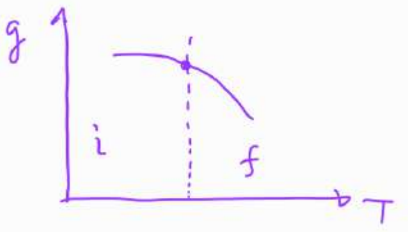
2nd order phase Transition

29/11/24 The phase transition in which entropy and volume remain the same but 2nd derivative of Gibs function show discontinuity, is called 2nd order phase transition.

$$\frac{c_p}{T} = \left(\frac{\partial s}{\partial T}\right)_p = \left[\frac{\partial}{\partial T}\left(-\frac{\partial g}{\partial T}\right)_p\right]_p = -\left(\frac{\partial^2 g}{\partial T^2}\right)_p$$

$$K v = -\left(\frac{\partial v}{\partial p}\right)_T = -\left[\frac{\partial}{\partial p}\left(\frac{\partial g}{\partial p}\right)_T\right]_T = -\left(\frac{\partial^2 g}{\partial p^2}\right)_T$$

$$\beta v = \left(\frac{\partial v}{\partial T}\right)_p = \left[\frac{\partial}{\partial p}\left(\frac{\partial g}{\partial p}\right)_T\right]_p = \left(\frac{\partial^2 g}{\partial T \partial p}\right)_{T,p}$$



Ehrenfest's eqn:

In case of 2nd order phase transition there is no change of entropy & volume, hence slope of G − T curve (when $s_1 = s_2$) or slope of G − P curve ($v_1 = v_2$) becomes continuous. So there are two forms of 2nd order transition based on constancy of entropy and constancy of volume.

Consider the transition with constancy of entropy in two phases i.e.

$s_1 = s_2$ at T, P

For a slight change of pressure, temp $T + dT$, $P + dP$ the entropy change

$$s_1 + ds_1 = s_2 + ds_2$$

$$\Rightarrow ds_1 = ds_2 \Rightarrow T ds_1 = T ds_2$$

$$\Rightarrow (C_P)_1 dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = (C_P)_2 dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$$

Isobaric volume expansion coefficient $\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$

$$(C_P)_1 dT - T\alpha_1 v\, dP = (C_P)_2 dT - T\alpha_2 v\, dP$$

$$\Rightarrow \left(\frac{dP}{dT}\right) = \frac{C_{P_2} - C_{P_1}}{Tv(\alpha_2 - \alpha_1)}$$ ✓

Another form: $dv_1 = dv_2$ [$v_1 = v_2$)

$$\Rightarrow v = v(T, P) \Rightarrow dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP = v\alpha\, dT - vK_T\, dP$$

$K_T = \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$

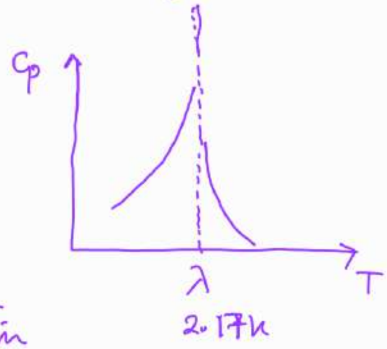
$$v\alpha_1 dT - vK_{T_1} dP = v\alpha_2 dT - vK_{T_2} dP$$

$$\frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{K_{T_2} - K_{T_1}}$$ ✓

Liquid He-I → liquid He-II at λ point (2.17K)
⇓ ⇓
(4.2K) superfluid

Ferromagnetism into paramagnetism at
Curie point

examples of 2nd order phase transition



<u>Gibs' phase rule:</u>

A phase is defined as a system which is homogeneous and has definite boundaries, may be chemically pure substance or may contain more than one component as in the case of air or a mixture of two liquids

<u>Component:</u> The smallest no. of independent variable constituents by means of which the composition of each phase present can be expressed.

<u>Degree of freedom:</u> The minimum no. of independent variables like pressure, temp, concentration required for describing the condition of equilibrium of a system is referred to as the D.o.f.

<u>Gibs phase rule:</u> Uninfluenced by magnetic or electric forces or gravity but influenced by temp/pressure/concentration the degree of freedom (F) of a system in equilibrium between a no. of phases 'P' and components 'C' is given by

$$\boxed{F = C - P + 2}$$

Appl^{n} : Show that max^{m} no of phases that can exist in eq^{m} for one component system is '3'

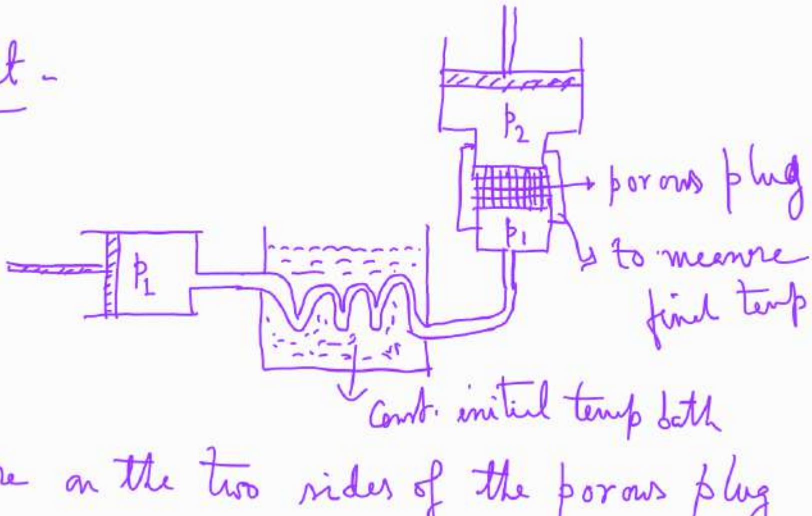
$$P = C - F + 2$$

Max^{m} of P corresponds to minimum of F which can be taken as 0, C = 1, P = 3

That is a pure substance can not have more than three phases co-existing in eq^{m}. Moreover since C = 1, phase rule tells us that for one phase F = 2 i.e. one can vary both T & P, for two phases F = 1 i.e. one can vary either P or T without disturbing eq^{m}.

For three phases to coexist we must have F = 0

Joule-Thomson Effect -



Suppose that the pressure on the two sides of the porous plug are kept const at values p_1, p_2 ($< p_1$) which can be achieved by moving pistons at const rate. If u_1, v_1 are the initial internal energy & volume of the gas and u_2, v_2 are that after the gas is throttled then the work done by the gas

$$W = \int p_2 dv_2 - \int p_1 dv_1 = p_2 v_2 - p_1 v_1$$

Since no heat enters the system, this work has to be performed at the expense of internal energy ⇒

$$u_1 - u_2 = p_2 v_2 - p_1 v_1 \Rightarrow u_1 + p_1 v_1 = u_2 + p_2 v_2$$

$$\Rightarrow H_1 = H_2 \Rightarrow \text{enthalpy const.}$$

To find out the change in temp with pressure

$$H = H(p,T) \Rightarrow dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT = 0$$

$$\Rightarrow \left(\frac{\partial H}{\partial T}\right)_p dT = -\left(\frac{\partial H}{\partial p}\right)_T dp$$

$$H = U + pV$$
$$dH = du + pdv + vdp$$
$$= \delta Q + vdp$$
$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$dH = Tds + vdp \Rightarrow \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T + v = -T\left(\frac{\partial v}{\partial T}\right)_p + v$$

$$dH = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp = 0 \quad [\because H \text{ const}]$$

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = \frac{T^2}{C_p}\left[\frac{\partial}{\partial T}\left(\frac{v}{T}\right)\right]_p$$

↓

J.T. coefficient

$$= -\frac{1}{C_p}\left[\left(\frac{\partial H}{\partial p}\right)_T\right]$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{-\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}$$

$$= -\frac{1}{C_p}\left[\left(\frac{\partial U}{\partial p}\right)_T + \left\{\frac{\partial}{\partial p}(pV)_T\right\}\right] \quad [H = U + pV]$$

$\Downarrow$ ↳ ⓒ

04/12/24

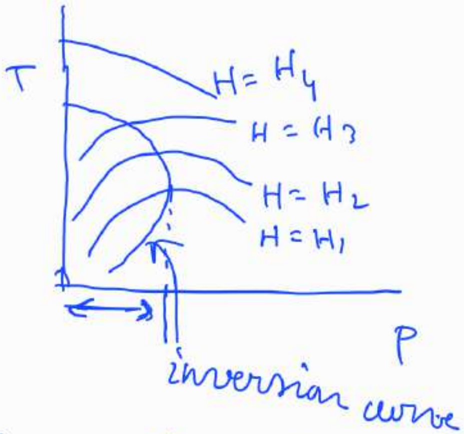
Explaination of the above expression

The 1st term is a measure of deviation from Joule's law $U = U(T)$ whereas the 2nd term gives deviation from Boyle's law. For a perfect gas both these terms are zero. Therefore if J-K coefficient vanishes for a gas then it is ideal gas. For a real gas the 1st term always contributes to cooling but the 2nd term may contribute to heating or cooling depending on the pressure & temp of the gas.

So the net effect would determined by the interplay of two terms i.e. $\mu = 0$ when cooling due to deviation from Joule's law exactly cancels heating due to deviation from Boyel's law

$$\left(\frac{\partial U}{\partial p}\right)_T + \frac{\partial}{\partial p}(PV)_T = 0 \Rightarrow \underline{T\left(\frac{\partial V}{\partial T}\right)_P - V = 0} \rightarrow ②$$

The eqn ② defines a curve in (T, P) plane & is known as inversion curve, which represents the locus of points for which $\mu = 0$. For a given initial temp



the gas will suffer cooling if the pressure is so chosen that the initial state lies within the inversion curve i.e. $\left(\frac{\partial T}{\partial p}\right)_H$ is +ve.

If the gas is initially at state falls outside the inversion curve where $\left(\frac{\partial T}{\partial p}\right)_H$ -ve, J-K expansion will warm up the gas

Result: 1. If the initial temp is sufficiently low, all gases suffer cooling effect.

2. As the initial temp is increased the drop in temp becomes smaller & at a particular value of $T = T_i$ the drop becomes zero. Finally if the initial temp has a value above T_i, the gas would be heated instead of cooling. The critical value of initial temp in which there is no change in temp due to throttling, is known as inversion temp. For N_2 $T_i = 621K$ $T_i^{H_2} = 195K$ $T_i^{He} = 23.6K$.

To have cooling effect the gas is to be taken below its inversion temp T_i

J-T effect for van der Waals's gas

$$\left(p + \frac{a}{V^2}\right)(V-b) = RT \Rightarrow \left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p - \frac{2a}{V^3}(V-b)\left(\frac{\partial V}{\partial T}\right)_p = R$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = R \Big/ \left[\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V-b)\right]$$

$$= \frac{R(V-b)}{RT - \frac{2a(V-b)^2}{V^3}} = \frac{V-b}{T\left[1 - \frac{2a(V-b)^2}{RTV^3}\right]}$$

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

$$= \frac{V}{T}\left(1 - \frac{b}{V}\right)\left(1 + \frac{2a}{RTV}\right) = \frac{V}{T}\left(1 - \frac{b}{V} + \frac{2a}{RTV}\right)$$

$$\Rightarrow T\left(\frac{\partial v}{\partial T}\right)_p - v = \frac{2a}{RT} - b \Rightarrow \mu = \frac{1}{c_p}\left[\frac{2a}{RT} - b\right]$$

So three possibilities may occur :-

1. If the intermolecular forces are so strong that $a \gg b$

   then $\frac{2a}{RT} > b \Rightarrow \mu > 0 \rightarrow$ gas cools down

2. If $b > \frac{2a}{RT}$ $\mu < 0$, gas warms up

3. If $b = \frac{2a}{RT}$, $\mu = 0 \rightarrow$ no change in temp

$$\Rightarrow T = T_i = \frac{2a}{Rb}$$

$T_B \rightarrow$ Boyle temp $= \frac{a}{bR}$ $T_c = \frac{8a}{27bR}$

$$T_i = 2T_B = \frac{27}{4}T_c$$

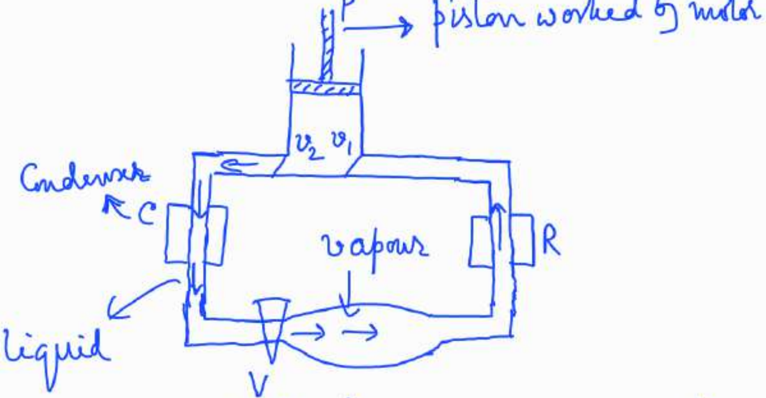
$$T_i : T_B : T_c = ?$$

$$\mu = \frac{b}{c_p}\left[\frac{T_i}{T} - 1\right]$$

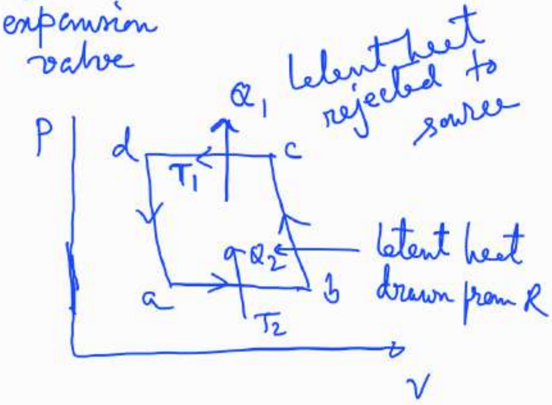
06/12/21

Refrigerator

Basic Principle



As piston P moves up, pressure within the cylinder falls below than that in R & vapour sucked in through the valve v_1, during forward movement of P, vapour is compressed & passes through v_2, gets liquified in condenser C and finally passes through expansion valve V, falling pressure to low value & evaporates in R extracting heat from refrigerating space.



$$Q_1 = W + Q_2$$

Working substance used is called refrigerant commonly →

NH_3, SO_2, carbonic acid, Freon (CCl_2F_2, CFC-12) or $CClF_3$. The choice of substance depends on large latent heat of vaporization, must be vapour at NTP but capable of being liquified when compressed.

$$\text{Coefficient of performance } \eta = \frac{\text{heat drawn}}{\text{Work done}} = \frac{Q_2}{W}$$

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

Concept of Absolute scale of Themperature
⇒ Thermodynamic scale of temp

A temperature that is independent of the nature of the working substance is called absolute or thermodynamic scale of temp. It is known that the efficiency of a Carnot engine is independent of working substance and depends on temp only & thus Carnot engine provides the basis of thermodynamic temp scale.

$V_t = V_0(1+\gamma t)$

$V_t = V_0\left(1+\boxed{\frac{t}{273}}\right)$

$\boxed{t = -273} = 0K$

$V_t = 0$

$\gamma = \frac{1}{273}$

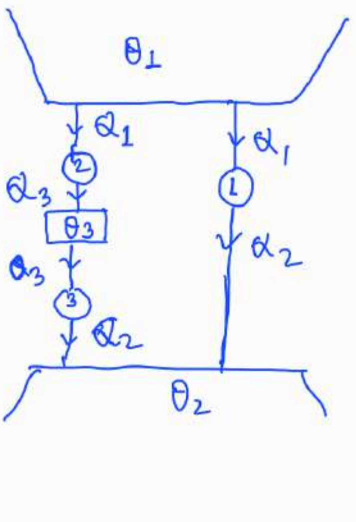
Kelvin scale → ideal gas scale temp

A Carnot engine absorbing Q_1 unit of heat from source at θ_1 & rejecting Q_2 unit of heat at sink at θ_2 has efficiency

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\theta_2}{\theta_1} \quad (\theta_1 > \theta_2)$$

$$= f(\theta_1, \theta_2) \Rightarrow \frac{Q_1}{Q_2} = \frac{1}{1 - f(\theta_1, \theta_2)}$$

Now let us consider three Carnot engines operating between three reservoirs where $\theta_1 > \theta_3 > \theta_2$



For engine ① ⇒ $\frac{Q_1}{Q_2} = f(\theta_1, \theta_2)$

For engine ② ⇒ $\frac{Q_1}{Q_3} = f(\theta_1, \theta_3)$ ③ → $\frac{Q_3}{Q_2} = f(\theta_3, \theta_2)$

$$f(\theta_1, \theta_3) = \frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \Big/ \frac{Q_3}{Q_2} = \frac{f(\theta_1, \theta_2)}{f(\theta_3, \theta_2)} \rightarrow ①$$

Now the temp θ_2 is arbitrarily chosen & since it does not appear in LHS of ① θ_2 must be dropped out in the ratio in RHS of ① & hence numerator can be written $\psi(\theta_1)$ & denominator $\psi(\theta_3)$ ⇒ $\frac{Q_1}{Q_3} = \frac{\psi(\theta_1)}{\psi(\theta_3)}$ ⇒ ratio on RHS as the ratio of two thermodynamic temp & is denoted by $\frac{\theta_1}{\theta_3} = \frac{Q_1}{Q_3} \rightarrow ②$

Hence the two temp on the thermodynamic scale are as the values of heat absorbed & rejected respectively by a Carnot engine operating between reservoir at these temp which is independent of working substance. Thus Carnot engine provides the universality that is lacking in the ideal gas temp scale.

To complete the defn of the thermodynamic scale we proceed to assign the arbitrary value of 273.16 K to the temp of the tripple point of water $\theta_{TP} = 273.16\,K$.

For a Carnot engine operating between reservoir at temp θ & θ_{TP} we have, $\frac{Q}{Q_{TP}} = \frac{\theta}{\theta_{TP}} \Rightarrow \theta = 273.16\,K \, \frac{Q}{Q_{TP}}$

which implies the smaller the value of Q, the lower the corresponding θ. The smallest possible value $Q = 0$ & the corresponding θ is absolute zero. Thus if a system undergoes a reversible isothermal process without transfer of heat the temp at which this process takes place is called absolute zero which holds for any substance.

Equality of ideal gas scale & thermodynamic scale

Ideal gas scale temp is defined in terms of the ratio of the pressure P to the pressure of the system at the tripple point of water P_{TP} in the limit as $P_{TP} \to 0$ i.e.

$$T = 273.16\,K \lim_{P_{TP}\to 0} \left(\frac{P}{P_{TP}}\right)$$

A Carnot engine of ideal gas operating between two reservoir having ideal gas scale temp T_1, T_2 $(T_1 > T_2)$ satisfies the relation

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \rightarrow ③$$

The thermodynamic scale defined by ② allows us to replace the ratio of heats by the ratio of thermodynamic temp to produce

$$\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2} \rightarrow ④$$

If θ_1, T_1 refer to any temp & θ_2, T_2 refer to tripple point of water then relation ④ becomes

$$\frac{\theta}{\theta_{Tp}} = \frac{T}{T_{Tp}}$$

Since $\theta_{Tp} = T_{Tp} = 273 \cdot 16\,K \Rightarrow \boxed{\theta = T}$

The Thermodynamic scale of temp is numerically equal to ideal gas scale of temp.

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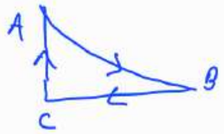
Problem - Soln:

Some points to solve problem:

1. Closed area in T-S diagram ⇒ Work done
2. Area under a curve with S-axis ⇒ Heat
3. Closed cycle area in P-V diag ⇒ Work done
4. Area under a curve by V-axis ⇒ Work done
5. Heat absorbed ⇒ $Q = U + W$
6. Heat absorbed in closed cycle
   → heat in different process closing the cycle $= Q_{AB} + Q_{BC} + Q_{CA}$



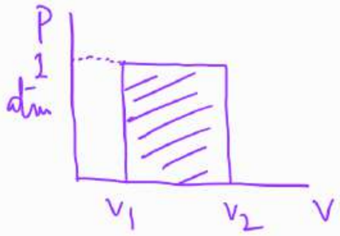
Problem: 1. One mole of N_2 gas is kept at const. pressure of 1.5 atm while its temp is raised from 127°c to 227°c. Calculate ΔU

$\Delta U = n C_v dT \qquad n = 1, \qquad \gamma_{N_2} = 1.41 \qquad \Delta T = 100$

$C_p - C_v = R \Rightarrow C_v = \frac{R}{0.41}$

$\Delta U = \frac{8.31 \times 100}{0.41}$ J

2. A cylinder contains one mole O_2 gas at $T = 27$°c. Gas is heated to $T_2 = 127$°c at const P. Calculate work done, ΔU, draw PV diagram if P = 1 atm.



$p_1 V_1 = RT_1 \Rightarrow V_1 = \frac{RT_1}{p}$, $V_2 = \frac{RT_2}{p}$ $p = 1$ atm $= 1.013 \times 10^6$ dyne/cm^2

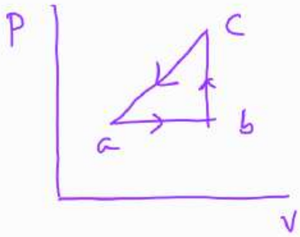
Work done = shaded area $= \int p dv$

$$= 1.01 \times 10^6 (V_2 - V_1) = p \frac{R}{p} (T_2 - T_1)$$

$$= 831 \text{ J}$$

ΔU same as before

3. When a system is taken through the process abc, 180 J of heat is absorbed & 80 J of work is done by it, but when it is taken through ac, it performs 60 J of work. What is the heat flow in this?

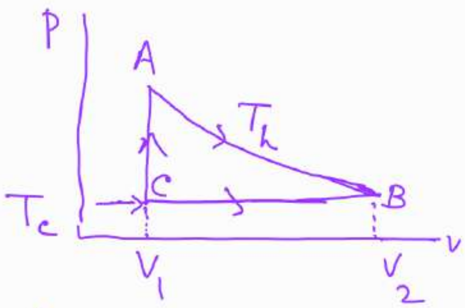


$$\int_{abc} dU = \int_{ac} dU$$ [as internal energy is path independent function]

$$\Rightarrow \int_{abc} (\delta Q - \delta W) = \int_{ac} (\delta Q - \delta W)$$

$$\Rightarrow (180 - 80) = (\delta Q - 60) \Rightarrow \delta Q = 160 \text{ J}$$

4. One mole of ideal gas undergoes reversible cycle ABCA in PV diagram, AB is isotherm at T_h.



Find out the net heat added to the system & W_{net}

$Q_{AB} = RT_h \ln\frac{V_2}{V_1}$, $Q_{BC} = C_p\,(T_c - T_h)$

$Q_{CA} = C_v\,(T_h - T_c)$

$$Q_{net} = RT_h \ln\frac{V_2}{V_1} + (T_h - T_c)\,(C_v - C_p)$$

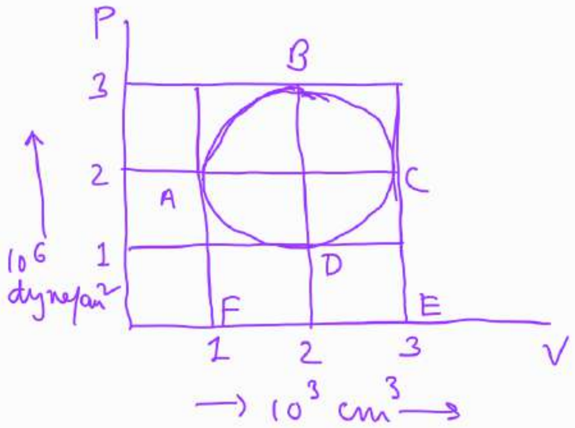
$$= RT_h \ln\frac{V_2}{V_1} - R\,(T_h - T_c)$$

$$W_{net} = W_{AB} + W_{BC} + W_{CA}$$

$$= RT_h \ln\frac{V_2}{V_1} + P_c\,(V_1 - V_2) + P_c \cdot 0 \;(\Delta V = 0)$$

$$= RT_h \ln\frac{V_2}{V_1} + \frac{RT_c}{V_1}\,(V_1 - V_2)$$

5. One mole of ideal gas is subjected to a cyclic quasi-static process which appears as a circle in PV diagram. Show that the net work done by the gas in one cycle is 314 J, internal energy difference of the gas between states C & A is 600 J, heat absorbed by the gas in going from A to C via ABC is 1157 J. $C_v = \frac{3}{2}R$.



Net work done in each cycle = area of PV diagram

$= \pi(1)^2 = \pi$ unit $= \pi \times 100 = 314$ J

One unit area $= pdv = 10^6 \times 10^3 = 10^9$ erg

$= 100$ J

$dU = C_v dT$, At A, $P_1 = 2\times10^6$, $V_1 = 10^3$ cm^3

$$T_1 = \frac{P_1 V_1}{nR} = \frac{2\times10^6 \times 10^3}{8.31\times10^7}$$

$$T_2 = \frac{2\times10^6\times 3\times10^3}{8.31\times10^7}$$

$$dU = \frac{3}{2}R\,(T_2 - T_1) = 600\,\text{J}$$

Work done in going from A to C along ABC

= area under the curve $\widehat{ABC}$ with volume axis

$$= \frac{\pi}{2} + \square ACEF = \left(\frac{\pi}{2}+4\right)100 = 557\,\text{J}$$

Heat absorbed $\delta Q = dU + \delta W = 600 + 557 = 1157$ J

6. Show that for a hydrostatic system $\frac{dV}{V} = \beta_p dT - \frac{dp}{B_T}$

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad B_T = -V\left(\frac{\partial p}{\partial V}\right)_T$$

$$f(p, V, T) = 0 \Rightarrow V = f(p, T) \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

$$= V\beta_p dT - \frac{V}{B_T}dp$$

$$\Rightarrow \quad \frac{dV}{V} = \beta_p dT - \frac{dp}{B_T}$$

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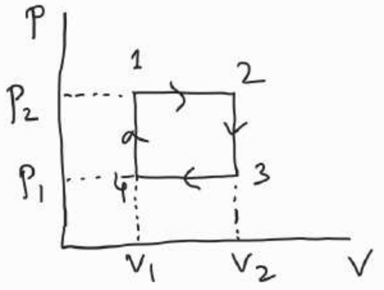
7. One mole of ideal gas is expanded from (T, P_1, V_1) to (T, P_2, V_2) in two stages: in 1st stage opposing pressure p', volume changes from $V_1 \to V'$, 2nd stage opposing pressure P_2, volume changes $V' \to V_2$. For what p' work done would be minimum].

$$W_T = p'(V' - V_1) + P_2(V_2 - V') \quad , \quad \underline{P_1V_1 = RT = P_2V_2 = p'V'}$$

$$= p'\left(\frac{RT}{p'} + \frac{RT}{P_1}\right) + P_2\left(\frac{RT}{P_2} - \frac{RT}{p'}\right)$$

$$= RT\left(2 - \frac{p'}{P_1} - \frac{P_2}{p'}\right) \Rightarrow \frac{dW_T}{dp'} = 0 \Rightarrow \underline{p' = \sqrt{P_1P_2}}$$

8. Find out the efficiency of the cycle.



$$T_1 = \frac{P_2V_1}{R} \, , \quad T_2 = \frac{P_2V_2}{R} \, , \quad T_3 = \frac{P_1V_2}{R}$$

$$T_4 = \frac{P_1V_1}{R}$$

$Q_{12} = C_p(T_2 - T_1) = C_p P_2(V_2 - V_1)/R \leftarrow$ heat absorbed

$Q_{23} = C_V(T_3 - T_2) = -C_V V_2(P_2 - P_1)/R \leftarrow$ rejected

$Q_{34} \to C_p(T_4 - T_3) = -C_p P_1(V_2 - V_1)/R \to$ rejected

$Q_{41} = C_V(T_1 - T_4) = C_V V_1(P_2 - P_1)/R \to$ absorbed

$Q_{ab} = Q_{12} + Q_{41} \qquad W = \square 12341 = (P_2 - P_1)(V_2 - V_1)$

$$\eta = \frac{W}{Q_{ab}} = \frac{(P_2-P_1)\,(V_2-V_1)}{C_p P_2 (V_2-V_1)/R + C_v V_1 (P_2-P_1)/R}$$

$$= \frac{R}{\frac{C_p P_2}{P_2-P_1} + \frac{C_v V_1}{V_2-V_1}} = \frac{\gamma-1}{\frac{\gamma P_2}{P_2-P_1} + \frac{V_1}{V_2-V_1}}$$

9. A cornot engine operates between two bodies of same mass and specific heat 'c'. until the temp are equal. If the initial temp of the bodies are 4T, T show that final temp is 2T & work done per unit mass by the engine is CT.

Initial internal energies of the two bodies

$U_1 = MCT_1 \quad U_2 = MCT_2$

$\delta Q_1 = MCdT_1$

$\delta Q_2 = MCdT_2$

For a Carnot engine $\frac{\delta Q_1}{T_1} = -\frac{\delta Q_2}{T_2}$

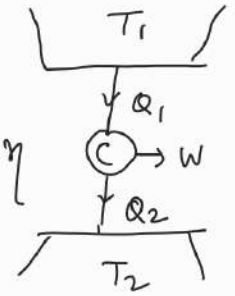
$$\Rightarrow \int_{T_1}^{T_f} \frac{dT}{T} = -\int_{T_2}^{T_f} \frac{dT}{T} \Rightarrow T_f = \sqrt{T_1 T_2}$$
$$= 2T$$

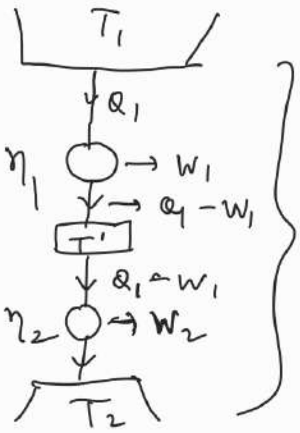
$$W = Q_1 - Q_2 = MC(4T-2T) - MC(2T-T)$$
$$= MCT = CT \quad (M=1)$$

or Energy conservation $\Rightarrow (U_1 - U) - (U - U_2) = U_1 + U_2 - 2U =$ work done

$$= MCT_1 + MCT_2 - 2MCT_f$$
$$= (4C + C - 4C)\,T = CT$$

10. A carnot engine operates between two heat reservoirs T_1, T_2 $(T_1 > T_2)$. A person proposes to increase the efficiency by running one engine between T_1 & T' & other between T', T_2 $(T_1 > T' > T_2)$ using the heat expelled by the 1st engine. Examine if proposal would be successful.





$$\eta = \frac{W}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\eta_1 = 1 - \frac{T'}{T_1} = \frac{W_1}{Q_1}$$

$$\Rightarrow W_1 = Q_1\left(1 - \frac{T'}{T_1}\right)$$

$$\eta_2 = 1 - \frac{T_2}{T'} = \frac{W_2}{Q_1 - W_1} \Rightarrow Q_1 - W_1 = Q_1 - Q_1 + Q_1\frac{T'}{T_1}$$

$$= Q_1 \frac{T'}{T_1}$$

$$W_2 = \left(1 - \frac{T_2}{T'}\right) Q_1 \frac{T'}{T_1} = Q_1\left[\frac{T'}{T_1} - \frac{T_2}{T_1}\right]$$

$$W_1 + W_2 = Q_1 - Q_1\frac{T'}{T_1} + Q_1\frac{T'}{T_1} - Q_1\frac{T_2}{T_1} = Q_1\left(1 - \frac{T_2}{T_1}\right) = W$$

$$\eta_{comb} = \frac{W_1 + W_2}{Q_1} = 1 - \frac{T_2}{T_1} = \eta \Rightarrow \text{efficiency same.}$$

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11. Starting from the internal energy of a paramagnetic system $U(S,M)$ construct $G(T,H)$, prove $\left(\frac{\partial S}{\partial H}\right)_T = \mu_0\left(\frac{\partial M}{\partial T}\right)_H$.
Show that in case of adiabatic demagnetisation $\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\,\mu_0\left(\frac{\partial M}{\partial T}\right)_H$

Elementary work done to develop small amount of magnetisation within the material by dM

$$\delta W = -\mu_0 H dM \Rightarrow dU = T ds + B dM \quad (B = \mu_0 H) \rightarrow ①$$

$$U = U(S,M) \Rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_M ds + \left(\frac{\partial U}{\partial M}\right)_S dM \rightarrow ②$$

$$① \,\&\, ② \Rightarrow \quad T = \left(\frac{\partial U}{\partial S}\right)_M = x \text{ (say)} \quad B = \left(\frac{\partial U}{\partial M}\right)_S = y \text{ (say)}$$

Using Legendre transformation

$$G(T,B) = U(S,M) - ST - MB = U - TS - BM$$

$$dG = dU - SdT - Tds - BdM - MdB = -SdT - MdB$$

$$\equiv M dx + N dy \Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\Rightarrow \left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B \Rightarrow \left(\frac{\partial S}{\partial H}\right)_T = \mu_0\left(\frac{\partial M}{\partial T}\right)_H$$

$$S = S(B,T) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_B dT + \left(\frac{\partial S}{\partial B}\right)_T dB$$

$$\Rightarrow T dS = T\left(\frac{\partial S}{\partial T}\right)_B dT + T\left(\frac{\partial S}{\partial B}\right)_T dB \qquad \left[\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B\right.$$

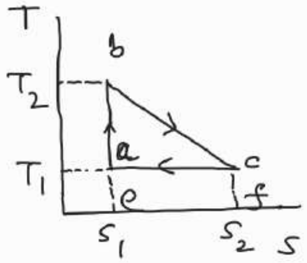
Maxwell's eqn
$dG = -SdT - MdB$

$$= C_H dT + \mu_0 T\left(\frac{\partial M}{\partial T}\right)_H dH$$

$= 0$ for adiabatic

$$\Rightarrow \left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\,\mu_0\left(\frac{\partial M}{\partial T}\right)_H$$

12 Calculate efficiency of the engine



Heat absorbed $Q_1 = \triangle abc + \square fcae$

$$= \frac{1}{2}(S_2-S_1)(T_2-T_1) + T_1(S_2-S_1)$$

$$= (S_2-S_1)\left(\frac{T_1+T_2}{2}\right)$$

Work done $W = \triangle abc = (S_2-S_1)\left(\frac{T_2-T_1}{2}\right)$

$$\eta = \frac{W}{Q_1} = \frac{T_2-T_1}{T_2+T_1}$$

13 A certain system is found to have Gibbs free energy

$$G(P,T) = RT\ln\frac{aP}{(RT)^{5/2}} , \quad C_p = ? \qquad a \to \text{cst}$$

$$G = U - TS + PV \Rightarrow dG = -SdT + VdP \Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -T\frac{\partial^2}{\partial T^2}\left[RT\ln aP - 5/2\, RT\ln(RT)\right]$$

$$= \frac{5}{2}R$$

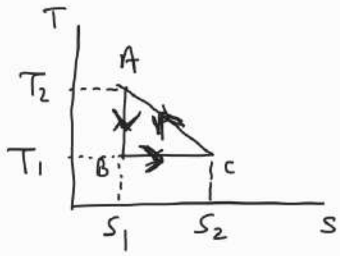
14 A 100Ω resistor is held at cst temp of 300 K. A current of 10 A is passed through it for 300 sec. What is the change in entropy of the resistor & that of universe?

Heat produced $Q = i^2Rt = 10^2 \times 100 \times 300 = 3\times10^6$ J

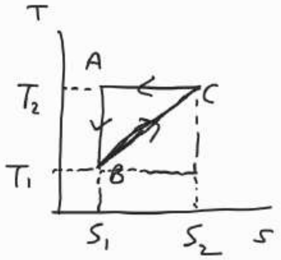
$\Delta S_R = 0$ as temp is maintained cst 300 K

$\Delta S_{surroun} = \frac{3\times10^6}{300} = 10^4$ J/K , $\Delta S_{universe} = 10^4$ J/K

14 Compare the efficiencies of the cycle ABCA



(I)



(II)

Heat absorbed $Q_I = \triangle ABC + \square S_2CBS_1$

$$= \frac{1}{2}(S_2-S_1)(T_2-T_1) + (S_2-S_1)T_1$$

$$= (S_2-S_1)\left(\frac{T_1+T_2}{2}\right)$$

$W_I = \triangle ABC = (S_2-S_1)\left(\frac{T_2-T_1}{2}\right)$ $\quad \eta_I = \frac{T_2-T_1}{T_2+T_1}$

$Q_{II} = \triangle ABC + \square CBS_1S_2 = \frac{1}{2}(S_2-S_1)(T_2-T_1) + \frac{1}{2}(S_2-S_1)(T_2-T_1) + (S_2-S_1)T_1$

$= T_2(S_2-S_1)$ $\quad W_{II} = \triangle ABC = \frac{1}{2}(S_2-S_1)(T_2-T_1)$

$$\eta_{II} = \frac{T_2-T_1}{2T_2} \qquad \eta_I/\eta_{II} = \frac{2T_2}{T_1+T_2}$$

15 Is the isothermal expansion of an ideal gas violates 2nd law?

$\delta Q = dU + \delta W = C_v dT + \delta W \Rightarrow \delta Q = \delta W \quad (dT = 0)$

i.e. whole heat is converted into work → apparent violation of 2nd Law ???

16 A carnot engine is operated between ice-point and steam point. a) if the engine receives 746 cal from hot reservoir in each cycle how much heat does it reject to the cold reservoir. b) if the engine is operated as a refrigerator and receives the same heat from the cold reservoir how much heat does it deliver to the hot reservoir? How much work done by the engine?

$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ $\quad T_1 = 373 \quad T_2 = 273 \quad Q_1 = 746 \quad Q_2 = ?$

$Q_2 = \frac{T_2}{T_1} Q_1 = \frac{273}{373} 746 = 546$, $W = Q_1 - Q_2 = 200$ cal

For refrigerator $Q_1 = Q_2 + W$ $\quad$ W → work done on it

→ heat received from cold reservoir

$$Q_2 = \frac{T_2}{T_1 - T_2} W \Rightarrow W = \frac{T_1 - T_2}{T_2} Q_2 = \frac{100}{273} 546 = 200 \text{ cal}$$

17 The specific volume of water at 0°C increases by 9.1% on freezing and latent heat of fusion of ice is 80 cal/gm at atm pressure. Calculate the pressure needed to lower the melting point of ice by 1°C.

$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}$ $\quad v_2 - v_1 = 0.1$ cc $\quad L = 80 \times 4.2 \times 10^7$ erg

$T = 273$, $dT = 1$

$$dp = 13.6 \times 10^7 \text{ dyne/cm}^2 = \frac{13.6 \times 10^7}{1.03 \times 10^6} = 134.7 \text{ atm}$$

18 A certain amount of monoatomic gas is compressed to half of its intial volume. By what factor does the pressure change if the compression is done isothermally & adiabatically. If the gas be diatomic then what would be the answer?

$V_2 = \frac{V_1}{2}$ $\qquad P_2 = \frac{V_1}{V_2} P_1 = 2P_1$

$PV^\gamma = ct \Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma$ $\qquad \gamma = 1.4$ for diatomic

$= 1.6 \rightarrow$ monoatomic

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

19 A body of mass 'm' with specific heat 'c' at 500K is brought into contact with an identical body at temp 100K & they are isolated from surrounding. Find ΔS

$$mc(500 - T_f) = mc(T_f - 100) \Rightarrow T_f = 300$$

$$\Delta S = mc \int_{T_1}^{T_f} \frac{dT}{T} + mc \int_{T_2}^{T_f} \frac{dT}{T} = mc \ln \frac{300}{500} + mc \ln \frac{300}{100}$$

$$= mc \ln \frac{9}{5}$$

Order parameter: It is a quantity for characterizing the transition between two phases which is non-zero below the transition temp T_c & zero above T_c, $\Delta\rho$, M are the O.P. of fluid & magnetic system.