



CSIR-NET

Council of Scientific & Industrial Research

PHYSICAL SCIENCE

VOLUME - VII

THERMO & STATICAL PHYSICS



THERMO DYNAMIC

1. Intro. Of Thermodynamics	1
2. Phase Transistor	25
3. Magnetic Properties of Solids	40
4. Statistical Mechanics	59
5. Contact b/w Thermo & Statistical Mechanics	87
6. Classical Ideal Gas	105
7. Harmonic Oscillator	108
8. Magnetic System	112
9. Fermi Gas	139
10. Black Body Radiation	144
11. Stephen's law	151
12. Grand Canonical Ensemble	178
13. Brownian Motion	185

Thermodynamics

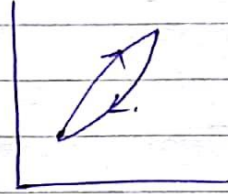
For path independent work $\int \vec{F} \cdot d\vec{r}$ should be Exact.

$$z = z(x, y)$$

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

$$dz = M dx + N dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \text{ - Cond}^n \text{ for Exact } \int$$



Thermodynamical State - P, V, T are thermodynamical state.

$$\text{eq}^n \text{ of state } \boxed{f(P, V, T) = 0}$$

directly.

For extensive quantity we can add these quantity.

eg. $V = V_1 + V_2$

$$m = m_1 + m_2$$

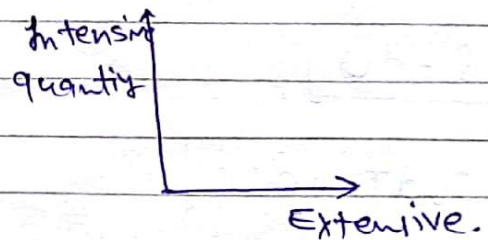
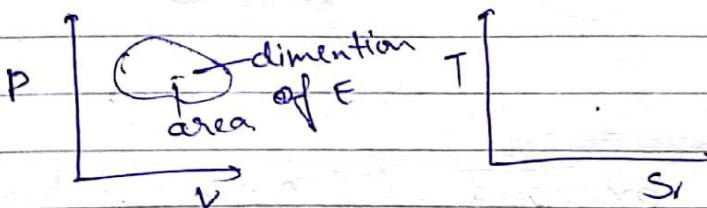
$$S = S_1 + S_2$$

$$U = U_1 + U_2$$

For intensive quantity we can't add these directly.

$$P \neq P_1 + P_2$$

$$T \neq T_1 + T_2$$



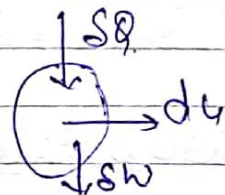
1st law of thermodynamics :-

$$du = \delta Q - \delta W$$

conservation of energy.

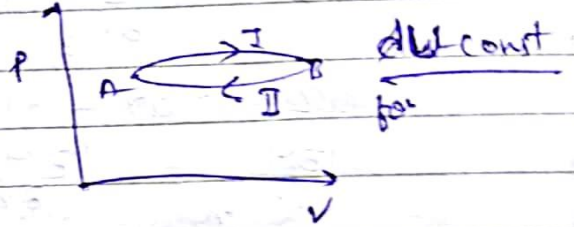
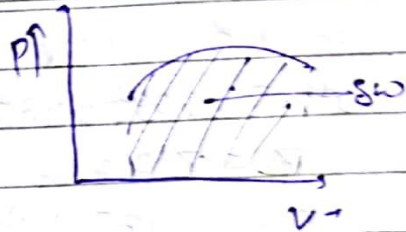
δQ & δW are path dependent process and du is

path independent process;



$$SW = \int \frac{F \cdot dx \cdot A}{A}$$

$$SW = \int P \cdot dV$$



Heat -

Specific Heat -

$$c = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right)$$

depend on the process

Ideal gas process -

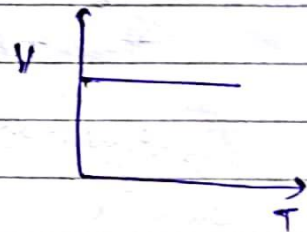
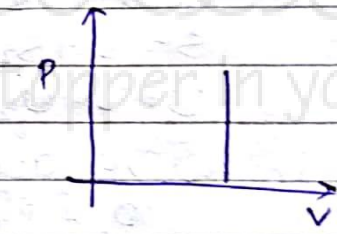
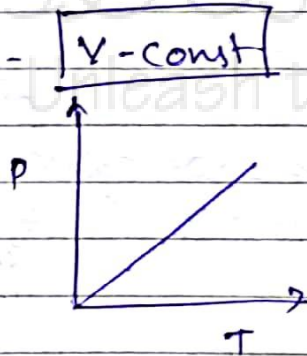
$$PV = nRT$$

i) Isochoric Process :- V = const

$$SW = PdV = 0$$

$$\boxed{SQ = dU}$$

$$\boxed{nc_v dT = dU}$$



In this process heat exchange is path independent and they are perfect differential.

→ Isochoric process will define the internal energy

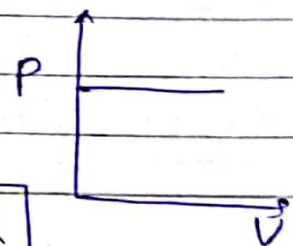
2. IsoBaric Process :- P = const

$$SQ = du + PdV$$

$$= nc_v dT + nRdT$$

$$\boxed{SQ = nc_p dT}$$

$$\boxed{c_p = c_v + R}$$



$$\frac{C_p}{C_v} = \gamma$$

$$C_p - C_v = R$$

$$C_v = \frac{R}{\gamma - 1}$$

$$C_p = \frac{\gamma R}{\gamma - 1}$$

$$\Delta Q = nR \frac{nRdT}{\gamma - 1} = \frac{\gamma}{\gamma - 1} nRdT$$

$$\Delta Q = \frac{\gamma}{\gamma - 1} \Delta W$$

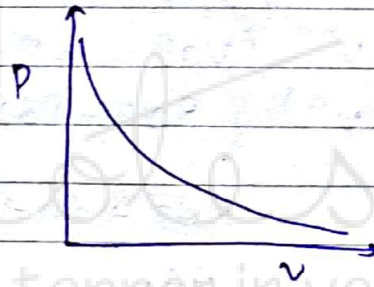
iii) Isothermal Process :- $T = \text{const}$

$$\Delta Q = \Delta W$$

$$= PdV$$

$$\int \Delta Q = nRT \int \frac{dV}{V}$$

$$\Delta U = 0$$



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

iv) Adiabatic Process - $Q = \text{const}$

$$\Delta Q = 0$$

$$\Delta W = -\Delta U$$

In this process work done is path independent.

$$\Delta W = -nC_v dT$$

$$= -\frac{nRdT}{\gamma - 1}$$

$$\Delta W = \frac{nR}{1 - \gamma} (T_2 - T_1) = \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}$$

$$PV^\gamma = \text{const}$$

Q. A Polytropic process $PV^n = \text{const}$ if c_v is specific heat for ideal gas then what will be Heat capacity?

Sol?

$$Q_v = \frac{1}{n} \quad C_v = \left(\frac{\partial Q}{\partial T} \right)_v$$

$$dQ = C_v dT \quad du = C_v dT$$

$$dQ = du + PdV$$

$$C_v dT = C_v dT + PdV$$

$$PV^n = \text{const.}$$

$$dP V^n + n P V^{n-1} dV = 0$$

$$PV = RT$$

$$V dP + P dV = R dT$$

$$V^{n-1} (V dP + n P dV) = 0$$

$$V^{n-1} (R dT - P dV + n P dV) = 0$$

$$R dT + (n-1) P dV = 0$$

$$P dV = \frac{R dT}{1-n}$$

$$C_v dT = C_v dT + \frac{R dT}{1-n} = \left(C_v + \frac{R}{1-n} \right) dT$$

$$C = C_v + \frac{R}{1-n}$$

2nd Law of Thermodynamics :-

1. Heat can't flow from lower temp to higher temp.
2. One can't make any heat engine which has 100% efficiency
+ the most efficient heat engine given by

Carnot cycle which is also not 100% efficient.

3. One can't make a natural process in which entropy of a universe will decrease. It will either increase or remain const.

Entropy is a measurement of disorder and randomness.
↳ no of ways

For irreversible process $\Delta S > 0$ (universe).

→ What is 'ideal reservoir'?

→ Ideal reservoirs have infinite heat capacity. So it can either heat or absorb or release, and during the exchange of heat temp of ideal reservoirs remain const.

→ Body - The specific heat or heat capacity of a body is finite and during exchange of heat the temp of a body will continuously change.

3rd law of thermodynamics -

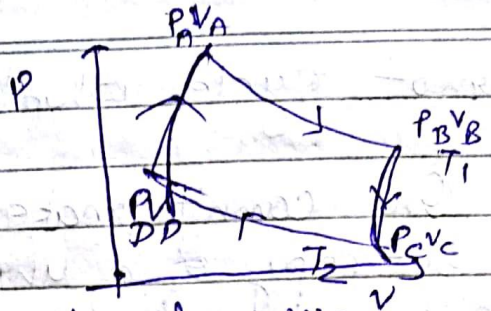
One can't achieve zero K temp. we can only tend to zero.

Zeroth law - If A & B will be in thermally eqⁿ. B & C will be in thermally eqⁿ then A & C ~~is~~ also in thermally eqⁿ.

Entropy

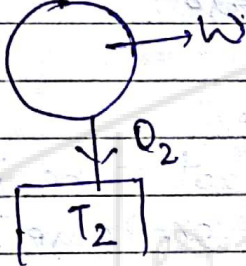
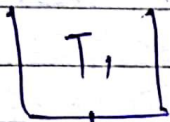
$$ds = \frac{\delta Q}{T}$$

$$Tds = du + PdV$$



$$\eta = \frac{W}{Q_1}$$

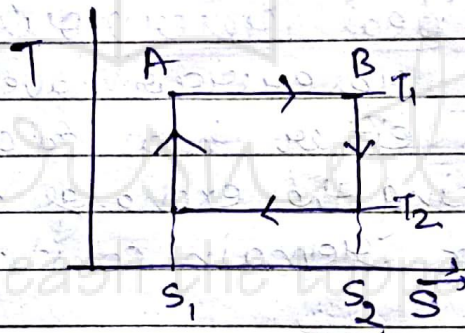
Q_1 - heat absorb. - +ve
 heat release - -ve



$$\eta = \frac{|Q_1| - |Q_2|}{|Q_1|} = 1 - \frac{T_2}{T_1} = 1 - \frac{|Q_2|}{|Q_1|}$$

For Carnot cycle

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



$$W = (T_1 - T_2)(S_2 - S_1)$$

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

Inequality of Clausius -

$$\eta_{\text{irr}} < \eta_c$$

$$1 - \frac{|Q_2|}{|Q_1|} < 1 - \frac{T_2}{T_1}$$

$$\frac{|Q_2|}{Q \cdot T_2} \geq \frac{|Q_1|}{T_1}$$

entropy of sink >
 entropy of
 source.

Q. m mass of water at hot temp T_h mixed with same mass of water with cold temp T_c . What will be eq^m temp.

i) What will be change in entropy of hot water.

ii) " " " " " " cold water.

iii) Prove that the mixing of water is irreversible process.

Solⁿ

$$mc(T - T_c) + mc(T - T_h) = 0$$

$$T = \frac{T_c + T_h}{2}$$

$$ds_h = \frac{mcdT}{T}$$

$$ds_h = \int_{T_h}^T \frac{mcdT}{T} = mc \ln \frac{T}{T_h}$$

$$ds_c = \frac{mcdT}{T} = \int_{T_c}^T \frac{mcdT}{T} = mc \ln \frac{T}{T_c}$$

$$\Delta S_h + \Delta S_c = mc \left(\ln \frac{T}{T_h} + \ln \frac{T}{T_c} \right)$$

$$= mc \ln \left(\frac{T^2}{T_h T_c} \right) = mc \ln \left(\frac{T_h + T_c}{2\sqrt{T_h T_c}} \right)^2$$

$$= 2mc \ln \left(\frac{T_h + T_c}{2\sqrt{T_h T_c}} \right)$$

$$\left\{ T_h + T_c > 2\sqrt{T_h T_c} \text{ (always)} \right.$$

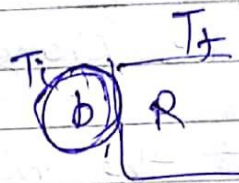
So $\Delta S = +ve$ So it is irreversible process.

Q. A body of const heat capacity C and temp T_i is put in contact with reservoir at temp T_f . Eq^m b/w reservoir and body establish. What will be change in entropy of body. ($T_f > T_i$)

What will be change in entropy of reservoirs.
 What will be change in entropy of universe.

Solⁿ

$$\Delta S_b = m \int_{T_i}^{T_f} \frac{cdT}{T}$$



$$\Delta S_b = mc \ln \frac{T_f}{T_i}$$

$$\Delta S_R = - \frac{\int_{T_i}^{T_f} mc dT}{T_f}$$

$\int_{T_i}^{T_f} mc dT$ - Heat taken by body

$$= - \frac{mc(T_f - T_i)}{T_f}$$

$$\Delta S_u = \Delta S_b + \Delta S_R = mc \ln \frac{T_f}{T_i} - \frac{mc(T_f - T_i)}{T_f}$$

Q A mole of an ideal gas under goes reversible isothermal expansion from volume V_1 to $2V_1$. what will be change in entropy of gas.

what will be change in entropy of universe. suppose that the same expansion can be achieved by free expansion. what will be entropy of gas and what will be entropy of universe.

Solⁿ - i) $\Delta S_g = nR \ln \frac{2V_1}{V_1} = nR \ln 2$

ii) $\Delta S_R = \frac{nC_v dT}{T} \neq 0$

$$\Delta S_R = -nR \ln 2$$

$$\Delta S_u = 0 \quad \text{so this is reversible}$$

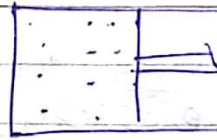
Free expansion

pull the piston very fastly higher than its rms speed.

so gas position of gas will not change at that time

so $\boxed{\delta W = 0}$

$\delta U = 0$ so $\delta Q = 0$



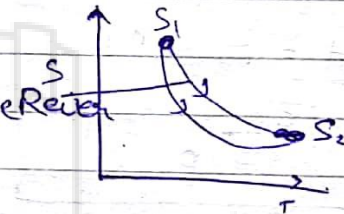
but change in entropy will not zero.



Entropy is path independent.

so we take one path reversible and for reversible process.

$\Delta S_g = nR \ln 2$



And for reservoir $\Delta S_R = 0$ Reservoir is not exchanging any heat.

$\Delta S_U = nR \ln 2$

Maxwell Relation and thermodynamical Potential:

$du = Tds - sdT$

$U(S, V) \rightarrow$ Internal energy

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

$P = -\left(\frac{\partial U}{\partial V}\right)_S$

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

$Mdx + Ndy$

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

Exact diff eqn

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

When process is adiabatic or isochoric then internal energy of the system is min.

Enthalpy -

$$\begin{aligned}
 H &= U + PV \\
 dH &= du + pdv + vdp \\
 &= Tds - pdv + pdv + vdp \\
 &= Tds + vdp
 \end{aligned}$$

$$H = H(S, P)$$

$$\left(\frac{\partial H}{\partial S} \right)_P = T$$

$$\left(\frac{\partial H}{\partial P} \right)_S = V$$

$$\begin{aligned}
 \eta &= S & \gamma &= P \\
 M &= T & N &= V
 \end{aligned}$$

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

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

When in a process which is isobaric and adiabatic then enthalpy is min.

Helmholtz Free Energy - $F = F(V, T)$

$$\begin{aligned}
 F &= U - TS \\
 dF &= du - Tds - sdt \\
 &= Tds - pdv - Tds - sdt \\
 &= -pdv - sdt
 \end{aligned}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T$$

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

$$\begin{aligned}
 M &= -P & N &= -S \\
 \eta &= V & \gamma &= T
 \end{aligned}$$

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

$$\begin{matrix} V & F & T \\ U & & G \\ S & n & P \end{matrix}$$

$$\begin{matrix} U \\ S & n & P \end{matrix}$$

$$dF = SdT - \frac{MdH}{M}$$

When process is isochoric and isothermal then Free energy will be min.

$U - TS$ is available energy for work done.

Gibbs Free Energy -

$$G = H - TS$$

$$dG = dH - Tds - SdT$$

$$= VdP + Tds - Tds - SdT$$

$$= VdP - SdT$$

$$G = G(P, T)$$

$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$\begin{matrix} M=V & N=-S \\ n=P & y=T \end{matrix}$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$

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

$$S = S(T, V)$$

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

$$Tds = C_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV$$

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

Or For ideal gas of const. specific heat is C_V and temp and vol^m changes from (T_1, V_1) to T_2, V_2 then what will be change in entropy.

$$PV = RT$$

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

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

$$ds = C_V \frac{dT}{T} + \frac{R}{V} dV$$

$$ds = \frac{C_v dT}{T} + \frac{R dv}{v}$$

$$\boxed{ds = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}}$$

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

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

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

$$\boxed{T ds = T \left(\frac{\partial S}{\partial T}\right)_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP}$$

$$\boxed{T ds = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP}$$

$$S = S(P, V)$$

$$ds = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

$$T ds = T \left(\frac{\partial S}{\partial P}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + T \left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV$$

$$\boxed{T ds = C_v \left(\frac{\partial T}{\partial P}\right)_V dP + C_p \left(\frac{\partial T}{\partial V}\right)_P dV}$$

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

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

$$dU = T ds - P dV$$

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

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P} \quad \text{1st energy eqn}$$

Q For the ideal gas prove that internal energy is not fun of volⁿ.

ii) If van der Waal eqⁿ $(P + \frac{a}{V^2})(V-b) = RT$ if vol^m will change from V_1 to V_2 at const temp what will be change in internal energy.

Solⁿ $PV = RT$

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

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

$$\partial U = \text{const} \cdot \left(\frac{\partial U}{\partial V}\right)_T = 0$$

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

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

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T \cdot \frac{R}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \Rightarrow U = \int \frac{a}{V^2} dV$$

$$= -a \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\Delta U = a \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$U_2 - U_1 = \frac{a}{V_2} - \left(-\frac{a}{V_1}\right)$$

$$\text{So } \left. \begin{aligned} U_1 &= -\frac{a}{V_1} \\ U_2 &= \frac{a}{V_2} \end{aligned} \right\}$$

If $F = -\alpha VT^4$ and $C_V = \beta S$ what is value of β .

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 4\alpha VT^3$$

$$C_V = \beta \cdot 4\alpha VT^3$$

$$\Rightarrow \beta = \frac{C_V}{4\alpha VT^3}$$

$$\left. \begin{aligned} C_V &= T \left(\frac{\partial S}{\partial T}\right) \\ &= 12\alpha T^3 \end{aligned} \right\}$$

$$\beta = 3$$

V F T
 U G
 S H P

$$\begin{aligned}
 \frac{\partial S}{\partial V} &= \frac{\partial P}{\partial T} \\
 \frac{\partial T}{\partial P} &= \frac{\partial V}{\partial S} \\
 \frac{\partial S}{\partial P} &= -\frac{\partial V}{\partial T}
 \end{aligned}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \alpha T^4$$

Q. If entropy of a system is given by

$$S = \frac{n}{2} \left[\sigma + 5R \ln \frac{U}{n} + 2R \ln \frac{V}{n} \right]$$

What will be internal energy and what will be C_V

Solⁿ $T = \left(\frac{\partial U}{\partial S} \right)_V$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V$$

$$\frac{\partial S}{\partial U} = \frac{5nR}{2} \cdot \frac{1}{U} \cdot \frac{1}{n} =$$

$$\frac{1}{T} = \frac{5nR}{2U} \Rightarrow U = \underline{\underline{\frac{5}{2} n R T}}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \underline{\underline{\frac{5}{2} n R}}$$

Q. $U = \alpha S^2 V^3$ what will be temp of a system

$$T = \left(\frac{\partial U}{\partial S} \right)_V = 2\alpha S V^3$$

Q. Prove that $U = -T^2 \left(\frac{\partial (F/T)}{\partial T} \right)_V$

$$F = U - TS$$

$$U = F + TS$$

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

Ensemble - collection

1. Microcanonical Ensemble. (N, V, E) - (Ideal situation)
 - Energy doesn't change - isolated wall
 - Volume " " - volume rigid wall
 - No. of particle " " - impenetrable wall.

2. Canonical Ensemble (T, V, N) -
 - wall = rigid, impenetrable or end conductor.
 - temp. doesn't change and energy exchange.

3. Grand Canonical Ensemble (T, V, μ) -
 - Rigid, conductor

Canonical Ensemble -

$$P(E_i) = A e^{-\beta E_i}$$

$$\sum P(E_i) = 1$$

$$A \sum e^{-\beta E_i} = 1$$

$$A = \frac{1}{\sum_i e^{-\beta E_i}}$$

$$P(E_i) = \frac{g_i e^{-\beta E_i}}{\sum g_i e^{-\beta E_i}}$$

$$Z = \sum_i g_i e^{-\beta E_i}$$

Quantum mechanical

$$\langle U \rangle = E = \frac{\sum E_i P(E_i)}{\sum g_i e^{-\beta E_i}}$$