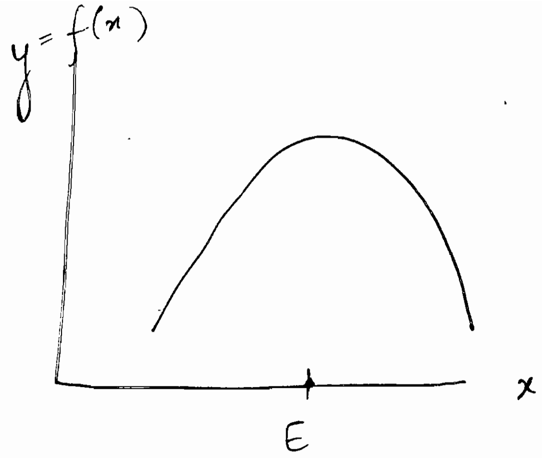
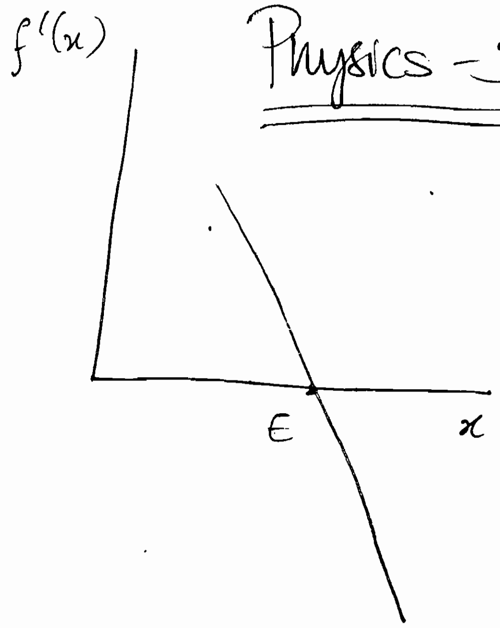
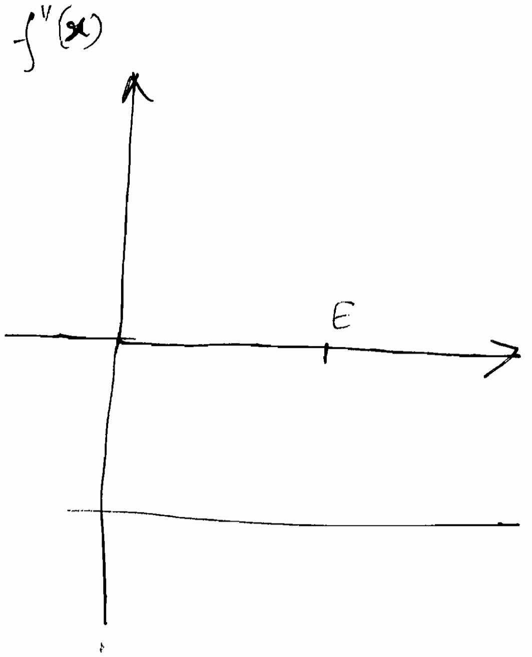
Physics - 3



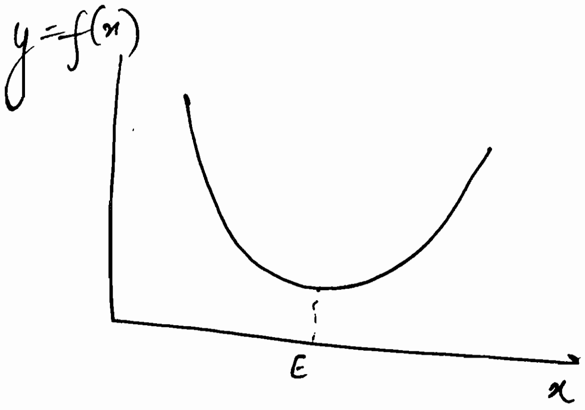


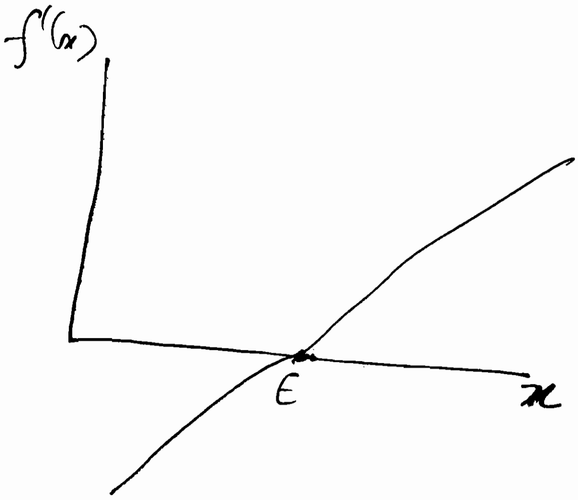


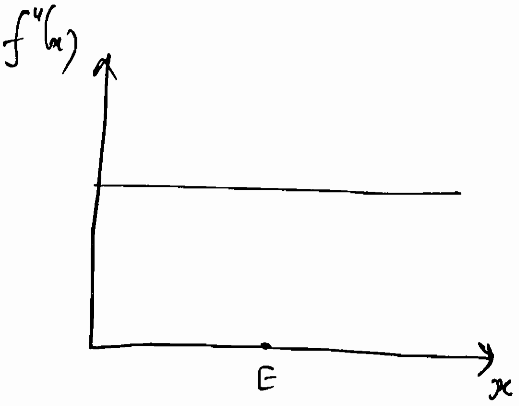
at Maxima, E

$$f'(x)\big|_E = 0$$

$$f''(x)\big|_E < 0$$







at minima E,

$$f'(x)\big|_E = 0$$

$$f''(x)\big|_E > 0$$

⊙ Vander Wall's Equation for Real Gas :

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

This equation is for 1 mole of real gas.

If moles are n and given Volume is V_0

⇒ Volume occupied by 1 mole $= \left(\frac{V_0}{n}\right)$

⇒ Equation for 1 mole becomes same :

$$\left[P+\frac{a}{\left(\frac{V_0}{n}\right)^2}\right]\left[\frac{V_0}{n}-b\right] = RT$$

⊙ Similarly $PV = RT$ is equation for 1 mole of ideal gas. If n moles and V_0 volume is given ⇒ Volume occupied by 1 mole of ideal gas $=\left(\frac{V_0}{n}\right)$. Pressure and Temp. remain same throughout

$$\Rightarrow \quad P\left(\frac{V_0}{n}\right) = RT$$

⊙ Avogadro's Number = 6×10^{23} molecules / mole

✪ $\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n}$

⊙ Helium has 2 isotopes (^3_2He and ^4_2He) which behave quite differently at low temperatures. This is because ^3_2He is a fermion ($s=\frac{1}{2}$) while ^4_2He is a boson ($s=1$)

✪ NTP : Normal Temperature & Pressure (20°C, 1 atm)

STP : Standard Temp. & Pressure (0°C, 1 atm)

SATP : Standard Ambient Temp. & Pressure (25°C, 1 atm)

✪ 31.4°C : Critical Temp. for CO_2

✪ $b = 4V_{(\text{all molecules})}$

Section B

26/12/2011

Units of viscosity

$\boxed{CGS}$

η : POISE

$\frac{\eta}{\rho}$: STOKE

$\boxed{SI}$

η : POISEUILLE (Pl)

where $\eta = \frac{F}{A\left(\frac{dv}{dz}\right)}$, ρ : density

Q5) 3 bits + 3 bits

Q6) Elec & Magn.

Q7) EM Theory + (1 bit at max of Thermal Physics)

Q8) Thermodynamics

$\boxed{\text{15 LECTURES}}$

$\Rightarrow$ 60+30+10 = 100 marks of Thermo

(a) Thermodynamics

① **Basic Concepts** : Terminology, Laws of thermodynamics, Work, different thermodynamic Processes.

② **Heat Engines** : Otto & Diesel Engines

③ **Entropy**

④ Thermodynamic Relations : Maxwell Relations
- → Clasius- Claperyon Eq^n.
- → Joule kelvin
- → Adiabatic demagnetization

⑤ VanderWal's Eqn

⑥ Specific Heat of Solids

⑦ Misc. Gibbs Phase Rule / Transport Phenomenon

(5) Statistical Physics

① Maxwell - Boltzman Statistics (Concept of negative Temprature)

② Fermi Dirac Statistics

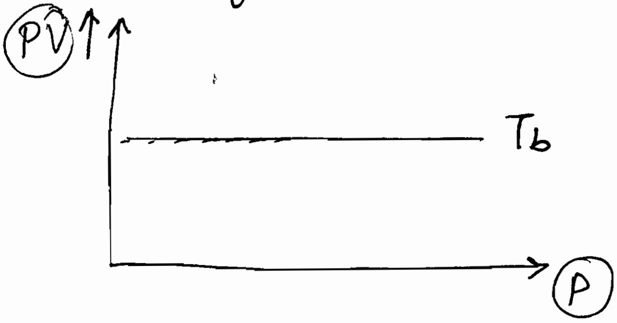
③ Bose Einstein Statistics → (Black Body Radiation) (Specific Heat of Gases)

14-15 classes

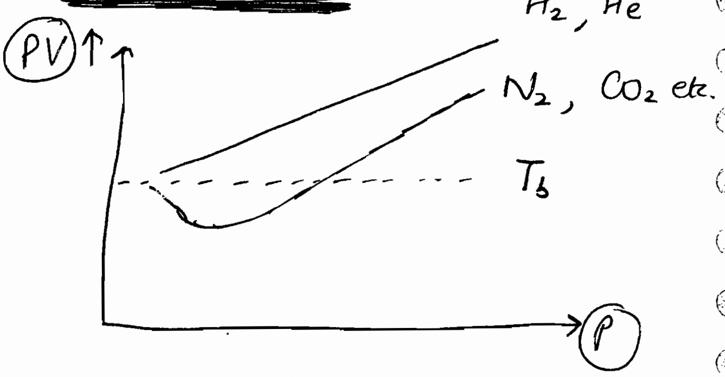
[B.Sc Honours Course of Thermodynamics]

(*) **Vapour**: usually applied to gas in equilibrium with its liquid (i.e. saturated vapour) or to a gas at a temperature below T_c. Its properties are similar to a gas.

(*) **For ideal gas**

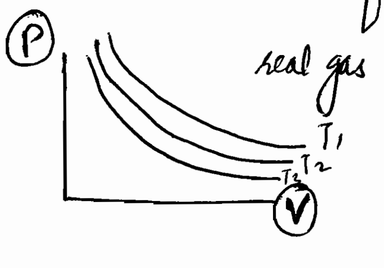


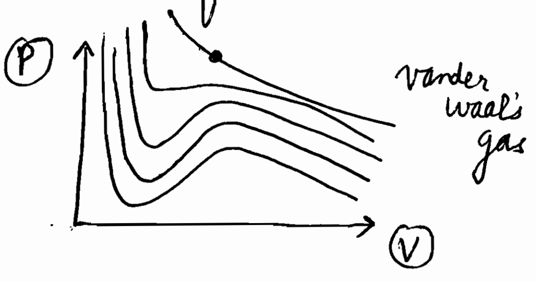
Actually observed



(*) T_b : Boyles Temperature, temp. at which Boyle's law holds for fairly wide range of Pressure.

(*) Triple Point of water : 0·01°C, 4.58 mm of mercury
Its used to define kelvin scale of Temperature.





Thermodynamics (1)

26/12/2011

Heat is a form of energy. Heat can be converted into Work and Work can be converted into Heat. This interconversion is the domain of thermodynamics.

3 techniques to study these interactions

1) Thermometry

✓ direct measurement of parameters and getting the relations, thereby.

✓ We are not concerned about consituents of system. i.e Not concerned about individual particles' behaviour

✓ We are interested in Macro variables.

2) Kinetic Theory of Gases

✓ trying to track down behaviour of individual molecules

✓ here also we can account for macro variable using integrated affect of individual molecules.

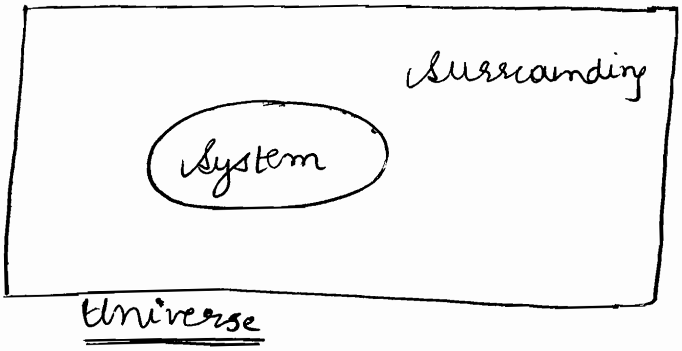
3) Statistical Thermodynamics:

✓ in between the previous 2 approaches

✓ we measure things at equilibrium: the most probable state of matter.

✓ we study aggregate behaviour or expectation values

Thermodynamic System



"A definite quantity of matter (i.e. can exchange mass and energy) with a distinct boundary."

Depending upon exchange of mass & energy b/w system and surrounding, we have:

1) Open System: Both energy & mass can be exchanged

2) Closed: Energy interaction allowed

3) Isolated: No interaction allowed.

Temperature and other thermodynamic variables

How hot or cold the system: Temperature

State of any system can be defined in terms of thermodynamic variables. They are of 2 types:

1) Intensive: independent of mass eg. Specific Heat Capacity
2) Extensive: dependend on mass eg. Heat Capacity

Also, we have variables as :

1) Macro : can be perceived by sense : aggregate behaviour
2) Micro : behaviour of individual particles

These variables are measured by the 3 techniques mentioned before.

Equation of state is nothing but relationship between thermodynamic variables.

eg. $\underline{f(P,V,T) = 0}$

eg for an ideal gas : $PV = nRT$

Boyles law $P \propto \frac{1}{V}$ } from Thermometry

Charles' law $V \propto T$

$$P = \frac{1}{3} \frac{Nm\bar{v}^2}{V}$$

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT$$

$$\Rightarrow PV = nRT$$

} from kinetic Theory

If thermodynamic system is dependent upon or described by 3 variables
⇒ only 2 are independent. Hence state is known only via 2 variables.

All the thermodynamic variables are measured at Equilibrium.

Thermodynamic Equilibrium

It means system is in : thermal equilibrium
mechanical equilibrium
chemical equilibrium

Ⓣ Thermal Equilibrium : No temperature gradient inside the system i.e. no heat flow within the system. Thermal Equilibrium defined by a particular temperature.

Concept of Temperature comes from 0^{th} law of temperature.

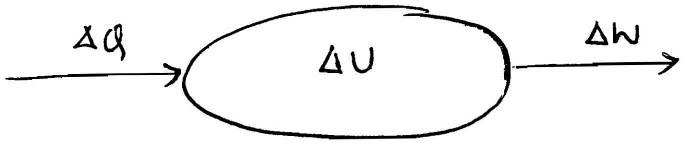
Ⓟ Mechanical Eqb : No unbalanced forces i.e. Pressure througout the system is same.

Ⓥ Chemical Eqb : There is no chemical concentration in any part of system. Volume is measured at chemical eqb.

If there are 2 eqb, 3^{rd} eqb. will automatically follow.

Laws of Thermodynamics:

1st law : Statement of Conservation of Energy.



$$\boxed{\Delta Q = \Delta U + \Delta W}$$

Heat given to system : ⊕ve
Work done by system : ⊕ve

⊛⊛

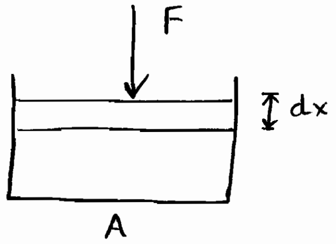
$$\Rightarrow \quad \underset{\Delta(\text{internal energy})}{\underset{\uparrow}{\Delta U}} = \underset{\text{heat given to system}}{\Delta Q} - \Delta W \leftarrow \text{Work done by System}$$

[The sum of total kinetic and potential energies of all molecules constitutes the internal energy of the system.]

We know $\Delta W = F \cdot dx$

$= P\ A\ dx$

$= P\ dV$



⊛ For solid $dW = 0$

$\Rightarrow \quad \Delta Q \propto \Delta T$

$\Delta Q \propto$ mass

$$\Delta Q = (\underset{\substack{\nearrow \\ \text{heat capacity} \\ (S)}}{m} \underset{\substack{\uparrow \\ \text{specific heat} \\ (s) \text{ or } (c)}}{s})\ \Delta T$$

Heat Capacity :-
Extensive Variabl

Specific Heat Capacity :
intensive variable

$$s = \frac{1}{M}\left(\frac{\Delta Q}{\Delta T}\right)$$

Solids have only 1 specific heat capacity since their volume is assumed to be const.

Thermodynamic Process

Going from 1 thermodynamic state of equilibrium to other equilibrium state.

We know (n-1) independent variables, 1 dependent variables. Usually the latter variable is kept const. during any thermodynamic process.

Process is named after that variable which is kept const.

eg. Isochoric Adiabatic
Isobaric Isothermal

eg. Volume is kept const. for determining specific heat of solids.

$$\boxed{C_V = \left(\frac{dQ}{dT}\right)_V}$$

i.e. $dQ = C_V\, dT$

Similarly we can define

$$\boxed{C_p = \left(\frac{dQ}{dT}\right)_P}$$

i.e. $dQ = C_P\, dT$

$C_p = C_v$ in case of solids

$C_p \neq C_v$ in case of liquids and gases.

dU: Internal Energy or Intrinsic Energy

Characteristics of molecules.

$$\boxed{dU = \underset{\substack{\uparrow \\ \text{due to} \\ \text{motion of molecules}}}{dU_{K.E.}} + \underset{\substack{\uparrow \\ \text{due to interaction} \\ \text{between molecules}}}{dU_{P.E.}}}$$

If there is no interaction between particles $dU_{P.E.} = 0$

eg. Ideal Gas have non-interacting particles.

$$\underline{dU_{\text{ideal gas}} = dU_{K.E.}}$$

$$\underline{dU_{K.E.} = f(T)}$$

⇒ for ideal gas : $\underline{U = U(T)}$: for non interacting molecules

$$\left.\begin{aligned} &\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0 \\ &\Rightarrow \left(\frac{\partial U}{\partial P}\right)_T = 0 \end{aligned}\right\} \text{Joule's law}$$

Inter Molecular Interactions are characterized by volume

⇒ $\underline{U = U(T,V)}$: for interacting molecules

[We could have taken (T,P) also, but we love $\underline{f(T,V)}$]

$$\boxed{dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV}$$

U is a state function i.e. dU is dependent upon initial and final equilibrium positions and independent of the process taken.

$$dQ = dU + P\,dV$$

$$C_V\,dT = dU + P.0 = dU$$

$$\Rightarrow \boxed{dU = C_V\,dT}$$

⊙ We have calculated $dU = C_V\,dT$ for $dV = 0$

If we assume dU as f(T) only, then we can say for same dT (as U is a state function)

$U = C_V\,dT$ (always)

But if we assume $U = f(T,$ as is the case normally, then we need to write

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

& cannot write in general that $dU = C_V d$

$$dQ = dU + dW$$

$$\Rightarrow C_p dT = C_v dT + P dV$$ (at Const. Pressure)

$$\Rightarrow \boxed{C_p = C_v + P\left(\frac{dV}{dT}\right)_P}$$

In case of solids $\left(\frac{dV}{dT}\right)_P = 0 \Rightarrow \boxed{C_p = C_v}$

For ideal gases $PV = RT \Rightarrow \left(\frac{dV}{dT}\right)_P = \left(\frac{R}{P}\right)$

$$\Rightarrow \boxed{C_p = C_v + R}$$

0th law of thermodynamics

If 2 system A and B are in thermal equilibrium and 2 systems B and C are in thermal equilibrium, this implies A and C are in thermal equilibrium.

$\Rightarrow$ At [redacted] thermal equilibrium, some thermodynamic property is const.

We define that property as Temperature. T

$\Rightarrow$ if $T_A = T_B$

and $T_B = T_C$

$\Rightarrow T_A = T_C$

$(13, 9) \Leftrightarrow$ Coprime

$(9, 26) \Leftrightarrow$ coprime

but $(13, 26) \not\Leftrightarrow$ coprime

✪ Note that if volume change $= 0$, then $dU = C_v dT$ always. But if volume change $\neq 0$, then

$$dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV$$ in general case

For ideal gas, Joule's law states that $\left(\frac{\partial U}{\partial V}\right)_T = 0 \Rightarrow \boxed{dU = C_v dT}$

2nd law of thermodynamics

100% of [redacted] conversion of heat into work is not possible.

[Heat → Work Conversion] via Heat Engine.

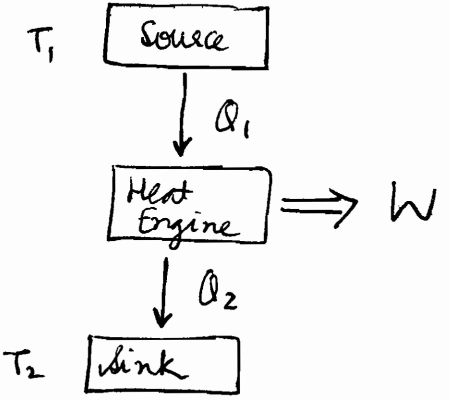
[Work → Heat] via Referigerator.

$$\eta = \frac{\text{Output}}{\text{Input}} = \frac{W}{Q}$$

$$\eta < 1$$

kelvin Planck Statement of 2nd law.

" It is impossible to contruct a device whose sole job is to take heat from source at higher temperature and perform equivalent amount of work w/o producing any other changes into parts of system."



$T_1 > T_2$

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

$$Q_1 = Q_2 + W \quad \Rightarrow \quad \eta = \left(\frac{Q_1 - Q_2}{Q_1}\right) = \left[1 - \left(\frac{Q_2}{Q_1}\right)\right]$$

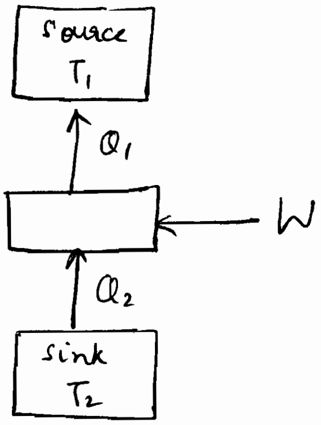
For $\eta = 100\% \rightarrow Q_2 = 0$ which is contradicted by kelvin Planck Statement.

~~Perpetual Machine of 1st kind : Heat Engine~~

~~Perpetual Machine of 2nd kind : Refrigerator~~

"Classius - Ostwald statement"

"It is impossible to contruct a device whose sole job is to get heat from a lower temperature, [redacted]) and release the heat at [redacted] higher temperature."



$T_1 > T_2$

$\left(\frac{Q_2}{W}\right)$: coefficient of Performance

Ostwald statement

"It is impossible to have a perpetual machine of 2nd kind."

3rd law of thermodynamics

(corollary to 2nd law)

$\eta < 1$

$1 - \frac{T_2}{T_1} < 1$

$\Rightarrow \boxed{T_2 > 0}$ always

- Absolute Zero is unattainable in a finite number of steps.

OR
- Entropy of a system cannot be reduced to zero in a finite number of operations.

OR
- Entropy of a perfect crystal at absolute zero is exactly equal to zero. (Only 1 available microstate)

Thermodynamic Processes for Ideal Gas

For an ideal gas : $PV = RT$ (for 1 mole)

Isothermal

$PV = \text{const.} = RT$

$\rightarrow dU = C_V\,dT = 0$ (ideal gas; otherwise $\left(\frac{\partial U}{\partial V}\right)_T dV$ term als

$\rightarrow dW = P\,dV = \left(\frac{RT}{V}\right) dV = RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{P_1}{P_2}\right.$

$V_2 > V_1 \Rightarrow$ Gas expanding $\Rightarrow$ ⊕ve work by system

$V_1 > V_2 \Rightarrow$ Gas compressing by external force $\Rightarrow$ ⊖ve work by system

$\rightarrow \bar{d}Q = dW = RT\ln\left(\frac{V_2}{V_1}\right)$

Isochoric

$PV = RT \Rightarrow \frac{P}{T} = \frac{R}{V} = \text{const.}$

$dW = P\,dV = 0$

$dU = C_v\,dT$

$dQ = dU = C_v\,dT$

Isobaric

$dW = P\,dV = P(V_2 - V_1)$

$dQ = C_p\,dT$

$dU = dQ - dW$

Adiabatic

$$dQ = 0$$

$$dW = -dU$$

$$dW = PdV$$

$$dU = -PdV$$

Perpetual Motion Machine of 1st type produces work w/o the input of energy. It thus violates the 1st law of thermodynamics.

Perpetual Motion Machine of 2nd type spontaneously converts thermal energy into mechanical work. When thermal energy is equivalent to work done, this does not violate the law of conservation of energy. However, it violates the 2nd law of thermodynamics.

⊙ We know η of a heat engine will always be less than 1. This means that to get some useful work done, some energy is always lost. The lost energy can add to thermal pollution in our surrounding leading to global warming.... We say so because usually source is not atmosphere but sink is more often than not, the atmosphere.

Thermodynamics (2)

27/12/2011

For adiabatic, we can derive 1 more equation for an ideal gas :-

(dU को $C_v dT$ लिख
means you are talkin
about Ideal Gas

$$dQ = 0$$

$$\Rightarrow dU + PdV = 0 \quad \Rightarrow \quad C_v\, dT + PdV = 0$$

$$\Rightarrow C_v\, dT + \frac{RT}{V}\, dV = 0$$

(we can replace P in real gas also)

$P + a$

$$\Rightarrow C_v \left(\frac{dT}{T}\right) + R\left(\frac{dV}{V}\right) = 0$$

$$\Rightarrow \left(\frac{dT}{T}\right) + \left(\frac{R}{C_v}\right)\left(\frac{dV}{V}\right) = 0$$

$$\boxed{\begin{gathered} \frac{C_P}{C_v} = \gamma \text{ (dependent on atomicity of gases)} \\ C_P - C_v = R \\ \Rightarrow (\gamma - 1) C_v = R \\ \Rightarrow \frac{R}{C_v} = (\gamma - 1) \end{gathered}}$$

Its called Gamma

$$\boxed{\gamma > 1}$$

$$\Rightarrow \left(\frac{dT}{T}\right) + (\gamma - 1)\left(\frac{dV}{V}\right) = 0$$

$$\Rightarrow \int \frac{dT}{T} + (\gamma - 1)\int \frac{dV}{V} = \ln(c) \quad \text{(say)}$$

$$\Rightarrow \ln T + (\gamma - 1)\ln V = \ln(c)$$

$$\Rightarrow \boxed{TV^{\gamma - 1} = c}$$

For ideal gas

$$\frac{PV}{R} \cdot V^{\gamma - 1} = c \quad \Rightarrow \quad \boxed{PV^{\gamma} = \text{const}}$$

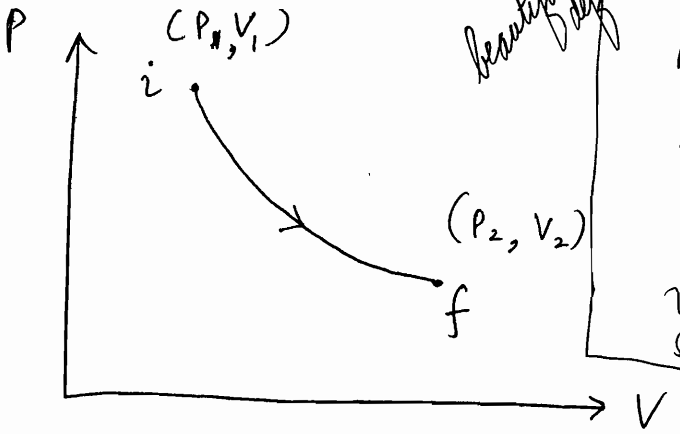
$$\boxed{PV^{n} = \text{const}}$$: depending on n $(0, 1, \infty, \text{any other})$ it can represent any process

isobaric → 0, isothermal → 1, isochoric → ∞, adiabati → any other

$dP\, V^{n} + P \gamma V^{n-1} dV = 0 \Rightarrow dV = -\frac{V\, dP}{nP}$ if $dV = 0 \Rightarrow n \to \infty \Rightarrow$ for isochoric $n = \infty$

Indicator diagram. (Or PV diagram)

Indicator diagram can be b/w (P, T) or (T, V) also. But area under PV curve gives Work. Hence preferred more.



beautiful def^n

★ If all the equilibrium points that a process undergoes while going from 1 state to another are represented on a graph of 2 thermodynamic variables, then the curve so obtained is called an indicator diagram

If we are able to measure P and V at every point i.e. a continuous curve, this implies process goes

✓ through infinite quasistatic processes st. equilibrium is maintained at all points. Quasistatic Process are carried very slowly. At all points condition of equilibrium holds.

✓ Also area under curve gives Work Done.

✓ Also the direction of curve indicates expansion / contraction.

Slopes for different Processes

For an isothermal process,

$$PV = \text{const}$$

$$\Rightarrow P\,dV + V\,dP = 0$$

$$\Rightarrow \left(\frac{dP}{dV}\right)_T = -\left(\frac{P}{V}\right)$$

For an adiabatic process,

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

$$\Rightarrow (\gamma) P V^{\gamma-1} dV + V^{\gamma} dP = 0$$

$$\Rightarrow \left(\frac{dP}{dV}\right)_{\text{adiabatic}} = -\gamma\left(\frac{P}{V}\right)$$

more slope than isothermal

For an isobaric process,

$dP = 0$

$$\Rightarrow P = \text{const} \Rightarrow \left(\frac{dP}{dV}\right)_P = 0$$

For an isochoric process

$dV = 0$

$$\Rightarrow \left(\frac{dP}{dV}\right)_V = \infty$$

Work done in ideal gas undergoing adiabatic process

For adiabatic (ideal) : $-dU = P\,dV$

$\Rightarrow W = -\int dU = -C_v \int d$

$= C_v \cdot (T_1 - T_2)$

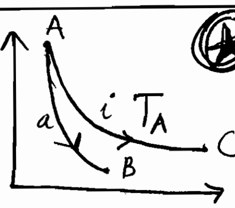
$= \frac{R}{\gamma - 1} (P_1V_1 - P_2V_2$

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

$\Rightarrow P = k\,V^{-\gamma}$

$$W = P\,dV = k V^{-\gamma}\,dV = \frac{k\,V^{(-\gamma+1)}}{(1-\gamma)} \Big|_{V_1}^{V_2} = k\left(\frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma}\right)$$

$$= \frac{P_2V_2^{\gamma}\,V_2^{1-\gamma} - P_1V_1^{\gamma}\,V_1^{1-\gamma}}{1-\gamma} = \left[\frac{P_2V_2 - P_1V_1}{1-\gamma}\right]$$



For an ideal gas,

$$W = -R\frac{(T_2 - T_1)}{(\gamma - 1)} = \frac{R\,(T_1 - T_2)}{(\gamma - 1)}$$

$$\boxed{W = \frac{R}{(\gamma-1)}(T_1 - T_2)}$$

In adiabatic Process 'a',

Temperature at any point along AB is less than T_A

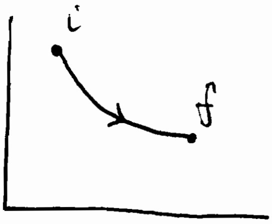
i.e. $T\downarrow \Rightarrow U\downarrow \Rightarrow dU < 0$. since $dQ =$

$\Rightarrow dW > 0$ in this process

Reverse is true for process -'a'....

अतः Area under the curve +ve है !!

Reversible Process : If I am able to retrace back from f to i backwards, then its reversible process.



It is ideal concept.

All processes are irreversible in nature

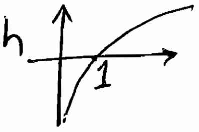
Reversible Process assumes 0 dissipative losses. In real process, some dissipation always occur. In indicator diagrams, the Quasi-static Processes are assumed to be reversible.

Some Maths......

if $Z = f(x, y)$

we know, $dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$

log का graph



$\log n > 0$ for $n >$

$\log n < 0$ for $0 < n$

Usually z is const. We always separate out the constant variable ⇒ $dz = 0$

→ Const. वाले को separate out कर लेते हैं और उसी के नाम पर Process का नाम रख देते हैं !!

eg. for Isothermal Process

$$T = f(P, V)$$

$$\Rightarrow 0 = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$\Rightarrow \boxed{\left(\frac{dy}{dx}\right)_z = \frac{-\left(\frac{\partial f}{\partial x}\right)_y}{\left(\frac{\partial f}{\partial y}\right)_x}} \quad \text{Or} \quad \boxed{\left(\frac{dy}{dx}\right)_z = \frac{-\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial y}\right)_z}}$$

remember by Physical interpretation

if $x\uparrow \Rightarrow z\uparrow \Rightarrow \left(\frac{\partial z}{\partial x}\right) > 0$

$y\uparrow \Rightarrow z\downarrow$ $\quad \left(\frac{\partial z}{\partial y}\right) < 0$

For const. z

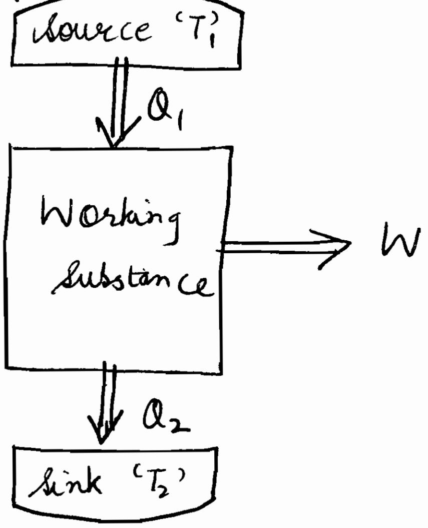
$x\uparrow$ and $y\uparrow$

$\Rightarrow \left(\frac{\partial y}{dx}\right) > 0$

Heat Engine

Heat Engine has 3 components :

1) Source 'T_1' ✓
2) Working substance ✓
3) Sink 'T_2' $(T_2 < T_1)$ ✓



Assuming heat absorption is ideal process, i.e. no wastage in conduction, radiation etc.

$$\Rightarrow \quad Q_1 = W + Q_2$$

$$\eta = \left(\frac{W}{Q_1}\right) = \frac{Q_1 - Q_2}{Q_1} = 1 - \left(\frac{Q_2}{Q_1}\right)$$

(ISOTHERMAL + ADIABATIC)

Carnot Engine

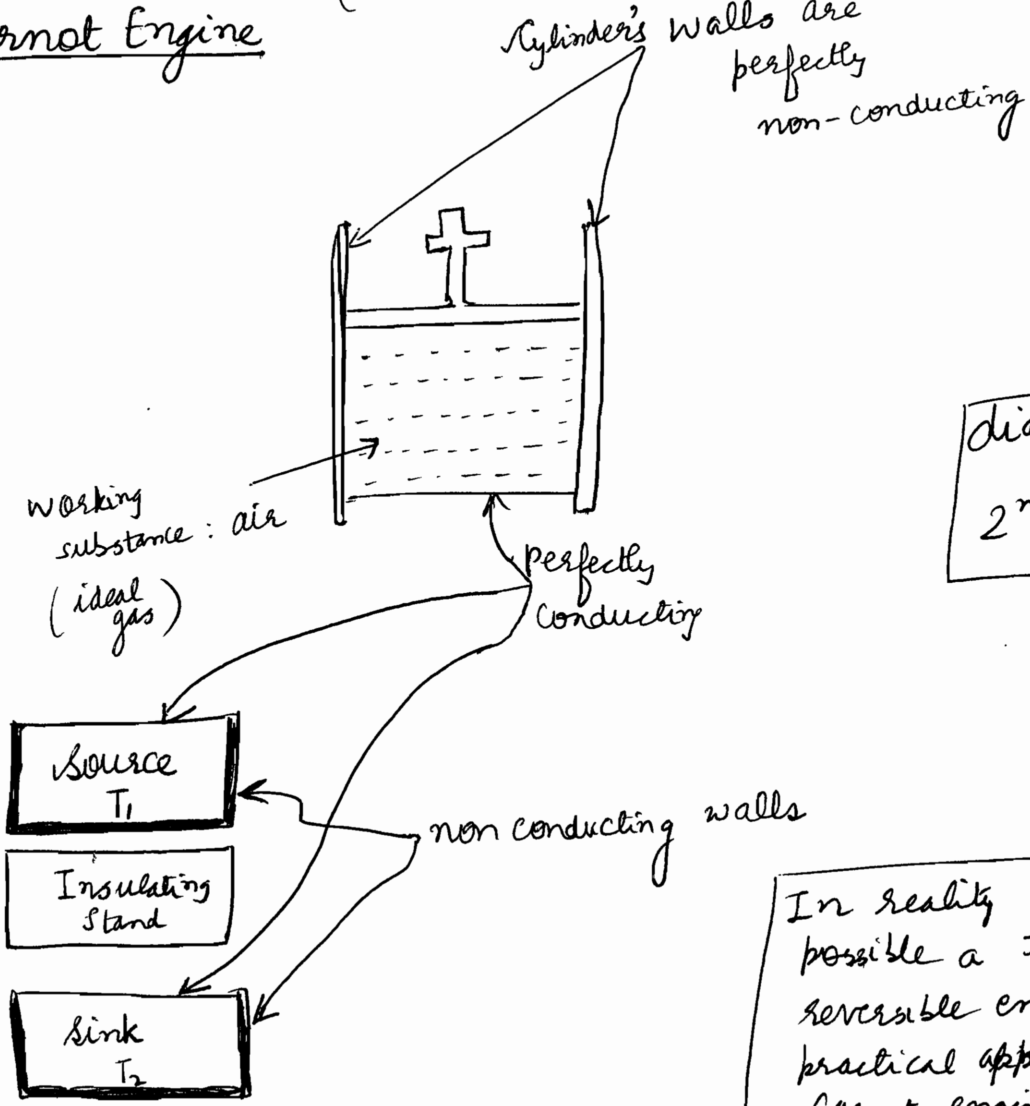


diagram of 2nd lecture

In reality it is not possible a thermodynamically reversible engine, so practical application of Carnot engine is restricted

[Isothermal Process are VERY slow processes
Adiabatic Process are VERY FAST processes.]

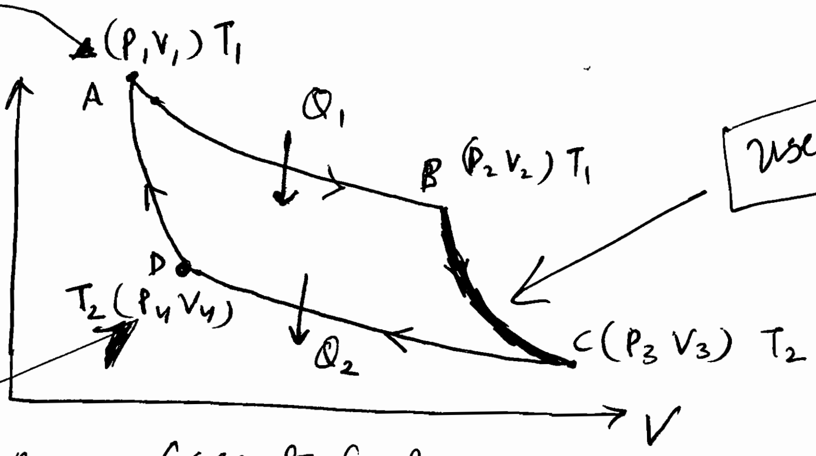
While suppling heat, conducting walls of source and cylinder are kept next to each other. Isothermal expansion occurs.

When adiabatic process is started, Insulating Stand is kept next to cylinders conducting wall. Heat supply is cut off.

While removing heat, sink is brought in contact with cylinder. Isothermal contraction occurs.

Finally insulation stand is again brought to achieve adiabatic compression.

Process starts with supply of heat



Useful work is done in adiabatic expansion

o We should start the cycle with this point for sake of analysis

Carnot Cycle

In adiabatic expansion, gas works on its own and hence useful work is done. Temperature falls down as internal energy is used up for performing the expansion or ⊕ve work. Hence $T_C < T_B$.

In BC, useful work has been done. Work of engine has been done. Now we have to bring back the system to previous state to again do the work.

CD : isothermal contraction

DA : adiabatic

Work done = $\Delta(ABCD)$

Note that all processes are assumed to be reversible.

Net Work Done

AB $\quad dU = 0$

$$dW_1 = Q_1 = RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

BC $\quad dQ = 0$

$$dW_2 = \frac{R}{(\gamma-1)}(T_1 - T_2)$$

CD $dU = 0$

$$dW_3 = Q_2 = T_2 R \ln\left(\frac{V_4}{V_3}\right)$$ ← all the terms are <

DA $dQ = 0$

$$dW_4 = \frac{R}{(\gamma - 1)} (T_2 - T_1)$$

$$\text{Net Work Done} = RT_1 \ln\left(\frac{V_2}{V_1}\right) + RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

We know $T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$, $T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$

$$\Rightarrow \boxed{\left(\frac{V_1}{V_2}\right) = \left(\frac{V_4}{V_3}\right)}$$

Use $TV^{\gamma-1}$ form

$$\Rightarrow \boxed{\text{Net Work Done} = R(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right)}$$

Also from Energy supplied

$$Q = RT_1 \ln\left(\frac{V_2}{V_1}\right) - RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$= R(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right)$$

$dU = 0$ for complete cycle

$$\Rightarrow \boxed{dQ = dW}$$

$$\eta = \frac{W}{Q_1} = \frac{R(T_1 - T_2) \ln\left(\frac{V_2}{V_1}\right)}{RT_1 \ln\left(\frac{V_2}{V_1}\right)} = \frac{T_1 - T_2}{T_1}$$

$$\Rightarrow \boxed{\eta = 1 - \left(\frac{T_2}{T_1}\right)}$$

⊙ $\eta = 1 - \frac{Q_2}{Q_1}$ in general

$= 1 - \left(\frac{T_2}{T_1}\right)$ for carnot engine

→ Remember that Carnot theorem has 2 components

★ All the reversible engines operating between same source and same sink will have same efficiency equals to $\left[1 - \left(\frac{T_2}{T_1}\right)\right]$: Carnot Theorem ①

★ Irreversible Engine will have lower efficiency than the reversible engine working between same sink & source

i.e. $\eta_{reversible} > \eta_{irreversible}$

<u>Carnot theorem</u> ②

i.e. $\left(1 - \frac{Q_2}{Q_1}\right)_{irreversible} < \left(1 - \frac{T_2}{T_1}\right)$ Proof in lecture 4

Note that both proofs follow the same things of applying Opposite Carnot cycle

★ For reversible cyclic engine,

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

[redacted] i.e. Operating high η as engine and lower η as referigerator!!

→ We can give the logic that any closed reversible process that be thought of consisting of many Carnot cycles $\Rightarrow \oint_{reversible} \frac{dQ}{T} = 0$

For irreversible

$$\frac{Q_2}{Q_1} > \frac{T_2}{T_1} \Rightarrow \frac{Q_2}{T_2} > \frac{Q_1}{T_1}$$

$$d\left(\frac{Q}{T}\right) = \left[\frac{Q_1}{T_1}\right] + \left[\frac{-Q_2}{T_2}\right] < 0 \Rightarrow$$ [redacted]

$$\Rightarrow \oint_{irreversible} \frac{dQ}{T} < 0$$

[redacted]

यह Carnot theorem से आया है!!

$$\Rightarrow \oint \left(\frac{dQ}{T}\right) \leqslant 0$$ (equality for reversible process) Classius Inequality

- Irreversible के लिए η कम है.....
  $\Rightarrow$ $-[dQ]$ वाला component ज्यादा है for some incoming heat
  $\Rightarrow \oint (dQ/T) \leqslant 0$

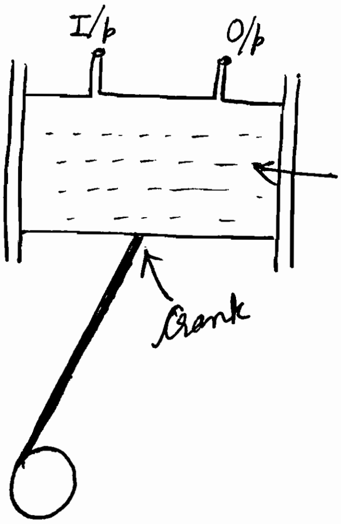
- Note that Clasius Inequality talks nothing about entropy change. It talks only about $\int \frac{dQ}{T}$

Internal Combustion Engines

Within cylinder-piston arrangement, provision of burning of fuel.

2 examples of ICEs are Otto Engine and Diesel Engine.

Otto Engine (ISOCHORIC + ADIABATIC)



Working substance: 1 gram-mole of air

→ mole = gram-mole
= gram-molecule
= avogadro no. of mole

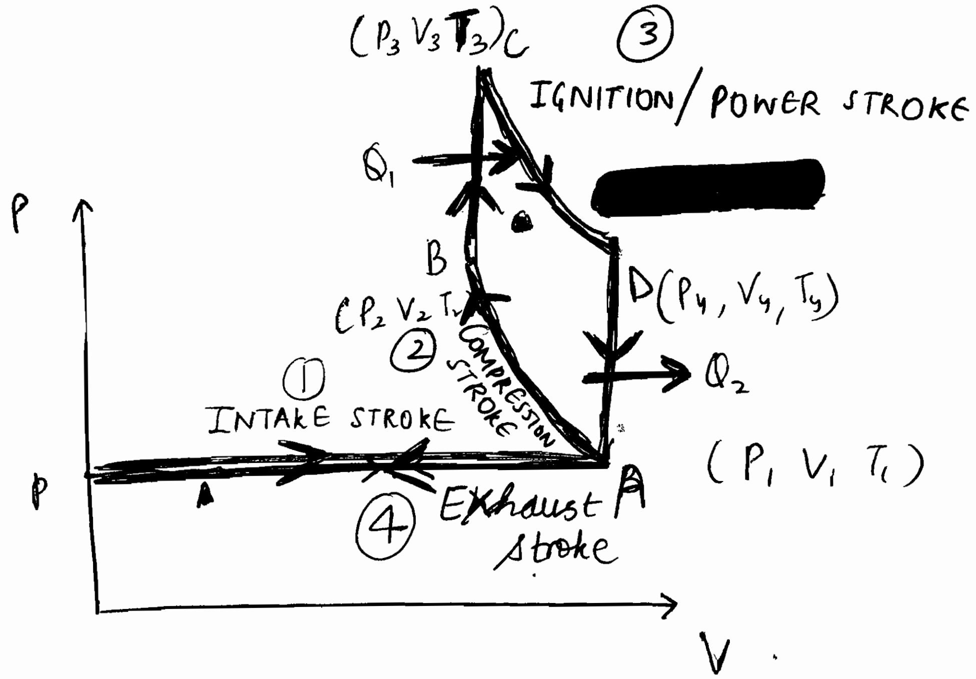
→ Otto engine designed by Nickolas Otto in 19th century.

→ Modified, advanced and fuel controlled versions of Otto Engines are used in cars all over the world.

→ Also called Petrol or Gasoline engine.

4 strokes, 2 valves engine
- Suction / Intake stroke
- Compression
- Working (Ignition)
- Exhaust (Heat Release)

① At the atmospheric pressure, 'I' is opened and a mixture of air and fuel is sucked in. T_1 : room temp.



[redacted]

② 2nd stroke is adiabatic compression

Maximum compression can be 6 times. $\boxed{AB}$

~~Compression Ratio~~ (e) ~~=~~ $\left(\frac{V_1}{V_2}\right) < 6$

More than 6, Pressure will be huge s.t. walls will burst.

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = T_1\,(6)^{+0.5} = 2.4\,T_1$$

③ Isochoric heat addition is done in 3rd stroke

$Q_1 = C_V(T_3 - T_2)$

$V_3 = V_2$

Compressed mixture is exploded by an electric spark to release heat which increase P and T. Piston is driven out adibatically.

Temperature is increased further.

Before commencing with derivation, its mandatory to mention:

① Use

② 4 strokes, with diagram

④ **Adiabatic Expansion** occurs due to high temperature. Crank is thrown out. **Useful work is done in this step.**

⑤ Isochoric Heat Rejection. This is the 4th stroke

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_v(T_4 - T_1)}{C_v(T_3 - T_2)}$$

$$\boxed{\eta = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)}}$$

↑

Beware of not writing $1 - \frac{C_v(T_1 - T_4)}{C_v(T_3 - T_2)}$

as 'Q_2' is a ⊕ve number

$\Rightarrow -Q_2 = dW = C_v(T_1 - T_4)$

$\Rightarrow \underline{Q_2 = C_v(T_4 - T_1)}$

(use $TV^{\gamma-1}$ form)

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_4 V_4^{\gamma-1} = T_3 V_3^{\gamma-1}$$

$V_3 = V_2$

$V_4 = V_1$

$$(T_4 - T_1) V_1^{\gamma-1} = (T_3 - T_2) V_2^{\gamma-1}$$

$$\Rightarrow \boxed{\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}} = 1 - \frac{1}{(\rho)^{\gamma-1}}$$

$$\eta_{max} = 1 - \frac{1}{6^{\gamma-1}} \approx 52\% \text{ (for } \gamma = 1.4)$$

(low efficiency)

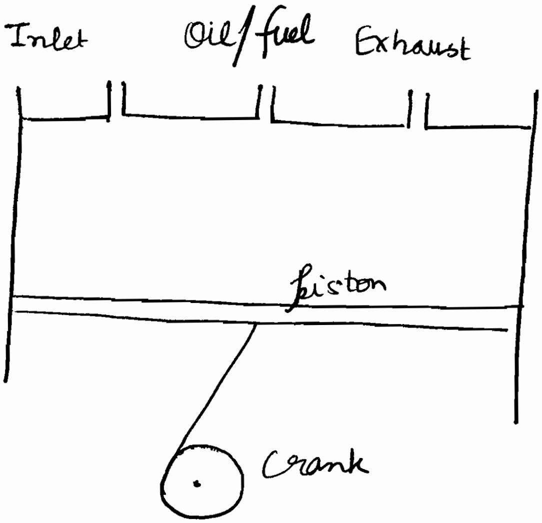
⊛ Note that compression ratio is, UNLIKE WHAT ITS NAME SUGGESTS, $\rho = \left(\frac{V_{more}}{V_{less}}\right)$

⊛ There is a single ρ for both expansion & compression, therefore, the 2nd and 4th process need to be ISOCHORIC.

✓ Compression Ratio, expansion ratio etc. are always greater than unity. $\rho_E > 1$, $\rho_C > 1$

Diesel Engine (ADIABATIC, ISOBARIC, ADIABATIC, ISOCHORIC)

- In this engine, air is compressed sufficiently to heat it enough to ignite the fuel & then fuel is sprayed in.
- Compression upto 34 atm.



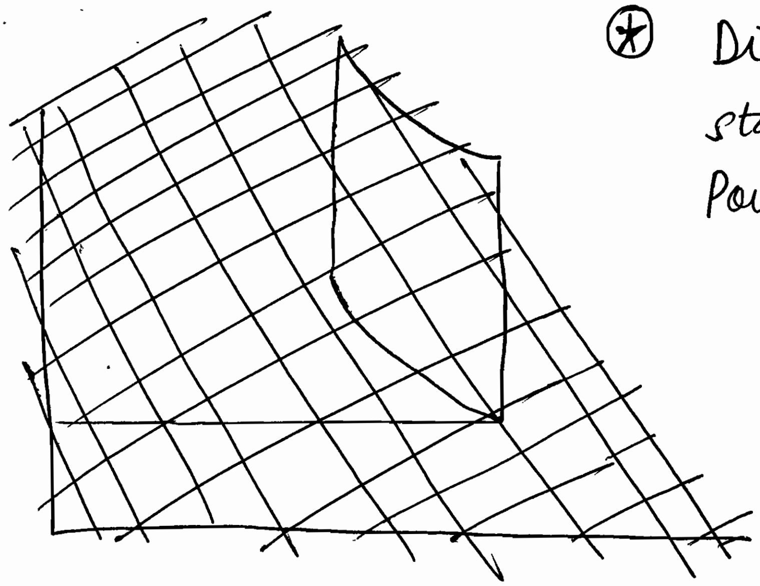
→ Designed by Rudolph Diesel at end of 19th century.

→ More Efficient than otto Engine

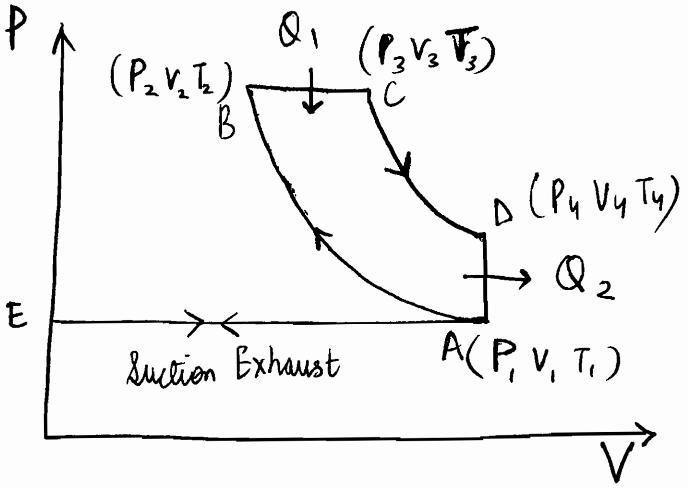
→ Diesel engines are found in virtually all heavy duty applications eg. truck, ships

✓ Walls have capacity to bear 34 atm.

✓ $\left(\frac{V_1}{V_2}\right)$ can be as high as 17



⊛ Difference only in starting phase of Power stroke



→ $P_3 = P_2$

isobaric expansion

$\Rightarrow V \propto T$ i.e. $\frac{V_3}{V_2} = \frac{T_3}{T_2}$

isochoric heat rejection

$V_1 = V_4$

- Note that after AB, $T \approx 1000^\circ C$, $P \approx 34\,atm$, $\rho_c \approx 17$, Now at this stage fuel is injected & combustion takes place.

$Q_1 = C_p (T_3 - T_2)$

$Q_2 = C_v (T_4 - T_1)$

⊛ Compression & Expansion ratios are defined only for adiabatic compressions and expansions....

$$\eta = 1 - \frac{C_v (T_4 - T_1)}{C_p (T_3 - T_2)}$$

$$= 1 - \frac{1}{\gamma}\left[\frac{\left(\frac{1}{\rho_e}\right)^{\gamma} - \left(\frac{1}{\rho_c}\right)^{\gamma}}{\left(\frac{1}{\rho_e}\right) - \left(\frac{1}{\rho_c}\right)}\right]$$

Compression > Expansion $\Rightarrow \rho_c > \rho_E \Rightarrow \left(\frac{1}{\rho_c}\right) < \left(\frac{1}{\rho_E}\right)$

ρ_e : expansion ratio $= \left(\frac{V_4}{V_3}\right) = \left(\frac{V_1}{V_3}\right)$ $\boxed{V_1 = V_4}$

ρ_c : compression ratio $= \left(\frac{V_1}{V_2}\right)$

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ $\qquad$ $T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}$

$(T_4 - T_1) V_1^{\gamma-1} =$ [redacted] $T_3 V_3^{\gamma-1} - T_2 V_2^{\gamma-1}$

$$\Rightarrow \eta = 1 - \frac{1}{\gamma} \cdot \frac{T_3 V_3^{\gamma-1} - T_2 V_2^{\gamma-1}}{V_1^{\gamma-1} (T_3 - T_2)}$$

Write only P,V equations for easy derivation.... done on next page

$$= 1 - \frac{1}{\gamma} \frac{\left(\frac{T_3}{T_2}\right) V_3^{\gamma-1} - V_2^{\gamma-1}}{(V_1)^{\gamma-1}\left[\left(\frac{T_3}{T_2}\right) - 1\right]} = \frac{\frac{V_3^{\gamma}}{V_2} - V_2^{\gamma-1}}{V_1^{\gamma-1}\left[\frac{V_3}{V_2} - 1\right]}$$

$$= \frac{V_3^{\gamma} - V_2^{\gamma}}{V_1^{\gamma-1}(V_3 - V_2)}$$

$$= \frac{\left(\frac{V_3}{V_1}\right)^{\gamma} - \left(\frac{V_2}{V_1}\right)^{\gamma}}{\left(\frac{V_3}{V_1}\right) - \left(\frac{V_2}{V_1}\right)} = \frac{\left(\frac{1}{\rho_e}\right)^{\gamma} - \left(\frac{1}{\rho_c}\right)^{\gamma}}{\left(\frac{1}{\rho_e}\right) - \left(\frac{1}{\rho_c}\right)}$$

$$\Rightarrow \boxed{\eta = 1 - \frac{1}{\gamma}\left[\frac{\left(\frac{1}{\rho_e}\right)^{\gamma} - \left(\frac{1}{\rho_c}\right)^{\gamma}}{\left(\frac{1}{\rho_e}\right) - \left(\frac{1}{\rho_c}\right)}\right]}$$

$$\left(\frac{T_4 - T_1}{T_3 - T_2}\right)$$

now eliminate "Pressure" terms

$$= \frac{P_4V_4 - P_1V_1}{P_3V_3 - P_2V_2} = \frac{(P_4 - P_1)V_1}{(V_3 - V_2)P_2}$$

$$= \frac{\left[P_3\left(\frac{V_3}{V_4}\right)^{\gamma} - P_2\left(\frac{V_2}{V_1}\right)^{\gamma}\right]V_1}{[V_3 - V_2]\,P_2}$$

$$= \frac{\left(\frac{V_3}{V_4}\right)^{\gamma} - \left(\frac{V_2}{V_1}\right)^{\gamma}}{\left(\frac{V_3}{V_1}\right) - \left(\frac{V_2}{V_1}\right)}$$

$$= \frac{\left(\frac{1}{\rho_e}\right)^{\gamma} - \left(\frac{1}{\rho_c}\right)^{\gamma}}{\left(\frac{1}{\rho_e}\right) - \left(\frac{1}{\rho_c}\right)}$$

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$
$P_2 = P_3$
$P_3V_3^{\gamma} = P_4V_4^{\gamma}$
$V_4 = V_1$

use PV^{γ} form

⊙ Claussius introduced the concept of entropy. He gave a quantitative criteria following which we can predict direction of evolution of a process. He showed that only such processes can occur for which entropy does not decrease.

⊙ Boltzmann showed that entropy is a measure of disorder in molecular arrangement of a system.

⊙ Since entropy characterizes the approach to equilibrium, it can be related to the probability of occurence of state. Thus, it helps to relate the results of thermodynamics to those of statistical mechanics.

Thermodynamics (3) 28/12/2011

Refrigerator

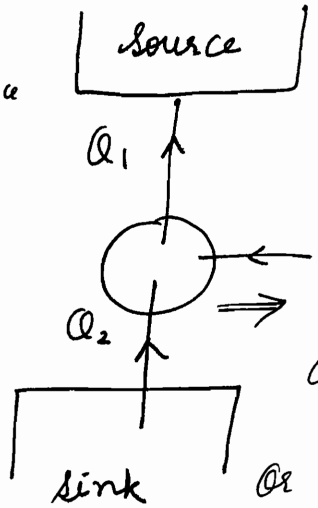
$\beta_{refrigerator}$ = Coefficient of performance

$= \left(\frac{Q_2}{W}\right)$

$Q_1 = Q_2 + W$

Opposite heat and work flows.

$$\boxed{\eta = \frac{1}{\beta + 1}}$$

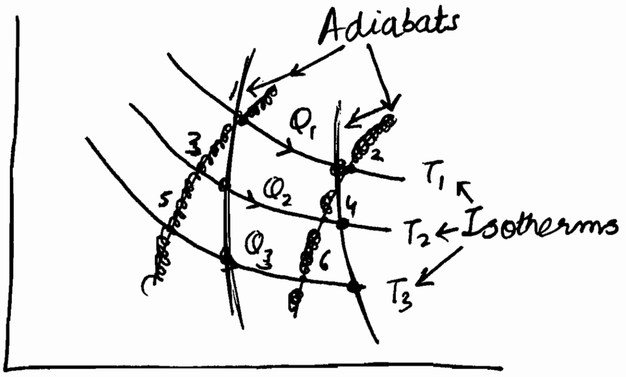


⟹ Note that the direction of cycle : clockw Or anti clockwise decides whether cycle is engine or refrigerator

★
★

- Clockwise cycle : ⊕ve work
- Anticlockwise cycle : ⊖ve work

Entropy



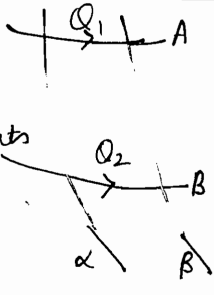
Going from 1 adiabatic to other via any isothermal process $\left(\frac{Q}{T}\right)$ remains const. [like equipotential lines, adiabats are equi-entropic lines.]

$$\left(\frac{Q_1}{T_1}\right) = \left(\frac{Q_2}{T_2}\right) = \left(\frac{Q_3}{T_3}\right) = \ldots\ldots \left(\frac{Q_n}{T_n}\right)$$

We defined this change as entropy

$$S_2 - S_1 = \left(\frac{Q_1}{T_1}\right)$$

We can take any 2 isotherms A and B. With the fixed adiabats α and β, they can make a Carnot engine



$\Rightarrow \frac{Q_1}{Q_2} = \frac{T_A}{T_B} \Rightarrow \left(\frac{Q_1}{T_A}\right) = \left(\frac{Q_2}{T_B}\right)$

Entropy is a thermodynamic variable. It is mathematically defines as, $\boxed{dS = \left(\frac{dQ}{T}\right)}$. It is a state function. It remains constant during reversible adiabatic process.

$\left(\begin{matrix} S = \text{const.} \\ dS = 0 \end{matrix}\right)$

$$\int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T}$$ → going from equilibrium state 1 to equilibrium state 2 via a reversible process.

1st law

★ We know, internal energy is difference of heat supplied and work produced. This increase in internal energy can be used to do more work via adiabatic expansion.

0th law

It gives the concept of temperature.

(If even some processes do not violate conservation of energy, they may violate $\Delta S_{univ} > 0$. Hence not allowed)

2nd law

It gives us the concept of entropy. Consider following points about Entropy:

2nd law ⇒ Carnot theorem ⇒ Clausius inequality ⇓ Concept of entropy

① Entropy change can be calculated as $\int \frac{dQ_{rev}}{T}$ only for reversible processes.

② Entropy change for reversible adiabatic process is 0.

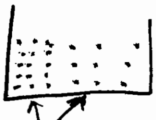
③ Note that, it is a state function, we are interested only in dS, not actual S. Hence, this enables us to calculate dS for irreversible processes.

$$\boxed{dS_{1,2\ \text{irreversible}} = dS_{1,2\ \text{reversible}}}$$

Replace actual process by reversible process from i to f states. Calculate $\int_1^2 \frac{dQ}{T}$

④ Entropy is a measure of disorder in the system. All natural process, that occur spontaneously, Create more chaos, more disorder, i.e. increase the entropy: law of increase of Entropy $\boxed{\Delta S > 0}$

⑤ Equilibrium is the most probable state.
Maximum disorder also means more probability.



concentration gradient
⇒ mixing will lead to more S and equilibrium

Equilibrium ⇒ $\text{Prob}_{\text{maximum}}$ ⇒ Maximum Entropy

Entropy is an additive quantity while Probability is multiplicative ⇒ log function is the relation.

⇒ $S \propto \ln \Omega$

$$\boxed{S = k \ln \Omega}$$

Ω : thermodynamic probability.
S : entropy
k : boltzmann's cons

⑥ From Classius Inequality, we have seen

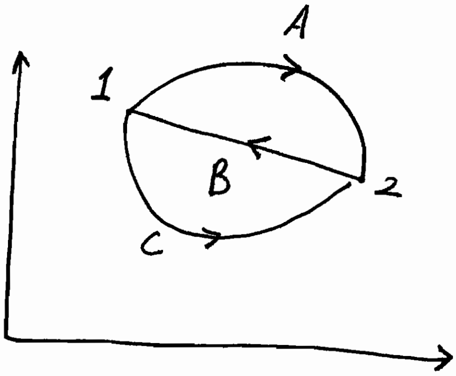
$$\oint \frac{dQ}{T} \leq 0$$

$$\int_1^2 \frac{dQ}{T} = dS\Big|_1^2 = S_2 - S_1$$

$$\& \oint_1^1 \frac{dQ}{T} \leq 0$$

To prove Entropy is path independent function

Let A, B, C are ~~reversible processes~~.



$$\int_1^2 dS = \int_1^2 \frac{dQ}{T} = S_2 - S_1$$

$$\oint_{AB} \frac{dQ}{T} = 0$$ [using classius inequality]

$$\Rightarrow \int_A \frac{dQ}{T} + \int_B \frac{dQ}{T} = 0 \quad — ①$$

$$\oint_{BC} \frac{dQ}{T} = 0$$ [classius inequality]

$$\Rightarrow \int_B \frac{dQ}{T} + \int_C \frac{dQ}{T} = 0 \quad — ②$$

→ Note that Classius inequality talks nothing about $\int dS$. It talks about $\oint \frac{dQ}{T}$

From ①

$$\underset{B}{\int} \frac{dQ}{T} = -\underset{A}{\int} \frac{dQ}{T}$$

From ②

$$\underset{B}{\int} \frac{dQ}{T} = -\underset{C}{\int} \frac{dQ}{T}$$

$$\Rightarrow \underset{A}{\int} \frac{dQ}{T} = \underset{C}{\int} \frac{dQ}{T} \Rightarrow \boxed{\text{Path Independent}}$$

Carnot theorem

$\Downarrow$

Clausius Inequality

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

$\Downarrow$

Concept of Entropy

$$\Delta S \geq 0$$

Now let us say process C is irreversible.

$$\underset{AB}{\oint} \left(\frac{dQ}{T}\right) = 0 \qquad \& \qquad \underset{BC}{\oint} \left(\frac{dQ}{T}\right) < 0$$

$$\Rightarrow \underset{A}{\int_{1}^{2}} \frac{dQ}{T} + \underset{B}{\int_{2}^{1}} \frac{dQ}{T} = 0$$

$$\Rightarrow \underset{B}{\int_{2}^{1}} \frac{dQ}{T} + \underset{C}{\int_{1}^{2}} \frac{dQ}{T} < 0$$

$$(S_2 - S_1) + \underset{B}{\int_{2}^{1}} \frac{dQ}{T} = 0$$

$$\Rightarrow \underset{B}{\int_{2}^{1}} \frac{dQ}{T} = (S_1 - S_2)$$

$\Rightarrow$ From ①

$$(S_1 - S_2) + \underset{C}{\int_{1}^{2}} \frac{dQ}{T} < 0$$

$$\Rightarrow \int_{1}^{2} \frac{dQ}{T} < (S_2 - S_1)$$

This shows that entropy of isolated ① system cannot decrease. For reversible changes entropy will remain const. while for irreversible changes, entropy must increase.

For isolated systems,
$dQ = 0$
$\Rightarrow \Delta S \geq 0$

This means that entropy of an isolated system tends towards maximum while it approaches equilibrium. i.e

$$\boxed{(S_2 - S_1) > \underset{\text{irreversible}}{\int_{1}^{2} \frac{dQ}{T}}} \quad \text{or} \quad \boxed{\underset{\text{irreversible}}{\int_{1}^{2} \frac{dQ}{T}} < (S_2 - S_1)}$$

✓

$$\Rightarrow S_2 - S_1 \geq \int_{1}^{2} \frac{dQ}{T}$$

equality holds good for reversible process.

$$\int_1^2 dS = \int_1^2 \frac{dQ}{T}$$

reversible process

Now dQ can be $\underline{\underline{C_v\,dT}}$ or $\underline{\underline{C_p\,dT}}$ or $\underline{\underline{ms\,dT}}$

let us say $dQ = C_v\,dT$ (solids or liquids)

$$\Rightarrow \int_1^2 dS = \int_1^2 C_v \frac{dT}{T} = C_v \ln\left(\frac{T_2}{T_1}\right)$$

Let us take ice (1kg) at -20°C. It is to be converted to steam (1kg) at 200°C. Calculate Entropy Change!!

1 kg Ice at -20°C (253k) to 0°C (273k)

$$\Delta S_1 = \int dS = \int \frac{dQ}{T} = \int \frac{C_v\,dT}{T} = C_{v_{ice}} \ln\left(\frac{273}{253}\right)$$

(assumed all along reversible process)

1 kg ice to 1kg water at 0°C : state change

$$\Delta S_2 = \int dS = \int \frac{dQ}{T} = \left(\frac{mL}{273}\right)$$

1 kg of water at 0°C to water at 100°C

$$\Delta S_3 = \int dS = C_{v_{H_2O}} \ln\left(\frac{373}{273}\right)$$

1 kg of water at 100°C to steam at 100°C

$$\Delta S_4 = \left(\frac{mL}{373}\right)$$

1 kg of steam at 100°C to 200°C

$$\Delta S_5 = C_{steam} \ln\left(\frac{473}{373}\right)$$

$$\Delta S = [\Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5]$$

Entropy is an additive process!!

Note that $\Delta S_1 = k \ln \Omega_1$

$\Delta S_2 = k \ln \Omega_2$

$\vdots$

$$\Rightarrow \Delta S = \sum_{i=1}^{5} \Delta S_i = k \sum_{i=1}^{5} \ln \Omega_i = k \ln (\Omega_1 \Omega_2 \Omega_3 \Omega_4 \Omega_5)$$

Entropy change calculations for 1 gram-mole of ideal gas.

We have, $PV = RT$

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

We know $S = f(T, V)$

$$dS = \frac{dQ}{T} = \frac{dU + P\,dV}{T} = \frac{C_v\,dT + P\,dV}{T}$$

$$= C_v\left(\frac{dT}{T}\right) + R\left(\frac{dV}{V}\right)$$

$$\Rightarrow \boxed{S = C_v \ln T + R \ln V + c_1}$$

or

$$\boxed{\Delta S = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)}$$

For isothermal : $\boxed{\Delta S = R \ln\left(\frac{V_2}{V_1}\right)}$

For isochoric : $\boxed{\Delta S = C_v \ln\left(\frac{T_2}{T_1}\right)}$

Also we can write, $S = f_2(T, P)$

$$dS = \frac{C_v\,dT + P\,dV}{T} = \frac{C_v\,dT + R\,dT - V\,dP}{T}$$

$$= (C_v + R)\left(\frac{dT}{T}\right) - \left(\frac{V}{T}\right)dP$$

$$= C_p\left(\frac{dT}{T}\right) - R\left(\frac{dP}{P}\right)$$

$$\Rightarrow \quad \boxed{S = C_p \ln T - R \ln P + C_2}$$

$$\boxed{\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)}$$

For isobaric : $\boxed{\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right)}$

Also we can write $S = f_3(P, V)$

$$dS = \frac{C_v\,dT + P\,dV}{T} = \frac{\frac{C_v}{R}(P\,dV + V\,dP) + P\,dV}{\frac{PV}{R}}$$

$$= \frac{(\cancel{P}C_v + \cancel{P}R)\,dV}{\cancel{P}V} + \frac{\cancel{V}C_v}{P\cancel{V}\cancel{R}}\,dP$$

$$= C_p\left(\frac{dV}{V}\right) + \frac{C_v}{\cancel{R}}\left(\frac{dP}{P}\right)$$

$$\Rightarrow \quad \boxed{S = C_p \ln V + C_v \ln P + C_3}$$

$$\boxed{\Delta S = C_p \ln\left(\frac{V_2}{V_1}\right) + C_v \ln\left(\frac{P_2}{P_1}\right)}$$

For 1 gram-mole gas undergoing :-

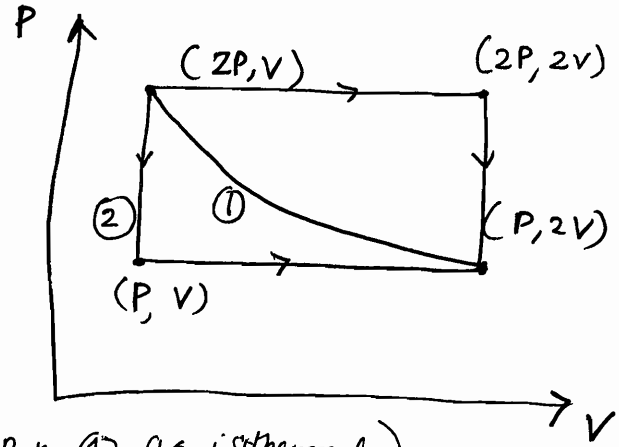
1) Isothermal $\quad S_2 - S_1 = \underline{R \ln\left(\frac{V_2}{V_1}\right)} = R \ln\left(\frac{P_1}{P_2}\right)$

2) Isobaric $\quad S_2 - S_1 = \underline{C_p \ln\left(\frac{T_2}{T_1}\right)} = C_p \ln\left(\frac{V_2}{V_1}\right)$

3) Isochoric $\quad S_2 - S_1 = \underline{C_V \ln\left(\frac{T_2}{T_1}\right)} = C_V \ln\left(\frac{P_2}{P_1}\right)$

(4) Adiabatic Process : $S_2 - S_1 = 0$

Q/ Illustrate, using 3 different paths, that ΔS is path independent.



Path 1

$S_2 - S_1 = C_p \ln 2 + C_v \ln\left(\frac{1}{2}\right)$

$= (C_p - C_v) \ln 2$

$= R \ln 2$

(rather than any reversible curve, take Path ① as isothermal curve. $\Rightarrow S_2 - S_1 = R \ln\left(\frac{2V}{V}\right) = \underline{R \ln 2}$)

Path 2

$\Delta S = \Delta S_1 + \Delta S_2$

$= C_v \ln\left(\frac{1}{2}\right) + C_p \ln\left(\frac{2}{1}\right)$

$= (C_p - C_v) \ln 2$

$= R \ln 2$

Path 3

$\Delta S = \Delta S_1 + \Delta S_2 = C_p \ln 2 + C_v \ln\left(\frac{1}{2}\right) = (C_p - C_v) \ln 2 = R \ln 2$

Thermodynamics (4)

29/12/2011

Tut21

Q6) $\Delta S_{resistor}$

$\Delta S_{universe} = \Delta S_{resistor} + \Delta S_{surrounding}$

Resistance remains same. $\Big\}$ NO change in state of resistor.
Temperature remains same. $\Big\}$ $\Rightarrow \Delta S_{res} = 0$

$\Delta S_{surrounding}$ per time $= \left(\frac{I^2Rt}{T}\right)/t = \left[\frac{I^2R}{T}\right]$

Q4) $\Delta S = \Delta S_A + \Delta S_B$ $\qquad Q = 10^4\ J/s$

$= -\frac{Q}{1500} + \frac{Q}{500}$

$= Q \cdot \frac{2}{1500}\ J/Ks$

$= 10^4 \cdot \frac{2}{1500} = \frac{200}{15} = \left(\frac{40}{3}\right) \frac{J}{Ks}$

Q9) Outside the course but do cover it from some book !!

Q14) Q20) $\Big\}$ Carnot's Theorem :- $\eta_R > \eta_{IR}$ working b/w same T_1 & T_2

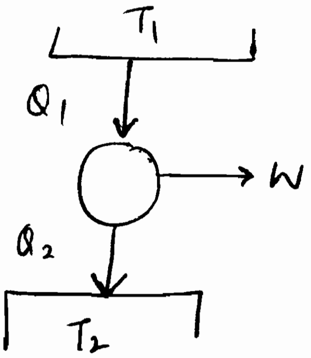
Proof

Proof is by contradiction.

Let us suppose $\eta_I > \eta_R$

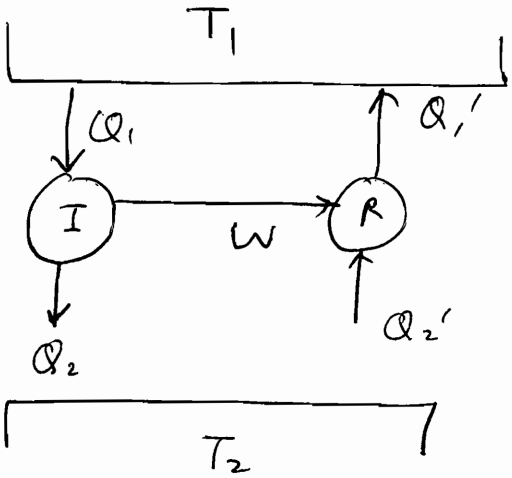
$\eta_I = \frac{W}{Q_1}$ $\qquad \eta_R = \frac{W}{Q_1'}$

$\Rightarrow Q_1' > Q_1$



Now reversible engine can be performed in backward direction also.

Let us couple I and R engine with R reversed



Now R acts as refrigerator

2^{nd} law states that its impossible for any device to take heat from lower temperature and transfer it to higher temperature.

2^{nd} law is violated in this system as $[Q_1' - Q_1] > 0$

↑ heat transferred

Hence contradiction

$\Rightarrow$ Our assumption is wrong

$\Rightarrow$ $\boxed{\eta_R > \eta_I}$

Q15) $\Delta U = 0$ $\Delta S = R \ln\left(\frac{V_2}{V_1}\right)$ $\Leftarrow$ assumption of ideal gas

$H = U + PV$

U is a state function $\Rightarrow$ H has to be a state function

$dH = d(PV) = P_2V_2 - P_1V_1$

Q17) ice → water at 0 → water at T ← water at 30

ΔS_1 ΔS_2 ΔS_3

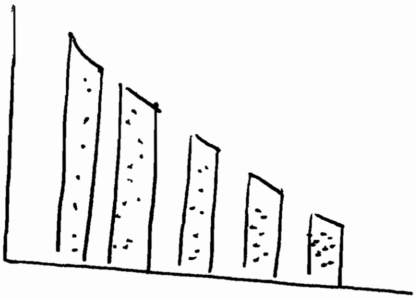
Tut 20

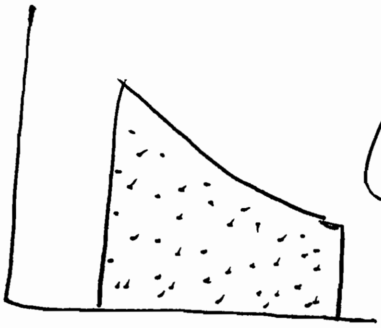
① Adiabatic Compression

Adiabatic Expansion

Slope : ⊖ve

④





do not attempt such question

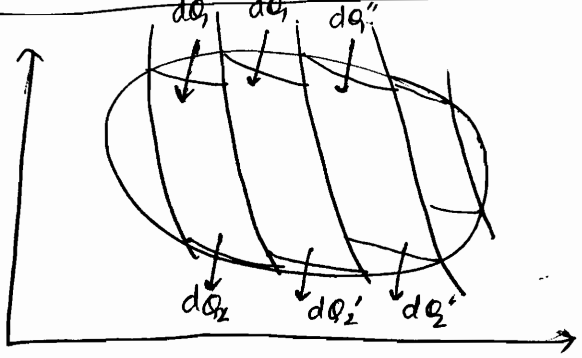
Δ (rev) > Δ (irrev)

GO FOR STANDARD QUESTIONS !!

⑥ Cooling ; adiabatic demagnetization ; useful work in engine ; travelling of sound waves

⑦ For diatomic gas : $\gamma = 1.4$

⑧ "increases n times".



→ Summing over all cycles of small isothermal - adiabatic curves

$$\frac{dQ_1}{T_1} = -\frac{dQ_2}{T_2}$$

$$\Rightarrow \oint \frac{dQ}{T} = 0$$

Thermodynamic Relationships

1^{st} Thermodynamic ~~Potential~~ : Internal Energy

1^{st} law of Thermodynamics

$$dQ = dU + PdV$$

2^{nd} law

$$dQ = T\,dS \qquad \text{[reversible process]}$$

Note that for any P, V, T system $dW = PdV$.
It is not just for ideal gas but for all P, V, T systems i.e. system described by state (P, V, T).

Combining,

$$TdS = dU + PdV$$

$$\Rightarrow \boxed{dU = T\,dS - P\,dV}$$

Internal Energy is 1 of the 4 thermodynamic potentials i.e.

Work done per unit quanta against the Force.

eg. $dV = \dfrac{dW}{m} = \dfrac{F.dr}{m}$ (gravitational)

$dV = \left(\dfrac{dW}{q}\right)$ (electromagnetic)

Always create such definitions!

Here, thermodynamic Potential [dU] = Work done on system in reversible adiabatic process is stored in form of internal energy.

$$dU = T\,dS - PdV$$

in adiabatic, $dU = -P\,dV$ = Work done on the system

$$U = U(S, V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow \boxed{\left(\frac{dU}{\partial S}\right)_V = T} \qquad \text{Also} \qquad \boxed{\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}}$$

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

We know if $z = f(x, y)$

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$:- Mathematical definition of Path independence

It is valid if z is <u>state function</u> i.e. <u>path independence</u>

$\Rightarrow$ dz is <u>exact differential</u>

$\Rightarrow$ above relation is valid

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

$$\Rightarrow \boxed{\left[\frac{\partial T}{\partial V}\right]_S = -\left[\frac{\partial P}{\partial S}\right]_V}$$ 1st Maxwell Relationship

Group 1	Group 2
P V	S T

OR $\left(\frac{d\alpha}{d\beta}\right)_\gamma$: (α, γ) : same group

Group का 1 variable vary करो और दूसरा constant रखो !!

belongs to same group $\Bigg\{$ vary const. $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$

2nd Potential — Helmholtz Free Energy

"Free energy" because it can be retrieved when the need arises.

Mathematically defined as $\boxed{F = U - TS}$

U is state function ⇒ F is state function

⇒ only dF is important.

$$dF = dU - TdS - S\,dT$$

IAPAC recommends symbol "A" for Helmholtz free energy

We know $dU = TdS - PdV$

$$\Rightarrow \boxed{dF = -PdV - S\,dT}$$

If dT is zero ⇒ isothermal process.

ie, In Reversible Isothermal Process, work done on the system is stored in form of Helmholtz Free Energy

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

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

$F = f(P, S)$

F is a state function of V and T

⇒ dF must be exact differential

$$\Rightarrow \left(\frac{\partial}{\partial T}\left[\frac{\partial F}{\partial V}\right]_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right)_T$$

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

2nd Maxwell Relation.

3rd Potential Enthalpy or Total Heat Function

Mathematically, $\boxed{H = U + PV}$

U : state function ⇒ H is a state function

$$dH = dU + PdV + VdP$$

$$= Tds - PdV + PdV + VdP$$

$$\boxed{dH = Tds + VdP}$$

As C_V corresponds to U.... on the similar lines C_P corresponds to H

$$\Rightarrow H = f(S,P)$$

In reversible Isobaric Process, Heat given is stored as enthalpy

$$dH = Tds + VdP$$

$$= Tds + 0 \qquad (\text{Isobaric})$$

$$= dQ \qquad (\text{reversible})$$

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

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

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

Components of defn of H

① Thermodynamic Potential

② mathematically defined as $H = U + PV$

③ heat given to system in reversible isobaric process stored as enthalpy.

④ state function ⇒ total differential gives 3rd Maxwell eqn

H : state function ⇒ Path independent ⇒ exact differential

$$\Rightarrow \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right]_P$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad \text{3rd Maxwell Relation}$$

4th Potential Gibbs Free Energy

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

H: state function ⇒ G : state function ⇒ dG: important

$$dG = dH - TdS - SdT$$

$$= TdS + VdP - TdS - SdT$$

$$\boxed{dG = \underbrace{V\,dP}_{\text{Mechanical Eqb.}} - \underbrace{S\,dT}_{\text{Thermal Eqb.}}}$$

✔ At equilibrium $dG = 0$ and minimum $\left[\text{i.e. } \frac{dG}{dP} = 0 \;\&\; \frac{d^2G}{dP^2} > 0\right]$

importance in chemistry

if $dG \neq 0$ ⇒ chemical reaction is going on ⇒ not yet equilibrium

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

Gibbs free energy is the maximum amount of non-expansive work that can be extracted from a closed system in a reversible process.

G: state function

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T$$

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

4th Maxwell Equation

Refer to End of ~~Notes~~ lecture!!

⊛ $\underbrace{P, V, T}_{\text{state variables}}, \underbrace{U, S, F, G, H}_{dx\,:\ \text{state functions}}$:- only 2 are independent variables

state variables ⇓ define a state

dx : state functions ⇓ define process

- We subtract the entropy part to get free energies

eg.

$$F = U - TS$$

$$G = H - TS$$

- Natural tendency of a spontaneous reaction is to decrease it free energy (Gibbs Free Energy)

$$\Rightarrow \Delta G_{\text{spontaneously reaction}} < 0$$

This energy released equals the maximum amount of work that can be performed as a result of the chemical reaction.

In contrast, if ΔG is ⊕ve ⇒ energy (in the form of Work) has to be added to the reacting system to make the reaction go.

- In Maxwell's relations, Television (TV) is negative

i.e. either $\left(\frac{\partial T}{\partial V}\right)_S$ or $\left(\frac{\partial V}{\partial T}\right)_P$ relationships bear a negative sign !!

- In Maxwell Relations, variable of LHS is constant of RHS and variable of RHS is const. of LHS.

Thermodynamics (5)

30 /12/11

पवरन

- All relations derived were of form $\boxed{\underset{0\ 1}{PV} = \underset{0\ 1}{ST}}$

From this relation, we have to do cross 1 by 1.

Ⅰ $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$: $dU = TdS - PdV$ 0,0

Ⅱ $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$: $dF = -PdV - SdT$ 0,1

Ⅲ $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$: $dH = TdS + VdP$ 1,0

Ⅳ $\left(\frac{\partial V}{\partial T}\right)_{\underset{\uparrow}{P}} = -\left(\frac{\partial S}{\partial P}\right)_{\underset{\uparrow}{T}}$: $dG = VdP - SdT$ 1,1

इनके constants का ध्यान रखना !! } refer एक देख end of Thermo Notes

- These Equations are very important. Questions like, "Does C_p varies with Pressure ?" or "Does C_V varies with volume ?"

i.e. ① $\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T} = 0$?

Solution $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \leftarrow$ no relation relating S and T as relations are cross in nature

Substituting
LHS $= \frac{\partial}{\partial V}\left[T\left(\frac{\partial S}{\partial T}\right)_V\right]_T = T\frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial V}\right)_T\right]_V$ (∵ S is path independent)

$= T\frac{\partial}{\partial T}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_V = \underline{\boxed{T\left(\frac{\partial^2 P}{\partial T^2}\right)_V}}$ [redacted]

For ideal gas $\Rightarrow$ $P = \left(\frac{R}{V}\right) T$

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

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = 0 \quad \text{for ideal gas}$$

↗ It comes out to be zero even for a real gas !!

if For a special gas : $PV = A + BT + CT^2$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{V}\left[B + 2CT\right]$$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{1}{V}\left[2C\right]$$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = \frac{2CT}{V} \neq 0$$

② $\boxed{\left(\frac{\partial C_P}{\partial P}\right)_T} = 0$?

Solution $C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$

$$\text{LHS.} = \frac{\partial}{\partial P}\left(T\left(\frac{\partial S}{\partial T}\right)_P\right)_T = T\frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial P}\right)_T\right)_P$$

$= T\frac{\partial}{\partial T}\Big($ [redacted] $\left(-\frac{\partial V}{\partial T}\right)_P\Big)_P = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$

$$= \boxed{-T\left(\frac{\partial^2 V}{\partial T^2}\right)_P}$$

Ideal Gas

Q1) $\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$ for $PV = RT$

$\left(\frac{\partial U}{\partial V}\right)_T = f(v)$ for $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

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

for ideal gas $= T\left(\frac{R}{V}\right) - P$

$= \underset{\sim}{0}$

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

$$\Rightarrow T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{TR}{V-b} - P = \boxed{\left(\frac{a}{V^2}\right)}$$

From above relations, we can gather a useful result :-

★ $U = U(T, V)$ [It can be written in form of any 2 variables]

$$\boxed{dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV}$$

← for a general process

Energy due to movement of molecules

C_V

Energy due to interaction of molecules

0 for ideal gas

$\left(\frac{a}{V^2}\right)$ for real gas

इन्हीं दो में क्यूँ लिखा, इस पर दिमाग नहीं !!

For an isochoric process :

- $dQ = \underset{\sim}{C_V\, dT}$
- $dW = \underset{\sim}{0}$
- $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV$

$= C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot 0 = \underset{\sim}{C_V\, dT}$

Q7) If Its written, "start from Maxwell Equation"

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

Multiply by T,

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

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

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

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

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

How to write in exam....
if says "starting from maxwell's equations, prove that....."

Coefficient of Elasticity of Gases : Bulk Modulus

Stress : dP Strain : $\left(\frac{dV}{V}\right)$

$$k = -\frac{dP}{\left(\frac{dV}{V}\right)}$$

[P↑ ⇒ V↓]
but
k is +ve

$$\Rightarrow \boxed{k = -V\left(\frac{dP}{dV}\right)}$$

So Process can be isothermal or adiabatic

- Isothermal Coefficient of Elasticity

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

- Isothermal Coefficient of Compressibility

$$\boxed{\beta_T = \frac{1}{k_T}}$$

Note that these symbols are not standard

- Adiabatic Coefficient of Elasticity

$$\boxed{k_s = -V\left(\frac{\partial P}{\partial V}\right)_s}$$

Adiabatic Coefficient of Compressibility

$$\boxed{\beta_s = \frac{1}{k_s}}$$

Volume Coefficient of Expansion of Gases

⊛ We also know volume of gases increase with Temp.

$$V_{(T)} = V_0(1 + \alpha T)$$ at const. Pressure ✓

$$\Rightarrow \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Q/ Show that $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$ ①

$$= -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 \quad ②$$

$$= \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \quad ③$$

$C_p = T\left(\frac{\partial S}{\partial T}\right)_P$ $\qquad$ $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

$$\text{LHS} = T\left[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V\right]$$

= [redacted]

Standard way !!

Let S be expressed as $f(T,V)$

①

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

कुछ न सूझे तो यह कर दो !!

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

} Refer to end of notes !!

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

$$\Rightarrow \text{LHS} = T\left[\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$= T\left[\underbrace{\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}\right] \checkmark$$

$$C_p - C_v = -T\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p^2$$

✓ since $\left(\frac{\partial V}{\partial T}\right)_p^2 \geq 0$ and $\left(\frac{\partial p}{\partial V}\right)_T \leq 0$ for all substances $\Rightarrow C_p - C_v \geq 0$ for all substances.

✓ At temp = 4°C for water, $\left(\frac{\partial V}{\partial T}\right) = 0$

$\Rightarrow C_p = C_v$

✓ As $T \to 0$, $C_p \simeq C_v$

③

3rd part

Let $U = f(T, V)$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V \cdot dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV$$

$$\Rightarrow TdS - PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

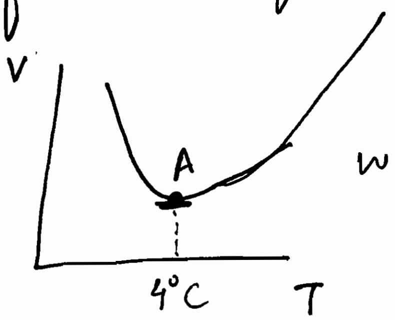
$$\Rightarrow TdS = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right) dV$$

Differentiating w.r.t. T at const P

$$\Rightarrow \left(\frac{\partial q}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$\Rightarrow C_p - C_v = \text{RHS}$

Now if we know equation of state $(C_p - C_v)$ can be calculated



water

at A : $\boxed{\left(\frac{\partial V}{\partial T}\right) = 0}$

$\Rightarrow C_p = C_v$

Q13) Similar 1st Part

$$\left[p + \frac{a}{V^2}\right]\left[\cancel{\frac{RT}{\left(p+\frac{a}{V^2}\right)}}\right] = R$$

$$C_p = C_v + R$$

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

$$\Rightarrow \boxed{C_p = C + R}$$

Using integration by Parts,

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

Using Binomial,

$$\Rightarrow R\left[1 + \frac{2a(V-b)^2}{V^3 RT}\right] + C = C_p$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_p = \frac{V-b}{T}\left[1 + \frac{2a}{RTV}\right]}$$

Whattaff formula for Real Gas

$$(V-b)^2 \approx V^2$$

$$\Rightarrow R\left[1 + \frac{2a}{VRT}\right] + C = C_p$$

$$\Rightarrow C_p = \text{[redacted]}\ R + \left(\frac{2a}{VT}\right) + C$$ ✓

For Vander wall's gas

$$\boxed{C_p - C_v = R + \frac{2a}{VT}}$$

This result can be more easily obtained via

$$\boxed{C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p}$$ ✓

★ For Vander Waal's Gas, for derivation of $\left(\frac{\partial V}{\partial T}\right)_p$, perform $+\frac{a}{V^2} - \frac{a}{V^2}$ in denominator to form $P + \frac{a}{V^2} - \frac{2a}{V^2}$ term and $\left(RT/_{V-b}\right)$ as common.

~~Q11)~~ $$C_p - C_v = -T\left(\frac{\partial P}{\partial V}\right)_T \underbrace{\left(\frac{\partial V}{\partial T}\right)_P^2}$$

We need to do "NO DERIVATION" in this answer !!

Reasoning : ⓐ ⊛ $\boxed{\left(\frac{\partial P}{\partial V}\right)_T \text{ cannot be } 0 \text{ For Water}}$, T cannot be 0

⊛ $\boxed{\left(\frac{\partial V}{\partial T}\right) = 0 \text{ at } T = 4°\text{C}}$

ⓑ For Real Gas ←

For Ideal Gas

$$-T\left(\frac{R}{V^2}\right)\left(\frac{R}{P}\right)^2 T$$

$$= \frac{R^3}{R^2T^2}\cdot T = R$$

Proof

Q) $$C_p - C_v = \underline{+T\kappa_T\alpha^2 V} \qquad (E_T = k_T)$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T \quad ②$$

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

from or from

If $z = f(x,y)$ or $f(x,y,z)=0$

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x = -1$$

$P = f(T,V)$

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

$$0 = \left(\frac{dP}{dT}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

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

Q/ In Iso Enthalfic Process, show that change ~~with~~ of Temp wrt. Pressure is given by

$$\frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

Joule kelvin
Coefficient is tough
i.e. TPH i.e. $\left(\frac{\partial T}{\partial P}\right)_H$

Solution

This is the Joule kelvin Process

To prove $\underbrace{\left(\frac{\partial T}{\partial P}\right)_H}_{} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$

(★) $\boxed{\frac{1}{C_p} < \quad >}$
और bracket में
volume के terms

Joule-kelvin Coefficient

$H = U + PV$

$dH = \underbrace{dU + PdV}_{} + VdP$

$\Rightarrow dH = dQ + V\,dP$

also $C_p = \left(\frac{\partial Q}{\partial T}\right)_P$

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

at const. Pressure

$dH = dQ$

We know

Cylic Process

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

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

deriving from function

Or $H = f(P, T)$

$\Rightarrow dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$

$\Rightarrow$ at const. H & doing $\left(\frac{\partial}{\partial T}\right)_H$

$0 = \left(\frac{\partial H}{\partial P}\right)_P \left(\frac{\partial P}{\partial T}\right)_H + \left(\frac{\partial H}{\partial T}\right)_P$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left[\frac{\partial}{\partial P}(PV)\right]_T$$

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

For real gas $\left(\frac{\partial U}{\partial P}\right)_T \neq 0$: deviation from Joule's law

Real gas $\left[\frac{\partial}{\partial P}(PV)\right]_T \neq 0$ deviation from Boyle's Law

Ideal gas $\left[\frac{\partial}{\partial P}(PV)\right]_T = 0$

$$\Rightarrow \boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H = 0 \quad \text{for ideal gases}}$$

For non-ideal gas in general

$$\mu = -\frac{1}{C_P}\left[T\left(\frac{\partial S}{\partial P}\right)_T \cancel{- P\left(\frac{\partial V}{\partial P}\right)_T} + V + \cancel{P\left(\frac{\partial V}{\partial P}\right)_T}\right]$$

$$= -\frac{1}{C_P}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

[illegible]

$$\boxed{\begin{aligned} dU &= T\,dS - P\,dV \\ \left(\frac{\partial U}{\partial P}\right)_T &= T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T \end{aligned}}$$

For ideal gas : 0

For real gas : $\frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$

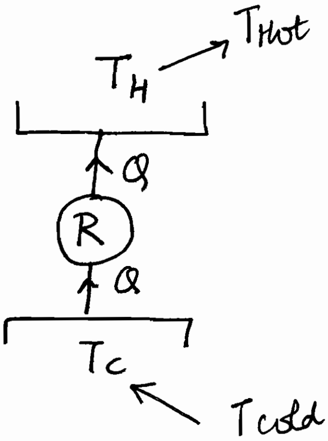
(H.W.)

★ [Heat Pump (or refrigerator) is the opposite of heat engine]

Kelvin Planck statement from Claussius

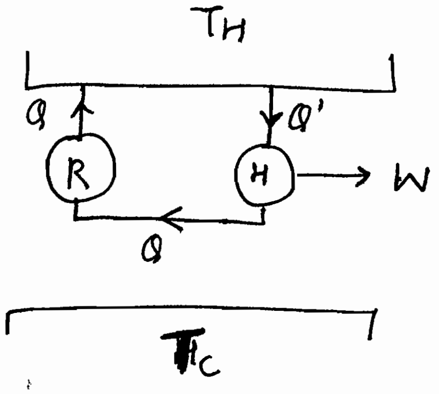
Say Claussius is wrong

⇒ Heat Pump (R) can be there :



We can couple it with Heat Engine (H) s.t. Heat remove by R be same as Heat Rejected from H.

⇒



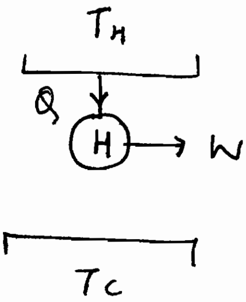
Now the combined is a heat engine that converts heat $(Q'-Q)$ to Work (W) without producing any external effect.

⇒ Violation of Planck-kelvin statment

Claussius Statement from kelvin Planck Statment

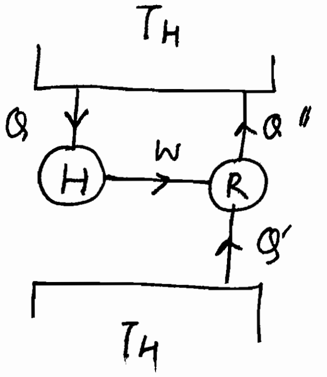
Say kelvin-Planck Statement is wrong.

Let us have Heat Engine (H) such that



We can couple it with Heat Pump (R), s.t. Work Produced by H by used by R such that

HW



$$W = Q \Rightarrow Q'' = W + Q' > W \Rightarrow Q'' > Q$$

⇒ Now the combined device transfers heat from lower temp. to higher temperature without using any external work

Thermodynamic Temperature Scale

We can use Carnot Principle to establish thermodynamic Temperature Scale. Carnot Theorem states that all reversible engines working between same heat reservoirs are equally efficient. Thus, any reversible heat engine operating between temperature T_1 and T_2 must have same efficiency, i.e. efficiency is a function of only temperatures.

$$\eta = 1 - \frac{q_c}{q_h} \Rightarrow \left(\frac{q_c}{q_H}\right) = f(T_C, T_H)$$

Let $T_1 > T_2 > T_3$

$$f(T_1, T_3) = \frac{q_3}{q_1} = \left(\frac{q_3}{q_2}\right)\left(\frac{q_2}{q_1}\right) = f(T_3, T_2)\; f(T_2, T_1)$$

LHS is not a function of T_2

⇒ in order to achieve this $f(T_1, T_2) = \left(\frac{g(T_2)}{g(T_1)}\right)$

and $f(T_2, T_3) = \left(\frac{g(T_3)}{g(T_2)}\right)$

s.t. $f(T_1, T_3) = \frac{g(T_3)}{g(T_2)} \cdot \frac{g(T_2)}{g(T_1)} = \frac{g(T_3)}{g(T_1)}$

As a matter of convenience, we choose $g(T) = T$. HW

Choosing 1 fixed reference as reference Temperature (i.e. Triple Point of water), we establish Thermodynamic Temperature Scale, as the other one [note that we need 2 points to make scale) is Absolute Zero.

① $\frac{Q_1}{Q_2} = \frac{T}{T_{ref}}$ Hence can define T.

By international standards, the unit is kelvin and Points are defined as:

1) Absolute Zero, the lowest possible temperature at 0k and −273.15 °C

2) Triple Point of water at 273.16 k and 0.01°C

This definition defines 3 things :-

a) It fixes the magnitude of kelvin Unit as being precisely 1 part in 273.16 parts the difference between Absolute Zero & Triple Point of water.

b) It establishes that one kelvin has precisely the same magnitude as 1-degree increment on Celcius scale

c) It establishes difference between 2 scales' null points as being precisely 273.16 k....

$\Rightarrow \boxed{T(V-b)^{R/C_V} = \text{Const.}}$

Adiabatic relation for Vander Wall gas

$$dU + P\,dV = 0 \quad \text{—} \quad ①$$

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

$$= C_V\,dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{} dV \quad \text{—} \quad ②$$

$\left(\frac{a}{V^2}\right)$ for real gas

$$\text{Now} \left(\frac{\partial U}{\partial V}\right)_T dV = \left(\frac{T\,dS - P\,dV}{dV}\right)_T dV = T\left(\frac{\partial S}{\partial V}\right)_T dV - P\,dV$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V dV - P\,dV \quad \text{—} \quad ③$$

$$\Rightarrow dU + P\,dV = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV - P\,dV + P\,dV = 0$$

$$\Rightarrow C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV = 0 \quad \Rightarrow C_V\,dT + \frac{RT}{V-b}\,dV = 0$$

Thermodynamics (6)

02/01/2012

Joule Thomson or Joule-kelvin Coefficient

$$\boxed{\mu = \left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]}$$

For ideal gases : $\boxed{\mu = 0}$ i.e. $dT = 0$

For real gases : $\boxed{\mu = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]}$

बचपन में Joule Thompson Effec

High Pressure से low Pressu में Gas release हुई तो उसका Temperature drop कर जाएगा !!

Joule - kelvin Effect

- Outcome of famous Porous Plug Experiment.
- Joule was interested in interaction of real gas molecules.
- In ideal gases, molecules are point particles while in real gases they occupy space, hence interact, while the former do not interact. ★
- H_2 and He are so small s.t. it can be treated as an ideal gas.
- Joule's law : $U_{\text{ideal gas}} = U(T)$

  i.e. $\left(\frac{\partial U}{\partial V}\right)_T = 0$; $\left(\frac{\partial U}{\partial P}\right)_T = 0$ ★★

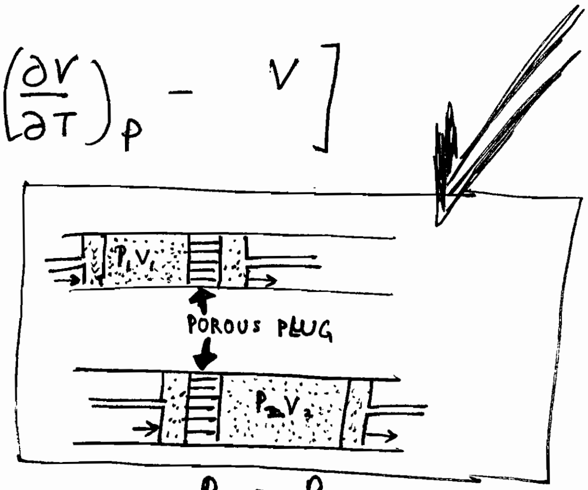
Joule wanted to prove, for real gases $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$ & $\left(\frac{\partial U}{\partial P}\right)_T \neq 0$

- Thomson improved the experimental set up and performed famous porous plug experiment, with Joule. Its also called Joule Thomson Experiment.

Aim : To find out inter-molecular interactions in real gases.

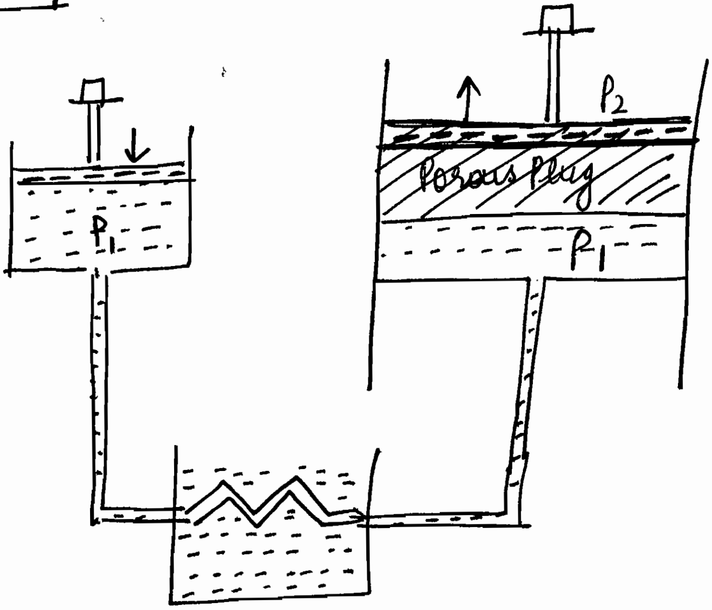
RESULT : "Whenever a real gas is subjected to Constant Pressure difference in an irreversible adiabatic process, resulting into change of its temperature, this change in temperature wrt. Pressure difference [redacted] is called Joule-Thomson Coefficient"

$$\mu = \left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$



$P_1 > P_2$

Set up :



Sensitive Heat Bath

P_1 : Const. High Pressure
P_2 : Const. low Pressure
⇒ ISOBARIC

$T_{gas} = T_{sensitive\ heat\ bath}$ (initially)

[Most of the gases, except H_2 & He ; T ↓ in Joule-Thomson Experiment]

Walls are totally insulated i.e. no heat flow allowed ⇒ Adiaba

Porous Plug : Cotton or silk

We have to do work to maintain Pressure P_1 & P_2.

[redacted]

$$\left[\begin{array}{l} W_{\text{done by external force}} = P_1V_1 - P_2V_2 \\ \Rightarrow W_{gas} = W_{sys} = W = (P_2V_2 - P_1V_1) \end{array}\right] ⊛$$

$$dW = P_2\, dV_2 - P_1\, dV_1$$

$$W = P_2V_2 - P_1V_1$$

$$dQ = 0 = dU + dW$$

$$\Rightarrow \underline{dW = -dU = U_1 - U_2}$$

$$⊛ \Rightarrow U_1 - U_2 = P_2V_2 - P_1V_1$$

$$\Rightarrow \boxed{U_1 + P_1V_1 = U_2 + P_2V_2}$$

⇒ **Isoenthalpic Process.**

⊛ Adiabatic + Const. Pressure difference (irreversible ⇓) ⬇ Isoenthalpic Process

This is an irreversible process

$$dP = P_1 - P_2 = \text{const.}$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right)$$

For real gases, $\mu = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$

$$\frac{T_1 - T_2}{P_1 - P_2} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

$$T_1 - T_2 = \left(\frac{P_1 - P_2}{C_p}\right)\left[\frac{2a}{RT} - b\right]$$

⊛ Now $\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T$

$$= \frac{-1}{C_P}\left[\underset{\substack{\Uparrow \\ \text{deviation from} \\ \text{Joule's law} \\ U = f(T)}}{\left(\frac{\partial U}{\partial P}\right)_T} + \underset{\substack{\Uparrow \\ \text{deviation} \\ \text{from Boyle's} \\ \text{law} \\ (PV)_T = \text{const.}}}{\left(\frac{\partial (PV)}{\partial p}\right)_T}\right]$$

Since ideal gas follow both the laws ⇒

$$\underset{\substack{\uparrow \\ \text{Joule-kelvin} \\ \text{Coefficient}}}{\mu}_{\text{ideal gas}} = 0$$

Cooling

⊙ $T_1 > T_2 \Rightarrow \frac{2a}{RT} - b > 0 \Rightarrow \boxed{T < \frac{2a}{Rb}}$

⊙ T: initial temperature or Temperature of heat bath.

Heating

⊙ $T_2 > T_1 \Rightarrow \boxed{T > \left(\frac{2a}{Rb}\right)}$

at $T = \left(\frac{2a}{Rb}\right)$: no change in Temperature.

It is the temperature of inversion (T_i)

$$\boxed{T_i = \left(\frac{2a}{Rb}\right)}$$

$T < T_i$: Cooling
$T > T_i$: heating
$T = T_i$: no change in temp.

✓ Note the dP is negative....

⊙ FOR H_2 and He, a and b are very small.
T_i for H_2 and He is very small.
$\Rightarrow T > T_i$: always heating

Other gases: $T_i \approx 1000$°K
$\Rightarrow T < T_i$: always cooling

Clasius Clapeyron Equation

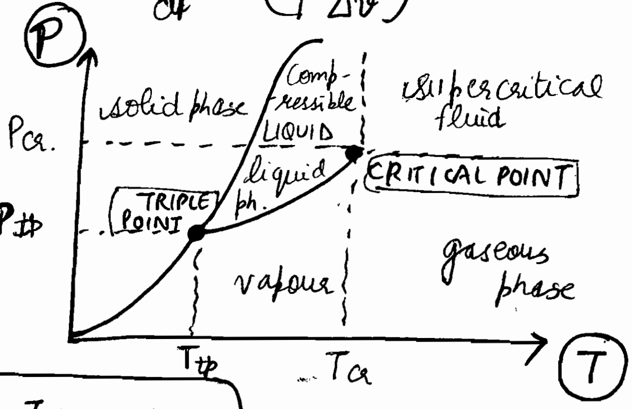
- (3 Proof) ⊙ 1st order : 2 applications
  ⊙ 2nd order : 2 examples
- It describes 1st order Phase Transition

eg. Melting
Freezing
Vapourization
Condensation

i.e. $\Delta S \neq 0, \ \Delta V \neq 0$

On a Pressure-Temp. (P-T) diagram, the line separating the 2 phases is known as the coexistence curve. This relation gives the slope of this curve.

$$\frac{dP}{dT} = \left(\frac{mL}{T\Delta v}\right)$$



3rd CT of Joule Thompson $\left(\frac{\partial P}{\partial T}\right)$

- If Cp changes ⇒ 2nd Order Phase Transition

- Gibbs Function $\boxed{dG = VdP - SdT}$

If $\left(\frac{\partial G}{\partial P}\right)_T = V$, $\left(\frac{\partial G}{\partial T}\right)_P = -S$ i.e. 1st derivatives

are discontinuous ⇒ 1st Order Phase Transition.

(★) discontinuous means that during change, both volume & entropy undergo a change. eg. melting, vapourization. Since $dT=0$, $[C_P, \alpha, k_T] \rightarrow \infty$

If n^{th} derivative is discontinuous ⇒ n^{th} Order Phase Transition

eg. $\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T$: if its discontinuous ⇒ 2nd order Phase Change

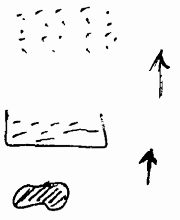
$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_P}{T}$: if Cp is discontinuous ⇒ 2nd Order Phase Change

Note that here, volume & entropy are usually continuous (remain same)

Note that 2nd order if any 1 is discontinuous or both.

- Note that we always talk about
  Solid → liquid transition
  and
  liquid → vapour transition

ऊपर की
ओर जाएँगे :

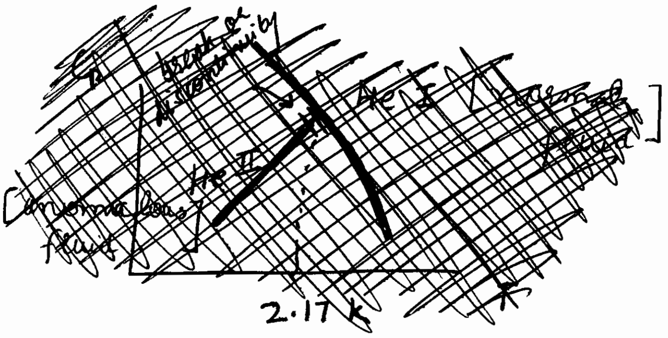


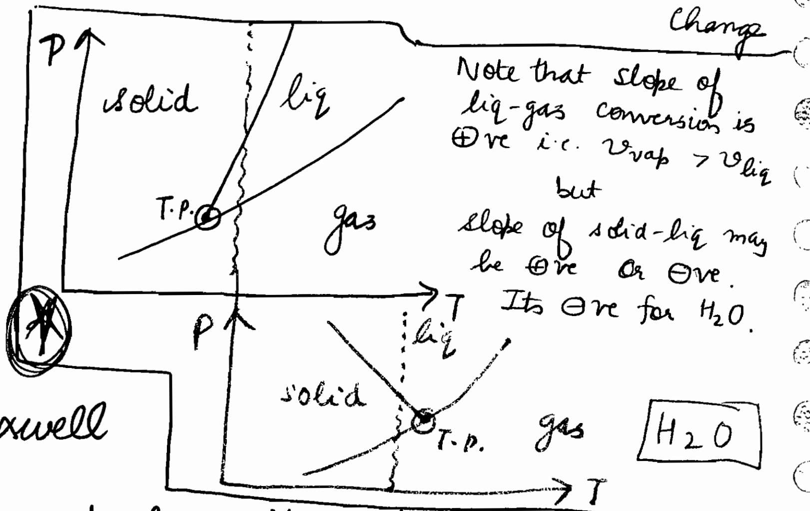
eg. Ferromagnetic Material $\xrightarrow[\text{Curie Temp.}]{\text{heating above}}$ Paramagnetic Material

its 2nd order ϕ-change

Normal Conductor $\xrightarrow[\text{certain Temp.}]{\text{Cooled below}}$ Super Conductor

examples of 2nd order Phase Change





Note that slope of liq-gas conversion is ⊕ve i.e. $v_{vap} > v_{liq}$ but slope of solid-liq may be ⊕ve or ⊖ve. Its ⊖ve for H_2O.

Clasius Clapeyron from Maxwell

⊙ Clasius- Clapeyron Equation deals with change of Phase Change Temperature upon application upon Pressure

$$\boxed{\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}}$$

$\boxed{V: \text{specific volume} = \frac{1}{\rho}}$

→ It is one of the most important formula of thermodynamics. It gives rate at which vapour Pressure must change with Temperature for 2 phases to coexist in equilibrium.

Inversely, we may investigate effect of Pressure on Boiling Point

$$\underset{V_1}{\text{Phase 1}} \xrightarrow{\text{at a}} \underset{V_2}{\text{Phase 2}}$$

- Temp T
- Pressure P
- $\Delta Q = L$

We know $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ [IInd Maxwell equation]

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

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

dQ : heat given to system... तबी उपर की ओर जाती है !!

$$\Rightarrow \frac{L}{T(V_2-V_1)} = \left(\frac{dP}{dT}\right)$$

liquid → vapour

(4) $$\frac{(6\text{ cm of Hg})}{dT} = \frac{2.3\times10^6}{373\left(\frac{1}{\rho_2}-\frac{1}{\rho_1}\right)}$$

⊙ for ex., For H_2O $(V_2-V_1)<0$ melting of ice

⇒ L.H.S is ⊖ve

⇒ If I increase Pressure, [redacted] $T_{melting}$ can be reduced i.e. even at −3°C ice can be melted upon application of enuff Pressure : REGELATION

⊛ Note that V and L are for 1 kg ⇒ $V = \frac{1}{\rho}$

or if m kg and corresponding volumes

$$\Rightarrow \frac{mL}{T(V_2-V_1)}$$

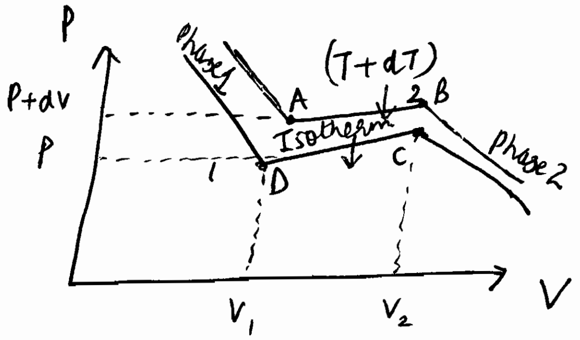
$$\left(\frac{\partial p}{\partial T}\right)_{saturation} = \frac{L}{T(v_{vap}-v_{liq})}$$

Since $v_{vap} > v_{liq}$ ⇒ $\left(\frac{\partial p}{\partial T}\right)_{sat.} > 0$

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

⇒ increase in Pressure raises the boiling point, and vice versa. Hence the concept of Pressure Cooker.

Clasius Clapeyron from Carnot Cycle



PV curve for Carnot Cycle

→ P and T are const.

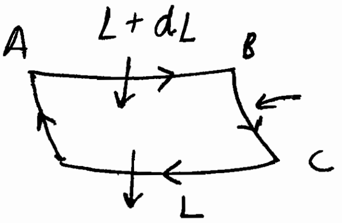
→ V changes

AB, CD : isotherms
BC, DA : adiabats

Quick I change the Pressure, corresponding T changes quickly ⇒ adiabatic process.

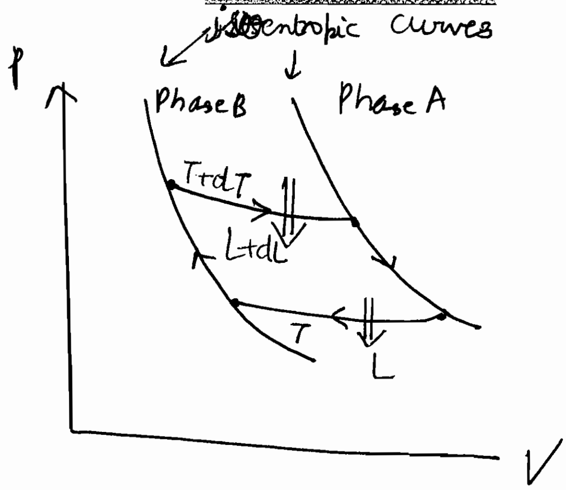
Let ABCD be a reversible Carnot Cycle.

Ph 1 : liquid
Ph 2 : vapour



I quickly reduce the P i.e. adiabatic expansio

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



$$\frac{L+dL}{L} = \frac{T+dT}{T}$$

$$\Rightarrow \frac{dL}{L} = \frac{dT}{T}$$

$$\Rightarrow \boxed{dL = \left(\frac{L}{T}\right) dT}$$

Work Done in Carnot Cycle $= Q_1 - Q_2$ [redacted]

$$= L + dL - L$$

$$= dL$$

$$= \frac{L}{T} dT$$

Work Done = Area of Curve $\approx dP(V_2 - V_1)$

$$\Rightarrow \frac{L}{T} dT = dP(V_2 - V_1)$$

$$\Rightarrow \boxed{\frac{L}{T(V_2 - V_1)} = \frac{dP}{dT}}$$ Hence, Proved

---

⊛ [In case of vapourization, $V_2 > V_1$ in all cases $\Rightarrow \frac{dP}{dT} > 0$

$\Rightarrow$ if $dP \uparrow \Rightarrow dT \uparrow$ and if $P \downarrow \Rightarrow T \downarrow$]

In case of melting, $\boxed{V_2 > V_1}$ or $\boxed{V_1 > V_2}$

eg. ice to water : $V_2 < V_1$

$$\Rightarrow (V_2 - V_1) < 0 \Rightarrow \left(\frac{dP}{dT}\right) < 0$$

similarly ice, gallium, bismuth

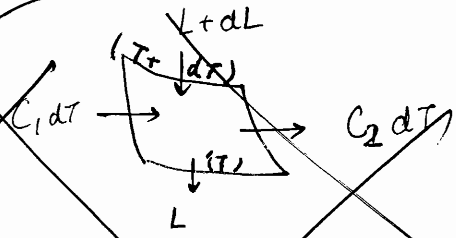
$V_2 < V_1$ BIG

$\Rightarrow$ if $P\uparrow \Rightarrow T\downarrow$

if $P\downarrow \Rightarrow T\uparrow$

eg. Wax on melting : $V_2 > V_1 \quad \Rightarrow \quad V_2 - V_1 > 0 \quad \Rightarrow \left(\frac{dP}{dT}\right) > 0$
Sulphur

$\Rightarrow$ if $P\uparrow \Rightarrow T\uparrow$
$P\downarrow \Rightarrow T\downarrow$



~~**Non Adiabatic**~~

~~If $A\to B : L + dL$~~
~~$B\to C : -C_2\, dT$: saturated vapour → normal vapour~~
~~$C\to A : \quad -L$~~

~~D-A: normal liquid → saturated liquid~~
~~$C_1 dT$~~

~~$\Rightarrow dQ = (L+dL) - (C_2 dT) - (L) + (C_1 dT)$~~

~~$dQ = dL + (C_1 - C_2)\, dT$~~

~~$\frac{L}{T} dT = \frac{dL}{[illegible]} + (C_1 - C_2)\, dT \quad \Rightarrow \boxed{C_2 - C_1 = \left(\frac{dL}{dT}\right) - \left(\frac{L}{T}\right)}$~~

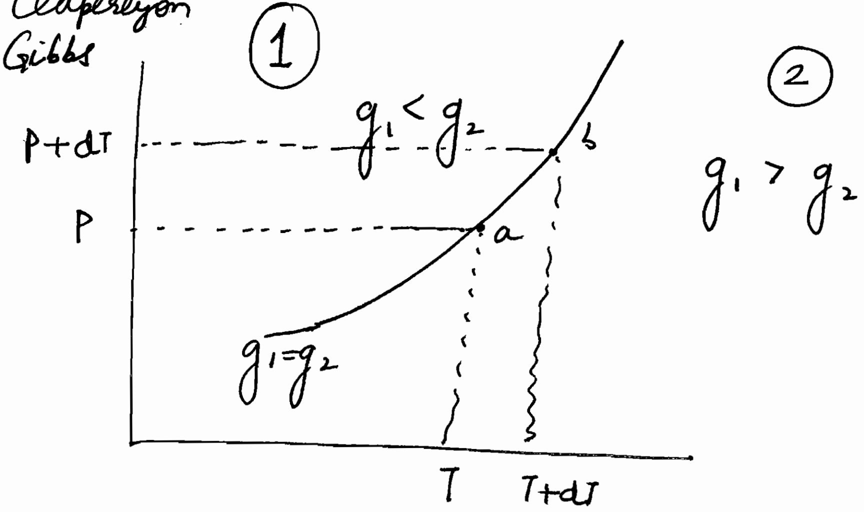
~~$\Rightarrow \frac{dQ}{dT} = \frac{L}{T} + C_1 - C_2$~~

PTO

⊛ For phase change, we draw PT curves
Also the slope is $\left(\frac{dP}{dT}\right)$ for clausius clapeyron equation .....

Clasius Clapereyon from Gibbs Energy

HW



PT curve always for phasechange

At both a and b, phases are in equilibrium, so the specific Gibbs free energy of 2 phases at each point are same i.e.

If dg is Δg between a and b

$$g_1^{(a)} = g_2^{(a)}$$
$$g_1^{(b)} = g_2^{(b)}$$
$$\Rightarrow \quad dg_1^{ab} = dg_2^{ab}$$

do this question from Tut Q1

⇓

[refer end of notes]

$$\Rightarrow \quad -s_1\,dT + v_1\,dP = -s_2\,dT + v_2\,dP$$
$$\Rightarrow \quad (s_2 - s_1)\,dT = (v_2 - v_1)\,dP$$
$$\Rightarrow \quad \underset{\sim\sim\sim}{\frac{dP}{dT}} = \frac{(s_2 - s_1)}{(v_2 - v_1)} = \underset{\sim\sim\sim}{\frac{L}{T(v_2 - v_1)}}$$

From IV th law, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha$

Hence for substances that expand on heating ⇒ $\alpha > 0$

$$\Rightarrow \left(\frac{dQ}{dP}\right)_T < 0$$

i.e. Heat is released upon compression

Relation between Specific Heats of Vapour and Liquid HW

(not related to Clausius Clapeyron eqn)

For a change in state from liquid to vapour at Temperature T, we have

s: saturated vapour
p: liquid

$$[S_s - S_p] = \left(\frac{L}{T}\right) \quad — ①$$

differentiating ① wrt T,

$$\frac{dS_s}{dT} - \frac{dS_p}{dT} = \frac{1}{T}\frac{dL}{dT} + L\left(\frac{-1}{T^2}\right)$$

$$\Rightarrow T.\frac{dS_s}{dT} - T\frac{dS_p}{dT} = \frac{dL}{dT} - \frac{L}{T}$$

[multiplying by T]

$$\Rightarrow \boxed{[C_s - C_p] = \left(\frac{dL}{dT}\right) - \frac{L}{T}}$$

Specific Heat of saturated vapour is negative, meaning $C_s < 0$, meaning that in order to raise the temperature, a certain quantity of heat is to be withdrawn from the body.

To change saturated vapour at one Temperature to saturated vapour at a higher temp, Pressure must be increased. If compression were effected adiabatically, i.e., without adding or subtracting heat, the vapour would become superheated, Consequently, during compression, some heat must be abstracted in order to keep the vapour in saturated condition. Hence T ↑ is accompanied by removal of heat ⇒ $C < 0$.

⊛ Vapour <
Saturated
⇓ adiabatic compression
Superheated

Thermodynamics (7)

03/01/2012

Adiabatic Demagnetization of Paramagnetic Salt

- **Magnetic Property of a material** :

1) Permeability μ
2) Susceptibility χ

[Corresponding electrical properties
→ Permittivity
→ Electrical Susceptibility]

$$\mu = \mu_0 [1 + \chi] = \mu_0 \mu_r$$

$\left(\frac{\mu}{\mu_0}\right)$: relative permeability : μ_r

Effects of $\vec{H}$

- **3 vectors of Magnetism** : $\vec{B}, \underbrace{\vec{H}}_{\text{Basic or Natural}}, \vec{M}$

$\vec{H}$: Magnetizing force that is applied on a [material that can be magnetized] or [magnetic material]. Magnetic Material has some property of acquiring magnetism eg. magnetic dipole via unpaired charge like unpaired electrons.

If these dipoles are aligned in direction of field ⇒ Magnetism

$\vec{M}$: no. of magnetic dipoles per unit volume

Fraction of $\vec{H}$ that has caused M is χ

i.e. $\boxed{\chi \vec{H} = \vec{M}}$

$\vec{B}$ or intensity of magnetic induction is the magnetic induced due to applied $\vec{H}$

i.e. $\boxed{\vec{B} = \mu \vec{H}}$

In free Space : $\vec{B} = \mu_0 \vec{H}$

In a material , some dipoles will align too

$$\Rightarrow \vec{B} = \mu_0 \vec{H} + \mu_0 \vec{M}$$
$$= \mu_0 (1+\chi) \vec{H}$$
$$= \mu \vec{H}$$

$\Rightarrow \boxed{\mu = \mu_0 (1+\chi)}$ $\mu_0 = 4\pi \times 10^{-7}$ SI un

On these properties , we can classify materials :

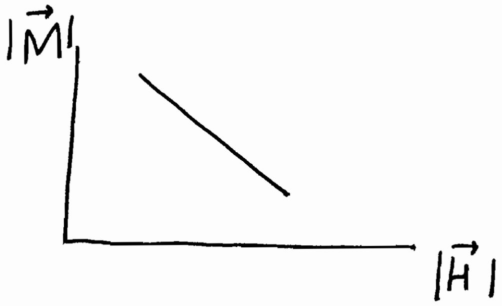
(1) ~~DIAMAGNETIC~~ :

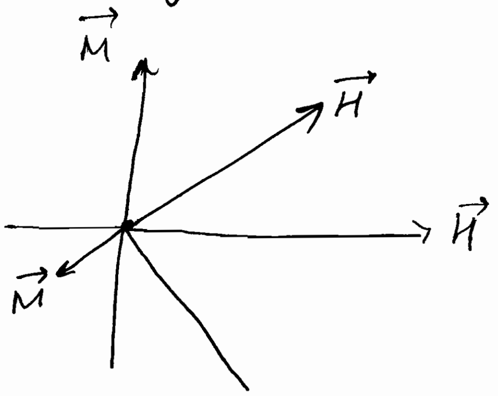
- χ is small negative quantity

$\Rightarrow \mu < \mu_0$

- We know $\vec{M} = \chi \vec{H}$

if χ is negative $\Rightarrow$ dipoles align weakly opposite to applied $\vec{H}$.





(χ diamagnetic is independent of temperature .)

- It happens in materials with paired electrons.

- SuperConductors are perfect diamagnetic materials

✪ χ is independent of Temperature for diamag

2) Paramagnetic Materials

- Small ⊕ve value of χ
- $\mu > \mu_0$
- Weakly aligned dipoles in direction of $\vec{H}$
- dependend on Temperature as inversely proportional

st. $\chi = \frac{M}{H} \propto \left(\frac{1}{T}\right)$

$\chi = \frac{c}{T}$ c: Curie's const.

i.e. $\boxed{\vec{M} = \frac{c\vec{H}}{T}}$

3) Ferromagnetic Materials :

- Large ⊕ve value of χ
- $\mu \gg \mu_0$
- $\boxed{\chi = \left(\frac{c}{T-\theta}\right)}$ Valid For $T > \theta$: Paramagnetic Material

Note that for $T < \theta$ it is Ferromagnetic Material

"It is called "Curie-Weiss law".
It describes magnetic susceptibility
χ of a ferromagnet in Paramagnetic
region above the Curie Point."
i.e. $T > \theta$

θ : Curie's Temperature

Below θ, ferromagnets has spontaneous magnetization.
No law governs its.

Experiment

★ just remember the starting point

$\boxed{S = S(T, H)}$

$\uparrow$ Temp $\uparrow$ magnetic field applied

$$dS = \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH$$

Multiply by T,

$$T\,ds = T\left(\frac{\partial s}{\partial T}\right)_H dT + T\left(\frac{\partial s}{\partial H}\right)_T dH$$

$$\Rightarrow T\,ds = \left(\frac{\partial Q}{\partial T}\right)_H dT + T\left(\frac{\partial s}{\partial H}\right)_T dH$$

[like Gases $dW = P\,dV$
here, $dW = -H\,dM$]

Work done by external field on system $= H\,dM$
$\Rightarrow$ Work done by system $= -H\,dm$

[like $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, we have
$\left(\frac{\partial s}{\partial H}\right)_T = +\left(\frac{\partial M}{\partial T}\right)_H$]

$$\Rightarrow T\,dS = \underbrace{\left(\frac{\partial Q}{\partial T}\right)_H}_{C_H} dT + T\left(\frac{\partial M}{\partial T}\right)_H dH$$ ✓

C_H : specific heat at constant $\vec{H}$

[redacted]

$$\Rightarrow \boxed{T\,ds = C_H\,dT + T\left(\frac{\partial M}{\partial T}\right)_H dH}$$

Note that H is here applied magnetic field and not enthalpy

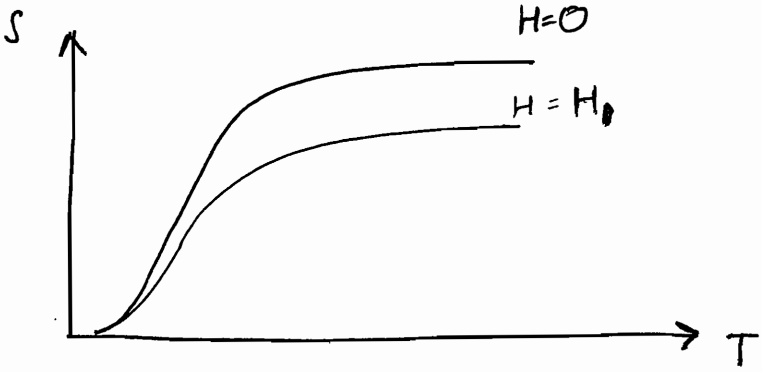
For paramagnetic salt, $M = \frac{cH}{T}$

$$\left(\frac{\partial M}{\partial T}\right)_H = \frac{-cH}{T^2}$$

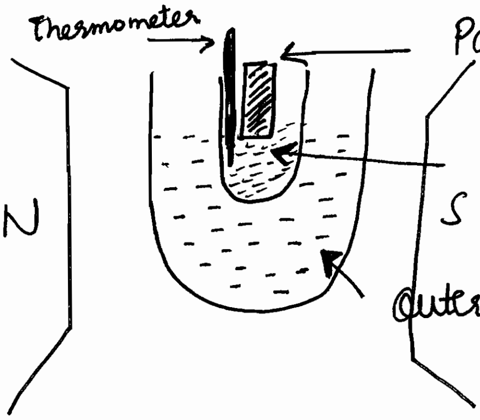
for paramagnetic

$$\Rightarrow \boxed{T\,dS = C_H\,dT - \left(\frac{cH}{T}\right) dH}$$

→ Adiabatic demagnetizati
is accompanied by fall in Temperature. Its called <u>Magneto Caloric Effect</u>.



Characteristic Curve of Paramagnetic Material



Paramagnetic salt : **Gadolinium Sulphate** [Rock Solid i.e. $PdV = 0$

inner bath : liquid Helium

outer Bath : liquid H_2

Specimen is at Temp. of liquid He initially

$$T_0 = T_{Helium}$$

There is no scale to determine Temp. below -200°C ....

NO WAY TO MEASURE ABOUT ABSOLUTE ZERO ??

We will evolve a magnetic Temperature Scale.

$$\chi_1 = \left(\frac{C}{T_1}\right) \quad : \quad \chi_1 ; T_1 : \text{known}$$

[assuming Curie's law is valid]

$$\chi_2 : \left(\frac{C}{T_2}\right) \qquad \chi_2 : \text{known}$$

T_2 : ?

$$\frac{\chi_1}{\chi_2} = \frac{T_2}{T_1}$$

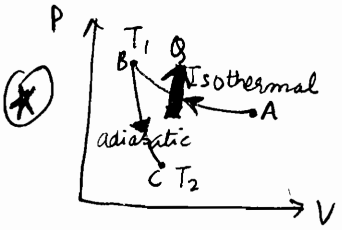
$$\Rightarrow \boxed{T_2 = T_1 \left(\frac{\chi_1}{\chi_2}\right)}$$

To measure χ : We put a coil in inner path and measure inductance.

Step 1 Isothermal Magnetization

- Let Temperature of liquid Helium be T_1
- Magnetic Field $\vec{H}$ is applied.
- Some dipoles will be aligned.
- Work Done = $\left[\int H\,dM\right]$ is stored in form of Potential Energy

Step 2 Adiabatic Demagnetization



Equivalent PV diagram

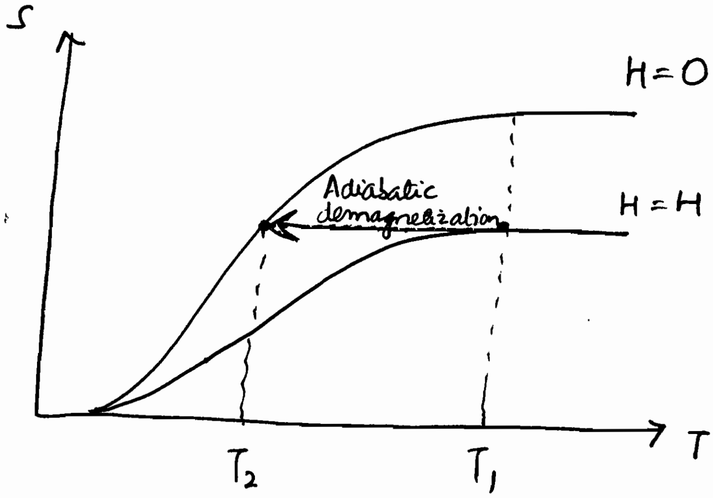
AB

$dQ < 0$
$dU = 0$
$dW < 0$
$dW_{ext} > 0$

BC

$dQ = 0$
$dW > 0$
$dU < 0$

- Quickly switch off the field.
- Internal Energy is used to bring back dipoles



$$T\,dS = C_H\,dT - \frac{cH}{T}\,dH$$

Adiabatic : $dS = 0$

$$\Rightarrow \int_{T_1}^{T_2} T\,C_H\,dT = + \; C\,\frac{H^2}{2}\Big|_H^0$$

$$\Rightarrow T_2^2 - T_1^2 = -\frac{C}{C_H}H^2$$

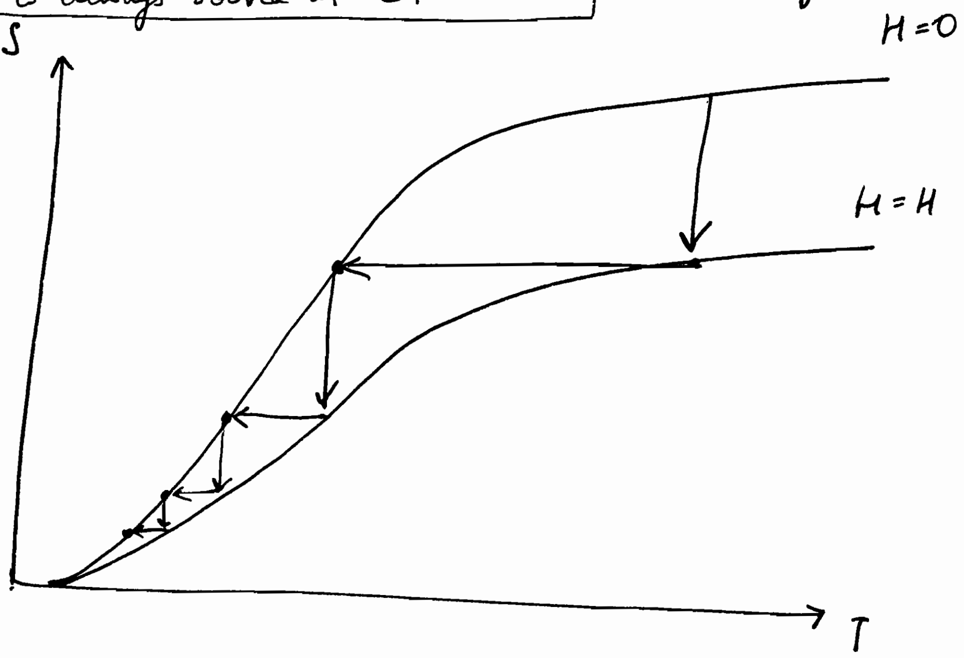
$$\Rightarrow (T_2 - T_1)(T_1 + T_2) = -\frac{C}{C_H}H^2$$

$$\Rightarrow \boxed{T_2 - T_1 = -\left(\frac{C}{C_H}\right)\frac{H^2}{2T}}$$

⊛ $\Delta T \propto \frac{1}{T}$: at high Temp, ΔT will be insignificant. ∴ first Cool by normal methods. Make ~~T~~ T low... then apply Magneto-caloric effect

• issues of dimensions in S.I. units, but in CGS units, $\mu_0 = 1$ and is dimensionless. Hence this question is always solved in CGS units

(H : oersted)



"When we apply Magnetic Field, dipoles are aligned in accordance. ~~work is done to align dipoles. It is stored as Potential Energy~~

Note that entropy is reduced in this process. ⇒ Heat released.

In adiabatic demagnetization, the internal energy is used to de align the dipoles in absence of $\vec{H}$. Hence the temperature drops".

"Temperature is measured by assuming the validity of Curie's law".

Disadvantages

① Cooling capacity is small and one cannot cool any large sized material.

② One cannot perform experiments that require absence of magnetic fields.

③ T already should be low.

④ Can we achieve T = 0? during isothermal magnetization, heat is removed which continuously needs to be removed from salt, for which at surrounding, an even lower T is reqd., which becomes increasingly difficult.

Vander Walls Equation of State for Real Gas

Thermometry :

For 1 mole of an ideal gas,

① Boyle's Law : $P \propto \frac{1}{V}$ (T = const.)

② Charles law : $V \propto T$ (P = const.)

Combining the ① and ②,

$$\boxed{PV = RT}$$

kinetic Theory :

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

$$PV = \frac{1}{3}Nmv^2$$

$$= \frac{1}{3}N\underbrace{mv^2} = \frac{1}{3}N\,3kT$$

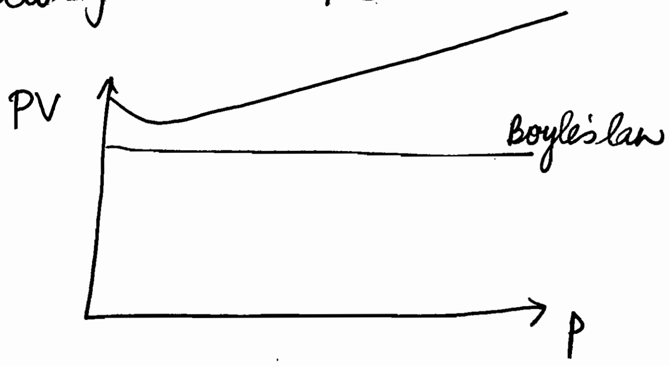
$$= NkT$$

$$\boxed{PV = RT} \qquad \boxed{R = Nk}$$

- Ideal Gas particles themselves do not occupy space ⇒ No interaction

But real gas interact !!

Correction for Real Gas



✓

① Finite size of Molecules:

Since volume of real gas particles $\neq 0$

⇒ Space for their movement or interaction is reduced

$$\Rightarrow \underset{\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim}{V_{real} = (V - b)_{available}}$$

b : Correction for volume occupied by molecules

② Correction for Intermolecular attraction.

$\left(\frac{\partial U}{\partial V}\right) = \frac{\partial U}{A \cdot \partial r} = \frac{F}{A} = P$ ✓

Vander Wall observed : $\underline{\frac{\partial U}{\partial V} \propto \frac{1}{V^2}}$ ✓

[Actually he observed : $\left(\frac{F(r)}{A}\right) = \frac{A}{r^6} - \frac{B}{r^{12}}$]

He considered : $\boxed{\frac{\partial U}{\partial V} = \frac{a}{V^2}}$

* drop in pressure caused due to inter-molecular interactions in the out-most layer $= \left(\frac{a}{V^2}\right)$

⇒ Pressure Correction : $\underline{P = P + \frac{a}{V^2}}$

⇒ in the ideal gas, we must replace p by the sum of observed pressure for a real gas and drop caused by intermolecular forces. i.e. $\left(p + \frac{a}{V^2}\right)$

So after applying both corrections,

$$\boxed{\left[P + \frac{a}{V^2}\right]\left[V - b\right] = RT}$$

here V is for 1 mole of gas

If V_0 is the volume for n moles

⇒ for 1 mole

Put $V = \left(\frac{V_0}{n}\right)$

For n moles, Put $V = \left(\frac{V}{n}\right)$

Real Gas $\left(P + \frac{an^2}{V^2}\right)\left(\left(\frac{V}{n}\right) - b\right) = RT$

Ideal Gas $P\left(\frac{V}{n}\right) = RT$ ★★★

⊙ Vandel Wall is a cubic in V.

i.e. $V^3 - bV^2 + \frac{a}{P}V - \frac{ab}{P} - \frac{RT}{P}V^2 = 0$

$= V^3 - \left[b + \frac{RT}{P}\right]V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$

Liquification of Gases

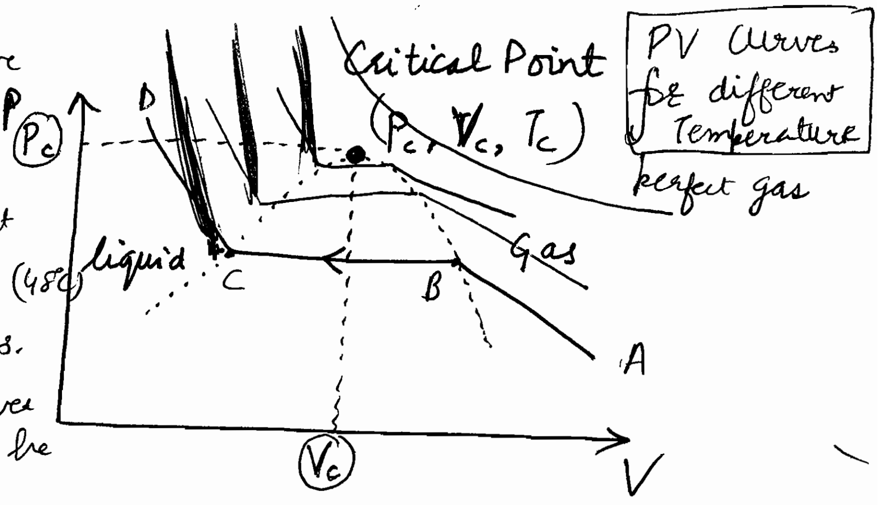
★ Important Curve

Andrew's Experiment on CO_2 liquification

Andrew carried very exhaustive experiments on compressibility of gases while attempting to liquify them. He found that

(a) Above a certain temperature (48°) CO_2 behaves like a perfect gas.

(b) At 31.4 °C, a kink is observed which suggests that gas can be liquified under compression.



(c) A → B : CO_2 behaves as a gas

B → C : liquid and vapour coexist & P const.

C → D : liquid

(d) in liquid phase slope is very high.

Application of P : easiest way of Compression

P_c : Critical Pressure

T_c : Critical Temperature

For (VAPOUR) $T < T_c$: Gas can be liquified via application of Pressure

(GAS) $T > T_c$: Gas can't be liquified just by application of Pressure

If $\left.\begin{matrix} P = P_c \\ T = T_c \end{matrix}\right\} \Rightarrow V = V_c$

For CO_2 : T_c : 31[redacted]°C
P_c : 73 atm

⊙ liquid state में हल्का सा भी compress करने के लिए, बहुत ज्यादा Pressure apply करना पड़ेगा। ∴ Very High slope of PV curve in liquid state.

$$V_c^3 - \left(b + \frac{RT_c}{P_c}\right) V^2 + \frac{a}{P_c} V_c - \frac{ab}{P_c} = 0 \quad \text{—} \quad ①$$

since V_c satisfied V ⇒ $V - V_c = 0$

or $(V-V_c)^3 = 0$

$$\Rightarrow V^3 - V_c^3 - 3VV_c(V-V_c) = 0$$

$$\Rightarrow V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad \text{—} \quad ②$$

① and ② are equivalent

→ Temperature ~~below~~ which it becomes possible to liquify gas under compression is known as **Critical temp.**

$$\Rightarrow 3V_c = b + \frac{RT_c}{P_c} \quad \text{—} \quad ③$$

→ Pressure just required to liquefy a gas at critical temperature is called **critical pressure**. and corresponding volume (for 1 mole of a gas) is called **critical volume**

$$3V_c^2 = \frac{a}{P_c} \quad \text{—} \quad ④$$

$$V_c^3 = \frac{ab}{P_c} \quad \text{—} \quad ⑤$$

dividing ④ and ⑤

$$\frac{3}{V_c} = \frac{1}{b} \Rightarrow \boxed{V_c = 3b} \qquad \boxed{b = \frac{V_c}{3}}$$

Putting in ④

$$27b^3 = \frac{ab}{P_c} \Rightarrow \boxed{P_c = \frac{a}{27b^2}} \qquad \boxed{a = 3P_cV_c^2}$$

Putting in ③

$$8b = \frac{RT_c}{a} 27b^2 \Rightarrow \boxed{T_c = \frac{8a}{27Rb}}$$

Critical Coefficient

$$= \frac{RT_c}{P_cV_c}$$

$$= \left(\frac{8}{3}\right)$$

Reduced Equation of State

$$\alpha = \frac{P}{P_c}$$

$$\beta = \frac{V}{V_c}$$

$$\gamma = \frac{T}{T_c}$$

Also note that for critical isother the point P is [illegible] inflection point. $\Rightarrow \left(\frac{\partial p}{\partial V}\right)_T = 0$ and $\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$ at critical point.

$$\boxed{\left(\frac{\partial p}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} \qquad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}}$$

This offers 2nd way to find out critica parameters. The two equations on Vander Walls gas give:

[redacted]

$\Rightarrow \boxed{V_c = 3b}$ & $\boxed{T_c = \frac{8a}{27bR}}$ Replacing in equation, we g P_c

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

→ We can get same results by placing P, V, T in terms of α, β, γ and a, b.

$$\left(\alpha P_c + \frac{3P_cV_c^2}{\beta^2 V_c^2}\right)\left(\beta V_c - \frac{V_c}{3}\right) = \gamma R T_c$$

$$\Rightarrow \left[\alpha P_c + \frac{3P_c}{\beta^2}\right]\left[\beta V_c - \frac{V_c}{3}\right] = \gamma R T_c$$

$$\Rightarrow (P_cV_c)\left(\alpha + \frac{3}{\beta^2}\right)\left(\beta - \frac{1}{3}\right) = \gamma R T_c$$

$$\Rightarrow \boxed{\left(\alpha + \frac{3}{\beta^2}\right)\left(\beta - \frac{1}{3}\right) = \frac{8}{3}\gamma}$$

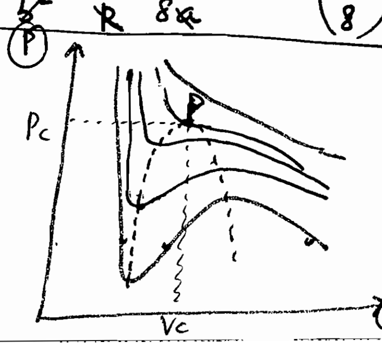
$$\boxed{P_cV_c = \frac{3}{8} R T_c}$$

[redacted]

Validity of derivation of critical constants

Vander Waals Equation is cubic in V. This means that for each pair of (p, T), V will have three values i.e. either all of them real or 1 real and 2 complex. For low temperatures, 3 +ve real roots exist. As T ↑, these roots approach one another. They become equal at $T = T_c$. Above $T > T_c$, only 1 real root exists for all p i.e. there can be no condensation in this region. ↑

$$\frac{\cancel{a}}{\cancel{27}\,\cancel{b^2}} \cdot \frac{3\cancel{b}}{\cancel{R}} \cdot \frac{\cancel{27}\,\cancel{R}\cancel{b}}{8\cancel{a}} = \left(\frac{3}{8}\right)$$



Law of Corresponding States

For Gas_1 : $[\alpha_1, \beta_1, \gamma_1]$

For Gas_2 : $[\alpha_2, \beta_2, \gamma_2]$

Only 2 Parameters are independent. 3rd can be derived from those 2.

says, if $\alpha_1 = \alpha_2$ & $\beta_1 = \beta_2$ $\Rightarrow$ $\gamma_1 = \gamma_2$

And the 2 gases are said to be in corresponding states.

eg. Gas 1 : $\begin{bmatrix} P_c : & 2 \text{ atm} \\ V_c : & 5 \text{ litre} \\ T_c : & 300 \text{ k} \end{bmatrix}$ @ $P = 1$ atm, $V = 25$ litre, $T : 4500$ k $\alpha_1 = \frac{1}{2}$, $\beta_1 = 5$, $\gamma_1 = 15$

Gas 2 : $\begin{bmatrix} P_c : & 5 \text{ atm} \\ V_c : & 30 \text{ litre} \\ T_c : & 800 \text{ k} \end{bmatrix}$ @ $P = 2.5$ atm, $V = 150$ litre, $T = 12000$ k $\alpha_1 = \frac{1}{2}$, $\beta_1 = 5$, $\gamma = 15$

$\Rightarrow$ Gas 1 and Gas 2 are in corresponding states.

→ Generic definition of corresponding states is that their reduced parameters are same!!

Q/ Calculate critical temperature of He if $P_c = 2.26$ atm. and critical density is $0.069\ g\,cm^{-3}$

A/ Critical volume is defined for 1 mole of gas.

$$\Rightarrow V_c = \frac{\text{Mass of 1 mole}}{\text{density}} = \frac{4g}{0.069\,g/cm^3} = \underline{\underline{57.97\ cm^3}}$$

$$\Rightarrow \frac{RT_c}{P_cV_c} = \frac{8}{3}$$

$$b = \frac{V_c}{3} = \underline{\underline{19.32\times10^{-6}\ m^3}}$$

$$\Rightarrow \underline{\underline{T_c = 4.2k}}$$

$$\frac{a}{27b^2} = 2.26\times10^5\ N/m^2$$

$$\Rightarrow T_c = \frac{8a}{27Rb} = \frac{8}{R}\left(\frac{a}{27b^2}\right)b = \frac{8b}{R}P_c$$

$$= \frac{8\times19.32\times10^{-6}\times2.26\times10^5}{8.31} = \underline{\underline{4.2\ k}}$$

✱ b is mathematically equivalent to 4 times the volume occupied by all the molecules

i.e. $\boxed{b = 4\times\left(\frac{4}{3}\pi r^3\right)\times N_A}$

eg. $b = 2.42\times10^{-5}\ m^3/mole$

$$\Rightarrow b = 4\times\frac{4}{3}\times\pi\times\frac{d^3}{8}\times N_A$$

$$\Rightarrow d^3 = \frac{3}{2}\frac{b}{\pi N_A} = 1.92\times10^{-29}\ m^3$$

$$\Rightarrow \boxed{d = 2.68\ \mathring{A}}$$

Thermodynamics (8)

04/1/2012

Gibbs Phase Rule & Chemical Potential

⇓ read this

$$dU = TdS - PdV$$
$$dF = -PdV - SdT$$
$$dH = TdS + VdP$$
$$dG = VdP - SdT$$

All these relations are valid for only HOMOGENOUS. systems. i.e. single composition system.

↑ (chemical composition)

eg. Ice + Water + steam : Homogenous Multi-Phase System

Ice + (water + sulphur) + Steam : Heterogenous or Multicomponent Multiphase System

For Heterogenous systems,

$$\boxed{F = U - TS + \mu N}$$

N → no. of molecules added

μ ↑ characteristic of added component called Chemical Potential

$$dF = -PdV - SdT + \mu dN$$

Similarly

$$dU = TdS - PdV + \mu_i dN_i$$
$$dF = -PdV - SdT + \mu_i dN_i$$
$$dH = TdS + VdP + \mu_i dN_i$$
$$dG = VdP - SdT + \mu_i dN_i$$

eg.

$$dU = T\,dS - P\,dV + \mu_1 dN_1 + \mu_2 dN_2$$

Read This

$$\mu_1 = \left(\frac{\partial U}{\partial N_1}\right)_{S,V,N_2} \quad \text{or} \quad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j}$$

similarly $$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{V,T,N_j}$$

$$\mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j}$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j}$$

- All these definitions are of $\boxed{\text{chemical Potential}}$. But in applications, we use $\boxed{\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j}}$

P, T are constant → Thermodynamic Equilibrium.

Gibbs Phase Rule

It describes thermodynamic $\overbrace{\text{equilibrium}}^{\text{Coexistence}}$ conditions for $\underbrace{\text{multi-component}}_{\text{('c' components coexisting in equilibrium)}}$ $\underbrace{\text{multi-phase}}_{\text{('p' phases coexisting in equilibrium)}}$ systems.

$$p \in \begin{bmatrix} \text{solid} \\ \text{liquid} \\ \text{Gas} \\ \text{Plasma} \\ \text{Bose Eistein Condensate} \end{bmatrix}$$

- Degree of Freedom at equilibrium

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

[i.e. F is the number of independent thermodynamic Coordinates or (variables) required to specify the state of thermodynamic equibrium]

given that equilibrium is not influence by forces of gravitational, electrostatic, magnetic & surface tension forces.

We know,

F = (Total number of thermodynamic variables) − (contraints)

⊙ For triple point of water,

$F = 1 - 3 + 2 = 0$

ie. every thing is fixed. It is a unique point.

Its Called 'INVARIANT SYSTEM'.

→ For ice-water state,

$F = 1 - 2 + 2 = 1$

Volume is changed in the process.

It is required to specify the system.

Its called 'MONOVARIANT SYSTEM'

⊛⊛ Refer [PTO to last Page] for Proof of Gibbs Phase Rule

G describes the equilibrium conditions

$$G = H - TS + \mu_1^1 N_1 + \mu_2^1 N_2 + \dots + \mu_c^1 N_c$$ 1 : specifies solid

$$+ \mu_1^2 N_1 + \mu_2^2 N_2 + \dots + \mu_c^2 N_c$$

$$\vdots$$

$$+ \mu_1^p N_1 + \mu_2^p N_2 + \dots + \mu_c^p N_c$$ p : p^th phase

$$dG = VdP - S\,dT + \sum_{i=1}^{c} \sum_{j=1}^{p} \mu_i \, dN_i^j$$

At equilibrium,

$$dG = 0$$
$$dP = 0$$
$$dT = 0$$

$$\Rightarrow \sum_{i=1}^{c} \sum_{j=1}^{p} \mu_i dN_i^{(j)} = 0$$

Let us consider, c component system existing in single phase:

$$G = H - TS + \mu_1^1 N_1 + \mu_2^1 N_2 + \dots \quad \mu_c^1 N_c$$

$$dG = VdP - SdT + \mu_1^1 dN_1 + \mu_2^1 dN_2 + \dots \quad \mu_c^1 dN_c$$

Equilibrium of c components in 1 phase

$$dP = 0 \quad dT = 0 \quad \underbrace{\sum \mu_1^{(1)} dN_1 + \mu_2^{(1)} dN_2 + \dots}_{\Rightarrow \ \text{independent} : \ (c-1)} = 0$$

$\Rightarrow$ For 'p' phase : independent = $p(C-1)$

Apart from that $dP = 0$
$dT = 0$

$\Rightarrow$ P, T are required

- Similarly considering 1 component in p phases :

$dG = 0 \quad dP = 0 \quad dT = 0$

$$\sum \begin{bmatrix} \mu_1^{(1)} dN_1 \\ \mu_1^{(2)} dN_1 \\ \mu_1 \, dN_1 \\ \vdots \\ \mu_1^{(P)} dN_P \end{bmatrix} = 0 \Rightarrow (p-1)$$

~~independent~~ constraints

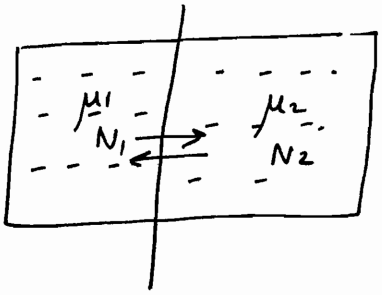
$$F = 2 + (C-1)P - (p-1)c$$

$$= 2 - P + C$$

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

(★) For triple point, $F = 0$ $(2 + 1 - 3 = 0)$

Hence $\underline{\underline{2 + C - p}}$ only !!



Membrane opened and particles allowed to interac

$$N = N_1 + N_2$$

$$dN = dN_1 + dN_2$$

$$\Rightarrow dN_1 = -dN_2$$

$$dG = V\,dP - S\,dT + \mu_1 dN_1 + \mu_2 dN_2$$

at equilibrium

$$(\mu_1 - \mu_2)\,dN_1 = 0$$

← [dynamic Equilibrium, dN_1 will not be zero at any instant. On the avg. dN_1 will be zero.....]

$\Rightarrow \mu_1 = \mu_2$ (i.e. chemical equilibrium)

~~[PTO to EOF] for Transport Phenomenon~~

Transport Phenomenon → Transports are measured per unit area per unit time per gradient.

It is used to describe

Viscosity of Gases : Transport of Momentum (to achieve mechanical eqb.)

Thermal Conductivity of gas : Transport of Heat Energy (to achieve Thermal Eqb.)

Diffusion of Gas : Transport of Mass (to achieve chemical Eqb.)

Heat Flow :

$$\frac{Q}{t} = k\,A\left(\frac{dT}{dz}\right) \Rightarrow \boxed{k = \frac{(Q/t)}{A\cdot\left(\frac{dT}{dz}\right)}}$$

Coefficient of Conductivity

Temperature Gradient

Viscous Flow :

$$\frac{(F/A)}{(dv/dz)} = \boxed{\eta} = \boxed{\frac{(dp/dt)}{A \cdot \left(\frac{dv}{dz}\right)}}$$

η ← Viscosity

$A \cdot \left(\frac{dv}{dz}\right)$ ← velocity gradient

Diffusion

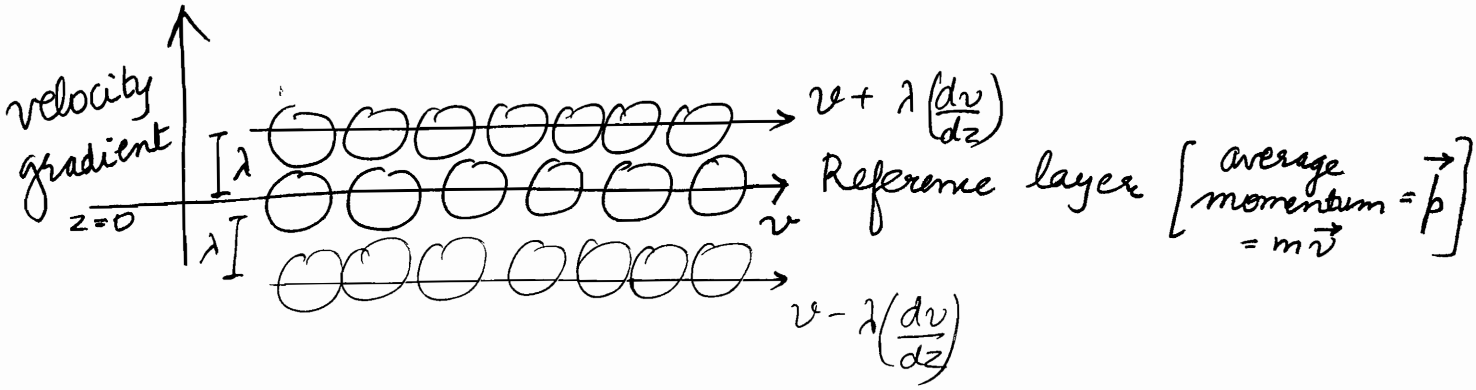
$$D = \frac{\left(\text{No. of Particles crossing per unit area per unit time}\right)}{\text{Concentration gradient}}$$

$$= \frac{(dN/dt)}{A\ (dn/dz)}$$

Viscosity of Gases as transport of Momentum

velocity ←

[note that velocity and velocity gradient are perpendicular]



λ : mean free path

→ There is relative motion between layers,

Δp when single molecule <u>crosses</u> upwards or downwards $= 2\lambda m \left(\frac{dv}{dz}\right)$

$n = \left(\frac{N}{V}\right)$: molecules per unit volume is known.

⑥ No. of molecules per unit area per unit time

$$\frac{N}{A\,dt} = \frac{N}{A\,dx}\left(\frac{dx}{dt}\right) = \frac{N}{V}\cdot\left(\frac{dx}{dt}\right) = n\bar{v}$$

In 1 particular direction, no. of <u>particles crossing per unit area per unit time</u>, $\frac{n\bar{v}}{3}$

No. of particles crossing only upwards $= \frac{n\bar{v}}{6}$

= No. of particles crossing only downwards <u>per unit area</u> <u>per unit time</u>

This is a statistical result that can be proved by calculati the avg. distance d below the reference plane where molecu makes its last collision. It comes out to be $\left(\frac{2\lambda}{3}\right)$. MENTION THIS

<u>Change in Momentum</u>, when a layer Crosses, either Upwards or downwards $= \left(\frac{n\bar{v}}{6}\right) * 2\lambda m\left(\frac{dv}{dz}\right)$

$$= \frac{1}{3} m n \bar{v} \lambda\left(\frac{dv}{dz}\right)$$

$$\Rightarrow \left[\frac{\left(\frac{F}{A}\right)}{\left(\frac{dv}{dz}\right)}\right] = \frac{1}{3} m n \bar{v} \lambda = \eta$$

Tangential Stress per unit

velocity gradient

$$= \frac{1}{3}\rho\bar{v}\lambda$$

$\because \frac{mN}{V} = \rho$

η is dependent only on temperature. However at very high Pressure, λ becom equal to molecular diameter & at very low Pressure, λ becomes comparable to dimensions of apparatus. So, η is f(P) only at very high & very low pressure

$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n}$$

d : diameter of molecule

For ideal gas : $PV = NkT \Rightarrow P = nkT$

$$\Rightarrow \eta = \frac{1}{3} \frac{m \bar{v}}{\sqrt{2} \pi d^2}$$

★ $$\boxed{\bar{v} = \sqrt{\frac{8kT}{m\pi}}}$$

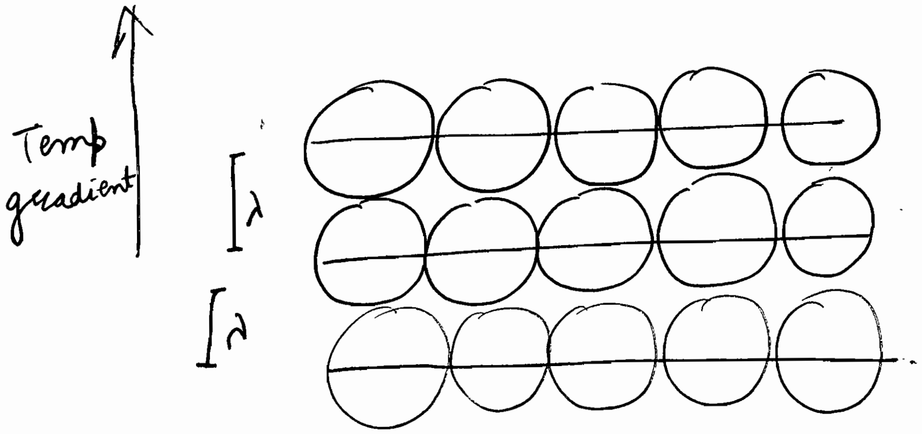
$\bar{v}$: avg velocity

$$\boxed{\begin{array}{l} \text{For gases} : \eta \propto T \\ \text{For liquids} : \eta \propto \frac{1}{T} \end{array}}$$ ← theoretically, not mathematically.

Thermal Conductivity

↑ Heat flow

→ Heat flow and Temp. Gradient are Parallel.



$E + \lambda\left(\frac{dE}{dz}\right)$ $T + \lambda\left(\frac{dT}{dz}\right)$

$E = C_v T$ T

$E - \lambda\left(\frac{dE}{dz}\right)$ $T - \lambda\left(\frac{dT}{dz}\right)$

↑ Writing in this fashion will be better

For 1 molecule crossing : $\Delta Q = 2\lambda\left(\frac{dE}{dz}\right)$

For whole layer : $\frac{1}{6} n \bar{v} * 2\lambda \frac{dE}{dz}$

Net flow of heat from higher Temperature region to lower Temperature region per unit area per unit time $= \frac{1}{3} n \bar{v} \lambda \left(\frac{dE}{dz}\right)$

$$dQ = mC_v\Delta T$$
$$= mC_v 2\lambda\left(\frac{dT}{dz}\right)$$

$$\Rightarrow k = \frac{\left(\frac{dq}{dt}\right)}{A\left(\frac{dT}{dz}\right)} \Rightarrow$$

$$= 2mC_v\lambda\frac{n\bar{v}}{6}$$

$$= \frac{1}{3}mn\bar{v}\lambda C_v$$

$$\boxed{E = mc_v T}$$

$$\left(\frac{dE}{dz}\right) = mc_v\left(\frac{dT}{dz}\right)$$

$$\frac{\left(\frac{dQ}{dt}\right)}{A} = \frac{1}{3}n\bar{v}\lambda m C_v\left(\frac{dT}{dz}\right)$$

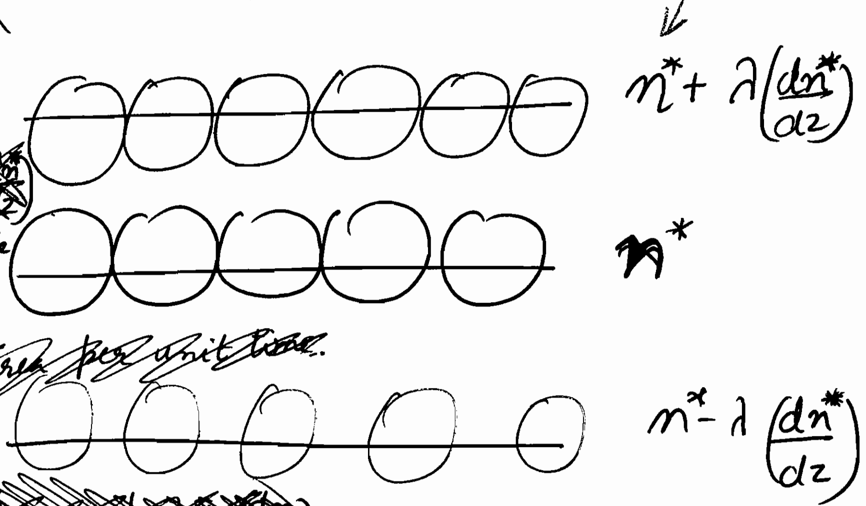
$$\Rightarrow \frac{\left(\frac{dQ}{dt}\right)}{A\left(\frac{dT}{dz}\right)} = \frac{1}{3}mn\bar{v}\lambda C_v = k$$

C_v: heat capacity per unit mass

If give molar heat capacity C
$$c = \left(\frac{C}{M}\right)$$

(*) We get $k = C_v\eta$. However actually $k = \epsilon\eta C_v$ where $1 < \epsilon < 2.5$ due to variation of molecular density with Temperature gradient.

Diffusion



~~Net Flow of molecules = $2\lambda\left(\frac{dn^*}{dz}\right)$ where n is the no. of particle in reference layer travelling in upward direction per unit area per unit time.~~

~~Now $n^* = \frac{n\bar{v}}{6}$~~

~~$\Rightarrow$ Net Flow = $2\lambda\frac{\bar{v}}{6}\left(\frac{dn}{dz}\right) = \frac{1}{3}\lambda\bar{v}\left(\frac{dn}{dz}\right)$~~

No. of particles crossing from higher conc. region to lower conc. region per unit area per unit time $= \frac{n}{6}\bar{v}$

$$\boxed{D} = \frac{1}{3}\bar{v}\lambda = \boxed{\frac{\left(\frac{dN}{dt}\right)}{A\left(\frac{dn}{dz}\right)}}$$

no. of molecules

this 'n' is molecules per unit volume

$$= \left(\frac{\eta}{\rho}\right)$$

PTO

- Frequency of Collision $= \left(\frac{\bar{v}}{\lambda}\right) = \left(\frac{1}{T_{\text{Collision}}}\right)$

- Density $\rho = mn$ $\qquad$ $\underline{m}$: mass of 1 molecule

---

We know numbers of particles crossing per unit area per unit time $= \frac{n\bar{v}}{6}$

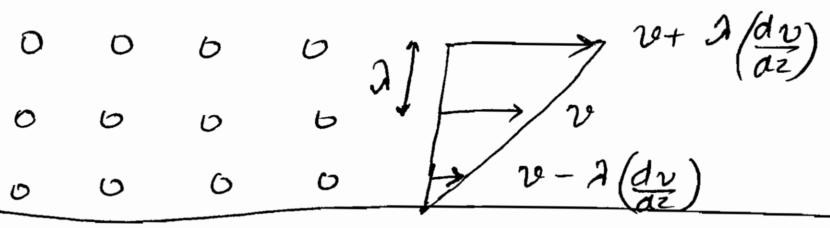
ΔN from upper surface $= \left(n + \frac{dn}{dz}\cdot\lambda\right)\frac{\bar{v}}{6}$

ΔN from lower surface $= \left(n - \frac{dn}{dz}\lambda\right)\frac{\bar{v}}{6}$

$\Rightarrow$ ΔN_{net} per unit area per unit time $= 2\,\frac{dn}{dz}\cdot\lambda\,\frac{\bar{v}}{6}$

$$\Rightarrow \boxed{\left[\frac{\left(\frac{\Delta N}{\Delta t}\right)}{\Delta A\cdot\left(\frac{dn}{dz}\right)}\right] = \frac{1}{3}\bar{v}\lambda = D}$$

Whenever in a gas, stored in a Container, there is concentration gradient, energy gradient etc. some phenomenon, singly or jointly come into play to destroy the cause of non-uniformity This phenomenon is called Transport Phenomenon.



* We take a reference layer with velocity v

- If particles are distinguishable, a specification of the energy state of each particle is said to define a $\boxed{\text{microstate}}$

Thermodynamics (9)

05/01/2012

STATISTICAL THERMODYNAMICS.

Thermodynamic state is described by thermodynamic variable. These variables are measured at equilibrium. To measure, one way is thermometry or calorimetry. 2^{nd} way is kinetic Theory : to track down motion of every particle. 3^{rd} way is statistical Physics.

~~Statistics~~

"Statistic" implies Probability distribution. (NOT STATISTICS)

- Thermodynamic Probability = 'Ω' = No. of accessible Microstates to a macrostate.

This is definition of Thermodynamic Probability. Do not confuse it with $0<p<1$ .... Probability of a Microstate may be $\left(\frac{1}{\Omega}\right)$

- Entropy $S = k \ln\Omega$ (bridge between statistics & Thermo)

Equilibrium ⇒ Maximum Ω ⇒ Maximum S

S : additive Ω : ~~Rso~~ Multiplication

$S = S_1 + S_2$ $\Omega = \Omega_1 \Omega_2$

⇒ we chose $S \propto \ln\Omega$

$$\Rightarrow \boxed{S = k\ln\Omega} \quad k : \text{Boltzmann Const.}$$

- Whether the particles are distinguishable or non distinguishable, a specification of the number of particles n_i in each energy level is said to define a macrostate of the assembly.

←

In thermodynamics, we encounter two types of distributions:

Statistical Distribution

Classical Statistics

(1860 - 1900)

eg. Maxwell - Boltzmann Statistics (1875)

↓ Energy

Energy emitted or absorbed is continuous.

↓ Nature of Particle

Valid for distinguishable particle.

↓ Spin

(Concept of Spin came in 1925)

Hence, spin is not the criteria.

↓ No. of Particles per cell

NO Restriction

Quantum Statistics (1926 - 30)

eg ① Bose - Einstein (1926)

② Fermi - Dirac (1928)

↓ Energy

Energy is quantized taking discrete values

↓ Nature of Particles

Valid for Indistinguishable particle.

↓ Spin

Here, spin is a criteria

Full Integral Spin :- Bose Einstein

Half Integral Spin :- Fermi Dirac

↓ No. of Particles per Cell

→ No restriction for Bose Einstein

→ Restrictions imposed on Fermi Dirac via Pauli's Exclusion Principle.

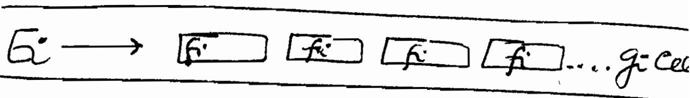
(*) Here cell means an energy level. n particles in a cell means n-fold energy level degeneracy. But there can be g cells for energy level E → $\boxed{gn}$ level of degeneracy....

Occupation Index or No. of Particles per Cell of Energy E_i at equilibrium Temp

or [Probability distribution function at Equilibrium temperature 'T']

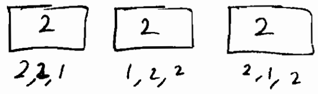
$n_{(E_i)}$: no. of particles ~~[redacted]~~ with energy level E_i

$g_{(E_i)}$: no of cells with energy level E_i



$$\boxed{\left(\frac{n_{E_i}}{g_{E_i}}\right) = \left(\frac{n_i}{g_i}\right) = f(\epsilon_i)}$$: OCCUPATION INDEX

eg. 9Δ :



$g_{9\Delta} = 3$ $f_{9\Delta} = 2$ $n_{9\Delta} = 6$

In Maxwell Boltzmann,

$$f(\epsilon_i) = A\, e^{-\beta \epsilon_i}$$

$$\boxed{\beta = \frac{1}{kT}}$$

$$\boxed{f(\epsilon_i) = e^{-(\alpha + \beta \epsilon_i)}}$$

where $\boxed{e^{-\alpha} = A}$

$$\Rightarrow \boxed{n_i = A g_i\, e^{-\left(\frac{\epsilon_i}{kT}\right)}}$$

In Bose-Einstein,

$$\boxed{f(\epsilon_i) = \frac{1}{e^{(\alpha+\beta\epsilon_i)} - 1}}$$

$$\beta = \frac{1}{kT} \qquad \alpha = -\left(\frac{\mu}{kT}\right)$$

(μ : chemical Potential) of BOSONS (integral spin)

For Photons : $\mu_{photon} = 0$

In Fermi Dirac,

$$\boxed{f(\epsilon_i) = \frac{1}{e^{(\alpha+\beta\epsilon_i)} + 1}}$$

$$\beta = \frac{1}{kT} \qquad \alpha = \left(\frac{\epsilon_f}{kT}\right)$$

(ϵ_f : fermi energy of FERMIONS) (half integral spin

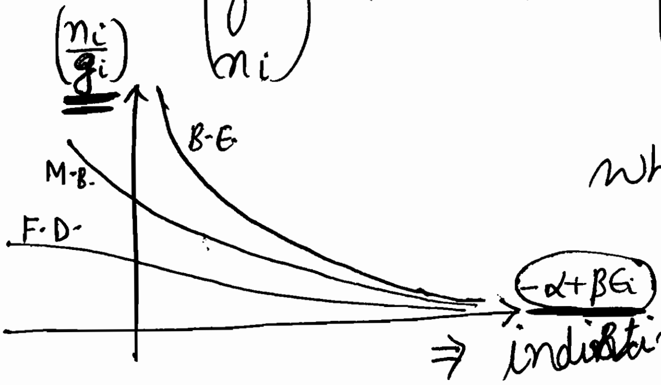
⊙ Power of 'e' or Exponent is always a pure number.

	MB	BE	FD
$\left(\frac{g_i}{n_i}\right)$	$\left(e^{\alpha+\beta\epsilon_i}\right)$	$\left(e^{\alpha+\beta\epsilon_i}-1\right)$	$\left(e^{\alpha+\beta\epsilon_i}+1\right)$
$e^{\alpha+\beta\epsilon_i}$	$\left(\frac{g_i}{n_i}\right)$	$\left(\frac{g_i}{n_i}\right)+1$	$\left(\frac{g_i}{n_i}\right)-1$

✓ → If $\left(\frac{g_i}{n_i}\right) = e^{(\alpha+\beta\epsilon_i)}$ is large, both Bose Einstein and Fermi Dirac will approach to Statistical Thermodynamics i.e. indistinguishable particles have become distinguishable, when no. of cells are much more than the particles that have to be placed in the cells. [Concept of unique roll number]

$$\left(\frac{g_i}{n_i}\right)-1 \longrightarrow \left(\frac{g_i}{n_i}\right) \longleftarrow \left(\frac{g_i}{n_i}\right)+1$$

when $\left(\frac{g_i}{n_i}\right)$ is large.



⇒ indistinguishable becomes distinguishable

✓ → Hence, Quantum Statistics are required when $\left(\frac{g_i}{n_i}\right)$ is small. It happens when Temperatures are small. In Ordinary temperatures, $\left(\frac{g_i}{n_i}\right)$ is large, hence classical statistics is sufficient.

⇒ Basic criteria for distinguishability : $\left(\frac{g_i}{n_i}\right)$ ← seats or cells ← students or particles

⇒ If $g_i > n_i$ ⇒ assign unique cell to each particle

⇒ distinguishable

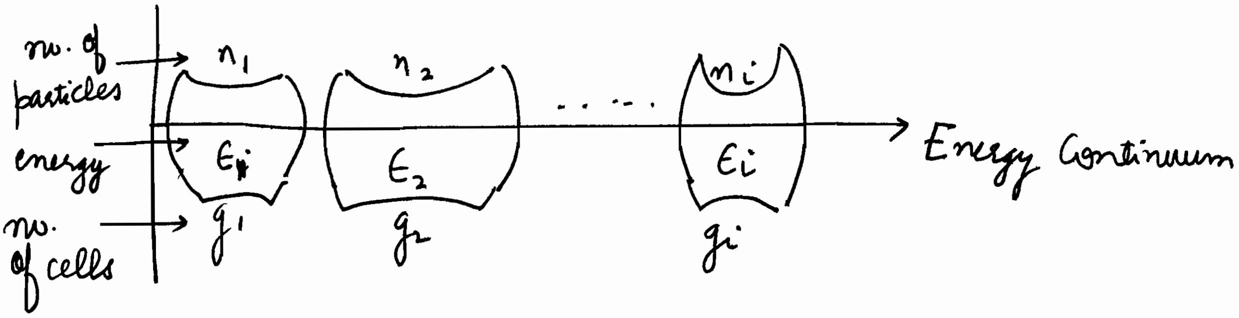
g_i : No. of cells with energy ϵ_i

- 0 Temp ⇒ No motion
- 0 is unattainable ⇒ Particles are always in motion

① $\sum n_i = N = \text{const.}$ (Total no. of particles)

② $\sum \epsilon_i n_i = E = \text{const.}$

} at equilibrium Temperature 'T'



$$\Omega(N, V, E) = ??$$

We have, 4 Assumptions :-

① $\sum n_i = N \Rightarrow \sum dn_i = 0$

② $\sum \epsilon_i n_i = E \Rightarrow \sum \epsilon_i dn_i = 0$

③ Entropy is maximum $\Rightarrow dS = 0$

$\Rightarrow d(\ln \Omega) = 0$

} at Equilibrium

④ Assumption of apriori equal probability

④ Assumption of Apriori Probability :

Before occupancy, all cells are equiprobable to be occupied.

- Macro State : 1 particular value of $\{n_1, n_2, \dots n_i\}$

eg $\{4, 10, 5\}$ is 1 macrostate

$\{10, 4, 5\}$ is other macrostate.

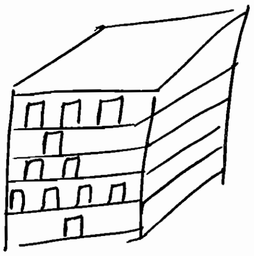
(बस number ही specify किया है, पहले में 4 ... कौन से चार, यह नहीं बताया, It won't matter in indistinguishable Particles but imp in distinguishables)

- Micro States : within 1 macro state, there can be multiple micro states depending upon filling of n_i in g_i (all g_i's are distinguishable)

$$\begin{bmatrix} \epsilon_1 \\ n_1 \\ g_1 \end{bmatrix} \begin{bmatrix} \epsilon_2 \\ n_2 \\ g_2 \end{bmatrix} \cdots \begin{bmatrix} \epsilon_i \\ n_i \\ g_i \end{bmatrix}$$

$N_5 = 2$
$N_4 = 1$
$N_3 = 1$
$N_2 = 2$
$N_1 = 1$

$g_5 = 3$
$g_4 = 1$
$g_3 = 2$
$g_2 = 4$
$g_1 = 1$



$$\Omega = \prod_i \overbrace{(n_i, g_i)}^{\text{ways of filling } n_i \text{ into } g_i}$$

For 1 particles,
We will measure

$$\left.\begin{matrix} x & \text{and} & p_x \\ y & \text{and} & p_y \\ z & \text{and} & p_z \\ \vdots & & \vdots \end{matrix}\right\} 1 \times 3 \times 2 = 6$$

$$\epsilon_x = \frac{p_x^2}{2m} = \frac{1}{2} m v_x^2$$

$$\epsilon_y = \frac{p_y^2}{2m} = \frac{1}{2} m v_y^2$$

$$\epsilon_z = \frac{p_z^2}{2m} = \frac{1}{2} m v_z^2$$

In general,
$1 \times f \times 2$

Phase Space

- derivation of $n(E)\,d(E)$

⊙ To specify dynamical configuration of any assembly of particles, we need 6 coordinates viz x, y, z, p_x, p_y, p_z

Cannonical Conjugate Variable : Measurement of 1 affects othe

$\Delta x\, \Delta p_x$ depends on Heisenberg Principle.

- say f : degrees of freedom $= 3$

$\Rightarrow$ Dimension of Phase Space $= 3 \times 2 = 6$ [general $2f$ dimensions of phase space]

$\boxed{\text{Volume Element in Phase Space : Cell}}$

$$\Delta x\, \Delta y\, \Delta z\, \Delta p_x\, \Delta p_y\, \Delta p_z$$

If continuous, $dx\, dy\, dz\, dp_x\, dp_y\, dp_z = \underline{d^3 r\, d^3 p}$: Cell

Cells represents mathematical space between

x and $(x+dx)$
y and $(y+dy)$
z and $(z+dz)$
p_x and (p_x+dp_x)
p_y and (p_y+dp_y)
p_z and (p_z+dp_z)

⊛ the smallest volume element

$= \Delta x\, \Delta y\, \Delta z\, \Delta p_x\, \Delta p_y\, \Delta p_z$

$= \Delta x\, \Delta p_x\;\; \Delta y\, \Delta p_y\;\; \Delta z\, \Delta p_z$

since $\Delta x\, \Delta p_x \approx h$

$= h^3$

⊙ In general, volume element in phase space,

$$(dx\, dy\, dz \ldots dq_f)\,(dp_x\, dp_y\, dp_z \ldots dp_f)$$

If $dx\, dp_x \approx h$ $\Rightarrow$ $\boxed{\text{Volume Element} = h^f}$

✓ In classical statistics, h can be any small const. It can be as small as possible ⇒ no. restriction on no. of cells ⇒ distinguishable.

✓ In quantum statistics, h is planck's const. ⇒ Restricted number of cells. ⇒ indistinguishable particles if more particles.

For 3-dimensional space,

No. of cells with energy E_i $\left[= \frac{p_x^2+p_y^2+p_z^2}{2m}\right]$

$$= g(E_i) = \frac{\text{Volume in phase space with energy } E_i}{\text{Volume of 1 cell}}$$

$$= \frac{\int_{\text{Phase Space}} d^3x\, d^3p}{h^3} = \frac{V}{h^3}\iiint dp_x\, dp_y\, dp_z$$

$$\boxed{\text{No. of cells with momenta b/w } p \text{ \& } (p+dp) = g(p)\,dp = g(p)\,dp : \text{Representation Only !!}}$$

We know, a sphere:

$$\left[\begin{aligned} p_x^2+p_y^2+p_z^2 &= p^2 \\ (p_x+dp_x)^2+(p_y+dp_y)^2+(p_z+dp_z)^2 &= (p+dp)^2 \end{aligned}\right]$$

$$\underbrace{dp_x\, dp_y\, dp_z}_{} = \underbrace{\frac{4\pi}{3}\left[(p+dp)^3-p^3\right]}_{} = 4\pi p^2\, dp$$

Both represent space b/w (p_x, p_x+dp_x), (p_y, p_y+dp_y), (p_z, p_z+dp_z)

$$g(p)\,dp = \int d^3x \; d^3p$$

$$\boxed{g(p)\,dp = \frac{V}{h^3} \cdot 4\pi p^2 \, dp} \quad ⊛$$

~~Upon integration~~

~~$g(p) = \frac{V}{h^3} 4\pi \frac{p^3}{3}$~~

Similarly,

$g(v)\,dv$: no. of cells with velocity between ~~with~~ v and $(v+dv)$

$g(\epsilon)\,d\epsilon$: no. of cells with energy between ϵ and $(\epsilon + d\epsilon)$

$$\boxed{\epsilon = \frac{p^2}{2m}}$$

$$\Rightarrow \boxed{p = \sqrt{2m}\sqrt{\epsilon}}$$

& $\boxed{dp = \sqrt{2m}\,\frac{1}{2}\,\epsilon^{-1/2}\,d\epsilon}$ [for non-relativistic energy]

we have, $g(\epsilon)\,d\epsilon = \frac{V}{h^3} \cdot 4\pi \, \cancel{2m}\epsilon \, \sqrt{2}\,m \, \frac{1}{\cancel{2}} \, \epsilon^{-1/2} \, d\epsilon$

$$\Rightarrow \boxed{g(\epsilon)\,d\epsilon = \frac{2\pi V}{h^3} \cdot (2m)^{3/2} \, \epsilon^{1/2} \, d\epsilon} \quad ⊛$$

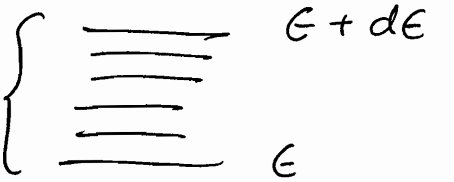
$$\Rightarrow \boxed{g(\epsilon)\,d\epsilon = C\sqrt{\epsilon}\;d\epsilon}$$

Density of State

No of cells/states

$\rightarrow$ $n(\epsilon)$ $= \int g(\epsilon)\, d\epsilon$

$d n(\epsilon)$



$$\rightarrow \boxed{g(\epsilon) = \left(\frac{d n(\epsilon)}{d\epsilon}\right)}$$

Note that density of state has no relation with number of particles. ⊛

We know

$$\boxed{g(p)\, dp = \frac{V}{h^3}\, 4\pi p^2\, dp}$$

In relativistic case, $\epsilon = \sqrt{p^2c^2 + m_0^2c^4}$

$$\epsilon^2 - m_0^2c^4 = p^2c^2$$

$$p^2 = \frac{\epsilon^2}{c^2} - m_0^2c^2$$

Photon For $m_0 = 0$, $p^2 = \frac{\epsilon^2}{c^2} \Rightarrow p = \frac{\epsilon}{c} \Rightarrow dp = \frac{d\epsilon}{c}$

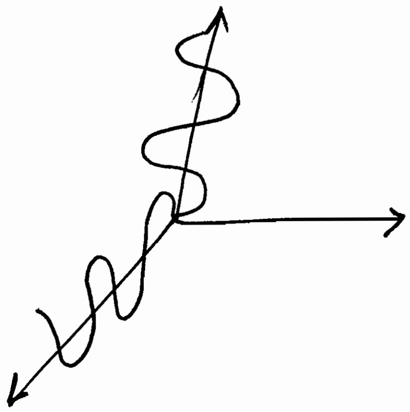
$$g(\epsilon)\, d\epsilon = \frac{V}{h^3} \cdot 4\pi \cdot \frac{\epsilon^2}{c^3}\, d\epsilon = \frac{4\pi V\, \epsilon^2 d\epsilon}{c^3h^3}$$

$$g(\nu)\, d\nu = \frac{V}{h^3} \cdot 4\pi \cdot \frac{h^2\nu^2}{c^2}\, \frac{h}{c}\, d\nu \qquad p = \frac{h\nu}{c}$$

$$\boxed{g(\nu)\, d\nu = \frac{4\pi V \nu^2}{c^3}\, d\nu}$$

Taking into account the polarization,

$$g(\nu)\, d\nu = \frac{8\pi V \nu^2 d\nu}{c^3}$$



Thermodynamics (10)

Conjuction !! [कंजंकसस्थ न]

⊙ Ω (N, V, E) : Ensemble

(Plural of Assembly i.e. Assembly of Assemblies)

⊙ ① $\sum n_i = N$ ② $\sum \epsilon_i n_i = E$ ③ $\sum d(\ln \Omega) = 0$

$\sum dn_i = 0$ $\sum \epsilon_i \, dn_i = 0$

④ Apriori Probability equal.

⊙ $$\underbrace{g(\epsilon_i)\, d\epsilon_i}_{} = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} \, d\epsilon$$

No. of cells b/w energy ϵ_i and $(\epsilon_i + d\epsilon_i)$

$$\int_0^{\epsilon} \boxed{g(\epsilon)}\, d\epsilon = \underline{n(\epsilon)}$$ ⇐ energy cells upto energy ϵ_i

[redacted]

$g(\epsilon)$ → no. of cells / density of state / Degree of degeneracy.

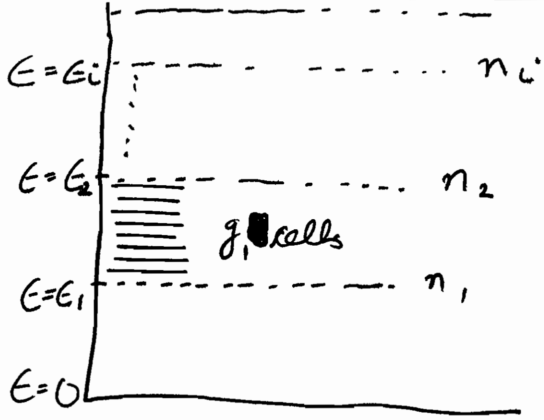
⊙ $$g(p)\, dp = \frac{d^3x \, d^3p}{h^3} = \frac{V}{h^3} d^3p = \frac{V}{h^3} 4\pi p^2 dp$$

⊙ Ω : Thermodynamic Probability

= No. of accessible microstates to a macrostate

⊙ From $\epsilon = \epsilon_1$ upto $\epsilon = \epsilon_2$,

✶ the cells are of energy ϵ_1 and are called g_1



* Problem is to put

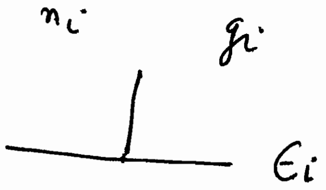
(n_1 particles in g_1 cells) &
(n_2 particles in g_2 cells) &
(n_3 particles in g_3 cells)....

$$= \prod_i \underbrace{(n_i, g_i)}_{\text{To put } n_i \text{ particles in } g_i \text{ cells}}$$

Example

$n_i = 2$
$g_i = 2$

eg.

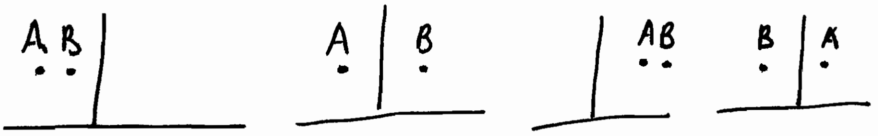


① decide distinguishable/ indistinguishable $n_i=2$ $g_i=2$

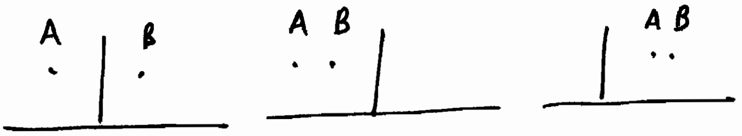
A B

② decide whether there is any restriction

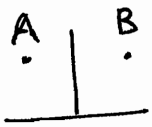
no restriction



Case 1 : distinguishable & no restriction : MB



Case 2 : indistinguishable & no restriction : BE



Case 3 : indistinguishable & restriction : F.D.

$(n_1, n_2, \dots n_i)$

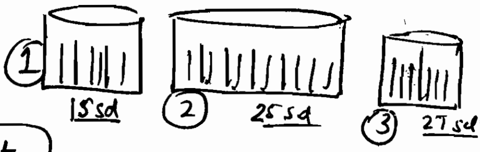
Macrostate
$\updownarrow$
Configuration

Maxwell Boltzmann

Macrostate = (3, 5, 2)

N=10 Balls of different colours.
Its a 2 step Problem......
i = 3 Tin को डिब्बे हैं of different numbers.

हर डिब्बे में subdivision हैं $n_1 = 15$
$n_2 = 25$
$n_3 = 27$



Probability of this Macrostate

$$= {}^{N}C_{n_1} \; {}^{N-n_1}C_{n_2} \; {}^{N-n_1-n_2}C_{n_3} \dots\dots$$

$$= \frac{\lfloor N}{\lfloor n_1 \, \cancel{\lfloor N-n_1}} \; \frac{\cancel{\lfloor N-n_1}}{\lfloor n_2 \, \cancel{\lfloor N-n_1-n_2}} \; \frac{\cancel{\lfloor N-n_1-n_2}}{\lfloor N_3 \, \lfloor N-n_1-n_2-n_3}$$

$$= \frac{\lfloor N}{\lfloor n_1 \, \lfloor n_2 \, \lfloor n_3 \dots \lfloor n_i}$$

No. of ways of Putting n_i balls in i^{th} box

$$= \frac{\lfloor 10}{\lfloor 3 \, \lfloor 5 \, \lfloor 2} = \underline{\underline{2520}}$$

Probability of Microstates to this Macrostate

$$= (g_1)^{n_1} \, (g_2)^{n_2} \dots\dots$$

$\leftarrow$ Now dividing the balls in each division = $(15)^3 (25)^5 (27)^2$

Hence,

$$\boxed{\Omega = \lfloor N_i \prod_i \frac{\text{[illegible]}}{\lfloor n_i} (g_i)^{n_i}}$$

★ Hence total no. of ways = Ω
$= 2520 \, (15)^3 (25)^5 (27)^2$
= Total no. of MICROSTATES TO MACROSTATE (3, 5, 2)

$$\ln \Omega = \sum_i \ln \lfloor N - \ln \lfloor n_i + n_i \ln g_i$$

$\uparrow$
Characteristic

$$d(\ln \Omega) = \sum_i d(\ln \lfloor N) - d(\ln \lfloor n_i) + \ln(g_i) \, dn_i$$

$$\boxed{\ln \lfloor n \approx n \ln n - n}$$

Stirling's Approximation for large n

$$\Rightarrow \boxed{d(\ln \lfloor n) \approx (n(1/n) + \ln n - 1)\, dn \approx \cancel{\ln(n)\, dn}}$$

$$\Rightarrow d(\ln \Omega) = \sum_i -\ln(n_i)\, dn_i + \ln g_i \, dn_i$$

$$\boxed{d(\ln\Omega) = \sum_i \ln\left(\frac{g_i}{n_i}\right) dn_i}$$

We know

$$\sum dn_i = 0$$

Let $\alpha \sum dn_i = 0$ — ①

α, β: Langrange multipliers

$$\sum \epsilon_i \, dn_i = 0$$

Let $\beta \sum \epsilon_i dn_i = 0$ — ②

$$\sum \ln\left(\frac{g_i}{n_i}\right) dn_i = 0 \quad \text{— ③}$$

(at equilibrium)
$S = \max$
$dS = 0$ i.e. $d(k\ln(\Omega)) = 0$
$\Rightarrow d(\ln\Omega) = 0$

① + ③ − ②

$$\sum_i \left(\ln\left(\frac{g_i}{n_i}\right) + \alpha - \beta\epsilon_i\right) dn_i = 0$$

If it holds for ∀ i

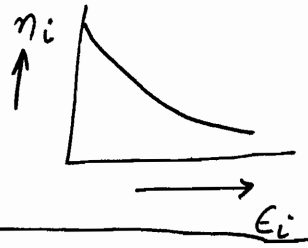
$$\Rightarrow \ln\left(\frac{g_i}{n_i}\right) + \alpha - \beta\epsilon_i = 0$$

$$\ln\left(\frac{g_i}{n_i}\right) = -(\alpha - \beta\epsilon_i)$$

$$\frac{g_i}{n_i} = e^{-(\alpha-\beta\epsilon_i)}$$

$$\boxed{\frac{n_i}{g_i} = e^{\alpha-\beta\epsilon_i}}$$

$$\Rightarrow \frac{n_i}{g_i} = A e^{-(\epsilon_i/kT)}$$



$$n_i = g_i \, e^{\alpha - \beta\epsilon_i} = A g_i \, e^{-\beta\epsilon_i} \text{ where } A = e^{\alpha}$$

$$\boxed{\sum' n_i = N = A \sum g_i \, e^{-\beta\epsilon_i}}$$

This equation is always used to find out random constants ....

$$\Rightarrow \boxed{A = \frac{N}{\sum g_i \, e^{-\beta\epsilon_i}}} \rightarrow Z = \sum g_i \, e^{-\beta\epsilon_i}$$

[Partition Function]

$$\Rightarrow \boxed{n_i = \frac{N}{Z} g_i \, e^{-\beta\epsilon_i}}$$

$P(\epsilon_i)$: Probability of occupancy of energy level ϵ_i at equilibrium temp T

$$\Rightarrow \boxed{P(\epsilon_i) = \frac{n_i}{N} = \frac{g_i \, e^{-\beta\epsilon_i}}{\sum_i g_i \, e^{-\beta\epsilon_i}}}$$

"i" represents an energy level. It is summation over all energy levels.

To determine β

$$S = k \ln\Omega$$

$$dS = k \, d(\ln\Omega)$$

$$TdS = kT \, d(\ln\Omega)$$

$$dE = TdS = \boxed{\sum' \epsilon_i \, dn_i = kT \, d(\ln\Omega)}$$

$$\Rightarrow \sum_i \epsilon_i \, dn_i = kT \sum_i -(\alpha - \beta\epsilon_i) \, dn_i$$

$$= -kT \sum_i (\alpha - \beta\epsilon_i) \, dn_i$$

$$\Rightarrow \sum \epsilon_i \, dn_i = \cancel{-\alpha kT \sum dn_i} + kT\beta \sum \epsilon_i \, dn_i$$

⊛ यह भी ठीक है !! $\sum \epsilon_i dn_i = 0$ when total energy is assumed as constant. Here, a little perterburbation considered to find dS

$$\Rightarrow \beta kT = 1$$

$$\Rightarrow \boxed{\beta = \frac{1}{kT}}$$

→ Proof of $\beta = \frac{1}{kT}$ is huge [4 Pages]

So simply write $\beta = \left(\frac{1}{kT}\right)$

Refer B.J. Mc Clelland Statistical Thermodyna..

Hence for Maxwell Boltzmann

$$\left(\frac{n_i}{g_i}\right) = A \, e^{-\beta\epsilon_i} \quad \text{where} \quad \boxed{A = \frac{N}{\sum g_i e^{-\beta\epsilon_i}}} \quad \boxed{\beta = \frac{1}{kT}}$$

$$P(\epsilon_i) = \frac{n_i}{N} = \left(\frac{g_i \, e^{-\beta\epsilon_i}}{\sum g_i \, e^{-\beta\epsilon_i}}\right)$$

Note that β is Const. at equilibrium

Z : Partition Function

Plays same role in Statistical Physics as Wave Function does in Quantum Physics.

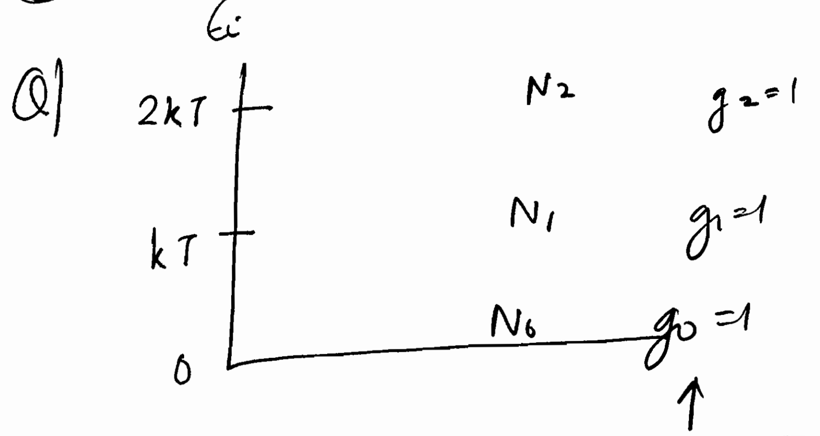
We know,

$$\langle x \rangle = \frac{\sum x\,(P(x))}{\sum P(x)}$$

[expectation value]

$$= \frac{\int_{-\infty}^{\infty} x\, p(x)\, dx}{\int_{\infty}^{\infty} p(x)\, dx}$$

Q)



100 particles to be filled

Not specified
⇒ assuming 1 cell per energy level

$n_0 = A.1.\,e^{0} = A$

$n_1 = A.e^{-1}$

$n_2 = A\,e^{-2}$

$\Rightarrow N = A[1 + e^{-1} + e^{-2}]$ $\Rightarrow$ $A = \left[\frac{N}{1 + e^{-1} + e^{-2}}\right]$

$$A = \frac{100}{1+0\cdot37+0\cdot09} = \frac{100}{1\cdot38} = 72$$

$$\Rightarrow n_0 = 72$$

$$n_1 = 26$$

$$n_2 = 2$$

$$P(\epsilon_i) = \frac{n_i}{N} = \begin{matrix} 0\cdot72 & \text{for } \epsilon_0 \\ 0\cdot26 & \text{for } \epsilon_1 \\ 0\cdot02 & \text{for } \epsilon_2 \end{matrix}$$

$$E = \sum \epsilon_i N_i = 0 \times 72 + kT \times 26 + 2kT \times 2$$

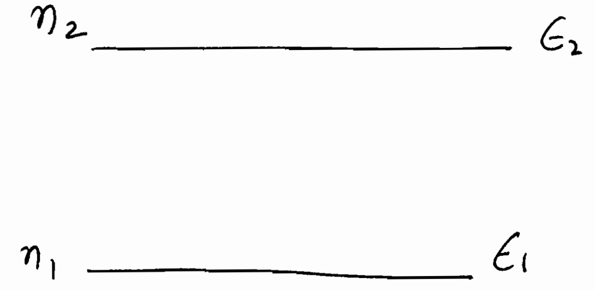
$$= 30kT$$

$$\langle E \rangle = \frac{\sum \epsilon_i P(\epsilon_i)}{\sum P(\epsilon_i)} = \sum \epsilon_i P(\epsilon_i) = \sum \frac{n_i}{N} \epsilon_i$$

$$= \frac{1}{N} \sum n_i \epsilon_i$$

$$= \left(\frac{E}{N}\right)$$

$$= \underline{0\cdot3 kT}$$



We know,

$$\boxed{n_1 = A g_i e^{-\beta \epsilon_1}}$$ ✪

this is what we always do.... remember Planck's derivation $u(\nu)\,d\nu$

$N_0 = N_0$
$N_1 = N_0 e^{-\frac{\Delta E}{kT}}$
$N_2 = N_0 e^{-\frac{2\Delta E}{kT}}$
$\vdots$

If not specified, take $g_i = 1$ ✪

Or take g_i = const. & same for all states. This way g_i will be absorbed in the const. A.

$$n_1 = A e^{-\beta \epsilon_1}$$

$$n_2 = A e^{-\beta \epsilon_2}$$

$$n_2 = \frac{n_1}{e^{-\beta \epsilon_1}} e^{-\beta \epsilon_2} = n_1 e^{-\beta(\epsilon_2 - \epsilon_1)} = n_1 e^{-\left(\frac{\Delta E}{kT}\right)}$$

$$\boxed{n_2 = n_1 e^{-\left(\frac{\Delta E}{kT}\right)}}$$ [at equilibrium]

Population Inversion : $n_2 > n_1$ $\Delta E > 0$

$\Rightarrow T < 0$

Concept of Negative Temperature

<refer end of notes>

Population Inversion is a very short duration phenomenon.

* By applying magnetic properties, population inversion can be achieved for a longer period of time !!

No. of particle within energy level b/w ϵ_i and $\epsilon_i + d\epsilon_i$

$= n(\epsilon)\, d\epsilon$ ⟸ Notation for dn

$= dn$

$= \underbrace{A e^{-\epsilon/kT}}_{f(\epsilon_i)} \quad \underbrace{g(\epsilon)\, d\epsilon}_{\circ}$ ⟸ Notation for no. of cells with energy b/w ϵ_i and $(\epsilon_i + d\epsilon_i)$

$= A e^{-\epsilon/kT} \cdot \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}\, d\epsilon$

$$\boxed{dn = \underbrace{B\, \epsilon^{(1/2)}\, e^{-\left(\frac{\epsilon}{kT}\right)}\, d\epsilon}}$$

This is ~~notation~~ formula of no. of particles between energy level ϵ and $(\epsilon + d\epsilon)$

$$\int_0^\infty dn = B \int_0^\infty \epsilon^{\frac{1}{2}} e^{-\frac{\epsilon}{kT}}\, d\epsilon$$

$$\Rightarrow N = B \int_0^\infty \epsilon^{1/2} e^{-\frac{\epsilon}{kT}}\, d\epsilon$$

$$n_i = A g_i e^{-\beta\epsilon_i}$$

$$\cancel{g(\epsilon_i) = \frac{2\pi V}{h^3} (2m)^{3/2} \frac{\epsilon_i^{3/2}}{(3/2)} = \frac{4\pi V}{3h^3} (2m)^{3/2} (\epsilon_i)^{3/2}}$$

$$n(p) = A\, g(p)\, e^{-\left(\frac{p^2}{2mkT}\right)} \qquad n(p)\,dp = A\, g(p)\,dp\, e^{-\frac{p^2}{2mkT}}$$

$$g(p)\,dp = \frac{V}{h^3}\,4\pi p^2\,dp$$

Similarly,

$$n(v)\,dv = A\frac{V}{h^3}\,4\pi m^3 v^2\,dv\;e^{-\left(\frac{mv^2}{2kT}\right)}$$

$$n(v)\,dv = B\,v^2 e^{-\left(\frac{mv^2}{2kT}\right)}\,dv$$

Maxwell Boltzmann Speed distribution

⊙ Note that we cannot leave it in terms of h and V; we have find the const B in terms of N.

⊙ $\int_0^\infty e^{-x} x^{n-1}\,dx = \Gamma n$ (gamma n)

$n > 1$

⊙ $\underset{\uparrow\ \text{Gamma}}{\Gamma n+1} = n\Gamma n = \underset{\uparrow\ \text{factorial}}{\lfloor n}$

⊙ $\Gamma\frac{1}{2} = \sqrt{\pi}$

$\Gamma\frac{5}{2} = \frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi}$

⊙ $$\int_0^\infty e^{-\alpha x^2} x^n\,dx = \frac{1}{2(\alpha)^{\frac{n+1}{2}}}\,\Gamma\frac{n+1}{2}$$

⊙ $$\int_0^\infty e^{-\alpha x^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$\Rightarrow \int_0^\infty n(v)\, dv = B \int v^2 e^{-\left(\frac{mv^2}{2kT}\right)} dv$$

$$N = B \frac{1}{2\left(\frac{m}{2kT}\right)^{3/2}} \cdot \Gamma\left(3/2\right) = \frac{B}{4}\left(\frac{\sqrt{\pi}}{\left(\frac{m}{2kT}\right)^{3/2}}\right)$$

$$N = \frac{B\sqrt{\pi}}{4}\left(\frac{2kT}{m}\right)^{3/2}$$

$$\Rightarrow \boxed{B = \left(\frac{2kT}{m}\right)^{-3/2} \frac{4N}{\sqrt{\pi}}}$$

GAMMA FUNC.

⊙ $\Gamma(\mu) = (\mu-1)! = \int_0^\infty x^{\mu-1} e^{-x}\, dx \quad : \quad \underset{\sim\sim}{\mu > 0}$

⊙ $\Gamma(\mu+1) = \mu\, \Gamma(\mu)$ $\qquad \int_{-\infty}^{\infty} e^{-\alpha x^2 \pm \beta x} dx = \sqrt{\frac{\pi}{\alpha}}\, e^{\left(\frac{\beta^2}{4\alpha}\right)}$

⊙ The argument of Γ : μ can be a rational no. and thereby $\Gamma(\mu+1) = \mu(\mu-1)(\mu-2)\ldots(1+p)\,p\,\Gamma(p)$ where $0 < p \leq 1$. For integer $\mu = n$, $\Gamma(n) = \underline{\lfloor n-1}$

⊙ $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

⊙ $I_\mu = \int_0^\infty x^\mu e^{-\alpha x^2} dx = \frac{1}{2} \frac{1}{\alpha^{\frac{(\mu+1)}{2}}} \Gamma\left(\frac{\mu+1}{2}\right)$

$\underset{\sim\sim}{\mu > -1}$

$$I_0 = \int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2\sqrt{\alpha}}\sqrt{\pi} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$I_1 = \int_0^\infty x e^{-\alpha x^2} dx = \frac{1}{2\alpha}(1) = \left(\frac{1}{2\alpha}\right)$$

⊛ $\underline{\lfloor 0} = 1$

$$I_2 = \int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{1}{2}\frac{1}{\alpha^{(3/2)}} \cdot \frac{1}{2} \cdot \sqrt{\pi} = \frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{\frac{1}{2}}$$

THERMODYNAMICS (II)

$$f(\epsilon_i) = \left(\frac{n_i}{g_i}\right) = A e^{-\beta \epsilon_i}$$: not valid at extremely low temperature !!

Maxwell Boltzmann Speed Dist^n Formula

Energy distribution

$$n(\epsilon) = g(\epsilon)\; f(\epsilon) = A\, g(\epsilon)\, e^{-\epsilon/kT}$$

$n(\epsilon)\, d\epsilon$ = [redacted] no. of particles [redacted] with energy between ϵ and $(\epsilon + d\epsilon)$ at equilibrium temperature T.

$$= A\, e^{-\epsilon/kT}\, \frac{2\pi V}{h^3} (2m)^{3/2}\, \epsilon^{1/2}\, d\epsilon$$

$$= B\, \epsilon^{1/2}\, e^{-\epsilon/kT}\, d\epsilon$$

$$N = B \int_0^\infty \epsilon^{1/2}\, e^{-\epsilon/kT}\, d\epsilon$$

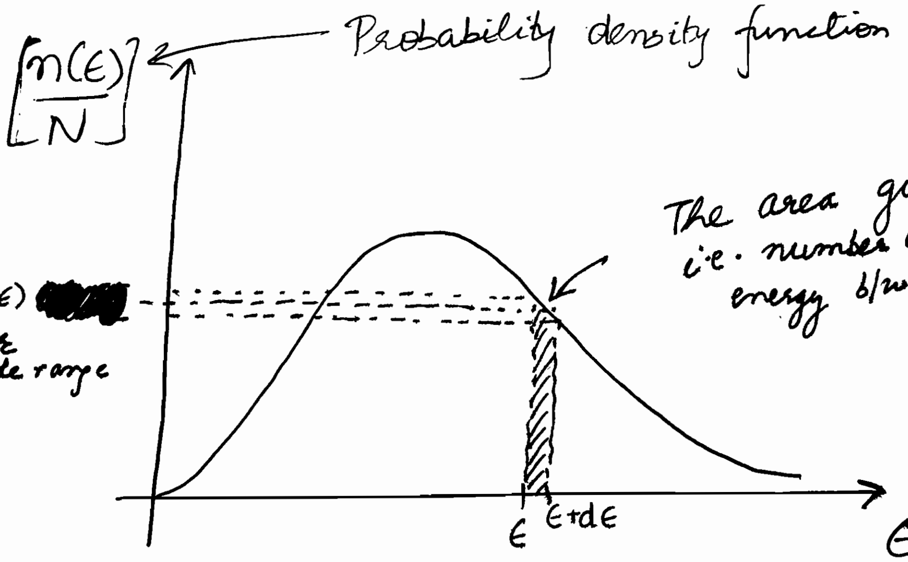
Put $\frac{\epsilon}{kT} = x \Rightarrow d\epsilon = kT\, dx$

$$\Rightarrow N = B (kT)^{3/2} \int_0^\infty x^{1/2}\, e^{-x}\, dx = B(kT)^{3/2}\, \Gamma\left(\tfrac{3}{2}\right)$$

$$\Rightarrow N = \frac{\sqrt{\pi}}{2} \cdot B\, (kT)^{3/2}. \quad \Rightarrow B = \frac{2N}{\sqrt{\pi}\,(kT)^{3/2}} = \frac{2\pi N}{(\pi k T)^{3/2}}$$

$$\Rightarrow \boxed{n(\epsilon)\, d\epsilon = \frac{2\pi N}{(\pi k T)^{3/2}}\, \sqrt{\epsilon}\; e^{-\left(\frac{\epsilon}{kT}\right)}\, d\epsilon}$$

This is Maxwell-Boltzmann Energy dist^n formula

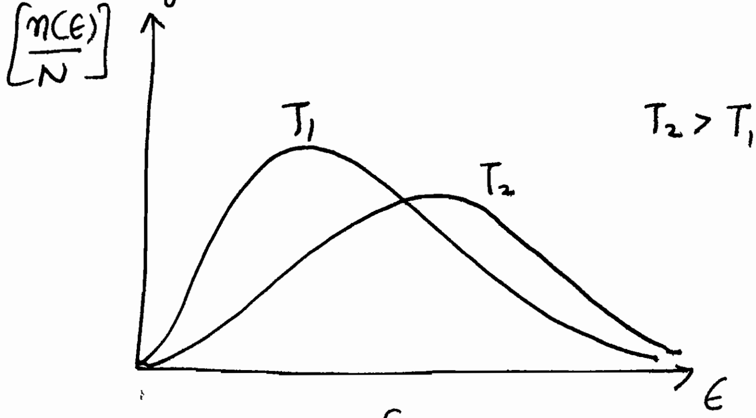


Probability density function

The area gives $n(\epsilon)\, d\epsilon$ i.e. number of particle with energy b/w ϵ and $(\epsilon + d\epsilon)$ ....

≈ $n(\epsilon)$ [redacted] for whole range

With increase in Temperature, the curve flattens since no. of particles or Area = const. ⇒ the following shapes:-



For a Probability distribution function

$$P_r[a \leq X \leq b] = \int_a^b f(x)\, dx$$

Note that $f(x)$ as such does not have much value. the area has a value i.e. the interval has a value

example If I measures width of an oak leaf, the result = 3.5 cm is possible but has Probability = 0, since there are uncountable possibilities even between 3.4 and 3.6. Each of the outcomes has Probability 0. But the outcome will fall b/w [3.4 and 3.6] has non-zero probability.

Most Probability Energy [redacted] when $\frac{d(n(\epsilon))}{d\epsilon} = 0$

[redacted]

$$\frac{dn}{d\epsilon} = 0$$

$$\Rightarrow \frac{1}{2} \epsilon^{-\frac{1}{2}} e^{-\left(\frac{\epsilon}{kT}\right)} + \epsilon^{\frac{1}{2}} e^{-\left(\frac{\epsilon}{kT}\right)} \frac{-1}{kT} = 0$$

$$\Rightarrow \frac{1}{2} \frac{1}{\sqrt{\epsilon}} = \frac{\sqrt{\epsilon}}{kT}$$

$$\Rightarrow \boxed{\epsilon = \frac{kT}{2}}$$

Most Probable Energy

$$\text{Mean Energy } \langle E \rangle = \frac{\int_0^\infty \epsilon \; n(\epsilon)\, d(\epsilon)}{\int_0^\infty n(\epsilon)\, d\epsilon} = \frac{2\pi}{(\pi kT)^{3/2}} \int_0^\infty \epsilon^{3/2} e^{-\frac{\epsilon}{kT}}\, d$$

Put $\frac{\epsilon}{kT} = x \Rightarrow d\epsilon = kT\, dx$

$$\Rightarrow \langle E \rangle = \frac{2\pi}{(\pi kT)^{3/2}} \int_0^\infty (kT)^{5/2} \cdot x^{3/2}\, e^{-x}\, dx$$

$$= \frac{2\pi\, (kT)^{5/2}}{(\pi)^{3/2}\, (kT)^{3/2}} \underbrace{\int_0^\infty x^{3/2}\, e^{-x}\, dx}$$

$$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi}$$

= [redacted] $\frac{2}{\sqrt{\pi}} (kT) \cdot \frac{3}{4} \sqrt{\pi}$

$$\boxed{\langle E \rangle = \frac{3}{2} kT}$$ Mean Energy

★★ rather than getting confused with constant. use $\dfrac{\int_0^\infty \epsilon\, n(\epsilon)\, d\epsilon}{\int_0^\infty n(\epsilon)\, d\epsilon}$ and cut out constants

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{\langle p_x^2 \rangle}{2m} + \frac{\langle p_y^2 \rangle}{2m} + \frac{\langle p_z^2 \rangle}{2m}$$

$\Rightarrow$ Per degree of freedom Energy $= \frac{1}{2} kT$

Momentum distribution.

$$n(p)\, dp = A\, e^{-\frac{p^2}{2mkT}}\, g(p)\, dp$$

= No. of particles with energy between p & $(p + dp)$

$$n(p)\, dp = A \cdot \frac{4\pi V}{h^3}\, p^2\, e^{-\frac{p^2}{2mkT}}\, dp$$

$$= B\, p^2\, e^{-\frac{p^2}{2mkT}}\, dp \quad \text{(say)}$$

$$N = \int_0^\infty n(p)\, dp = B \int_0^\infty p^2\, e^{-\frac{p^2}{2mkT}}\, dp$$

$$= \frac{B}{4} \left(\frac{\pi}{\left(\frac{1}{2mkT}\right)^3} \right)^{1/2}$$

$$\Rightarrow B = \frac{4N}{\sqrt{\pi}\,(2mkT)^{3/2}} = \frac{4\pi N}{(2\pi mkT)^{3/2}}$$

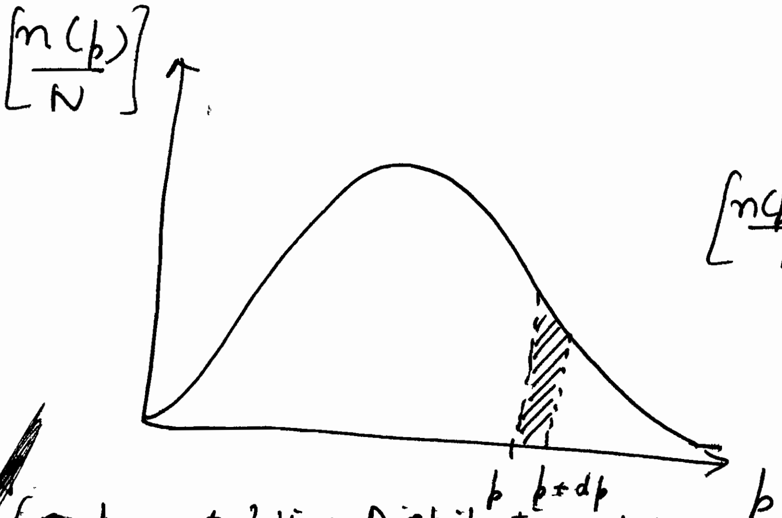
$$\Rightarrow \boxed{n(p)\,dp = \frac{4\pi N}{(2\pi mkT)^{3/2}}\, p^2\, e^{-\frac{p^2}{2mkT}}\, dp}$$

Velocity Distribution

Using $p = mv$

$$n(v)\,dv = \frac{4\pi N\, m^3}{(2\pi mkT)^{3/2}}\, v^2\, e^{-\frac{mv^2}{2kT}}\, dv$$

$$\boxed{\cancel{n(v)\,dv} = \frac{4\pi N m^3}{(2\pi mkT)^{3/2}}\, v^2\, e^{-\frac{mv^2}{2kT}}\, dv}$$



$\left[\frac{n(p)\,dp}{N}\right]$ = Area b/w p and $(p+dp)$

= fraction of particles with momentum between p and $(p+dp)$

Component Wise Distribution of Momentum

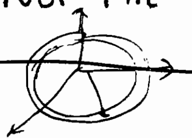
We can write

$$P(p)\,dp = \frac{n(p)\,dp}{N}$$

$P(p)\,dp = P(p_x)\,dp_x$ ★ $P(p_y)\,dp_y$ ★ $P(p_z)\,dp_z$

P: Probability distribution function

[NOTE THAT IT IS NOT THE PROBABILITY]



$$P(p)\,dp = [P(p_x)\,P(p_y)\,P(p_z)]\,[dp_x\, dp_y\, dp_z]$$

$$= P(p_x)\,P(p_y)\,P(p_z)\ \underline{4\pi p^2\, dp}$$

$$P(p)\,dp = \frac{1}{(2\pi mkT)^{3/2}}\, 4\pi p^2 \left[e^{-\frac{p_x^2}{2mkT}}\, dp_x\ e^{-\frac{p_y^2}{2mkT}}\, dp_y\ e^{-\frac{p_z^2}{2mkT}}\, dp_z\right.$$

where $p^2 = p_x^2 + p_y^2 + p_z^2$

We can write component wise,

$$P(p_x)\,dp_x = \frac{1}{(2\pi mkT)^{1/2}}\, e^{-\left(\frac{p_x^2}{2mkT}\right)}\, dp_x$$

$$P(p_y)\,dp_y = \frac{1}{(2\pi mkT)^{1/2}}\, e^{-\left(\frac{p_y^2}{2mkT}\right)}\, dp_y$$

$$P(p_z)\,dp_z = \frac{1}{(2\pi mkT)^{1/2}}\, e^{-\left(\frac{p_z^2}{2mkT}\right)}\, dp_z$$

on R.H.S. write $4\pi p^2 dp$ as $dp_x\, dp_y\, dp_z$

On LHS write $n(p)\,dp$ as $n(p_x)\,dp_x \cdot n(p_y)\,dp_y\, n(p_z)\,dp_z$

Its called Component Distribution formula ✓ Component wise formula

[Note that while Probabilities are multiplicative, the fractions or numbers are additive]

Different velocities

$$n(p_q)\,dp_q = \frac{N}{(2\pi mkT)^{3/2}}\, e^{-\left(\frac{p_q^2}{2mkT}\right)}\, dp_q$$

Following the same steps as analysis of energy,

$$g(v)\,dv = \text{[redacted]}\ \frac{d^3r\, d^3v}{h^3} = \frac{4\pi V}{h^3}\, v^2\, dv$$

$$n(v)\,dv = f(v)\, g(v)\, dv$$

$$= A\, e^{-\frac{mv^2}{2kT}} \cdot \frac{4\pi V}{h^3}\, v^2\, dv$$

$$N = \int n(v)\,dv = A\,\frac{4\pi V}{h^3} \int_0^\infty v^2\, e^{-\frac{mv^2}{2kT}}\, dv$$

$$= B \int_0^\infty v^2\, e^{-\left(\frac{m}{2kT}\right)v^2}\, dv = B\,\frac{1}{4}\left[\frac{\pi}{\left(\frac{m}{2kT}\right)^3}\right]^{\frac{1}{2}}$$

$$\Rightarrow B = 4\left(\frac{m}{2kT}\right)^{3/2} \frac{N}{\sqrt{\pi}}$$

$$\Rightarrow n(v)\,dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{-\frac{mv^2}{2kT}}\, dv$$

↑ We can this formula straight from Momentum dist^n..... Momentum dist^n can be derived from Energy dist^n.

$$P(v) = \frac{n(v)\,dv}{N}$$

For most Probable velocity

$$\frac{d\,P(v)}{dv} = 0$$

$$v_{M.P.} \Rightarrow \left.\frac{d\,n(v)}{dv}\right|_{v=v_{MP}} = 0$$

$$\Rightarrow \cancel{2v}\; \cancel{e^{-\left(\frac{mv^2}{2kT}\right)}} + v^2\, \cancel{e^{-\frac{mv^2}{2kT}}} \cdot -\frac{m}{2kT}\,\cancel{2v} = 0$$

$$\Rightarrow 1 = \frac{mv^2}{2kT}$$

$$\Rightarrow \boxed{v = \sqrt{\frac{2kT}{m}}}$$

Most Probable Velocity

Most important expression is of that of $n(\epsilon)\,d\epsilon$

$$n(\epsilon)\,d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}}\,\epsilon^{1/2} e^{-\frac{\epsilon}{kT}}$$

Mean value or Expectation Value or Average velocity

$$\langle v\rangle = \frac{\int_0^\infty v\, n(v)\,dv}{\int_0^\infty n(v)\,dv} = \frac{4\pi N}{N}\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3 e^{-\frac{mv^2}{2kT}}\,dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2}\, \frac{1}{\left(\frac{m}{2kT}\right)^2} \cdot \Gamma(2)$$

$$= \frac{2\pi}{\pi^{3/2}} \frac{1}{\left(\frac{m}{2kT}\right)^{\frac{1}{2}}} = \sqrt{\frac{4}{m\pi}\cdot 2kT} = \sqrt{\frac{8kT}{\pi m}}$$

$$\boxed{\langle v\rangle = \sqrt{\frac{8\,kT}{\pi\, m}}}$$

Average Velocity

Easier derivation will be done when we mutually cancel the constant. and perform both integrations....

Note that $\langle v\rangle_{avg} > v_{most\ probable}$

$$= \frac{\int_0^\infty v^3 e^{-\alpha v^2}\,dv}{\int_0^\infty v^2 e^{-\alpha v^2}\,dv} = \frac{\sqrt{2}\,\alpha^{3/2}}{\alpha^2\sqrt{3/2}} = \sqrt{\frac{8k}{\pi}}$$

Root Mean Square Velocity

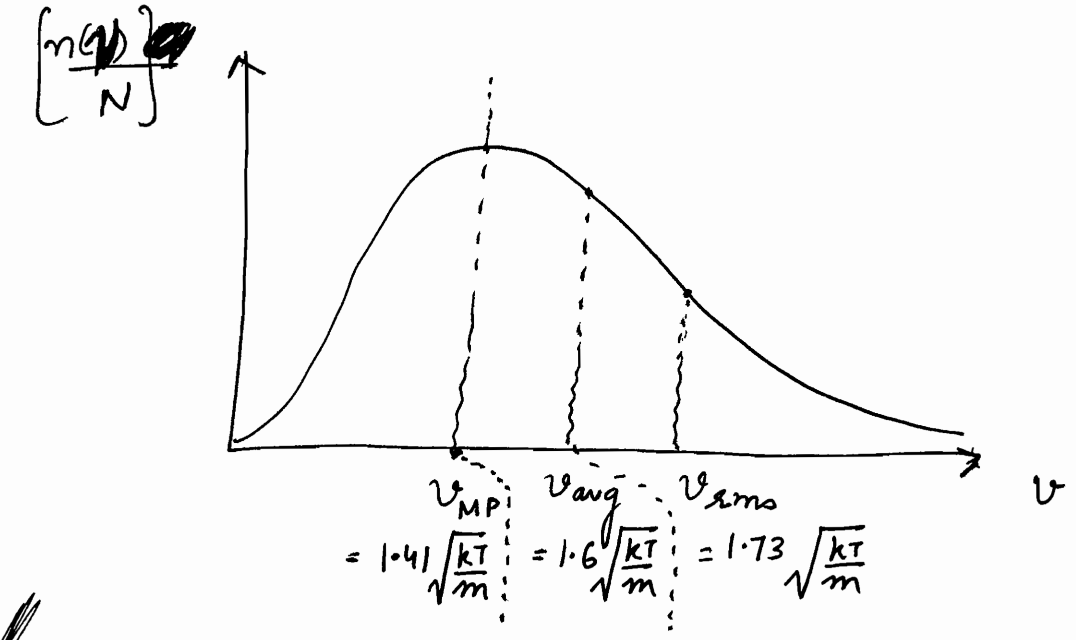
$$v_{rms} = \sqrt{\frac{\int_0^\infty v^2 \, n(p) \, dp}{\int_0^\infty n(p) \, dp}}$$

$$= \sqrt{4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 \, e^{-\frac{m}{2kT}v^2} \, dv}$$

$$= \sqrt{4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{m}{2kT}\right)^{\frac{5}{2}} \Gamma\left(\frac{5}{2}\right)}$$

$$= \sqrt{\frac{\cancel{4\pi}}{\cancel{\pi^{3/2}}} \frac{1}{\left(\frac{m}{\cancel{2}kT}\right)} \frac{1}{\cancel{2}} \cdot \frac{3}{\cancel{2}} \cdot \frac{1}{\cancel{2}} \cancel{\sqrt{\pi}}}$$

$$\boxed{v_{rms} = \sqrt{\frac{3kT}{m}}}$$ Root Mean Square Velocity



Component wise distribution of velocities

Following the same techniques as in momentum components

i.e. $dv_x \, dv_y \, dv_z = 4\pi v^2 \, dv$

Hence $P(v)\,dv \left(= \frac{n(v)\,dv}{N}\right)$

$= P(v_x)\,P(v_y)\,P(v_z)\,dv_x\,dv_y\,dv_z$

$= P(v_x)\,P(v_y)\,P(v_z)\,4\pi v^2\,dv$

$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{-\frac{m}{2kT}\left[v_x^2+v_y^2+v_z^2\right]}\,dv$

$$\Rightarrow \boxed{\begin{aligned} P(v_x)\,dv_x &= \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\left(\frac{m v_x^2}{2kT}\right)}\,dv_x \\ P(v_y)\,dv_y &= \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\left(\frac{m v_y^2}{2kT}\right)}\,dv_y \\ P(v_z)\,dv_z &= \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\left(\frac{m v_z^2}{2kT}\right)}\,dv_z \end{aligned}}$$

Only thing to note is that it is of $A e^{-\frac{\epsilon(v_x)}{kT}}$ d

ek dum normalized curves $\overset{¥}{\varepsilon}$!!

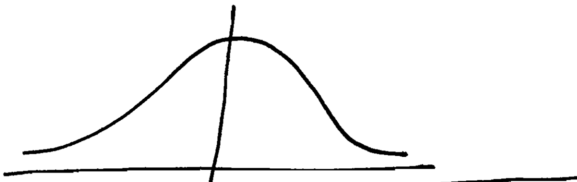
We used,

$P(v)\,dv = P(v_x)\,dv_x \cdot P(v_y)\,dv_y \cdot P(v_z)\,dv_z$

$= P(v_x)\,P(v_y)\,P(v_z)\,dv_x\,dv_y\,dv_z$

$= P(v_x)\,P(v_y)\,P(v_z)\,4\pi v^2\,dv$

Note that the curve for $P(v_x)\,dv_x$ is symmetric about $v_x = 0$ i.e. $v_{x\,avg} = 0$



$\langle v_x^{2n-1}\rangle = 0$

$$\boxed{\langle v_x^2\rangle = \frac{kT}{m}}$$

num $= \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot \frac{1}{4}\left[\frac{\pi}{\left(\frac{m}{2kT}\right)^3}\right]^{\frac{1}{2}}$

$= \frac{\sqrt{\pi}}{4\left(\frac{m}{2kT}\right)}\,\frac{1}{\sqrt{\pi}} = \frac{kT}{2m}$

den $= 2\cdot\frac{1}{2}\,\frac{\sqrt{\pi}}{\left(\frac{m}{2kT}\right)^{\frac{1}{2}}}\cdot\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}$

$= 2\,\frac{\sqrt{\pi}}{2\sqrt{\pi}} = (1)$

$\int_{-\infty}^{\infty} v^2 = 2\int_0$

$\Rightarrow \langle v_x^2\rangle = \left(\frac{kT}{m}\right)$

Most Probable velocity of $v_x = 0$

Note that $\int_0^{\infty} n(v_x)\,dv_x = \left(\frac{N}{2}\right)$

To get N, we need to integrate from $(-\infty,\infty)$

Equipartition of Energy Principle

[PTO to last Page of notes for Proof]

For, Any thermodynamic system at equilibrium temperature T, the energy per degree of freedom is $\left(\frac{1}{2}kT\right)$, provided it is expressible in form of $E_q = aq^2$.

$$U_x = \frac{1}{2}kx^2 \; ; \; U_y = \frac{1}{2}ky^2 \; ; \; U_z = \frac{1}{2}kz^2$$

$$\boxed{\left[\frac{n(q)\,dq}{N}\right] = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\left(\frac{aq^2}{kT}\right)} dq}$$

$$\boxed{P(q) = \frac{n(q)}{N}}$$

$$\langle \epsilon_q \rangle = \frac{\int \epsilon_q \, p(q)\, dq}{\int p(q)\, dq} = \frac{\int_0^\infty aq^2 \, p(q)\, dq}{\int_0^\infty P(q)\, dq}$$

$$= \frac{\int_0^\infty aq^2 \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} . \, e^{-\frac{aq^2}{kT}} dq}{\int_0^\infty \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{aq^2}{kT}} dq}$$

$$= \frac{\int_0^\infty aq^2 \, e^{-\frac{aq^2}{kT}} dq}{\int_0^\infty e^{-\frac{aq^2}{kT}} dq}$$

$$= a\left(\frac{I_2}{I_0}\right) = \frac{a \, \frac{1}{4} \, \frac{\sqrt{\pi}}{\alpha^{3/2}}}{\frac{1}{2} \, \frac{\sqrt{\pi}}{\alpha^{1/2}}} = \frac{a}{2} \, \frac{1}{\alpha}$$

$$= \frac{a}{2} \cdot \frac{1}{\left(\frac{a}{kT}\right)} = \underline{\underline{\left(\frac{kT}{2}\right)}}$$

For 1 Gm-Mole **Ideal Gas**,

Read this page

$$U = N \cdot f \cdot \frac{1}{2} kT = f \cdot \frac{1}{2} RT$$

$dU = C_V\, dT$

$= \frac{f}{2} R\, dT$

$\Rightarrow \boxed{C_V = \frac{f}{2} R}$

- $C_V = \frac{fR}{2}$
- $C_P = C_V + R = \left(\frac{f}{2} + 1\right) R$
- $\left[\frac{C_P}{C_V}\right] = \dfrac{1 + \frac{f}{2}}{\frac{f}{2}} = 1 + \frac{2}{f} = \gamma$

Mono atomic Gas $f = 3 \Rightarrow \gamma = 1 + \frac{2}{3} = 1.66$

Diatomic Gas $f = 5 \Rightarrow \gamma = 1 + \frac{2}{5} = 1.4$

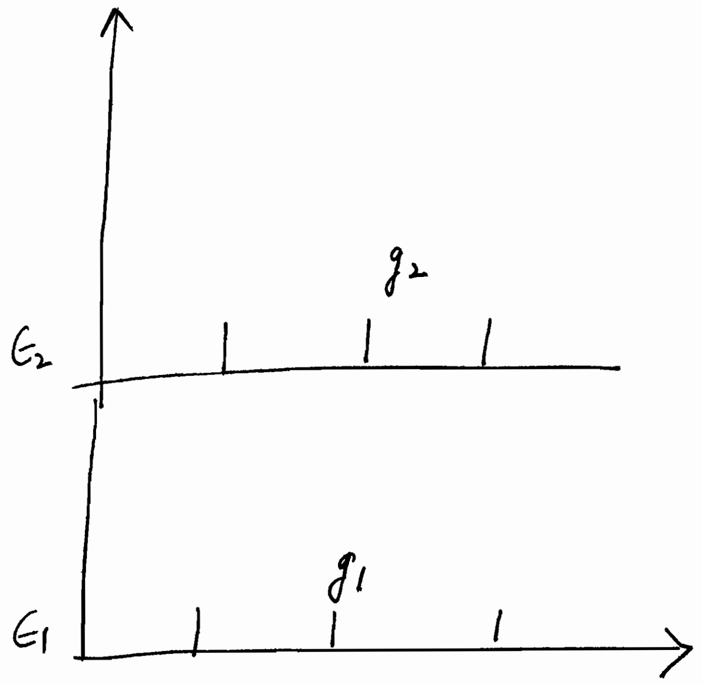
Triatomic Gas
or
Polyatomic Gas $\gamma = (1.29, 1.42)$ [3N−k
N=3 (Triatomic)]

Note that while deriving law of equipartition of energy, we assumed energy to have a continuous spectrum which is not the case.

Thus equipartition law breaks down at the level of low temperatures where kT is significantly smaller than spacing between energy levels. Here arises the need of quantum theory.

FERMI DIRAC STATISTICS

(Thermodynamics)
(12)
9/1/2012



(*) Note that 2 spin states are actually 2 different cells

⇓

$g(\epsilon)d\epsilon$ is multiplied by 2

→ always remember that cells (g_i) are always distinguishable
Rather they are the unique role numbers.

[illegible]

Difference b/w FD and BE is restriction on no. of particles per cell due to Pauli Exclusion Principle.

For F.D., $g_i \geq n_i$ For Pauli Exclusion Principle to hold true.

i.e. no. of cells must be more than no. of particles

⇒ way of choosing is to choose n_i cells out of g_i to fill particles in them. i.e. $\prod_i {}^{g_i}C_{n_i}$

$$\boxed{\Omega = \prod_i \frac{\lfloor g_i}{\lfloor n_i \lfloor g_i - n_i}}$$

Here also conceiving it as 2 step problem (3, 5, 2)

$\Omega = \Omega_1 \Omega_2$

⇒ $\Omega_1 = 1$ (as all particle are indistinguish

∴ which 3, which 5 etc. do not matter)

⇒ $\Omega_2 = \prod_i {}^{g_i}C_{n_i}$

$$\ln \Omega = \sum \ln \lfloor g_i - \ln \lfloor n_i - \ln \lfloor g_i - n_i$$

$$d(\ln \Omega) = \sum \underset{\overset{\uparrow}{0}}{d(\ln \lfloor g_i)} - d(\ln \lfloor n_i) - d(\ln \lfloor g_i - n_i)$$

$$= \sum d\{-n_i \ln n_i + n_i\} - d\{(g_i - n_i)\ln(g_i - n_i) - (g_i - n_i)\}$$

$$= \sum -n_i \cdot \cancel{\frac{1}{n_i}} - \ln n_i \overset{dn_i}{} + \cancel{dn_i} + \cancel{dn_i}$$
$$+ (g_i - n_i)\left(\cancel{\frac{1}{g_i - n_i}}\right) + \ln(g_i - n_i)\, dn_i$$

$$= \sum \ln\left(\frac{g_i - n_i}{n_i}\right) dn_i \quad \text{———} \quad ③$$

We know

$$\alpha \sum dn_i = 0 \quad \text{———} \quad ①$$

$$\beta \sum \epsilon_i dn_i = 0 \quad \text{———} \quad ②$$

Doing ① + ③ − ②

$$\sum_i \left[\ln\left(\frac{g_i - n_i}{n_i}\right) + \alpha - \beta\epsilon_i\right] dn_i = 0$$

⇒ If hold good $\forall i$, ⇒ $dn_i \neq 0$ for all i

$$\Rightarrow \ln\left(\frac{g_i - n_i}{n_i}\right) + \alpha - \beta\epsilon_i = 0$$

$$\Rightarrow \left[\frac{g_i - n_i}{n_i}\right] = e^{-(\alpha - \beta \epsilon_i)}$$

To find variables, $S = k \ln \Omega$

$$T\,dS = Tk\,d(\ln \Omega)$$

$$\sum \epsilon_i\, dn_i = -kT \sum (\alpha - \beta \epsilon_i)$$

$$\Rightarrow \boxed{\beta = \frac{1}{kT}}$$

- $d(\ln \Omega)$ may be different but in terms of α and β, it is same
Hence. β की same ही तो value आएगी !!

$$\Rightarrow \frac{g_i - n_i}{n_i} = \left(\frac{g_i}{n_i}\right) - 1 = e^{-(\alpha - \beta \epsilon_i)}$$

$$f(\epsilon_i) = \frac{1}{\left(\frac{g_i}{n_i}\right)} = \frac{1}{1 + e^{-(\alpha - \beta \epsilon_i)}} = \frac{1}{1 + e^{-\left(\alpha - \frac{\epsilon_i}{kT}\right)}}$$

define $\boxed{\alpha = \frac{\epsilon_f}{kT}}$ where ϵ_f : characteristic energy of fermions called fermi energy at temperature T

$$\Rightarrow \boxed{f(\epsilon_i) = \left(\frac{n_i}{g_i}\right) = \frac{1}{1 + e^{\left(\frac{\epsilon_i - \epsilon_f}{kT}\right)}}}$$

Fermi Dirac Distribution

Note that α can be $+\frac{\epsilon_f}{kT}$ or $-\frac{\epsilon_f}{kT}$ depending upon whether we do ①+③-② or -①+③-② ... etc. Finally we should get this formula of distribution.

$$f(\epsilon) = \frac{n(\epsilon)}{g(\epsilon)} = \frac{1}{1+e^{(\epsilon-\epsilon_f)/kT}} \quad — ①$$

○ Note that $f(\epsilon)$ is always less than 1. It makes sense as no. of particles per energy ~~level~~ cell cannot be more than 1.

@ T = 0K [just for definition ; its unattainable]

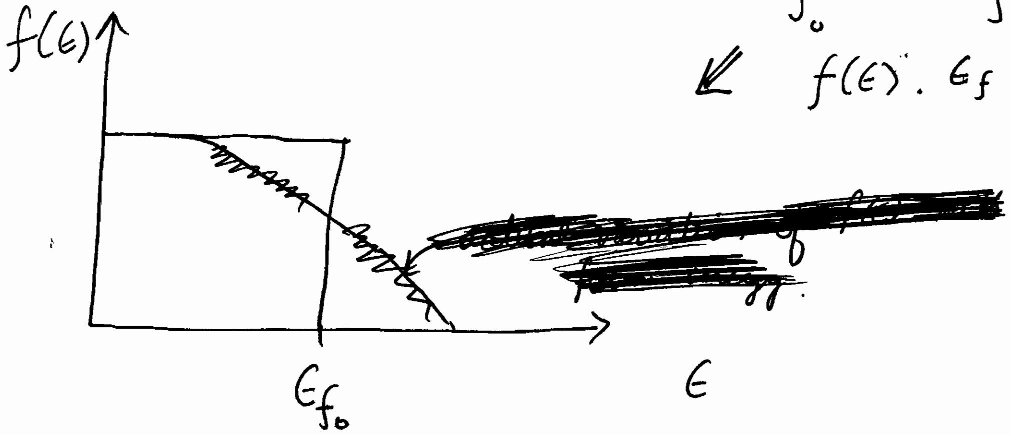
From ①,

if $\epsilon < \epsilon_{f_0}$, we get $f(\epsilon) = 1$ (all states are fully occupied)

if $\epsilon > \epsilon_{f_0}$, we get $f(\epsilon) = 0$ (no state is occupied)

$$\int_0^\infty f(\epsilon) \Leftrightarrow \int_0^{\epsilon_f} f(\epsilon)$$

↙ $f(\epsilon) . \epsilon_f$



Hence 2 parts of complete defⁿ of ϵ_f :

✓① Characteristic of fermions at Temp T.

✓② @ 0k, energy below which all states are fully occupied and above which no state is occupied.

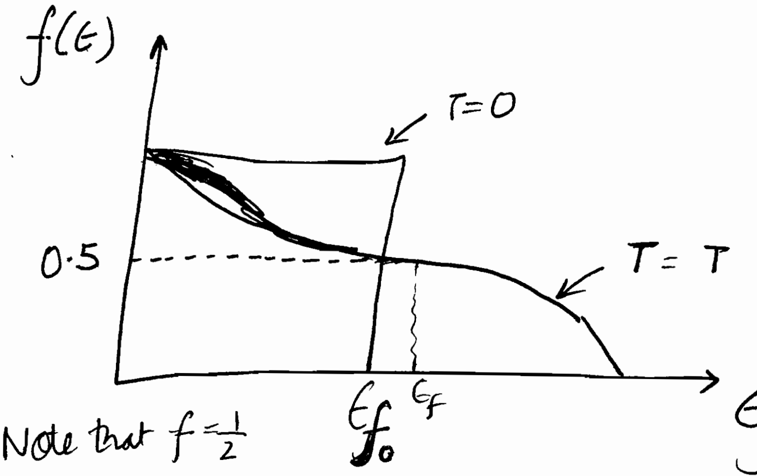
Now 2 analysis in syllabus

① @ T = 0 , (i) find ϵ_{f_0} (iii) find P_0
(ii) find E

② @ T = T Use $\int_0^\infty f(x-x_0)\, x^n\, dx = \frac{x_0^{n+1}}{n+1}\left[1 + \frac{\pi^2}{6}\frac{n(n+1)}{x_0^2} + \dots\right]$

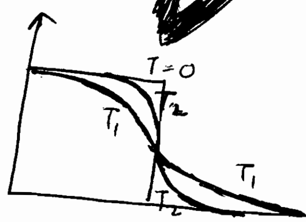
in order to
(i) find $\epsilon_f(T)$
(ii) Contribution of Energy by e-
(iii) find C_v, P_T

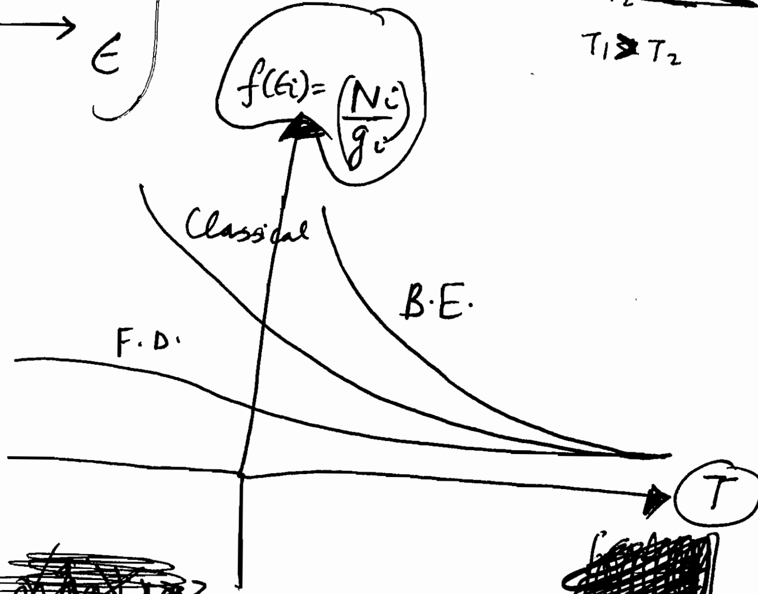
Use $\frac{4\pi V}{h^3}(2m)^{\frac{3}{2}} = \frac{3}{2}\frac{N}{\epsilon_{f_0}^{3/2}}$ in both



⊛ Note that $f=\frac{1}{2}$ at ϵ_f and not ϵ_{f_0}. ϵ_f lies close to but not at ϵ_{f_0}

Q4 and Q7





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⑩

$$\epsilon = a q^2$$

$$\langle \epsilon \rangle = \frac{\int \epsilon \, P(\epsilon) \, d\epsilon}{\int P(\epsilon) \, d\epsilon} = \frac{\int_0^\infty \epsilon \, f(\epsilon) \, d\epsilon}{\int_0^\infty \epsilon \, f(\epsilon) \, d\epsilon}$$

$$= \frac{\int \epsilon \, e^{-(\alpha + \beta \epsilon_i)} d\epsilon}{\int e^{-(\alpha + \beta \epsilon_i)} d\epsilon} = \frac{\int \epsilon \, e^{-\beta \epsilon_i} d\epsilon}{\int e^{-\beta \epsilon_i} d\epsilon}$$

Let $\beta \epsilon = x \Rightarrow d\epsilon = \frac{dx}{\beta}$

$$= \frac{1}{a\beta}\,\frac{\Gamma 2}{\Gamma 1} = \frac{1}{a\beta}$$

$$\beta = \frac{1}{kT}$$

[redacted]

⋮

check for errors.

<u>2nd way</u>

Put $\epsilon = aq^2$ $\qquad d\epsilon = 2aq\,dq$

$$a\beta q^2 = x$$

$$\sqrt{a\beta}\; q = \sqrt{x}$$

$$q = \frac{1}{\sqrt{a\beta}}\sqrt{x}$$

$$dq = \frac{1}{2\sqrt{a\beta}}\; x^{-1/2}\; dx$$

$$\boxed{\frac{1}{\beta}}$$

$$\beta = \frac{1}{kT}$$

$$f(\epsilon) = \frac{1}{1+e^{(\epsilon-\epsilon_f)/kT}}$$

$$@\ 0k : \quad f(\epsilon) = 1 \qquad \epsilon < \epsilon_f$$
$$\qquad\qquad = 0 \qquad \epsilon > \epsilon_f$$

No. of fermions at 0 k

$$\int dn_i = \int f(\epsilon_i)\ g(\epsilon_i)\ d\epsilon_i$$

$$= \int_0^{\epsilon_{f_0}} 1.\ \overbrace{\frac{2\pi V}{h^3}\ (2m)^{3/2}\ \epsilon^{1/2}}^{\text{space degeneracy}}.\ d\epsilon$$

$$\boxed{N = \frac{2\pi V}{h^3}.\ (2m)^{3/2} \left[\frac{(\epsilon_{f_0})^{3/2}}{(3/2)}\right]}$$

in general at temp T,

$$N = \frac{2\pi V\ (2m)^{3/2}}{h^3} \int_0^\infty \frac{f}{1+e^{(\epsilon-\epsilon_f/kT)}}\ \epsilon^{1/2}\ d\epsilon$$

If spin degeneracy is also taken into account, $g = g_{space} * g_{sp}$

$$g(\epsilon)_{space} = \frac{2\pi V}{h^3}.(2m)^{3/2}\ \epsilon^{1/2}$$

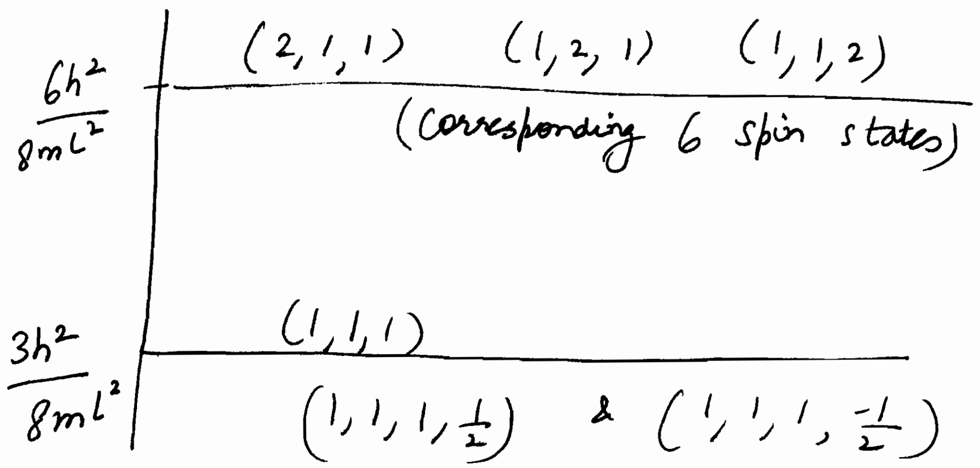
or degeneracy of state or no. of particular energy level or no. of prob. states per energy leve

cells per

$$g_{spin} = (2S+1)$$

For e^- : $S = \frac{1}{2} \Rightarrow g_{spin_e} = 2$

Hence $2e^-$ can be put in same space or cell if spin is taken into account.



(*) Fermions like e^-, proton, neutron have $S = \frac{1}{2}$

⇒ every energy level ϵ can have 2 particles.
(here we mean every cell)

⇒ $N = 2 * N_{\text{space degeneracy}}$

* बस 1 constant का ही फर्क पड़ेगा !!

$$N = 2 \times \frac{2\pi V}{h^3} (2m)^{3/2} \left[\frac{(\epsilon_{f0})^{3/2}}{3/2} \right]$$

$$\Rightarrow \boxed{\frac{4\pi V}{h^3} (2m)^{3/2} = \frac{3}{2} \frac{N}{\epsilon_{f0}^{3/2}}}$$

✓ This is important !!

$n = \frac{N}{V} \Rightarrow 3\pi^2 n \hbar^3 = (2m\epsilon_{f_0})^{3/2}$

$\hbar = \frac{h}{2\pi}$ (h cross) $\Rightarrow \boxed{\epsilon_{f_0} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}}$

at 0 k

$n = \frac{\rho N}{M} = \left(\frac{N}{V}\right)$

If $T = T \neq 0 \Rightarrow$ we have to integrate $\int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{1+e^{(\epsilon-\epsilon_f)/kT}}$

Note the limits

Use
$$\boxed{\int_0^\infty f(x-x_0)\, x^n\, dx = \frac{x_0^{n+1}}{n+1}\left[1 + \frac{\pi^2}{6}\frac{n(n+1)}{x_0^2} + \cdots\right]}$$

Sommerfield lemma

by Putting $\frac{\epsilon}{kT} = x$ and $\frac{\epsilon_f}{kT} = x_0$

Total no. of particle at a finite Temperature

$$N = \left[\frac{4\pi V}{h^3}(2m)^{3/2}\right]\int_0^\infty \frac{(kT)^{3/2} x^{1/2}\, dx}{1+e^{x-x_0}}$$

$$N = \left[\frac{3}{2}\cdot\frac{N}{\epsilon_{f_0}^{3/2}}(kT)^{3/2}\right](x_0)^{3/2}\,\frac{2}{3}\left[1 + \frac{\pi^2}{6}\times\frac{1}{2}\times\frac{3}{2x_0^2} + \cdots\right]$$

$$\Rightarrow 1 = \left(\frac{\epsilon_f}{\epsilon_{f_0}}\right)^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{kT}{\epsilon_f}\right)^2 + \cdots\right]$$

$$\boxed{\epsilon_f(T) = \epsilon_{f_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2 + \cdots\right]}$$

⊛ Remember $\frac{\epsilon_f}{kT} = \alpha$ (const)

$\Rightarrow \epsilon_f = f(T)$

But remember approximation like $(g_i + n_i) \gg 1$ were used. Hence expression for ϵ_f is complex

defining $\boxed{\epsilon_f = kT_f}$

↑

fermi temperature

$$\boxed{\epsilon_f(T) = \epsilon_{f_0}\left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_f}\right)^2 + \cdots\right]}$$

$T_f > 10^4$ i.e. very high values hence $\epsilon_f(T)$ and ϵ_0 have little difference ....

For $\epsilon_f = 3.2\,eV$ $T_f \simeq 10^4$

$$N = \left[\int f(p)\, g(p)\, dp\right] * \left[(2s+1)\right]$$ (if spin taken into account)

$$f(p) = \frac{1}{1 + e^{\frac{p^2 - p_f^2}{2mkT}}}$$

define : $\epsilon_f = \frac{p_f^2}{2m}$

@ $T = 0k$: for $p < p_f$ $f(0) = 1$

$p > p_f$ $f(0) = 0$

$$\int 2 * f(p) \; \frac{V}{h^3} \; 4\pi p^2 \, dp$$

$$N = \frac{8\pi V}{h^3} \; \frac{p_{f_0}^2}{3}$$

Total Energy

$$E = \int \epsilon \, dn_\epsilon = \int \epsilon \, n(\epsilon) \, d\epsilon$$

$$= \int \epsilon \, f(\epsilon) g(\epsilon) \, d\epsilon$$

$$= \int_0^\infty \epsilon \cdot \frac{4\pi V}{h^3} \cdot (2m)^{3/2} \frac{\epsilon^{1/2} \, d\epsilon}{1 + e^{\left(\frac{\epsilon - \epsilon_f}{kT}\right)}}$$

$$\boxed{E = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} \, d\epsilon}{1 + e^{(\epsilon - \epsilon_f)/kT}}}$$

~~03/8/9~~ @ T=0

$$\frac{4\pi V}{h^3} (2m)^{3/2} \int_0^{\epsilon_f} e^{3/2} \, d\epsilon$$

$$\frac{3N}{2} (\epsilon_{f_0})^{-3/2} \; \frac{2}{5} \, \epsilon_f^{5/2}$$

$$\boxed{E = \frac{3}{5} N \epsilon_{f_0}}$$

This shows that unlike classical particle, a fermion has appreciable energy even at 0 k.

Also $C_V = \left(\frac{\partial E}{\partial T}\right)_v = 0$ at 0K

$$\frac{E}{N} = \frac{3}{5} \epsilon_{f_0} =$$ 60% of fermi energy at 0 k

✓ $\boxed{PV = \frac{2}{3}E}$ ⊛ (Considering fermions as an ideal gas)

$$P = \frac{2}{3}\left(\frac{E}{V}\right) = \frac{2}{3}\cdot\frac{3}{5}\frac{N}{V}\epsilon_{f_0} = \underbrace{\frac{2}{5}\frac{N}{V}\epsilon_{f_0}}$$

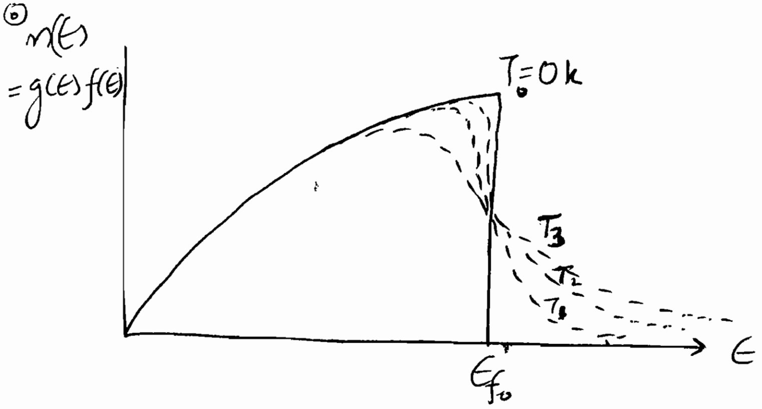
$$= \frac{2}{5} n \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

$$\Rightarrow \boxed{P \propto n^{5/3}}$$

* This high pressure is counter balanced by coulomb attraction of e⁻ by ions.

⊙ In an ideal fermi system, there is no inter-fermionic interaction

⊙



$T_1 < T_2 < T_3$

Thermodynamics (13)

10/01/2012

$$\int_0^\infty f(x-x_0)\, x^n \, dx = \frac{x_0^{n+1}}{n+1}\left[1 + \frac{\pi^2}{6}\frac{n(n+1)}{x_0^2} + \dots\right]$$

$$\int_0^\infty \frac{e^{-x}}{x^{n-1}}\, dx = \underset{\substack{\uparrow \\ \text{Gamma}}}{\Gamma n}\ \underset{\substack{\uparrow \\ \text{Zita}}}{\zeta(n)}$$

We know : ~~Con~~tribution of e^- ~~to~~ Internal Energy

F.D.

$$f(\epsilon) = \frac{n(\epsilon)}{g(\epsilon)} = \frac{1}{1 + e^{(\epsilon-\epsilon_f)/kT}}$$

$$\underset{\substack{\uparrow}}{n(\epsilon)} = f(\epsilon)\, g(\epsilon)$$

In MB and BE, we can put all particles in these energy level as there is no restriction....

$$dn = n(\epsilon)\, d\epsilon = \underset{\substack{\uparrow}}{2} * f(\epsilon) * g(\epsilon)$$

spin degeneracy

$$n = \int_0^\infty 2 * f(\epsilon) * g(\epsilon)$$

$$E = \int_0^\infty \epsilon \cdot dn$$

At 0 k, $n = \int_0^{\epsilon_{f_0}} 2\, g(\epsilon)\, d\epsilon$

$$E = \int_0^\infty \epsilon \quad 2 \quad f(\epsilon) \quad g(\epsilon) \quad d\epsilon$$

$$E = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} \, d\epsilon}{1 + e^{(\epsilon - \epsilon_f)/kT}}$$

$$E = \frac{3N}{2 \, \epsilon_{f_0}^{3/2}} \int_0^\infty \frac{\epsilon^{3/2} \, d\epsilon}{1 + e^{(\epsilon - \epsilon_f)/kT}}$$

$\uparrow$

Energy Contribution to internal energy by ~~fermions~~ / electrons..... Note that it is electronic contribution, not lattice (ions) contribution

Put $\frac{\epsilon}{kT} = x$

$d\epsilon = kT \, dx$

$$\Rightarrow E = \frac{3N}{2 \, \epsilon_{f_0}^{3/2}} (kT)^{5/2} \int_0^\infty \frac{x^{3/2} \, dx}{1 + e^{(x - x_0)}}$$

$$\boxed{x_0 = \frac{\epsilon_f}{kT}}$$

$$\boxed{n = 3/2}$$

$$\Rightarrow E = \frac{3N}{\cancel{2} \, \epsilon_{f_0}^{3/2}} \cancel{(kT)^{5/2}} \frac{\cancel{2}}{5} \frac{(\epsilon_f)^{5/2}}{\cancel{(kT)^{5/2}}} \left[1 + \frac{\pi^2}{6} \cdot \frac{3}{2} \, \frac{5}{2} \left(\frac{kT}{\epsilon_f} \right)^2 + \cdots \right.$$

$$\Rightarrow \boxed{E = \frac{3}{5} N \frac{\epsilon_f^{5/2}}{\epsilon_{f_0}^{3/2}} \left[1 + \frac{5\pi^2}{8} \left(\frac{kT}{\epsilon_f} \right)^2 + \cdots \right]}$$

@ $T = 0\,k$, $E = \frac{3}{5} N \epsilon_{f_0}$

simplifying further, expressing ϵ_f in terms of ϵ_{f_0}

$$E = \frac{3N}{5\,\epsilon_{f_0}^{3/2}}\,\epsilon_{f_0}^{5/2}\left[1+\frac{\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2+\cdots\right]^{5/2}\left[1+\frac{5\pi^2}{8}\left(\frac{kT}{\epsilon_f}\right)^2+\cdots\right]$$

$$E = \frac{3N\epsilon_{f_0}}{5}\left[1-\frac{5\pi^2}{24}\left(\frac{kT}{\epsilon_f}\right)^2+\frac{5\pi^2}{8}\left(\frac{kT}{\epsilon_f}\right)^2+\cdots\right]$$

$$\boxed{E = \frac{3}{5}N\epsilon_{f_0}\left[1+\frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_f}\right)^2\right]}$$

$\uparrow$

Contribution of Fermions or electronic contribution.....

Specific Heat of Gases

Here we talk about "Ideal Fermi Gas" or "Ideal Fermi System".

→ Fermi Gas : Particles obey Pauli Exclusion Principle.

→ Ideal Fermi Gas : Non interacting particles

This does not mean particles are in gaseous state. It just means no interaction among particles.

$$C_v = \left(\frac{dE}{dT}\right)_V = \overbrace{\frac{3}{5}N\epsilon_{f_0}\left[\frac{5\pi^2}{12}\left(\frac{k}{\epsilon_f}\right)^2\right]}^{A}2T+\cdots$$

$$\approx AT \qquad A = \frac{N\epsilon_{f_0}\pi^2k^2}{2\,\epsilon_f^2}$$

$$dQ = C_v \, dT$$

$$dS = \frac{dQ}{T} = \frac{C_v \, dT}{T} = A \, dT$$

$$P(T) = \frac{2}{3} \frac{E(T)}{V}$$

$$\left[\begin{array}{l} \frac{1}{2} mnv^2 = E \\ \frac{1}{3} mnv^2 = PV \end{array} \right]$$

↑

Pressure exerted by electrons $= \frac{2}{3} * \frac{3N\epsilon_{f_0}}{5V} \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{\epsilon_f} \right)^2 + \dots \right]$

$$\boxed{P(T) = \frac{2}{5} n \epsilon_{f_0} \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{\epsilon_f} \right)^2 + \dots \right]}$$

Even at 0k, $P = \frac{2}{5} n \epsilon_{f_0}$

This Pressure is balanced by attraction b/w ions and electrons. Whenever this balanced is maintained, star survives. The limit after which star collapses, is called Chandra Shekhar limit.

Important Points in F.D.

→ derivation along with graph is important

→ fermi energy, total no. of particles: typically at $T = 0\,k$

$$E_f = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

→ Total Energy $E = \frac{3}{5} N \epsilon_{f_0}$

Strong degeneracy : all levels below E_f : fully occupied
all levels above E_f : empty.

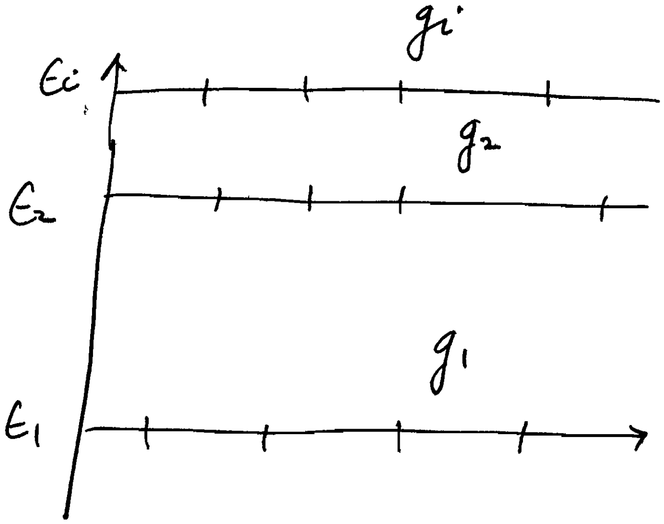
Bose - Einstein Statistics

Valid for indistinguishable particle having full integral spin, having no restriction on no. of particles per degeneracy level.

eg. **Photons** (quanta of energy of EM waves)

Phonons (minimum energy or quanta of elastic waves)

even Mass Number A → $^{4}_{2}He$ (all even A nuclei)



← no of ways to put n_i in g_i degeneracy leve

$$\Omega = \prod_i \binom{g_i}{n_i}$$

let

$n_1 = 3$

$g_1 = 2$

No. of ways : $(g_1)(g_1-1)\ldots(n_1-g_1$

Total no. of ways $= {}^{(n_i+g_i-1)}C_{(n_i)}$

Consider it as 2 step Problem (3,5,2)

$\Omega_1 = 1$ (as all are indistinguishable)

Consider $n=3$ box :

$$= \frac{\underline{|n_i+g_i-1}}{\underline{|n_i}\ \underline{|g_i-1}}$$

Let particles be lettered (a, b, c, d ....). Let levels gi be numbered (1, 2, 3...)

The distn of particles among levels may be written as :

1 (ab) 2 (c) 3 4 (def) ..... Ⓘ

If the numbers are arranged in all possible sequences, provided the sequence begins with a no., the no. of ways are $g_i\,(N_i+g_i-1)!$

But Ⓘ is equivalent to

2(c) 3 1(ab) 4(def) .... Ⓘⓘ

Hence there will be $\underline{|g}$ such sequences.

Also Ⓘ is equivalent to

1 (f, g) 2 (a) 3 4 (b, c, d) ....

since the particles are indistinguishable, distinguishable particles can be arranged in $\underline{|n}$ ways

$\Rightarrow$ Total No. of Ways $= \dfrac{\underline{|n_i+g_i-1}}{\underline{|g_i-1}\ \underline{|n_i}}$

$\Rightarrow \Omega_2 = \prod_i (n_i+g_i-1)!/(g_i-1)!\,n_i!$

n_i's are not distinguishable but g_i's are distinguishable ~~for~~ sure

$$\Omega = \prod_i \frac{\underline{|n_i+g_i-1}}{\underline{|n_i}\ \underline{|g_i-1}}$$

approximating $n_i+g_i \gg 1$

do not miss this step

$$\Rightarrow n_i+g_i-1 \approx n_i+g_i$$

$$\Rightarrow \Omega = \prod_i \frac{\underline{|n_i+g_i}}{\underline{|n_i}\ \underline{|g_i-1}}$$

$$\ln\Omega = \sum \ln\left(\underline{|n_i+g_i}\right) - \ln\underline{|n_i} - \ln\underline{|g_i-1}$$

$$= \sum (n_i+g_i)\ln(n_i+g_i) - (n_i+g_i) - n_i\ln n_i + n_i - \ln\underline{|g_i-1}$$

$$d(\ln\Omega) = \sum \ln(n_i+g_i)\,dn_i - \ln(n_i)\,dn_i$$

$$= \sum_i \ln\left[\frac{n_i+g_i}{n_i}\right] dn_i$$

For $\Omega(N, V, E)$,

$$\alpha \sum dn_i = 0$$

$$\beta \sum \epsilon_i \, dn_i = 0$$

$$\sum \ln\left(\frac{n_i + g_i}{n_i}\right) dn_i = 0$$

$\Big[$ $d(\ln \Omega) = \frac{dS}{k}$

$= 0$ at equilibrium

$$\Rightarrow \sum \left(\ln\left(\frac{n_i+g_i}{n_i}\right) + \alpha - \beta\epsilon_i\right) dn_i = 0$$

$$\Rightarrow \frac{n_i + g_i}{n_i} = e^{-(\alpha - \beta\epsilon_i)}$$

$\Big[$ to be valid ∀ i $\Big]$

$$\Rightarrow \boxed{f(\epsilon_i) = \left(\frac{n_i}{g_i}\right) = \frac{1}{e^{-(\alpha-\beta\epsilon_i)} - 1}} \boxed{= \frac{1}{A e^{\beta\epsilon_i} - 1}}$$

$A \leq 1$

FUGICITY

$\beta = \left(\frac{1}{kT}\right)$ as we found for other 2 distributions

Chemical potential of assembly of bosons

Assume

$e^{-\alpha} = A$ or $\boxed{\alpha = +\frac{\mu}{kT}}$

$$\boxed{f(\epsilon_i) = \frac{1}{e^{\left(\frac{\epsilon_i - \mu}{kT}\right)} - 1}}$$

In assembly of Photons, $\underline{\mu = 0}$

$$f(\epsilon_i) = \frac{1}{e^{\epsilon_i/kT} - 1}$$

$$f(\nu) = \frac{1}{e^{h\nu/kT} - 1}$$

$\mu = 0$ for $T < T_B$ and Photons

For Photon $g(\epsilon)\, d\epsilon = g(\nu)\, d\nu$

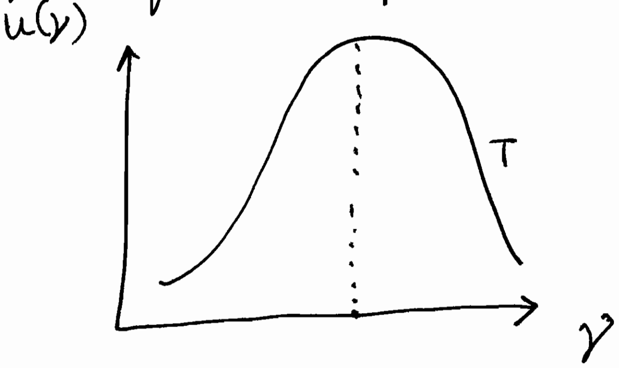
$$g(p)\, dp = \frac{d^3r\, d^3p}{h^3}$$

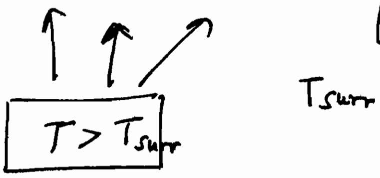
Blackbody Radiation

Planck's Radiation Formula :

$$u(\nu)\, d\nu = \frac{8\pi h \nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}$$

Energy density radiated in between frequency ν and $(\nu + d\nu)$ at equilibrium Temp 'T'





If heat transfer w/o heating the intervening medium : Radiation

BlackBody : Body at higher Temperature, able to radiate out heat.

$\underline{E_{radiated} \text{ per unit volume of blackbody}} = \underline{\text{Energy density}}$

As T ↑, colour of radiation shifts from Red to Blue.

$$\frac{E(\nu)\, d\nu}{V}$$

3 postulates of Planck's Quantum Theory

→ Atoms of Blackbody behave like oscillating particles.

① They radiate energy, not continuously, but discretely in quantum of energies.

EM quanta : Photons

Solid Body : Elastic waves : Phonons

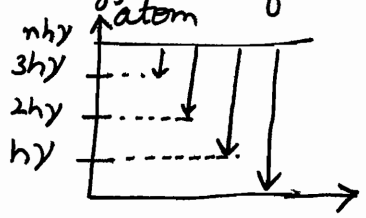
② $E_{\substack{radiation\\quanta}} \propto \nu$

$E_{\substack{radiated\\or}} = h\nu$ h : Planck's const.

$E_{absorbed}$

③ $E_{\substack{emission\\or\\absorption}} = nh\nu$ $n = 1, 2, 3, \ldots$

Energy levels of atom



⇒ energy levels in an atom are always discrete

→ Blackbody radiation chamber emits photons of energy $h\nu$.

$$E = \sum \epsilon_i \, dn_i = \int \epsilon \, dn$$

$$= \int h\nu \, dn$$

dn will come from BE distribution due to Photons being bosons.

$$= \int h\nu \; f(\epsilon) \, g(\epsilon) \, d\epsilon$$

$$= \int h\nu \; \frac{1}{e^{\left(\frac{h\nu}{kT}\right)} - 1} \; g(\nu) \, d\nu$$

To find $g(\nu) \, d\nu$:

$$g(p) \, d(p) = \frac{d^3r \, d^3p}{h^3}$$

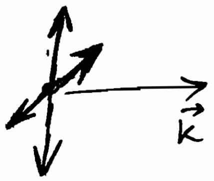
$$= \frac{V}{h^3} \cdot 4\pi p^2 \, dp$$

$$\boxed{\begin{array}{l} p = \frac{h\nu}{c} \\ dp = \frac{h}{c} \, d\nu \end{array}}$$

$$= \frac{4\pi V}{h^3} \frac{h^2}{c^2} \nu^2 \frac{h}{c} \, d\nu$$

$$= \frac{4\pi V}{c^3} \nu^2 \, d\nu = g(\nu) \, d\nu$$

But EM wave can have 2 modes of polarization



$$\Rightarrow \boxed{g(\nu) \, d\nu = \frac{8\pi V}{c^3} \nu^2 \, d\nu}$$

$$\Rightarrow \quad \underset{\substack{\uparrow \\ \text{No. of Photons emitted}}}{dN} = f(\epsilon)\, g(\epsilon)\, d\epsilon$$

$$= \frac{1}{e^{\left(\frac{h\nu}{kT}\right)} - 1} \left(\frac{8\pi V}{c^3}\right) \nu^2\, d\nu$$

$\boxed{\text{No. of photons}}$ at temp 'T' in any blackbody radiating EM radiation, per unit volume.

$$\left(\frac{N}{V}\right) = n = \int dn$$

$$= \int_0^\infty \left(\frac{8\pi}{c^3}\right) \frac{\nu^2\, d\nu}{(e^{h\nu/kT} - 1)}$$

Put $\frac{h\nu}{kT} = x$

$$d\nu = \left(\frac{kT}{h}\right) dx$$

$$n = \frac{8\pi}{c^3} \int_0^\infty \left(\frac{kT}{h}\right)^3 \frac{x^2\, dx}{(e^x - 1)}$$

$$= 8\pi \left(\frac{kT}{ch}\right)^3 \int \frac{x^2\, dx}{e^x - 1}$$

$$\Rightarrow \boxed{n \propto T^3}$$

⊛ No. of Photons in a cavity vary as T^3 while energy varies as T^4

$$dE = h\nu\, dN \Rightarrow u(\nu)\, d\nu = \frac{dE}{V} = \frac{8\pi h \nu^3\, d\nu}{c^3 \left[e^{\frac{h\nu}{kT}} - 1\right]}$$

$$\underset{\text{per unit volume}}{E} = \int h\nu \, dn$$

$$= \int h\nu \quad 8\pi \left(\frac{kT}{ch}\right)^3 \cdot \frac{x^2}{(e^x - 1)} \, dx$$

$$= \int 8\pi \frac{(kT)^4}{(ch)^3} \quad \frac{x^3}{(e^x - 1)} \, dx$$

We can also write

$$\underset{\text{per unit volume}}{dE \, d\nu} = 8\pi \frac{\cancel{(kT)^4}}{c\cancel{h^3}} \cdot \left(\frac{h\nu}{\cancel{kT}}\right)^3 \frac{1}{\left(e^{\frac{h\nu}{kT}} - 1\right)} \left(\frac{h}{\cancel{kT}}\right) d\nu$$

$$\Rightarrow \boxed{u(\nu)\, d\nu = \frac{8\pi h \nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}}$$

This formula that we got after solving G.P.s and A.G.P.s of M.B. distn is found directly with B.E. distn

Thermodynamics (14)

Criteria for Classical Statistics to hold good

① $\left(\frac{g_i}{n_i}\right) = e^{\alpha+\beta\epsilon_i} \pm 1$

$$\underbrace{\left(\frac{g_i}{n_i}\right) \mp 1}_{\text{quantum mechanical}} = \underbrace{e^{\alpha+\beta\epsilon_i}}_{\text{Classical}}$$

Whenever $\boxed{\left(\frac{g_i}{n_i}\right) >> 1}$, then quantum statistics (QS) converges to classical statistics (CS), i.e. indinguishable particles become distinguishable.

② • Volume occupied by 1 Particle = $\left(\frac{V}{N}\right)$

length available for 1-d motion (assume cube) = $\left(\frac{V}{N}\right)^{1/3}$

- Characteristic of a Particle: DeBroglie's Wavelength

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2mkT}}$$

We can also use $\frac{3}{2}kT$... No differente

↑ E for 1 degree of freedom = kT

- For distinguishable, there should be no overlap of particles,

$$\text{i.e. } \lambda = \frac{h}{\sqrt{2mkT}} < \left(\frac{V}{N}\right)^{1/3}$$

→ this is the usual case: 1 kinetic and 1 potential

Hence for this condition, Classical statistics is valid. Otherwise, we have to consider Quantum Effects.

$$\frac{h}{\sqrt{2mkT}} < \left(\frac{V}{N}\right)^{1/3}$$

$$\boxed{T > \left(\frac{N}{V}\right)^{\frac{2}{3}} \frac{h^2}{2mk}}$$

$$\left(\frac{N}{V}\right)^{1/3} \frac{h}{\sqrt{2mkT}} < 1$$

$$n^{1/3} \frac{h}{\sqrt{2mkT}} < 1$$

$$\left[\frac{n}{T^{3/2}}\right] \frac{h^3}{(2mk)^{3/2}} < 1$$

i.e. $\boxed{\frac{n}{T^{3/2}} \left(\frac{h^2}{2mk}\right)^{3/2} < 1}$ Region of validity of Classical Statistics

Specific Heat of Solids

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \underset{\substack{\uparrow \\ 0}}{\left(\frac{\partial V}{\partial T}\right)_P}$$

(for solids)

$$\Rightarrow C_p = C_v$$

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

① Dulong-Petit law

For ideal gas, 1 gm-Mole

$$E = N * f * \frac{1}{2} kT$$

$$= \frac{f}{2} * R * T$$

$$\Rightarrow \boxed{C_V = \frac{f R}{2}}$$

[independent of Temperature for ideal gas]

(*) dulong and petit's laws is experimentally valid at room temperature i.e. at room temperature all solids have $C_v \simeq 25 \ J \ mol^{-1} k^{-1}$

Dulong Petit (1870) : Classical
Eistein Theory (1907) } : Quantum
Debye Theory (1910) }

For solids, $E(T) = ?$

For solid to be solid, every molecule is bound to the solid even while moving/oscillating.

And at any Temp T, molecules are in motion

⇒ Molecules are under elastic force.

This elastic force is responsible for inter molecular forces.

For 1 particle, $E = \frac{1}{2} m\dot{x}^2 + \frac{1}{2} kx^2$ [for 1-d motion]

It is classical energy, as for any x we can have any E, thus E is continuous.

$$= \frac{1}{2} kT + \frac{1}{2} kT \quad \text{(equipartition of energy)}$$

$$= kT$$

(*) Now we can consider each particle to be composed of 3 oscillators vibrating in all 3 directions.

[redacted], $\Rightarrow E = 3kT$

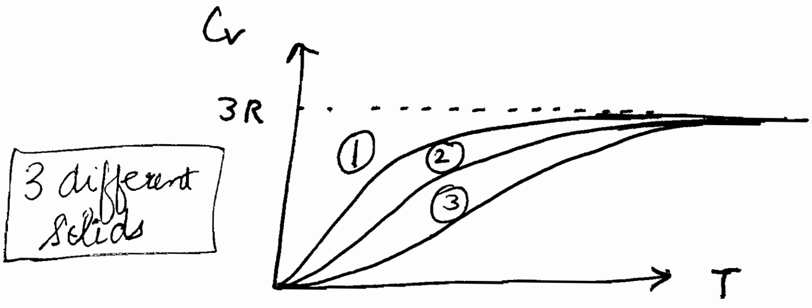
$$E_{Total} = N * 3kT = 3RT \Rightarrow \boxed{C_V = 3R}$$

dulong & petit formula

② Einstein Theory

- Dulong & Petit formula valid for high Temperatures.
(∵ law of equipartition is valid only for higher temperatures)

But we have seen that Cv varies with Temperature



No one was able to interpret these graphs upto 30 years till 1907.

By applying Planck's Quantum Theory, Eistein was able to explain this variation.

Minimum energy which an atom can have is Phonon.

Its vibrational energy.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$E \propto \nu$$

$$E = h\nu$$

Note that elastic waves are not transverse waves.

① Eistein said that all molecules are vibrating with same frequency. This frequency is characteristic of solid.

② Each molecule has 3 degrees of freedom

③ Energy emission and absorbtion is in multiples of $h\nu$

④ Planck gave avg. Energy of 1 molecule per degree of freedom

$$\boxed{\langle E \rangle = \frac{h\nu}{e^{\left(\frac{h\nu}{kT}\right)} - 1}}$$

(Proof of this @ end of copy)

For 1 gm mole,

$$E = N * 3 * \underbrace{\left(\frac{h\nu}{e^{\left(\frac{h\nu}{kT}\right)} - 1}\right)}$$

it was (kT) in classical statistics

$\langle E \rangle$: average energy of a molecule using Planck's Quantum Theory. Also called average energy of Planck Oscillator.

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3N\cancel{h}\nu\left[\frac{+1}{\left(e^{\frac{h\nu}{kT}}-1\right)^2} e^{h\nu/kT}\left(\frac{h\cancel{\nu}}{k\cancel{T}}\right)\frac{1}{T^2}\right]$$

$$= 3Nk\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{\left(e^{\frac{h\nu}{kT}}-1\right)^2}$$

$$\boxed{C_v = 3R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{(h\nu/kT)}}{\left[e^{(h\nu/kT)}-1\right]^2}}$$

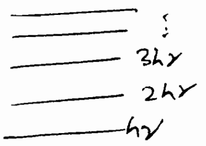
$\left(\frac{h\nu}{k}\right) = \theta_E$: eisteins Temperature

ν = characteristic frequency.

$\left(\frac{\theta_E}{T}\right)$: reduced Temperature

⊙ do not think too much frequency is same

these are overtones of same frequency.

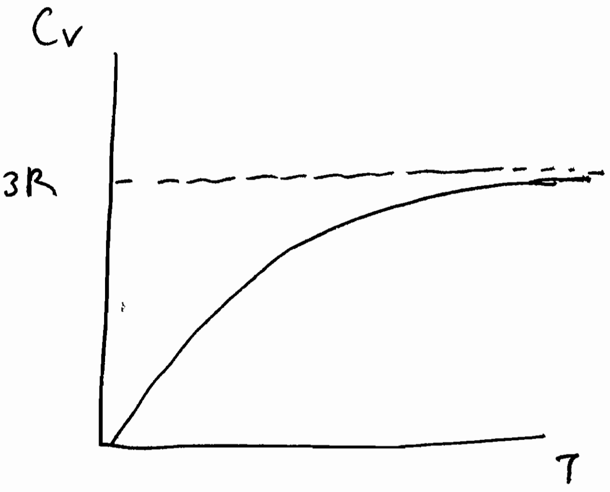


something like $\left(n+\frac{1}{2}\right)\hbar\omega$

$$\Rightarrow \quad \boxed{C_v = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{(\theta_E/T)}}{\left[e^{(\theta_E/T)}-1\right]^2}}$$

Specific Heat of solid, at given Temperature T, is given be Einstein Formula.

where R is (Nk) where k is _, N is _
θ_E is $(h\nu/k)$ where h is _, ν is _, k is _
T is temperature



Shortcoming : ① It does not explain observed C_v at very lower temperatures.
② How to know θ_E ??

At higher temperatures, $\frac{\theta_E}{T}$ is small

$$\text{s.t.} \quad e^{\frac{\theta_E}{T}} = 1 + \left(\frac{\theta_E}{T}\right)$$

$$\Rightarrow \quad C_v = 3R \cancel{\left(\frac{\theta_E}{T}\right)^2} \cdot \frac{\left(1+\frac{\theta_E}{T}\right)}{\left[\cancel{1+\frac{\theta_E}{T}-1}\right]^2} \approx 3R$$

As $T \to 0$ $\quad \frac{\theta_E}{T}$ is large

$$e^{\theta_E/T} >> 1$$

$$\Rightarrow C_v = 3R \frac{\left(\frac{\theta_E}{T}\right)^2}{e^{\left(\frac{\theta_E}{T}\right)}} = \frac{3R\left(\frac{\theta_E}{T}\right)^2}{1 + \left(\frac{\theta_E}{T}\right) + \frac{1}{\lfloor\underline{2}}\left(\frac{\theta_E}{T}\right)^2 + \frac{1}{\lfloor\underline{3}}\left(\frac{\theta_E}{T}\right)^3}$$

$$= \frac{3R}{\frac{1}{\left(\frac{\theta_E}{R}\right)^2} + \frac{1}{\left(\frac{\theta_E}{R}\right)} + \frac{1}{\lfloor\underline{2}} + \frac{1}{\lfloor\underline{3}}\left(\frac{\theta_E}{T}\right) + \cdots}$$

$$\approx \frac{3R}{\cancel{\frac{1}{\lfloor\underline{2}}} + \frac{1}{\lfloor\underline{3}}\left(\frac{\theta_E}{T}\right) + \cdots} \longrightarrow \frac{3R}{\infty} \longrightarrow 0$$

This is explained satisfactorily.

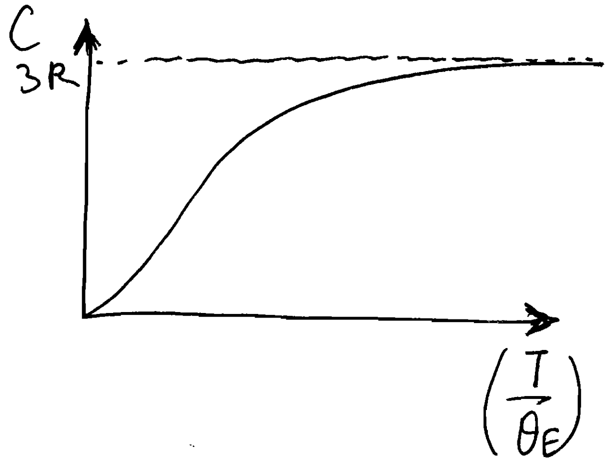
Method of determination of characteristic frequency of solids

Einstein gave an innovative method to determine ν_E.

Method of Curve Fitting

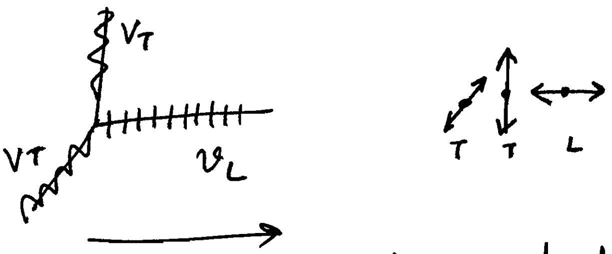
Here the shortcoming is Arbitrary fixation of ν_E without any empirical measure.

i.e. Plot empirically the variation of C_v
Now fix the Plot of C_v as given by Eistein's Formula upon the above Plot and find ν for the material.



③ Debye's Theory of Specific Heat of Solids

- ✓ All molecules are not vibrating with same [redacted]. frequency. They are vibrating forming a discrete frequency spectrum. $(\nu_1, \nu_2, \ldots \nu_m)$
- ✓ Vibrations of molecules are said to form elastic waves. Elastic Waves are longitudinal & transverse. Minimum quanta $= h\nu$
- ✓ Total modes of vibrations of solids are limited in number $= 3N$



direction of wave propagation

Modes $g(p)\,dp = \frac{V}{h^3}\,4\pi p^2\,dp$ $\quad p = \frac{h\nu}{v}$

⊛ Momentum of a wave $= \frac{h}{\lambda}$ $= \left(\frac{h\nu}{v}\right)$

$$\frac{V}{h^3} \cdot 4\pi \frac{h^2}{v^2}\cdot\frac{h}{v} \; \nu^2 d\nu$$

$$g(\nu)d\nu = V \frac{4\pi \nu^2 d\nu}{v^3}$$

⊛ No. of molecules vibrating in frequence range ν and $\nu + d\nu$ is

$dn = f(\nu)\, g(\nu)\, d\nu$

Assume $f(\nu) = 1$

(like we assume $g(\nu) = 1$ in equipartition proof)

(b'coz we are finding no. of states)

$\Rightarrow dn = g(\nu)\, d\nu \Rightarrow 3N = \int_0^{\nu_m} g(\nu)\, d\nu$

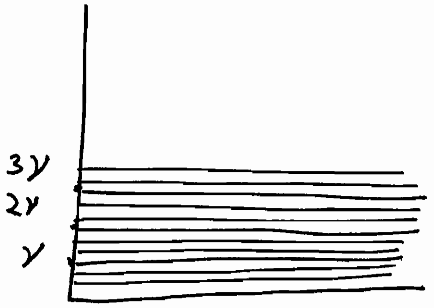
In a solid of volume V,

$$g(\nu)\, d\nu_{(\text{longitudinal})} = \frac{4V\pi \nu^2}{v_L^3} d\nu$$

$$g(\nu)\, d\nu_{(\text{transverse})} = \frac{8\pi V \nu^2}{v_T^3} d\nu$$

Total modes of vibration of solid in volume V in frequency range ν and $\nu + d\nu$

~~Total Modes~~ $= 4\pi V \nu^2 \left[\frac{1}{v_L^3} + \frac{2}{v_T^3} \right] d\nu$



$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Althought it was conceptualized discrete mode, for simpler analysis we treat them as continuous from (0 to ν_m)

$$4\pi V \int \nu^2 \left(\frac{1}{V_L^3} + \frac{2}{V_T^3} \right) d\nu = 3N$$

Since total number of Modes are finite, it puts a cap on maximum value of frequency in the spectrum.

$$4\pi V\left(\frac{1}{V_L^3}+\frac{2}{V_T^3}\right)\frac{\nu_m^3}{3} = 3N$$

$\nu_m : \nu_{max}$

$$\boxed{4\pi V\left(\frac{1}{V_L^3}+\frac{2}{V_T^3}\right) = \left[\frac{9N}{\nu_m^3}\right]}$$

Hence,

$$\boxed{\frac{9N}{\nu_m^3}\nu^2 d\nu \quad : \text{Modes of vibration between frequency } \nu \text{ and } \nu+d\nu}$$

dE : Energy of solid at equilibrium Temperature T with frequency b/w ν and $(\nu+d\nu)$

= (Modes of vibration) * (Energy of 1 mode)

$$= \frac{9N}{\nu_m^3}\nu^2 d\nu \underbrace{\frac{h\nu}{e^{h\nu/kT}-1}}$$

Note that this already contains $f(\epsilon)$ as well as ϵ

Hence no need of separate $f(\epsilon)$ ✓

$$\Rightarrow \boxed{dE = \left[\frac{9Nh}{\nu_m^3}\right]\frac{\nu^3 d\nu}{(e^{h\nu/kT}-1)}}$$

$$E = \int_0^{\nu_m}\frac{9Nh}{\nu_m^3}\frac{\nu^3 d\nu}{(e^{h\nu/kT}-1)}$$

Let $\frac{h\nu}{kT} = x \qquad \nu = \frac{kT}{h}x \qquad d\nu = \frac{kT}{h}dx$

$$E = \frac{9Nh}{\nu_m^3} \int_0^{\frac{h\nu_m}{kT}} \left(\frac{kT}{h}\right)^4 \frac{x^3\,dx}{e^x - 1}$$

$$= \frac{9Nh}{\nu_m^3} \left(\frac{kT}{h}\right)^4 \int_0^{\frac{h\nu_m}{kT}} \frac{x^3\,dx}{e^x - 1}$$

$$9Nk \left(\frac{k}{h\nu_m}\right)^3 T^4$$

$\frac{h\nu_m}{k} = \theta_D$: Debye Temperature

$$\boxed{E = 9R\,\frac{T^4}{\theta_D^3} \int_0^{(\theta_D/T)} \frac{x^3\,dx}{e^x - 1}}$$ ✓

where $\theta_D = \frac{h\nu_m}{k}$

$x = \left(\frac{h\nu}{kT}\right)$

Note that
हमने हर अगले
step में 1-1 चीज
change करते हैं !!

	[degree of freedom] < E_{av} >	C_v
Dulong & Petit	$3N \ast kT$	$\underline{\underline{3R}}$
Einstein	$3N \ast \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$	$3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)}$
Debye	$\frac{9N\nu^2 d\nu}{\nu_m^3} \ast \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$ although total modes are still 3N	$9R\left[4\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} - \left(\frac{\theta_D}{T}\right) \frac{1}{e^{(\theta_D/T)} - 1}\right]$

Thermodynamics (15)

12/01/2012

By debye's Theory,

$$E = 9R\frac{T^4}{\theta_D^3}\int_0^{h\gamma_m/kT}\frac{x^3\,dx}{e^x-1}$$

where $\theta_D = \frac{h\gamma_m}{k}$

$= $ Debye's Temp.

$x = \frac{h\gamma}{kT}$

$$C_v = \left(\frac{dE}{dT}\right)_v = \frac{9R}{\theta_D^3}\frac{d}{dT}\left[T^4\int_0^{h\gamma_m/kT}\left(\frac{x^3\,dx}{e^x-1}\right)\right]$$

$$= \frac{9R}{\theta_D^3}\left[4T^3\int_0^{\theta_D/T}\frac{x^3dx}{e^x-1} + T^4\frac{d}{dT}\int_0^{(\theta_D/T)}\frac{x^3\,dx}{e^x-1}\right]$$

Leibnitz Rule

$$\frac{d}{dt}\int_{u(t)}^{v(t)} f(x)\,dx = f(v)\left(\frac{dv}{dt}\right) - f(u)\left(\frac{du}{dt}\right)$$

Using this rule

$$\frac{d}{dT}\int_0^{(\theta_D/T)}\frac{x^3dx}{e^x-1} = \frac{(\theta_D/T)^3}{e^{\theta_D/T}-1}\cdot\left[-\frac{\theta_D}{T^2}\right]$$

$$= \frac{-\theta_D^4}{T^5(e^{\theta_D/T}-1)}$$

$$\Rightarrow C_v = \frac{9R}{\theta_D^3}\left[4T^3 \int_0^{\theta_D/T} \frac{x^3\,dx}{e^x-1} + T^4 \cdot \frac{-\theta_D^4}{T^5\left(e^{\theta_D/T}-1\right)} \right]$$

$$\boxed{C_V = 9R\left[4\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x-1}\,dx - \left(\frac{\theta_D}{T}\right) \frac{1}{e^{\theta_D/T}-1} \right]}$$

$\Uparrow$

This is "DEBYE SPECIFIC HEAT FORMULA"

Q4/24

	Einstein	Debye
①	const. ν	discret frequency spectrum
②	$\nu_1 = \nu_2 = \dots$	Definite upper bound $\nu_1, \nu_2 \dots \nu_m$
③	3 dof	No meaning of individual dof

At higher Temperature region : $T >> \theta_D$

$\Rightarrow \underline{\left(\frac{\theta_D}{T}\right) << 1}$

x is small

$\Rightarrow \underline{e^x \approx 1+x}$

$$C_v = 9R\left[4\left(\frac{T}{\theta_D}\right)^3 \int_0^{(\theta_D/T)} \frac{x^3}{x}\,dx - \frac{\theta_D}{T} \frac{1}{\left(\frac{\theta_D}{T}\right)}\right.$$

$$= 9R\left[4\left(\frac{T}{\theta_D}\right)^3 \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3 - 1\right]$$

$$= 9R . \left[\frac{4}{3} - 1\right]$$

$$\boxed{C_V = 3R}$$

At lower Temperature region $\quad T << \theta_D$

x is large

$\frac{\theta_D}{T} >> 1 \quad$ i.e. $\frac{\theta_D}{T} \rightarrow \infty$

$$C_V = 9R\left[4\left(\frac{T}{\theta_D}\right)^3 \int_0^\infty \frac{x^3\,dx}{e^x - 1} - \underset{\uparrow}{0}\right]$$

by expanding e^x

$$= 9R\left[4\left(\frac{T}{\theta_D}\right)^3 \int_0^\infty \frac{x^3\,dx}{e^x - 1}\right]$$

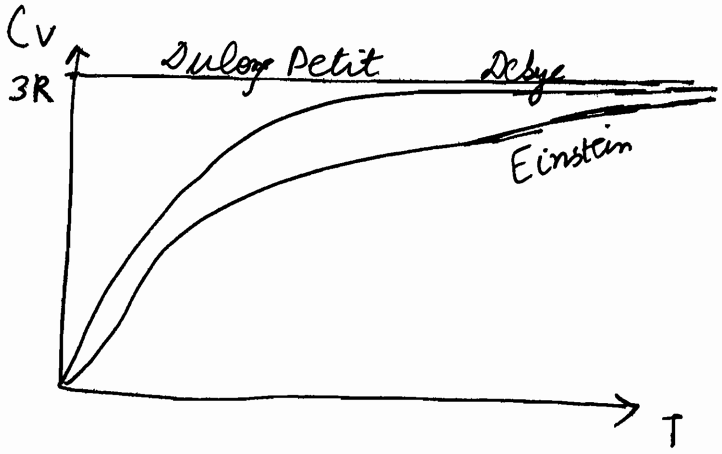
$$= \left[\frac{36R}{\theta_D^3} \int_0^\infty \frac{x^3}{e^x - 1}\,dx\right] T^3$$

→ also used in derivation of Stefan Boltzmann's law

$$\boxed{\int_0^\infty \frac{x^3}{e^x - 1}\,dx = \left(\frac{\pi^4}{15}\right)} \approx 6.5$$

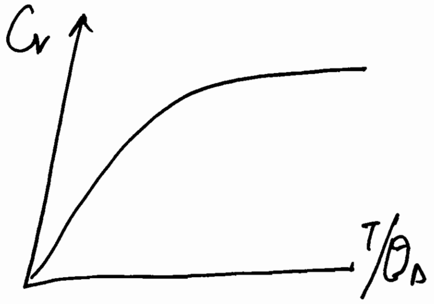
$$\boxed{C_V = A T^3}$$

where $A = \frac{36R}{\theta_D^3} \int_0^\infty \frac{x^3}{e^x - 1}\,dx$



Q5 | Tut 24

Debye Theory valid for isotropic solids



There are some variations in Anisotropic Solids.

Q|8 Corresponding States

2 solids are said to be in correspondence states if their reduced parameters are same, then then specific heat are also same.

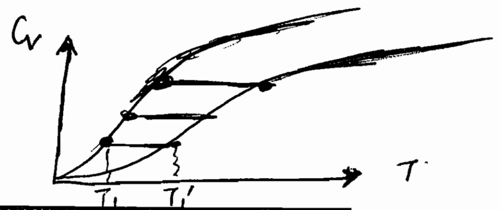
$$\frac{\theta_{D_1}}{T_1} = \frac{\theta_{D_2}}{T_2} \Rightarrow C_{v_1} = C_{v_2}$$: Debye's Theory

Similarly if,

$$\frac{\theta_{E_1}}{T_1} = \frac{\theta_{E_2}}{T_2} \Rightarrow C_{v_1} = C_{v_2}$$: Einstein's Theory

$$C_{v_1} = C_{v_2} \Rightarrow \frac{\theta_{E_1}}{T_1} = \frac{\theta_{E_2}}{T_1'}$$

$$T_1' = T_1\left(\frac{\theta_{E_2}}{\theta_{E_1}}\right)$$



Tut 26/10

$$n_i = g_i \, e^{-\alpha - \beta \epsilon_i}$$

$$\langle E \rangle = \frac{3}{2} kT = \frac{\int \epsilon_i \, dn_i}{\int dn_i}$$

$$= \frac{\int \epsilon \, g(\epsilon) \, e^{-\beta \epsilon} \, d\epsilon}{\int g(\epsilon) \, e^{-\beta \epsilon} \, d\epsilon}$$

Use $\epsilon = a q^2$ $\qquad g(\epsilon) = c \, \epsilon^{1/2}$

Bose-Einstein Condensation

In Bose-Einstein Distribution,

$$\frac{n_i}{g_i} \geqslant 0 \Rightarrow e^{\frac{\epsilon - \mu}{kT}} \geqslant 1$$

$$\Rightarrow \frac{\epsilon - \mu}{kT} \geqslant 0$$

$$\Rightarrow \epsilon \geqslant \mu \Rightarrow \boxed{\mu \leq 0}$$ as ϵ can be 0 also

$$\frac{n(\epsilon)}{g(\epsilon)} = f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/kT} - 1} = \frac{1}{\left(\frac{1}{A}\right) e^{\epsilon/kT} - 1} \quad ①$$

$$\boxed{\text{Always : } \mu \leq 0}$$

$$\boxed{A = e^{\mu/kT}}$$

[Fugacity of Assembly of Bosons]

① is valid for all ϵ,

Putting $\epsilon = 0$

$$\frac{n(\epsilon)}{g(\epsilon)} = \frac{1}{\left(\frac{1}{A}\right) - 1}$$

$$\Rightarrow \frac{1}{A} \geqslant 1 \Rightarrow \boxed{A \leqslant 1}$$

$$\ln A \leqslant \ln 1$$

$$\Rightarrow \frac{\mu}{kT} \leqslant 0$$

$$\Rightarrow \boxed{\mu \leqslant 0}$$ ✓

✓ Bose Einstein characteristics are acquired when T is close to 0

we are cooling down Boson.

A stage is reached when μ becomes 0.

Number of Bosons in ground state (minimum energy state)

$$n(\epsilon)\, d\epsilon = g(\epsilon)\, f(\epsilon)\, d\epsilon$$

$$N = N_0 + \frac{2\pi V}{h^3} \cdot (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{e^{(\epsilon-\mu)/kT} - 1}\, d\epsilon$$

A stage is reached at $T = T_B$, $\mu = 0$!! [strongly degenerate gas]

$$N = N_0 + \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{e^{\epsilon/kT} - 1}$$

$$= \left[\frac{2\pi V}{h^3} \cdot (2m)^{3/2}\right] (kT_B)^{3/2} \underbrace{\int_0^\infty \frac{x^{1/2}\, dx}{e^x - 1}}_{\Gamma\left(\frac{3}{2}\right)\ \zeta(3/2)}$$

↑ Zeta

$$N = N_0 + \underbrace{\left[\frac{2.612}{h^3} (2m\pi)^{\frac{3}{2}} V\right]}_{\text{let this be } \frac{N}{(KT_B)^{3/2}}} (KT)^{3/2}$$

$\frac{1}{2}\sqrt{\pi}$, 2.612.

① We can write

$$\Rightarrow (kT_B)^{3/2} = \frac{h^3\, 4\pi^2}{(2m)^{3/2}} \left(\frac{N}{V}\right) \cdot \frac{1}{\Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right)}$$

$\Longleftarrow T \geq T_B$, $N_0 = 0$ $\Rightarrow$ $\underbrace{\left[\frac{2.612 (2\pi m)^{3/2}}{h^3} V\right]}_{\alpha} (kT_B)^{3/2} = N$

$$\alpha = \frac{N}{(KT_B)^{3/2}}$$

$$(kT_B)^{3/2} = \left(\frac{\hbar^2}{2m}\right)^{3/2} 4\pi^2 n \, \frac{1}{\Gamma(\frac{3}{2})\,\zeta(\frac{3}{2})}$$

$$\Rightarrow \boxed{T_B = \frac{2\pi\hbar^2}{mk_B}\left[\frac{n}{\zeta(\frac{3}{2})}\right]^{2/3}}$$

$$\Rightarrow kT_B = \left(\frac{\hbar^2}{2m}\right)(4\pi^2 n)^{2/3}\left(\frac{1}{\Gamma(\frac{3}{2})\,\zeta(\frac{3}{2})}\right)^{2/3}$$

$$\Rightarrow \boxed{T_B \propto n^{2/3}}$$ ..... Bose Einstein Temperature

Characteristic temperature of Bosons when $\mu = 0$.

② We can also write ✓

$$\frac{N}{(kT_B)^{3/2}} = \underbrace{\frac{2\pi V}{h^3}(2m)^{3/2}}\,\Gamma(\tfrac{3}{2})\,\zeta(\tfrac{3}{2})$$

nothing but written the same thing.....

$$\Rightarrow \boxed{N_{ex} = \left[\Gamma(\tfrac{3}{2})\,\zeta(\tfrac{3}{2}) \quad \int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\epsilon/kT}-1}\right](kT)^{3/2}}$$

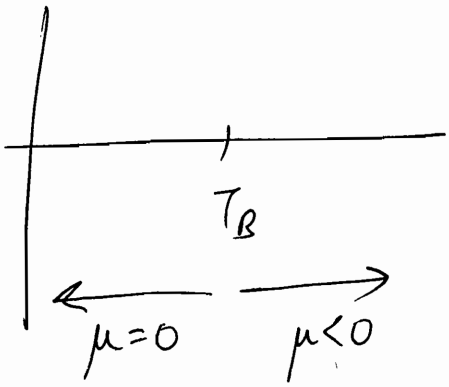
Note that this does not take into account energy at ground state.

(*) [It does not matter in FD b'coz in F.D. only some particles can come in ground state.]

$$\Rightarrow N = N_g + \frac{N}{(kT_B)^{3/2}\,\Gamma(\frac{3}{2})\,\zeta(\frac{3}{2})} \int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\epsilon/kT}-1}$$

$\underline{\mu=0}$

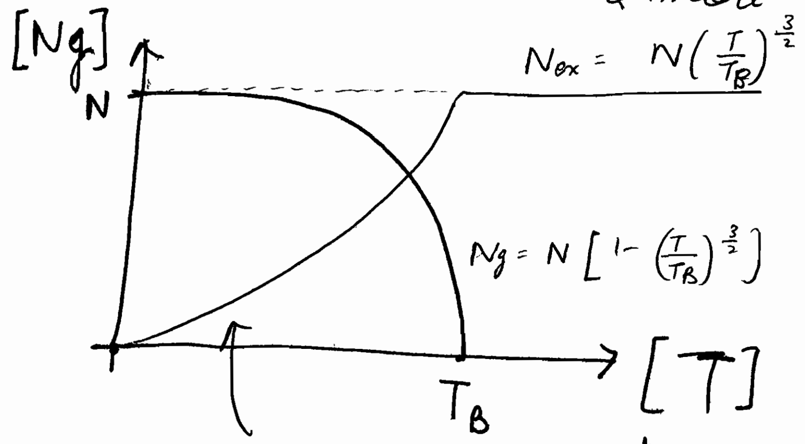
$$= N_g + \frac{N}{(kT_B)^{3/2}}\,(kT)^{3/2}$$



$$\Rightarrow N_g = N - N\left[\frac{T}{T_B}\right]^{3/2}$$

$$\Rightarrow \boxed{N_g = N\left(1-\left(\frac{T}{T_B}\right)^{3/2}\right)}$$

→ Refer to more theory @ end of lecture & more maths from end of copy



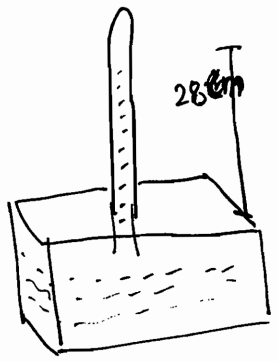
As Temp falls below T_B, population increases rapidly in ground state

At T=0, all particles will be in ground state.

Bose-Einstein Condensate

⇑

5th state of matter



It is responsible for abnormal properties exhibited by ^4_2He when it is cooled below $T_B = 2.17$ K. Below T_B, it is called Helium 2. It is anamolous fluid. It becomes superfluid i.e. $\eta = 0$. No opposition to flow.

Fountain Effect in Capillary Tubes immersed in bath of Helium 2.

VIRIAL THEOREM OF CLASIUS

$$\boxed{\overline{T} = -\frac{1}{2}\sum \vec{F_i}\cdot\vec{r_i}}$$

Or

$$\boxed{2\overline{T} + \overline{V} = 0}$$

where $\overline{V} = \sum \vec{F_i}\cdot\vec{r_i}$
= "Virial"

where $\vec{F_i} = m_i \frac{d^2 r_i}{dt^2} = m_i \frac{dv_i}{dt} = \left(\frac{dp_i}{dt}\right)$

Derivation

Let $\phi = \sum \vec{p_i}\cdot\vec{r_i}$ [illegible] } ϕ : mathematical construct

ϕ is either periodic or aperiodic

If Periodic, $\phi(\tau) = \phi(0)$

If aperiodic, τ is very large.

$$\frac{d\phi}{dt} = \sum \vec{p_i}\cdot\frac{dr_i}{dt} + \sum \frac{dp_i}{dt}\cdot\vec{r_i}$$

$$\left(\frac{d\phi}{dt}\right) = 2T + \sum \vec{F_i}\cdot\vec{r_i}$$

Taking Time average,

$$\frac{\int_0^\tau \left(\frac{d\phi}{dt}\right) dt}{\tau} = 2\overline{T} + \overline{\sum \vec{F_i}\cdot\vec{r_i}}$$

$$\frac{\phi(\tau)-\phi(0)}{\tau} = 2\overline{T} + \overline{\sum \vec{F_i}\cdot\vec{r_i}}.$$

$$= 2\overline{T} + \overline{V}$$

V: Virial

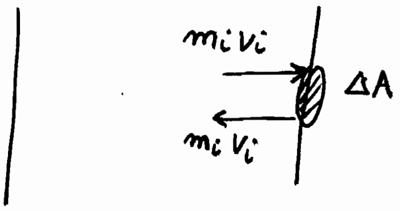
L.H.S. = 0 whether ϕ is periodic or aperiodic

$$\checkmark\ \underline{(\text{num}=0)} \qquad \checkmark\ \underline{(\text{den}=\infty)}$$

$$\Rightarrow\ 2\overline{T} + V = 0 \qquad V = \overline{\sum F_i \cdot r_i}$$

Application

Pressure exerted by molecules of an ideal gas



$$F_i = \frac{2 m_i \vec{v_i}}{\tau} = P_i \Delta\vec{A}$$

$$\mathbb{V} = +\frac{1}{2}\sum P_i \Delta\vec{A}\cdot\vec{r} = +\frac{P}{2}\sum \Delta\vec{A}\cdot\vec{r}$$

$$= +\frac{P}{2}\int_S d\vec{A}\cdot\vec{r}$$

$$\boxed{\nabla\cdot\vec{r} = 3}$$

$$= +\frac{P}{2}\int_V \nabla\cdot\vec{r}\, dV = +\frac{P}{2}\int 3\, dV = +\frac{3PV}{2}$$

$$T = -\frac{3}{2} PV$$

Also, we can use

$$\bar{T} = \frac{3}{2} NkT$$

$$\Rightarrow \boxed{PV = RT}$$

Time Avg. : $\bar{T} = \sum \frac{1}{2} m_i (v_i^2)$

$$= \frac{1}{2} m . N \overline{v_i^2}$$

$$\Rightarrow \frac{3}{2} PV = \frac{1}{2} m N \overline{v_i^2}$$

$$\Rightarrow \boxed{PV = \frac{1}{3} m N \overline{v_i^2}}$$

Bose Einstein Condensate

BEC is a state of matter of dilute gas of weakly interacting bosons cooled to temperatures very near absolute zero. Under such conditions, very large fraction of bosons occupy the lowest quantum state at which point quantum effects become apparent on macroscopic scale.

This transition occurs below a critical temperature, which for a uniform non interacting boson gas is given by

$$T_B = \frac{2\pi \hbar^2}{m k_B} \left[\frac{n}{\zeta\left(\frac{3}{2}\right)} \right]^{\frac{2}{3}} \simeq 3.31 \left(\frac{\hbar^2 n^{2/3}}{m k_B} \right)$$

n : particle density
m : mass per boson
$\hbar$: reduced Planck Const.
k_B : Boltzmann Const.
$\zeta\left(\frac{3}{2}\right)$: Reimann Zeta Function $\simeq 2.61$

Two examples of materials containing BECs are super conductors and superfluids.

No resistance in super conductor.
No viscosity in fluid. eg. He

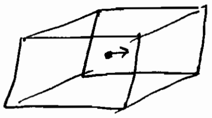
Also refer to back page !!

KINETIC THEORY OF GASES

Basic Postulates:

- ✓ Gas consists of very small particles i.e. total volume of particles $<< V_{container}$
  i.e. avg. distance between particles >> size of particles
- ✓ These particles have same mass.
- ✓ They are in const., random motion, colliding elastically with walls of container, without interacting with each other
- ✓ N (no. of molecules) is so large that statistical treatment can be applied
- ✓ $K.E._{avg}$ depends only on Temperature.

Derivations



Pressure is explained by kinetic theory by assuming it to arise from forces exerted by molecules impacting on walls of container.

$$\Delta p_x = 2mv_x \qquad \Delta t = \left(\frac{2L}{v_x}\right) \qquad \Rightarrow F = \frac{\Delta p}{\Delta t} = \left(\frac{mv_x^2}{L}\right)$$

$$F_{Total} = \frac{N m \overline{v_x^2}}{L} = \frac{Nm}{L}\overline{v_x^2}$$

Since particles are assumed to move randomly,

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \left(\frac{\overline{v^2}}{3}\right)$$

$$\Rightarrow F = \frac{Nm}{L}\frac{\overline{v^2}}{3}$$

$$P = \frac{Nm}{L^3}\left(\frac{\overline{v^2}}{3}\right) = \frac{n m \overline{v^2}}{3}$$

where n is the number density of gas

$$\boxed{P = \frac{1}{3} m n \overline{v^2}}$$

From ideal gas law

$$PV = N k_B T$$

$$\Rightarrow \quad PV = \frac{N m \overline{v^2}}{3} = N k_B T$$

$$\Rightarrow \quad T = \frac{m \overline{v^2}}{3 k_B} = \frac{m v_{rms}^2}{3 k_B}$$

From this,

$$\boxed{(k.E)_{molecule} = \frac{1}{2} m v_{rms}^2 = \frac{1}{2} . 3 k_B T = \frac{3}{2} k T}$$

$$\boxed{(k.E.)_{system} = \frac{1}{2} N m v_{rms}^2 = \frac{1}{2} . 3 N k_B T = \frac{3}{2} R T}$$

$$\text{Also} \quad PV = N k_B . \frac{2}{3} \frac{k.E.}{N k_B} = \frac{2}{3} k.E.$$

$$\Rightarrow \quad \boxed{PV = \frac{2}{3} kE}$$

---

3 Tds equations

$$S = f(T,V): T\,dS = C_v\, dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$S = f(T,P): T\,dS = C_p\, dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$S = f(P,V): T\,dS = C_v . \left(\frac{\partial T}{\partial P}\right)_V . dP + C_p . \left(\frac{\partial T}{\partial V}\right)_P dV$$

Mathematics

- All thermodynamic quantities can be divided into 2 groups : functions of state & functions of a process.
  (S, U etc.) (Q, W)

Only functions of state are path or process independent and hence ONLY FOR THEM

$$\left.\begin{array}{l} \text{if} \quad dz = M\,dx + N\,dy \\ \Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \end{array}\right\} \text{Its called Total Differential}$$

IT IS NOT VALID FOR PATH DEPENDENT VARIABLES.

- If $dz = 0$ i.e. $z =$ const.

$$\Rightarrow \left(\frac{\partial z}{\partial x}\right)_y \cdot dx + \left(\frac{\partial z}{\partial y}\right)_x \cdot dy = dz = 0 \qquad \text{—} ①$$

$$\Rightarrow \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = 0$$

$$\Rightarrow \boxed{\left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z = 0}$$

$$\Rightarrow 1 + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = 0$$

$$\Rightarrow \boxed{\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = -1}$$

Or

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1} \longleftarrow \text{cyclic}$$

Differentiating ① with respect to x keeping a Property OF STATE λ Const.

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

We get,

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_\lambda = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_\lambda}$$

It allows us to get relation between partial derivatives of one & the same quantity calculated, however, on the basis of different const. parameters, eg. C_p and C_v.

So basically if we require $\left(\frac{\partial X}{\partial a}\right)_{p_1} - \left(\frac{\partial X}{\partial a}\right)_{p_2}$, write $X = f(a, p_1)$ or $X = f(a, p_2)$

★ Global Warming does not violate the 2nd law of thermodynamics. Some people suggest that as Earth is souce of heat and CO_2 is thus colder, it cannot make the Earth hotter.

Note that Global Warming is not that Earth surface is getting hotter. Its just that heat is being trapped in CO_2 and its loss to outer space is slowed down.

Its similar to wearing a blanket. Body radiates heat. Blanket prevents heat getting lost. Its not that blanket transfers heat from outside to body.

TRANSPORT PHENOMENON

- Bad Pointer.

The Proofs done in class are Perfect.

Revise the Proof

Law of Equipartition of Energy

Energy of a particle is in general a function of a number of different parameters. These might be velocity components, amplitude of oscillation etc. Each of these [redacted] parameters is called a degree of freedom.

Let z reepresent any such parameters and $E(z)$ represent the energy associated with that parameter.

If energy can be represent as a continuous function of parameter $E(z) = az^2$, then MB distn lead to result that avg. no. of particles within a range Δz of the parameter is given by

$$n(z)\, dz = A\, e^{-\left(\frac{E(z)}{kT}\right)}\, dz \qquad \left[\text{assuming } g(z) = \text{const.}\right]$$

eg. velocity components.

$$N = \int n(z)\, dz$$

$$= \int A\, e^{-\frac{E(z)}{kT}}\, dz = \int A\, e^{-\frac{az^2}{kT}}\, dz$$

$$\text{Total Energy } E = \int E(z)\, dN = \int A\, az^2\, e^{-\frac{az^2}{kT}}\, dz$$

$$\Rightarrow \overline{E(z)} = \frac{E(z)}{N} = \frac{\int A\, az^2\, e^{-\frac{az^2}{kT}}\, dz}{\int A\, e^{-\frac{az^2}{kT}}\, dz} = \frac{1}{2} kT$$

That is, for every degree of freedom for which above conditions are fulfilled, the mean energy per particle, in an assembly in equilibrium at temp T, is $\left(\frac{kT}{2}\right)$

eg. $U(x) = \frac{1}{2}kx^2$

$E(v_x) = \frac{1}{2}mv_x^2$

① Notfulfilled for $E(y) = mgy$

② Not fulfilled for energies at quantum level that take discrete values and considering energy as a continuous function is erroneous. For eg. rotational motion.

Expansivity and Elasticity

⊙ $p = p(V, T)$

$$\Rightarrow dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V \cdot dT$$

We know $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$: Coefficient of volume expansion or expansivity

Also $K = -V\left(\frac{\partial P}{\partial V}\right)_T$ Isothermal Elasticity

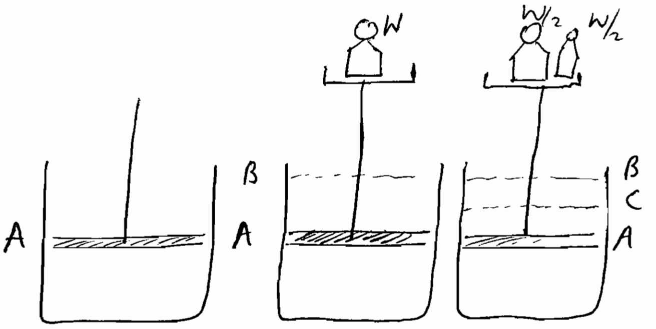
$$\Rightarrow dp = -\left(\frac{K}{V}\right)dV + \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p dT$$

$$= -\left(\frac{K}{V}\right)dV + \frac{K\alpha \cancel{V}}{\cancel{V}} dT$$

$$\boxed{dp = -\frac{K}{V}dV + K\alpha\, dT}$$

Q/ Reversible process is an ideal process & can never be achieved in practice. Explain

Ans Consider a gas in cylinder. We wish to change the volume of gas from V to 2V.



1st Way

Rapid Movement of piston from A to B.
This process is irreversible as all intermediate states are non equilibrium states.

2nd Way

Piston is spring loaded s.t. it remains at A when weight W is put on top and at once moves to B as soon as W is removed. But even now process is irreversible

3rd Way

Now we can place 2 weights ($\frac{W}{2}$ each). On removing 1 weight, intermediate equilibrium state C is reached.

So if use n weights ($\frac{W}{n}$ each), we can realize (n-1) equilibrium states between A and B. Thus if n is made very large ($n \to \infty$), we can have equilibrium states that do not differ much from each other.
This obviously is not practicable.

The problem of non-realizability of reversible process in thermodynamics is overcome by quasi-static process i.e. process is worked out very slowly.

Q1 A block of Copper whose expansivity is $48 \times 10^{-6}\ K^{-1}$ and isothermal elasticity is $1.30 \times 10^{11}\ Nm^{-2}$ is at atm. pressure and at a temp. of 0°C. Its temp. is raised to 10°C. Calculate final pressure when

(a) Volume is kept const.

(b) volume changes from 1000 cc. to 1000.1 c.c.

A1 let $p = p(V, T)$

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

Now given; $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = 48 \times 10^{-6}\ k^{-1}$

$$k_T = -V\left(\frac{\partial P}{\partial V}\right)_T = 1.3 \times 10^{11}\ N/m^2$$

$$\Rightarrow dp = -\frac{k_T}{V} dV + \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial p}\right)_T} dT$$

$$= -\frac{k_T}{V} dV + \alpha V \cdot \left(\frac{\partial p}{\partial V}\right)_T dT$$

$$= -\frac{k_T}{V} dV + \alpha V \frac{k_T}{V} dT$$

$$\Rightarrow \boxed{dp = -\frac{k_T}{V} dV + \alpha k_T\, dT}$$

(a) $dV = 0 \Rightarrow dp = \alpha k_T \cdot (10)$

$\Rightarrow p_2 = p_1 + \alpha k_T . 10 = 10^5 + 624 \times 10^5 = 625\ atm$

(b) $dV \neq 0 \Rightarrow dp = -\frac{1.3 \times 10^{11}}{1000\ \cancel{cc}} \times 0.1 + 625\ atm$

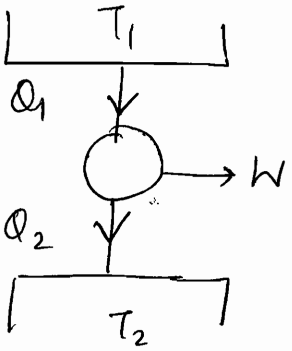
$= -130 + 624 = 494\ atm$

$\Rightarrow \boxed{p_2 = 495\ atm}$

When specimen is allowed to expand, Pressure is very less

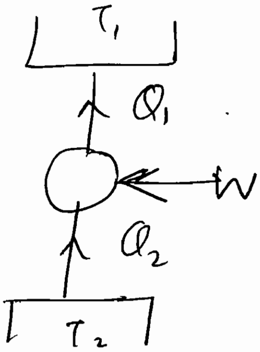
Q/ A carnot engine is Operated b/w ice point & steam point. (a) If engine receives 746 calories from hot reservoir in each cycle, how many calories does it reject to cold reservoir? (b) If engine is Operated as a referigerator and receives the same heat from cold reservoir, how many calories does it deliver to hot reservoir. (c) How much Work is done by engine in each case?

A/



Heat Engine

Fig (a)



Referigerator

Fig (b)

(a) Refer to Fig (a)

For carnot cycle, $1-\frac{Q_2}{Q_1} = 1-\frac{T_2}{T_1}$

$\Rightarrow 1-\frac{Q_2}{746} = 1-\frac{273}{373} \Rightarrow$ $Q_2 = 546$ calories

W = 200 cal

(b) Refer to Fig (b)

For Carnot referigerator, again $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$ (same formula holds as cycle is just reversed)

$\Rightarrow Q_1 = \frac{Q_2 \cdot T_1}{T_2} = \frac{746 \times 373}{273} = 1019$ calories

W = -273 cal

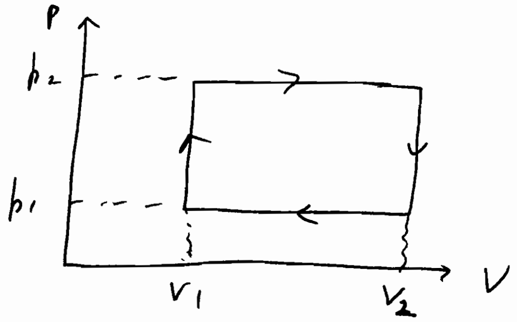
⊛

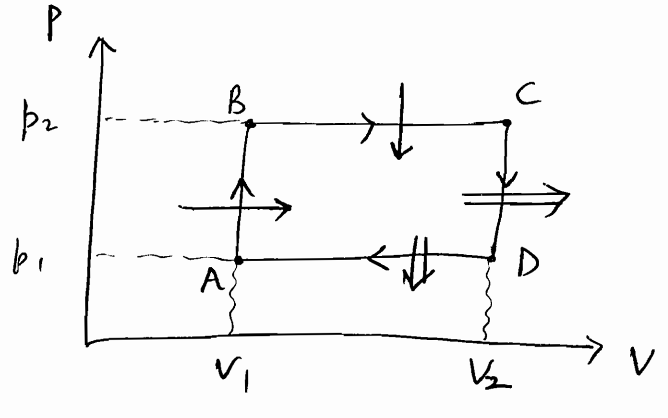
Note that in both cases, Q₁ is more

Q/ Calculate during the cycle

a) Work Done

b) η





A/

a) Work Done = Area of PV curve = $(p_2-p_1)(V_2-V_1)$

b) $\eta = \dfrac{W}{Q_{AB}+Q_{BC}}$

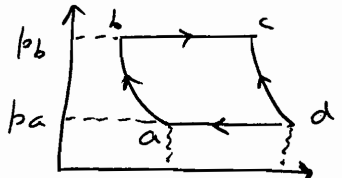
$Q_{AB} = C_V\, dT = \dfrac{C_V}{R}(p_2-p_1)\,V_1$

$Q_{BC} = C_P\, dT = \dfrac{C_P}{R}(V_2-V_1)\,P_2$

$$\Rightarrow \eta = \frac{(p_2-p_1)(V_2-V_1)}{\left(\frac{1}{\gamma-1}\right)(p_2-p_1)V_1 + \left(\frac{\gamma}{\gamma-1}\right)(V_2-V_1)\,p_2}$$

$$= \frac{\gamma-1}{\left(\frac{V_1}{V_2-V_1}\right)+\left(\frac{\gamma p_2}{p_2-p_1}\right)}$$

Q/ Calculate η in terms of (p_a, p_b, γ)



A/ $\eta = 1 - \dfrac{Q_{da}}{Q_{BC}} = 1 - \left(\dfrac{T_D-T_A}{T_C-T_B}\right)$

$\left(\dfrac{T_D}{T_C}\right) = \left(\dfrac{P_a}{P_b}\right)^{\frac{\gamma-1}{\gamma}}$; $\left(\dfrac{T_A}{T_B}\right) = \left(\dfrac{P_a}{P_b}\right)^{\frac{\gamma-1}{\gamma}}$ $\Rightarrow$ $\boxed{\eta = 1 - \left(\dfrac{P_a}{P_b}\right)^{\frac{\gamma-1}{\gamma}}}$

Q/ An ideal gas through a cycle consisting of
a) isochoric, adiabatic and isothermal lines.
When isothermal occurs at minimum Temperature, calculate the η if absolute Temperature varies n fold within the cycle.

A/ By the given conditions, fig. 1 represents the appropriate cycle.

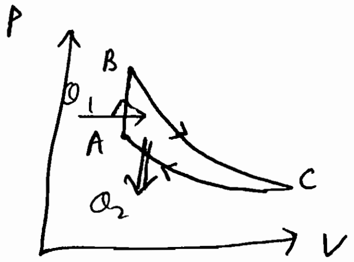


Fig 1

$$\eta = 1 - \frac{Q_2}{Q_1}$$

$$= 1 - \frac{RT\ln\left(\frac{V_C}{V_A}\right)}{C_V.(nT-T)}$$

$$= 1 - \frac{(\gamma-1)}{(n-1)}\ln\left(\frac{V_C}{V_A}\right) = 1 - \frac{(\gamma-1)}{(n-1)}\ln(n)^{\frac{1}{\gamma-1}} = 1 - \frac{\ln n}{(n-1}$$

$$\left[T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1} \Rightarrow nT \cdot V_A^{\gamma-1} = T V_C^{\gamma-1} \Rightarrow \left(\frac{V_C}{V_A}\right) = n^{\frac{1}{\gamma-1}}\right]$$

Q/ Calculate pressure of air in vessel being evacuated, as a function of evacuation time t. Volume of vessel is V and initial pressure is p_0. Process is assumed to be isothermal and evacuation rate (i.e. Volume being evacuated per second) is C. C is independent of Pressure.

A/ Now the numbers of molecules are changing.

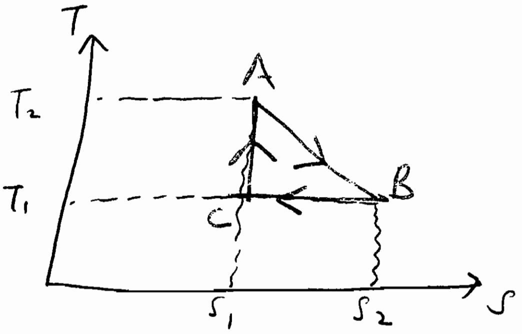
$$PV = nRT \Rightarrow P\cancel{dV} + V\,dP = RT\,dn \Rightarrow V\,dP = RT\,d$$

Also $dn = -\frac{nC\,dt}{V}$

$$\Rightarrow V\,dP = -\frac{RT}{V}\,n\,C\,dt \Rightarrow \int\frac{dP}{P} = -\int\frac{C}{V}\,dt$$

$$\Rightarrow \ln\left(\frac{P}{P_0}\right) = -\frac{Ct}{V} \Rightarrow \boxed{P = P_0 e^{-\frac{Ct}{V}}}$$

Q/ Calculate Efficiency of the cycle



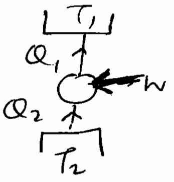
A/ AB $\rightarrow dQ_1 > 0$ as $TdS > 0$

BC $\rightarrow dQ_2 < 0$ as $TdS < 0$

CA $\rightarrow dQ = 0$: Adiabatic Process

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\left(\frac{1}{2}\right) \times (T_2 - T_1)(S_2 - S_1)}{\frac{1}{2} \times (T_2 + T_1)(S_2 - S_1) + T_1(S_2 - S_1)} = \left(\frac{T_2 - T_1}{T_2 + T_1}\right)$$

Q/ Prove Claussius Inequality for referigeration cycles.



A/ $\eta_{rev} \geq \eta_{irr} \Rightarrow \left(\frac{Q_2}{Q_1 - Q_2}\right)_{rev} \geq \left(\frac{Q_2}{Q_1 - Q_2}\right)_{irr.}$

$$\Rightarrow \left(\frac{1}{\frac{Q_1}{Q_2} - 1}\right)_{rev} \geq \left(\frac{1}{\frac{Q_1}{Q_2} - 1}\right)_{irr.} \Rightarrow \left(\frac{1}{\frac{T_1}{T_2} - 1}\right)_{rev} \geq \left(\frac{1}{\frac{Q_1}{Q_2} - 1}\right)_{irr}$$

$\Rightarrow$ (For same Temperature limits)

$$\Rightarrow \frac{Q_1}{Q_2} \geq \frac{T_1}{T_2} \Rightarrow \frac{Q_1}{T_1} \geq \frac{Q_2}{T_2} \Rightarrow \boxed{\frac{Q_2}{T_2} + \left(\frac{-Q_1}{T_1}\right) \leq 0}$$

Q/ m gram of water at temperature T_1 is isobarically and adiabatically mixed with equal amount of water at Temperature T_2. Show $\Delta S = 2mC_p \ln\left(\frac{T_{av}}{\sqrt{T_1 T_2}}\right)$

A/ Now $dQ_1 = dQ_2 \Rightarrow mC_p(t - T_1) = mC_p(T_2 - t)$

$\Rightarrow t = T_{avg} = \left(\frac{T_1 + T_2}{2}\right)$

$$\Rightarrow \Delta S = \Delta S_1 + \Delta S_2$$

$$= mC_p \ln\left(\frac{t}{T_1}\right) + mC_p \ln\left(\frac{t}{T_2}\right)$$

$$= mC_p \ln\left(\frac{t_{avg}^2}{T_1 T_2}\right) = 2mC_p \ln\left(\frac{T_{avg}}{\sqrt{T_1 T_2}}\right)$$

Q A heat engine receives 100 k cal of heat from a source at 1000 k. It ejects 50 kcal, 75 kcal and 25 kcal of heat at 500k to surroundings. Investigate natur of change.

A To know nature of change, we have Classius Inequality with us.

(a) $\oint \frac{dQ}{T} = \frac{100}{1000} - \frac{50}{500} = 0$: reversible process

(b) $\oint \frac{dQ}{T} = \frac{100}{1000} - \frac{75}{500} = -0.05 \text{ kcal } k^{-1}$: irreversible process

(c) $\oint \frac{dQ}{T} = \frac{100}{1000} - \frac{25}{500} = 0.05 \text{ kcal } k^{-1}$: CANNOT OCCUR.

Note that in 3rd case efficiency is more than 50% which is violation of Carnot's Theorem.

[Carnot Theorem puts a theoretical limit on efficiency which can be obtained or checked by Clausius Inequality.]

Q Consider a system at Temperature T_s in thermal contact with a heat bath at T_h $(T_s < T_h)$. If heat capacity of system remains const. over interval (T_s, T_h), show that temperature equalization is accompanied by increase in entropy.

When we say entropy, we say that of universe......

A Final temperature $= T_h$

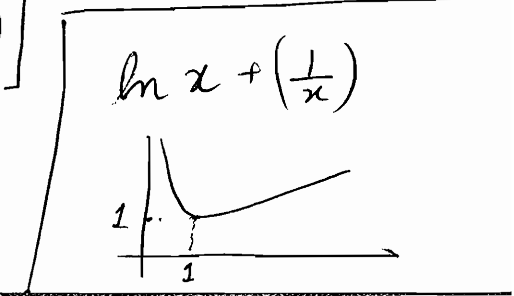
$$dS_{system} = \int \frac{dQ}{T} = \int_{T_s}^{T_h} C_s \cdot \frac{dT}{T} = C_s \ln\left(\frac{T_h}{T_s}\right)$$

$$dS_{surrounding} = \int \frac{dQ}{T} = -C_s \frac{(T_h - T_s)}{T_h} = -C_s\left(1 - \frac{T_s}{T_h}\right)$$

$$dS_{Total} = C_s \left[\ln\left(\frac{T_h}{T_s}\right) - 1 + \left(\frac{T_s}{T_s}\right)\right]$$

Now, $\left[\ln x + \left(\frac{1}{x}\right) > 1\right]$ $\forall x$

Hence $\boxed{dS_{Total} > 0}$ [irrespective of hot or cold bath]



Q/ Prove that entropy always increases

A/ Here we have 2 cases

① Isolated system : from Clausius inequality $\Delta S \geq 0$

② Heat from body at T_1 to body at T_2

$$\Rightarrow dS = \frac{dQ}{T_2} - \frac{dQ}{T_1} = dQ\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

since heat flows from higher Temp to lower temp.

$$\Rightarrow \frac{1}{T_2} \geq \frac{1}{T_1} \Rightarrow dS \geq 0$$

Q/ 10A current is passed through insulated resistor of $25\,\Omega$ (placed at 300k) for 1s. Find $\Delta S_{res.}$ and $\Delta S_{univ.}$ if $m = 10g$ and $C_p = 0.84\ J\ g^{-1}\ k^{-1}$

A/ Since resistor is insulated $\Rightarrow \Delta S_{surr} = 0 \Rightarrow \Delta S_{univ} = \Delta S_{res}$

Also $\Delta Q = mC_p\,\Delta T \Rightarrow 100 * 25 * 1 = 10 \times 0.84 \times \Delta T$

$\Rightarrow \Delta T = 297.61 \Rightarrow T_2 = 597.6\ k$

$$\Rightarrow \Delta S_{res} = \int \frac{dQ}{T} = mC_p\int\frac{dT}{T} = 8.4 * \ln\left(\frac{T_2}{T_1}\right)$$

$$= 5.78\ \cancel{J}/k$$

Q/ Calculate ΔS_{univ} if $1\,\mu F$ capacitor is connected to 100 V reversible cell ~~of~~ @ 0°C.

A/ Since Heat is not involved in charging the capacitor $dQ = 0$ and $dS = 0$

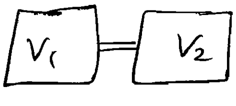
Q/ 1 mole of He and 1 mole of H_2 are mixed at a const. Temperature. Calculate entropy change.

A/ Assuming isothermal process and $V_1 = V_2 = V_0$

$\Delta S = \Delta S_{H_2} + \Delta S_{He}$

$= 2R\ln\left(\frac{V_f}{V_i}\right) = 2 \times 2\,cal/k/mol \times \ln 2$

$= 2.77\ cal/k$



Q/ Show that $C_p = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial p}{\partial T}\right)_S$.

A/ By definition $C_p = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$

To Convert '1' differential into '2', we know cyclic rule.

$$\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T = -1 \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial S}{\partial P}\right)_T$$

$$\Rightarrow C_p = -T\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial S}{\partial P}\right)_T = -T\left(\frac{\partial P}{\partial T}\right)_S * \left[-\left(\frac{\partial V}{\partial T}\right)_P\right]$$

P V S T

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

Q/ A Gas obey equation $[P(V-b) = RT]$ where b is a const. Gas has const. value of C_v. Show that

(a) U is a function of 'T' only

(b) During adiabatic process, gas follows $p(V-b)^{\gamma} =$ Const

A/ We will prove 1st part by contradiction.

Let $U = f(V)$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T \neq 0 \quad \Rightarrow \underline{L.H.S} = \left(\frac{T\,dS - P\,dV}{dV}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$= T.\left(\frac{\partial P}{\partial T}\right)_V - P = T.\frac{R}{(V-b)} - P = P - P = 0 \neq \underline{RHS}$$

Hence contradicted.

Similarly let $U = f(P)$

$$\Rightarrow \left(\frac{\partial U}{\partial P}\right)_T \neq 0 \quad \underline{L.H.S.} = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{dV}{\partial P}\right)_T$$

$$= -T.\left(\frac{\partial V}{\partial T}\right)_p - P\left(\frac{\partial V}{\partial P}\right)_T = -T.\frac{R}{p} - P.-\left(\frac{V-b}{P}\right)$$

$$= -\frac{RT}{p} + (V-b) = -(V-b) + (V-b) = 0 \neq \underline{R.H.S}$$

Hence Contradicted $\Rightarrow \boxed{U = f(T) \text{ only}}$

(ii) $p(V-b) = RT$

Now $C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T.\frac{R}{(V-b)}.\frac{R}{p}$

$$= \frac{T.R^2}{RT} = R$$

Also, $\frac{C_P}{C_V} = \gamma$

$$\Rightarrow \boxed{C_V = \left(\frac{R}{\gamma-1}\right)}$$

Also during adiabatic process

$dQ = 0 \Rightarrow dU + PdV = 0$

$\Rightarrow C_V dT + PdV = 0$ (now we know $U = f(T)$ only $\Rightarrow dU = C_V dT$)

$\Rightarrow \frac{R}{\gamma-1}.dT + \frac{RT}{(V-b)}dV = 0$

$\Rightarrow \frac{dT}{T} + (\gamma-1)\frac{dV}{(V-b)} = 0$

$\Rightarrow \ln T + (\gamma-1)\ln(V-b) = A$

$\Rightarrow T(V-b)^{\gamma-1} = A_1$

$\Rightarrow \frac{p(V-b)}{R}(V-b)^{\gamma-1} = A_1$

$$\Rightarrow \boxed{p(V-b)^{\gamma} = \text{Const}}$$

Q/ A system undergoes phase transition at a const. temp T and pressure P. If it suffers a change ΔV in its volume, show that $\Delta U = T^2 \frac{\partial}{\partial T}\left[\frac{p}{T}\right]_V \Delta V$

A/ Let $U = f(T,V)$

$\Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = \left(\frac{\partial U}{\partial V}\right)_T dV = \left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right]\Delta V$

$= \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\Delta V = T^2\frac{\partial}{\partial T}\left(\frac{p}{T}\right)_V \Delta V$

Q/ The Coefficient of viscosity of He is 2×10^{-5} poise at 27°C. Calculate the diameter of He molecule..

$N_A = 6 \times 10^{23}\ mol^{-1}$; $k_B = 1.38 \times 10^{-23}\ J k^{-1}$, $A[He] = 4$

A/ From Transport Phenomenon.

$$\eta = \frac{1}{3} m n \bar{v} \lambda = \frac{1}{3} m \cancel{n} \bar{v} \frac{1}{\sqrt{2} \pi d^2 \cancel{n}} = \frac{m \bar{v}}{3\sqrt{2} \pi d^2}$$

$$\Rightarrow d^2 = \left(\frac{m \bar{v}}{3\sqrt{2}\ \pi \eta} \right)$$

Now

$$m = \frac{4g}{6 \times 10^{23}} = 6.6 \times 10^{-24} g = \underline{\underline{6.6 \times 10^{-27} kg}}$$

$$\bar{v} = \sqrt{\frac{8}{\pi} \frac{kT}{m}} = \sqrt{\frac{8 \times 1.38 \times 10^{-23} \times 300}{3.14 \times 6.6 \times 10^{-27}}} = \sqrt{159.81 \times 10^2}$$

$$= \underline{\underline{1264\ ms^{-1}}}$$

$$\Rightarrow d^2 = \frac{6.6 \times 1264 \times 10^{-27}}{3\sqrt{2} \times 3.14 \times 2 \times 10^{-5}} = 313.1 \times 10^{-22}$$ [redacted]

$$\Rightarrow \boxed{d = 1.769\ \text{Å}}$$

$\boxed{\text{Also note that 'mn'} = \rho}$

Q/ Calculate the thermal conductivity of air using the following data: $\rho = 1.29\ kg\ m^{-3}$, $\bar{v} = 460\ ms^{-1}$, $\lambda = 6.4 \times 10^{-8} m$, $M = 29$, $\gamma = 1.4$ and $R = 8.31\ kJ\ kmol^{-1}k$

A/ We know $k = \frac{1}{3} m n \bar{v} \lambda \underset{\sim}{c_v}$

↑ Cv per unit mass

per unit mole

↓

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

$mn = \rho = 1.29$

$\bar{v} = 460$

$\lambda = 6.4 \times 10^{-8}$

$$c_v = \frac{C_V}{M} = \frac{R}{(\gamma - 1) M} = \frac{8.31}{0.4 \times 29 \times 10^{-3}} = 716.37$$

$$\Rightarrow \boxed{k = 9.06 \times 10^{-3}\ W m^{-1} k^{-1}}$$

Q/ The coefficient of viscosity and diffusion for O_2 are 1.95×10^{-5} N s m^{-2} and 1.22×10^{-5} $m^2 s^{-1}$. If avg. molecular speed is 440 ms^{-1}, calculate density and mean free path of molecules.

A/ $\eta = \frac{1}{3} m n \bar{v} \lambda$

$D = \frac{1}{3} \bar{v} \lambda$

$\Rightarrow \rho = mn = \frac{\eta}{D} = 1.6$ kg/m³

$\lambda = \frac{3D}{\bar{v}} = \frac{3 \times 1.22 \times 10^{-5}}{440}$

$= 8.32 \times 10^{-8}$ m

Q/ Calculate mass of N_2 diffusing through an area of 10^{-2} m^2 in 10 s if the concentration gradiatent is 1.26 kg m^{-4}, the mean free path = 10^{-7} m and $\bar{v} = 476$ ms^{-1}.

A/ $D = \frac{1}{3} \bar{v} \lambda = \frac{dN}{A.t.\left(\frac{dn}{dz}\right)}$

$\Rightarrow dN = \frac{1}{3} . \bar{v} . \lambda . A . t \left(\frac{dn}{dz}\right)$

$\Rightarrow dM = \frac{1}{3} . \bar{v} . \lambda . A . t \left[\underline{m \left(\frac{dn}{dz}\right)} \right] = \frac{1}{3} \bar{v} \lambda A t \left(\frac{d\rho}{dz}\right)$

$= \frac{1}{3} \times 476 \times 10^{-7} \times 10^{-2} \times 10 \times 1.26 = \underline{1.99 \times 10^{-6} \text{ kg}}$

Q/ What fraction of volume must liquid ether occupy at room temperature in order to pass into critical state when critical temperature is reached? For ether $T_c = 467$ k ; $P_c = 35.5$ atm ; density = 720 kg/m³ & A = 74

A/ $T_c = \frac{8a}{27Rb} = \frac{8b}{R}\left(\frac{a}{27b^2}\right) \Rightarrow$ $b = 13.64 \times 10^{-5}$ m³

$\Rightarrow V_c = 3b = \underline{40.94 \times 10^{-5} \text{ m}^3}$

$\frac{RT_c}{P_c V_c} = \frac{8}{3}$

Now since its in critical stage volume of vessel $= V_c = 40.94 \times 10^{-5}$ m³

Also since V_c is defined for 1 mole, for liquid ether (before evaporation), Volume $= \frac{74 \times 10^{-3}}{720 \text{ kg/m}^3} = \underline{10.27 \times 10^{-5} \text{ m}^3}$

$\Rightarrow$ Fraction occupied = 25%

अरे भय्या !! Constants को ध्यान रखना

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

A From P V S T

if we see $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ 1st Maxwell

लेकिन Constants तो कुछ और हैं !!

Therefore instead of Order of numerator and denominator, we can look for const.

For ex. if LHS const if P ⇒ ~~denominator~~ of RHS is P

⇒ numerator of LHS is V

⇒ equation to use is

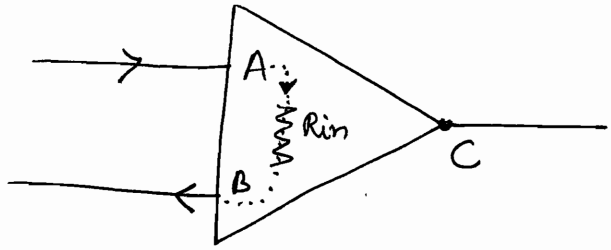
$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{OR} \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

We can see it is 2nd one

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$: 4th Maxwell Equation

Remember $\left(\frac{\partial A}{\partial B}\right)_C$ A and C are neighbours like PV or ST

OPAMP



Ideal Opamp

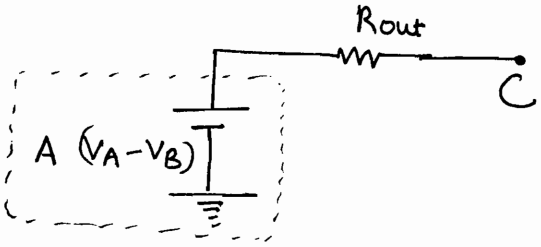
$V_C = A(V_A - V_B)$

$A \to \infty \Rightarrow V_A = V_B$

② $R_{in} = \infty \Rightarrow I_A = I_B = 0 \quad \left[\frac{V_A - V_B}{R_{in}}\right]$

③ $R_{out} = 0$

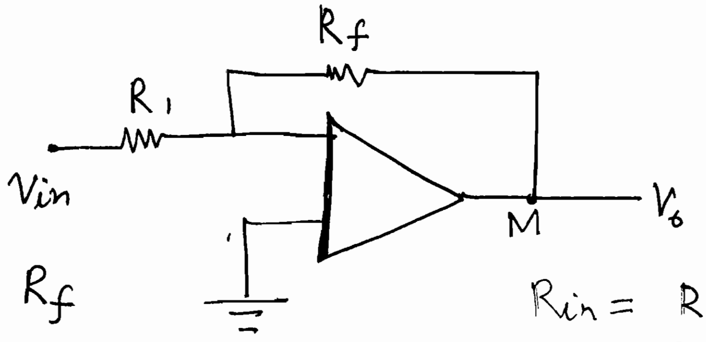
→ This is short ckt.



Opamp Circuit

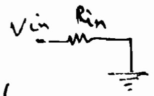
AMPLIFIER

a) Inverting

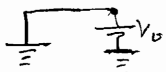


$V_o = -\frac{V_{in}}{R_1} \cdot R_f$

$R_{in} = R_1$

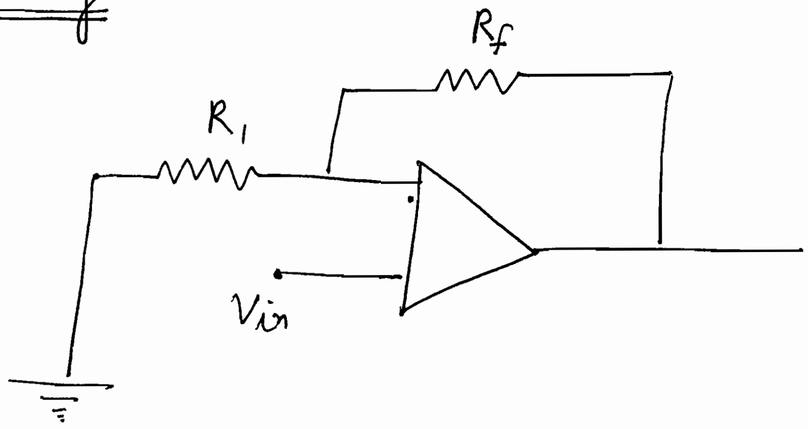


$R_{out} = 0$



If R' b/w M and V_o, R_{out} : R'

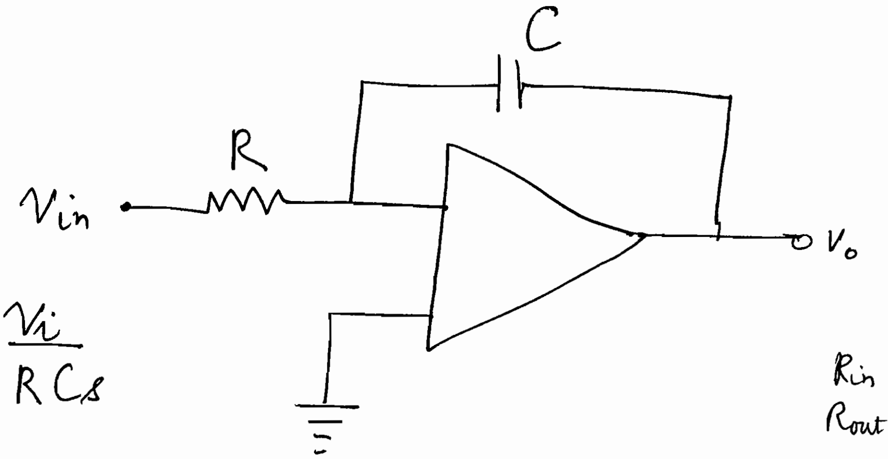
b) Non Inverting



$$V_o = V_{in}\left[\frac{R_f}{R_1} + 1\right]$$

$R_{in} = \infty$
$R_{out} = 0$

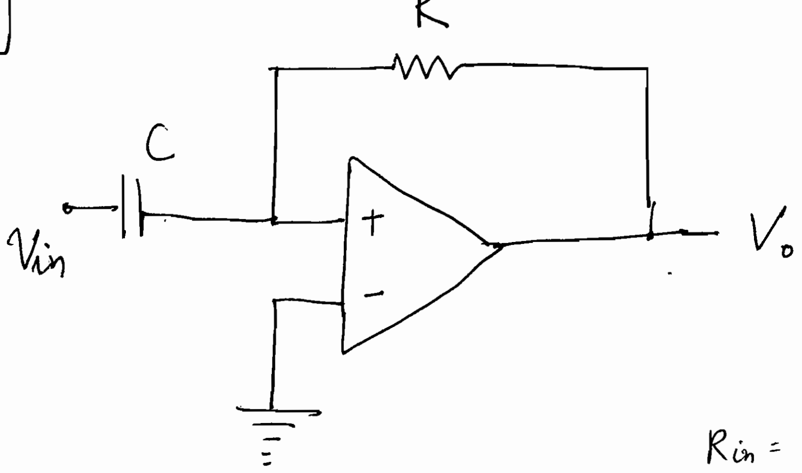
INTEGRATOR



$$V_o = -\frac{V_i}{RCs}$$

$R_{in} = R$
$R_{out} = 0$

DIFFERENTIATOR



$$V_o = \frac{-V_{in}R}{\left(\frac{1}{Cs}\right)}$$

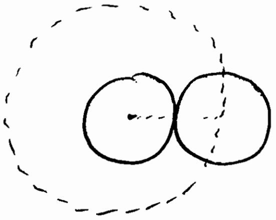
$$= -V_{in}RCs$$

$R_{in} = \infty$

$R_{out} = 0$

$\boxed{b}$

Since molecules are not point particles, they cover some volume and the space available to molecules is less than the volume of container.



Sphere of influence of each molecule is of radius $2r$ and since this is shared by 2 interacting molecules, value of b is half of total no. of molecules times the volume of sphere of influence

$$b = \frac{1}{2} * N * \frac{4}{3}\pi(2r)^3 = \underline{\underline{4Nv}}$$

Clausius Virial Theorem

Assuming that particles obey Newtonian mechanics.

$$m_i \frac{d^2\vec{r}_i}{dt^2} = \vec{F}_i = \dot{\vec{p}}_i$$

define $\phi = \sum_i \vec{P}_i \cdot \vec{r}_i$ $\quad$ $\boxed{\vec{P}_i : \text{momentum}}$

$$\left(\frac{d\phi}{dt}\right) = \sum \dot{\vec{P}}_i \cdot \vec{r}_i + \sum \vec{P}_i \cdot \dot{\vec{r}}_i = \sum \vec{F}_i \cdot \vec{r}_i + \sum m_i \vec{v}_i \cdot \vec{v}_i$$

$$= \sum \vec{F}_i \cdot \vec{r}_i + 2T$$

Taking time average of $\left(\frac{d\phi}{dt}\right)$

$$\left\langle \frac{d\phi}{dt} \right\rangle = \frac{1}{\tau}\int_0^\tau \left(\frac{d\phi}{dt}\right) . dt = \frac{1}{\tau}\int_0^\tau \sum \vec{F}_i \cdot \vec{r}_i \, . dt + \frac{2}{\tau}\int_0^\tau T \, dt$$

$$\Rightarrow \frac{1}{\tau}\left(\Phi_\tau - \Phi_0\right) = \overline{\sum \vec{F}_i \cdot \vec{r}_i} + \overline{2T}$$

Choose τ st. $\Phi_\tau = \Phi_0$, we get

$$\boxed{\overline{\sum \vec{F}_i \cdot \vec{r}_i} = -2T}$$

L.H.S. is called Virial

Fi includes

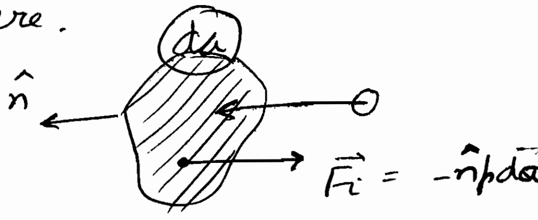
- → Force of impact on molecules due to collision with the walls of container
- → Force of collision between molecules
- → Force of interaction between molecules.

Application

1) **Pressure due to ideal gas**

Only 1st component of force is there.

$$\vec{F}\cdot\vec{r} = -p\, da\, \hat{n}\cdot\vec{r}$$



$\boxed{p : \text{pressure}}$

$$\text{Virial} = -\frac{1}{2}\overline{\sum \vec{F}_i\cdot\vec{r}_i}$$

$$= \frac{1}{2}p\,\overline{\sum \vec{ds}\cdot\vec{r}_i}$$

$$= \frac{1}{2}p\cdot\overline{\int \vec{r}_i\cdot\vec{ds}}$$

$$= \frac{1}{2}p\cdot\int\left(\vec{\nabla}\cdot\vec{r}_i\right)dv$$

$$= \frac{1}{2}p\cdot\ \overline{3.V}$$

$$= \frac{3}{2}pV$$

$[\vec{\nabla}\cdot\vec{r}_i = 3]$
$(\overline{3V} = 3V)$

$$\Rightarrow \frac{3}{2}pV = \overline{T} = \frac{3}{2}RT \quad \text{(for 1 mole of gas)}$$

$$\Rightarrow \boxed{pV = RT} \quad \& \quad \boxed{p = \frac{2}{3}\frac{\overline{T}}{V}}$$

Quasi Static Process

If during state of non-equilibrium, if external forces be varied only slightly, so that resulting unbalanced forces are infinitisimally small, the process is assumed to be in equilibrium & is called Quasi Static Process.

For quasistatic process, $dw = P\,dV$

Efficiency increase of Carnot engine

$$\eta = 1 - \left(\frac{T_2}{T_1}\right)$$

$$\left(\frac{d\eta}{dT_1}\right) = \left(\frac{T_2}{T_1^2}\right)$$

$$\left(\frac{d\eta}{d(-T_2)}\right) = \left(\frac{1}{T_1}\right)$$

$$\Rightarrow \left(\frac{d\eta}{d(-T_2)}\right) > \left(\frac{d\eta}{dT_1}\right)$$

$\Rightarrow$ Its preferable to reduce T_2 than to increase T_1

Internal vs External Combustion

- In steam engine, heat is produced in a separate boiler outside the cylinder : External Combustion Engine
- When heat is produced inside the cylinder by explosion of fuel, its called Internal Combustion Engine. It has Much higher efficiency.

Application of Claussius Inequality : Maximum Work

Q/ 2 bodies of identical mass and heat capacity C are at temp. T_1 and T_2. What is the max. work that can be done?

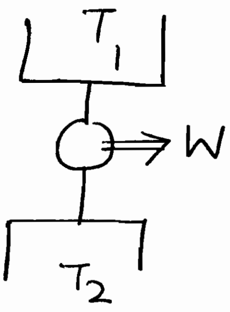
A/ Let final temp be T_f

$$Q_1 = C(T_1 - T_f)$$
$$Q_2 = C(T_f - T_2)$$

Now we cannot equate the two, as $W_{done} \neq 0$

$$W = Q_1 - Q_2$$
$$= C[T_1 + T_2 - 2T_f]$$

For maximum work, we need to find out minimum value of T_f.



We know $\oint \frac{dq}{T} \leq 0$

$$\Rightarrow \underbrace{\int_{T_1}^{T_f} -\frac{C\,dT}{T}}_{\text{increase in entropy}} + \underbrace{\int_{T_2}^{T_f} \frac{C\,dT}{T}}_{\text{decrease in entropy}} \leq 0$$

Heat released by hot reservoir $= -C\,dT$

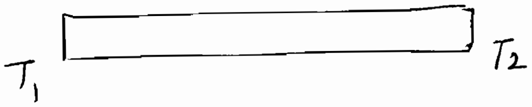
Heat gained by cold reservoir $= +C\,dT$

$$\Rightarrow -C\ln\left(\frac{T_f}{T_1}\right) + C\ln\left(\frac{T_f}{T_2}\right) \leq 0$$

$$\Rightarrow C\ln\left[\frac{T_f^2}{T_1T_2}\right] \geq 0$$

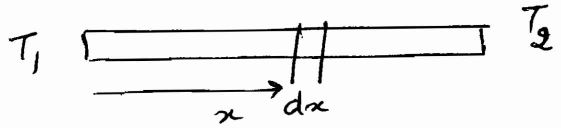
$$T_f^2 \geq T_1T_2$$

$$\Rightarrow W_{max} = C[T_1 + T_2 - 2\sqrt{T_1T_2}]$$

⊙ 

Find Entropy change after a long time.

Ans



For element dx

$$T_i = T_1 - \left(\frac{T_1-T_2}{L}\right)x$$

$$T_f = \frac{T_1+T_2}{2} \quad \text{(for the whole rod)}$$

$$dm = \frac{M}{L}.\,dx$$

$$dS = \frac{dQ}{T} = dm.\,c.\,\frac{dT}{T} = \frac{M}{L}c\,dx.\int_{T_i}^{T_f}\frac{dT}{T}$$

$$= \frac{Mc}{L}\,dx.\ \ln\left[\frac{\left(\frac{T_1+T_2}{2}\right)}{T_1-\left(\frac{T_1-T_2}{L}\right)x}\right] \quad \checkmark$$

For whole rod

$$\Delta S = \int dS$$

$$= \int_0^L \frac{Mc}{L}\ \ln\left[\frac{T_1+T_2}{2T_1 - \frac{(T_1-T_2)}{(L/2)}x}\right]dx$$

$$= \int_0^L \frac{Mc}{L}\ln\left(\frac{T_1+T_2}{2}\right)dx - \int_0^L \frac{Mc}{L}\ln\left(T_1-\left(\frac{T_1-T_2}{L}\right)x\right)dx$$

$\checkmark$

IBP

$$\int \ln\left(T_1 - \left(\frac{T_1-T_2}{L}\right)x\right)\cdot 1\ dx$$

$$= \ln\left(T_1 - \left(\frac{T_1-T_2}{L}\right)x\right)x\Big|_0^L - \int_0^L \frac{x}{T_1-\left(\frac{T_1-T_2}{L}\right)x}\left(\frac{T_1-T_2}{L}\right)dx$$

$$= \ln\left(\frac{T_2}{L}\right) - \int_0^L \frac{x}{\left(\frac{T_1 L}{T_1 - T_2}\right) - x}\, dx \quad \checkmark$$

$$= L \ln\left(\frac{T_2}{L}\right) - \int_0^L \frac{x - \left(\frac{L T_1}{T_1 - T_2}\right)}{\left(\frac{L T_1}{T_1 - T_2}\right) - x}\, dx + \frac{\left(\frac{L T_1}{T_1 + T_2}\right)}{x - \left(\frac{L T_1}{T_1 - T_2}\right)}\, dx$$

$$= L \ln\left(\frac{T_2}{L}\right) + L + \left(\frac{L T_1}{T_1 + T_2}\right) \ln\left(x - \frac{L T_1}{T_1 + T_2}\right)\Big|_0^L$$

$$\vdots$$

$$\Rightarrow \langle \epsilon \rangle = \frac{E}{N}$$

$$= \frac{\dfrac{h\nu N_0 \, e^{-\frac{h\nu}{kT}}}{\left(1-e^{-\frac{h\nu}{kT}}\right)^2}}{\left(\dfrac{N_0}{1-e^{-h\nu/kT}}\right)}$$

$$= \left[\frac{h\nu}{1-e^{-h\nu/kT}}\right] e^{-\frac{h\nu}{kT}}$$

$$= \boxed{\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}}$$

⊙ To prove $\langle \epsilon \rangle = \left[\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}\right]$

① Note that till time of Plank only Maxwell distribution was there.

② Assume $g(\epsilon) = 1 \quad \forall\ \epsilon$

Now lets support particles at ground level $= N_0$

$$\Rightarrow \quad N_1 = N_0 e^{-\frac{h\nu}{kT}}$$

$$N_2 = N_0 e^{-\frac{2h\nu}{kT}}$$

$$N_3 = N_0 e^{-\frac{3h\nu}{kT}}$$

$$\vdots$$

$$\Rightarrow N = N_0 + N_1 + N_2 + \ldots$$

$$= N_0 \left[1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \ldots \right]$$

$$= \frac{N_0}{1 - e^{-\left(\frac{h\nu}{kT}\right)}}$$

Also

$$E = N_0\epsilon_0 + N_1\epsilon_1 + N_2\epsilon_2 + \ldots$$

$$= 0 + h\nu N_0 e^{-\frac{h\nu}{kT}} + 2h\nu N_0 e^{-\frac{2h\nu}{kT}} + 3h\nu N_0 e^{-\frac{3h}{k}}$$

$$e^{-\frac{h\nu}{kT}} E = \qquad h\nu N_0 e^{-\frac{2h\nu}{kT}} + 2h\nu N_0 e^{-\frac{3h\nu}{kT}}$$

$$E\left(1 - e^{-\frac{h\nu}{kT}}\right) = h\nu \left[N_0 e^{-\frac{h\nu}{kT}} + N_0 e^{-\frac{2h\nu}{kT}} + \ldots\ldots \right]$$

$$= h\nu \frac{N_0 e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}}$$

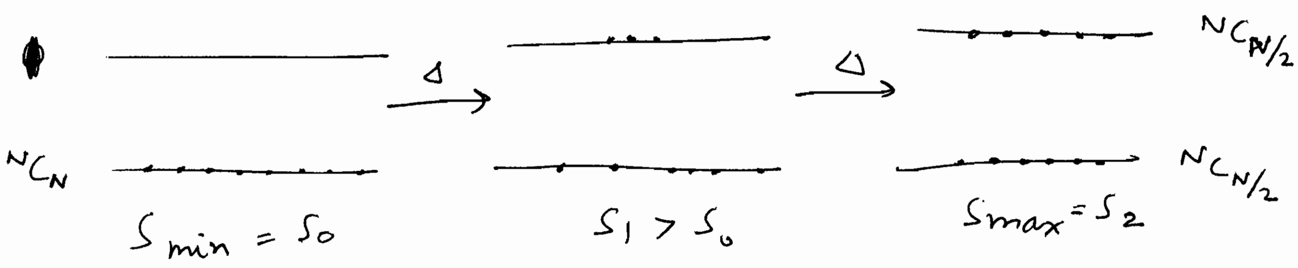
$$\Rightarrow E = \frac{h\nu N_0 e^{-h\nu/kT}}{\left(1 - e^{-h\nu/kT}\right)^2}$$

Concept of Negative Temperature

★ Temperature is defined as $dS = \frac{dQ}{T}$

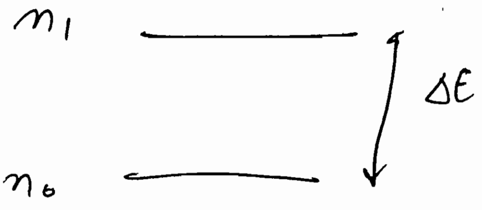
$$\Rightarrow \quad T = \left(\frac{dQ}{dS}\right)$$

Negative temperature if entropy drops on supplying heat.



if more heat supplied, more particles move up ⇒ entropy drops ⇒ negative temperature

★ When $n_1 > n_0$, we say that substance is at negative temperature.

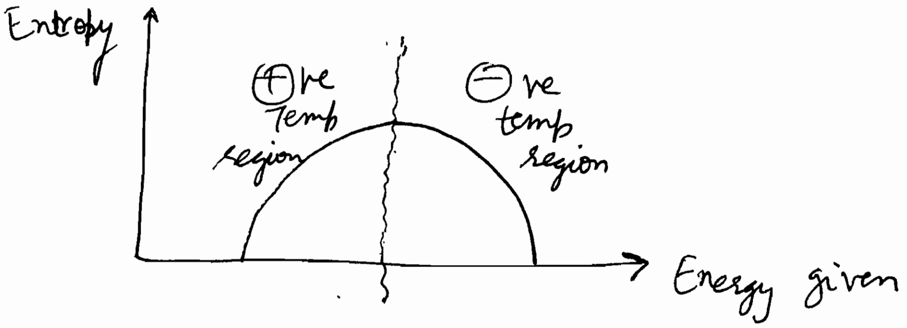


$$N_1 = N_0 \, e^{-\left(\frac{\Delta E}{kT}\right)}$$

if $N_1 > N_0$ and $\Delta E > 0$

⇒ **T** is negative

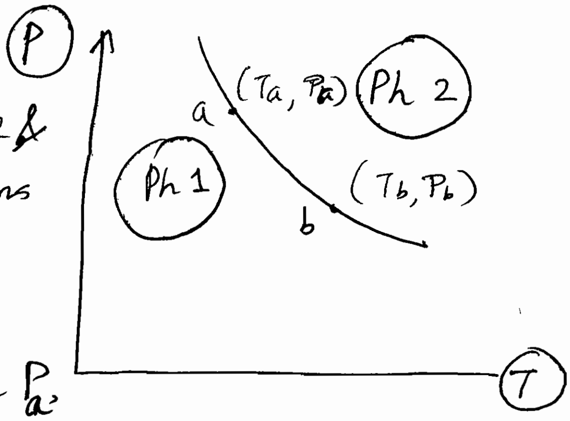
★



(*) Nuclear spin systems can be brought to negative temperature by radio frequency techniques.

Clasius Claypeyron Equation from Gibbs Free Energy

[redacted]



For two substances in reversible equilibrium at constant temperature & Pressure, the Gibbs function remains same.

Hence, for a change of phase (phase 1 to phase 2) at T_a and P_a, the specific gibbs functions are equal for two states

$$\boxed{g_a^{(1)} = g_a^{(2)}}$$

Similarly for a phase change at $(T+dT)$ $(=T_b)$ and $(P+dP)$ $(=P_b)$,

$$g_b^{(1)} = g_b^{(2)} \quad \text{or} \quad \boxed{g_a^{(1)} + dg^{(1)} = g_a^{(2)} + dg^{(2)}}$$

$$\Rightarrow dg^{(1)} = dg^{(2)}$$

$$\Rightarrow -s^{(1)} dT + v^{(1)} dP = -s^{(2)} dT + v^{(2)} dP$$

$$\Rightarrow (s^{(2)} - s^{(1)}) dT = (v^{(2)} - v^{(1)}) dP$$

$$\Rightarrow \frac{dP}{dT} = \frac{s^{(2)} - s^{(1)}}{v^{(2)} - v^{(1)}} = \underline{\underline{\frac{L}{T(v^{(2)} - v^{(1)})}}}$$

Hence Claussius Clapeyron equation relates change in Pressure dP with change ~~with~~ in Boiling / Melting Point.

Negative Temperature in a magnetic field

Let a system with just 2 magnetic energy levels due to a field H & dipoles of magnetic moment μ_B.

Particles aligned $\parallel$ to $\vec{H}$: $E_1 = -\vec{\mu_B}\cdot\vec{B} = -\mu_B B$

Particles aligned antiparallel to $\vec{H}$: $E_2 = -\vec{\mu_B}\cdot\vec{B} = \mu_B B$

No. of particles at $E_1 = N_1 = A e^{-\frac{E_1}{kT}}$

" " " " $E_2 = N_2 = A e^{-\frac{E_2}{kT}}$

Now, $\frac{N_2}{N_1} = e^{\left(\frac{E_1 - E_2}{kT}\right)}$ $\Rightarrow \ln N_2 - \ln N_1 = \frac{E_1 - E_2}{kT}$

$$\Rightarrow \boxed{T = \frac{E_2 - E_1}{k(\ln N_1 - \ln N_2)}}$$

Now $E_2 > E_1$

and normally $N_1 > N_2$

hence $T > 0$

However, if suddenly H is reversed.

E_1 becomes $\mu_B B$

E_2 becomes $-\mu_B B$

The particles take some time to realign & for that time T becomes negative.

Bose Einstein Condensation

For Bose Einstein distribution, we calculate N as

$$N = \left[\frac{2\pi V}{h^3} (2m)^{\frac{3}{2}}\right] (kT)^{\frac{3}{2}} \int_0^\infty \frac{x^{1/2}}{e^x - 1}\, dx$$

For that we took $g(\epsilon)\, d\epsilon$ as $\frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$.

Note that we have given zero weight to $E=0$ level. This is not justified in quantum mechanics.

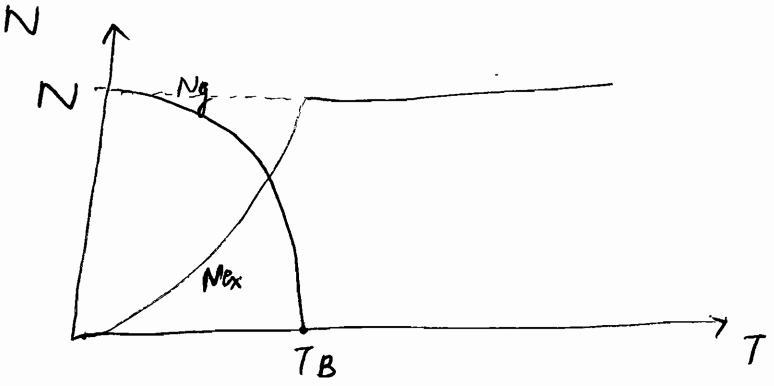
Hence we have to take care of N_g also.

$$\Rightarrow N = N_g + \underbrace{CV \int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{e^{\frac{\epsilon}{kT}} - 1}}_{N_{ex}\ :\ \text{particles with non zero energy}}$$

$$N_g = N - N_{ex} \quad \text{and} \quad \frac{N_{ex}}{N} = \left(\frac{T}{T_B}\right)^{3/2}$$

$$= N - N\left(\frac{T}{T_B}\right)^{3/2}$$

$$\boxed{N_g = N\left[1 - \left(\frac{T}{T_B}\right)^{\frac{3}{2}}\right]}$$ ✓



He Bose Einstein Condensate

For ^{4}He $T_B = 3.13$ k (from formula)

actual value $= 2.17$ k

(PTO)

$$N_{else} = \left[\frac{2\pi V}{h^3}(2m)^{3/2} \cdot \int_0^\infty \frac{x^{1/2}}{e^x - 1}\, dx\right] (kT)^{3/2}$$

$$= \alpha (kT)^{3/2} \quad \text{(say)}$$

Define $\alpha = \dfrac{N}{(kT_B)^{3/2}}$, we get

$$N_{else} = N\left(\frac{T}{T_B}\right)^{3/2}$$

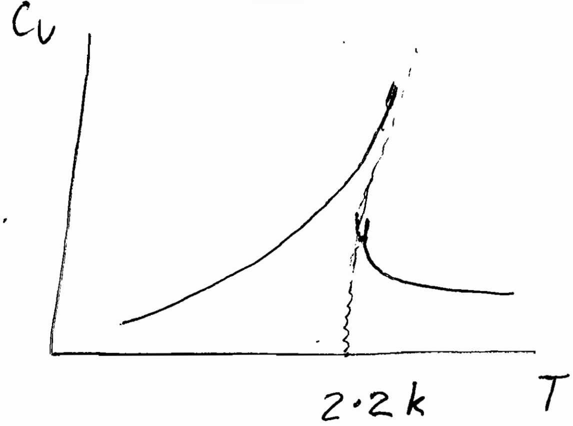
$$\Rightarrow N = N_g + N_{else}$$

$$\Rightarrow \boxed{N_g = N\left[1 - \left(\frac{T}{T_B}\right)^{3/2}\right]}$$

★ In Free expansion of an ideal gas, Temperature remains same.

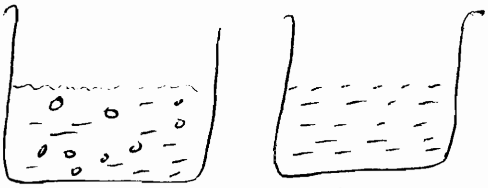
At atmospheric pressure, helium condenses into a normal liquid at 4·2k. As the temperature is lowered further, it undergoes phase transition once again at 2·17k. One would normally expect Helium to solidify at this transition. Instead, liquid He changes into another liquid of vastly different properties.

Transition is accompanied by an anomalous behaviour of heat capacity. The heat capacity has a shape similar to Greek letter λ. Hence transition temperature is also referred to as **LAMBDA POINT**.



The new fluid has

(i) apparently zero viscosity
(ii) infinite thermal conductivity.
(iii) no bubbles.


above λ-point
below λ-point

Lack of viscosity means that superfluid can flow through smallest of cracks without impediment. Another effects that superfluid Helium shows are that of fountain effect & second sound.

Gibbs Phase Rule

Let us consider a system of c components in p phases.

For a multicomponent system,

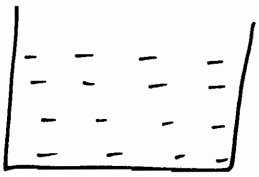
$$G = G(P, T, x_1, x_2, x_3, \dots x_c) \quad \text{for every phase} \quad (1)$$

where P : Pressure of system
T : Temperature of the system.

Mole Fractions $x_j = \left(\frac{N_j}{N}\right)$ sum to unity, hence only (c-1) mole fractions are independent, thereby making the no. of variable unknown equal to $2 + p(c-1)$

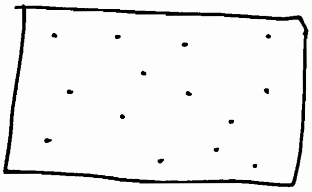
Note that we can consider, each separate phase as a simple system and the given system as a composite system of the different simple systems.

eg



liquid system

+



Gaseous system

+

Solid system

At the condition of equilibrium, for example, if water converts to steam, the chemical potentials

$$\mu^L_{water}(T, P, x^L_1) = \mu^G_{steam}(T, P, x^G_1) \quad (2)$$

Similarly for every component one for every phase

We will have,

$c(p-1)$ conditions or equation similar to ②

$(p-1)$ because, $\mu_s = \mu_L$ and $\mu_L = \mu_g$ gives $\mu_s = \mu_g$
hence 2 equations for 3 phases are independent

Total no. of variables which can be arbitrarily assigned $= f = 2 + p(c-1) - c(p-1)$
= degrees of freedom

$$= \underline{2 + c - p}$$

This Phase Rule applies a lot of restriction on the 1st Order Phase Transitions.

eg. ① 5 Phases cannot coexist for a 2 component system.

② For a 2 components, 3 phase system at a (T, P)
variables are $3(1) = 3$
equations are $2(2) = 4$
hence no solution would be possible in general; thereby indicating that we are not free to specify P and T apriori.
It is possible to select both T and P arbitrarily and then to find a 2-Phase state, a 3-Phase state can exist only for a particular Temperature if Pressure is satisfied.

③ For single component system,

$$F = 2 + C - P = 3 - P$$

For One phase $F = 2$ i.e. one can vary both T and p, hence system is called <u>bivarient</u>.

For 2 phases $F = 1$, i.e. one can vary only 1 variable either p (then T will be specific) or vice versa. hency system is called <u>monovariant</u>.

For 3 phases ~~phases~~ to coexist in equilibrium $F = 0$ i.e. all variables need to be fixed, only then all 3 phases can coexist in equilibrium. Such a system is called <u>Invariant</u> ⇒ Triple Point of water is unique.

Blackbody Radiation

- A blackbody is defined as a body that absorbs all radiations that fall on the surface. Actual black bodies do not exist in nature - though approximated by a hole in a box filled with highly absorbtive material.

- According to Stefan Boltzmann's law, radiation energy per unit time is given as

$$q = \sigma T^4 A$$

A : area of emitting body

T : Temperature of body's surface

σ : 5.6×10^{-8} W/m²K⁴

- For gray bodies, $q = \varepsilon \sigma T^4 A$

ε : emissivity of object (= 1 for blackbody)

- Net radiation loss = $\varepsilon \sigma A (T_{body}^4 - T_{surr}^4)$

$\boxed{\text{absorptivity = emmissivity}}$

① derivation of Gibbs Phase Rule ?

② density of state ?

③ Transport Phenomenon of diffusion ?

④ $\langle v_x^2 \rangle = \frac{kT}{m}$ or $\frac{kT}{2m}$?

⑤ $v_x = 4\pi p^2 v$??

⑥ $\left(\frac{\partial P}{\partial T}\right)_V = 0$? or $\left(\frac{\partial V}{\partial T}\right)_P = ?$ for solids

---

Q Explain why distribution of speeds of molecules emerging through a small hole in an effusive molecular beam source is not a maxwellian dist^n.

A Beams < Effusive ($\text{diameter}_{\text{orifice}} < \lambda_{\text{mean free path}}$)
Supersonic ($\text{diameter}_{\text{orifice}} > \lambda_{\text{mean free path}}$)

$\Downarrow$

[Gas Escaping from high Pressure to low pressure]

In effusive beam, molecules effectively wander out of hole whenever they collide with it, the M-B dist^n of the molecular speeds in source is more or less maintained. The dist^n is actually somewhat skewed towards higher velocities since molecules with higher speeds undergo more collisions with walls & are more likely to exit.

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PHYSICS PAPER - I: THERMAL PHYSICS
TUTORIAL SHEET: 20
Basic Concepts

1. Calculate the work done in compressing adiabatically 10^{-3}kg of air initially at STP to one - half its original volume. (Given density of air at STP = 1.293 kg./m^3 and $\gamma = 1.4$
(1990)

2. Establish that for an adiabatic process in an ideal gas $TV^{\gamma-1}$ = constant, where the symbols have their usual meanings.
(1991)

3. One gram of hydrogen gas at 27° C is compressed isothermally from 100 litres to 25 litres. Calculate the energy needed.
(1991)

4. Show that the work done in a reversible expansion of an ideal gas from volume V_1 to V_2 is greater than the corresponding work done in an irreversible expansion against a constant pressure P_2.
(1994)

Copy

5. Explain the concept of 'internal energy' of a system. Formulate mathematically the first law of thermodynamics. Calculate the work done in an isothermal compression of a gas.
(1999)

6. What is an adiabatic process? Give three engineering examples of adiabatic process, which are in common use?
(2000)

7. One mole of an ideal gas is compressed at constant temperature T from a volume V_1 to a volume V_2. Find the work done and heat absorbed by the gas. The gas now expands adiabatically to a volume 2V. Taking the gas to be diatomic, calculate the final temperature of the gas.
(2008)

9. Consider one mole of an ideal gas whose pressure changes with volume as $P = \alpha V$, where α is a constant. If it is expanded such that its volume increases m times, find the change in internal energy, work done by the gas and heat capacity of the gas.
(2010)

Universal gas constant

$R = 8.314$ SI units

Q8 State 2nd law. Prove no engine operating b/w 2 given temp is more efficient than a Carnot engine between 2 temperature

γ : specific heat ratio $= \left(\frac{f+2}{f}\right)$

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TUTORIAL SHEET: 21
Carnot's Cycle and Entropy

1. A Carnot's engine is made to work between 0° C and -200°C. Calculate its efficiency. Derive the expression you use for calculation.
(1988)

2. A volume of one gm. mole of an ideal gas expands isothermally to four times its initial volume. Calculate the change in its entropy in terms of gas constant.
(1988)

3. 1kg of ice at 0°C is melted and converted to water at 0°C. Compute the change in entropy.
(1989)

4. A and B are two huge blocks of same metal. The blocks are connected by a huge rod of the same material. The temperatures of A and B are 1500 K and 500 K respectively. The rate of heat conduction is 10^4 J/sec. Estimate the rate of entropy increase of the universe due to this process.
(1992)

5. Define entropy. Write a general expression for the elementary entropy change dS for 1 mole of an ideal gas. How would this become for cases where the change is (i) isothermal (ii) isochoric (iii) isobaric? Deduce expressions for $S_2 - S_1$ for each of these cases, where (i) and (ii) refer to the initial and final stage entropies respectively. Constants Cp, Cv, R may be used to express the results.
(1993)

6. A 10 ohm resistor carrying 3 ampere current is cooled by running water so as to keep the temperature at 300K. Discuss the change in entropy per second (i) of the resistor (ii) of the universe?
(1994)

7. Define entropy. Derive expressions for the entropy of a perfect gas in terms of (i)T and V (ii) T and P. The symbols have their usual meanings.
(1995)

8. Explain the concept of entropy. The specefic heat Cp of a material depends on temperature T according to the relation $Cp = a + bT + cT^2$ where a, b, c are constants. Derive an expression for the change in its entropy when the temperature changes from T_1 to T_2.
(1996)

9. How is absolute scale of temperature obtained with the help of Carnot cycle? Hence define absolute zero.
(1996)

10. Prove that $\int_A^B \frac{\delta Q}{T}$ evaluated along a reversible path joining the states A and B does not depend on the path chosen. Hence define the entropy function. Calculate the entropy change in an ideal gas undergoing a state change from (V,P) to (2V, P/2) for three suitably chosen different paths and show that the result turns out to be the same in all the cases.
(1998)

11. Define the efficiency of a Carnot Engine. An engine is designed to have an efficiency of 25% and to absorb heat at a temperature of 267°C. Find the maximum temperature at which it can exhaust heat.
(2000)

12. Calculate the increase in entropy when 1 kg ice melts at zero degree centigrade. The Latent heat of fuse of ice is $3.36 \times 10^{+5}$ Joules/kg. (Assume that the melting is an isothermal reversible process).

(2001)

13. Describe Carnot cycle and show that efficiency is given by $H=Q_1-Q_2 / Q_1 = T_1-T_2 / T_1$ where symbols ~~hence~~ their usual meaning.

(2002)

14. Describe Otto cycle and obtain an expression for the efficiency is lower than that of a Carnot cycle operating between the highest and lowest temperature of otto cycle.

(2003)

15. A gas expands isothermally from the pressure P_1 and Volume V_1 to the pressure P_2 and the volume V_2 Calculate:
   (i) the change in internal energy
   (ii) the change in entropy
   (iii) the change in enthalpy
   What will be corresponding quantities when gas expands adiabatically?

(2004)

16. Show that the entropy of one gas mole of an ideal gas is given by $S=C_p \text{ lv } V + C_v \ln P + S_0$

(2004)

17. 1 kg of ice at 0^0c floats on 10 kg of water at 30^0c, the whole system being thermally isolated. What will be the change in entropy of the system when thermal equilibrium is reached ?
[Specific heat of water = 4.2 kJ kg^{-1} K^{-1} and latent heat of fusion of ice = 336 kJ kg^{-1}]

(2006)

18. Prove the law of increase of entropy. Show that for a system at fixed temperature and pressure to be in equilibrium, its Gibbs free energy should be minimum.

(2007)

19. A system at temperature T_1 is brought in contact with a reservoir at temperature $T_2 > T_1$. When the system and the reservoir reach thermal equilibrium, calculate the change in entropy of the universe assuming the heat capacity of C_p of the system to be constant. Discuss whether the considered change is positive or not.

(2007)

20. State second law of thermodynamics. Prove that no engine operating between two given temperatures is more efficient than a carnot engine operating between same two temperatures.

(2008)

20 21. Define entropy. How is it related to disorder? Hence, derive the Boltzmann relation $S = k \log \Omega$, where Ω is the probability and k is the Boltzmann constant.
Show that for any type of process, involving a closed system

$$\Delta S \geq \frac{\Delta Q}{T}$$

Where the equality sign applies for internally reversible processes and the inequality for internally irreversible processes.

(2009)

$L_{ice} = 3.36 \times 10^{-5}$ SI units

TUTORIAL SHEET : 22

Thermodynamic relationships

1. Obtain the clausius clapeyron equation

$$\frac{dp}{dT}=\frac{L}{T(V_2-V_1)}$$ where the symbols have their usual meanings.

(1989, 1994)

2. Establish the relation $Cp - Cv = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$

(1991)

3. Write down the general expression for the Joule - Kelvin effect and define Joule - Kelvin coefficient, μ. Show that for an ideal gas $\mu = 0$

(1991)

4. The density of steam at 100°C is nearly 0.60×10^{-3} kg/litre and its latent heat is 2.3×10^6 J/kg. Calculate the change in the boiling point of water if air pressure changes from 76.0cm to 70.0 cm. of Hg.

U, F, H, G

(1991)

5. Define the thermodynamic energy functions. Using these function establish the following relations:

(i) $\left(\frac{\partial T}{\partial V}\right)_\phi = -\left(\frac{\partial P}{\partial \phi}\right)_V$ (ii) $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial \phi}{\partial V}\right)_T$

(iii) $\left(\frac{\partial T}{\partial P}\right)_\phi = \left(\frac{\partial V}{\partial \phi}\right)_P$ (iv) $\left(\frac{\partial \phi}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

(1992)

6. Calculate the Joule - Thomson coefficient for Nitrogen gas at 293 K and 100 atm. pressure taking

$Cp = 8.21$ cal deg^{-1} mole^{-1}
$a = 1.39$ litre^2 - atm - mole^{-2}
$b = 3.92 \times 10^{-2}$ litre mole^{-2}

(1994)

7. Using Maxwell's thermodynamic relations, show that the internal energy of an ideal gas at a constant temperature is independent of its volume while for a real gas it is a function of volume also.

(1996)

8. Define Helmholtz free energy F and Gibb's free energy G. What does decrease in G and F signify? Show that the internal energy U at temperature T is given by $U = F - T\left(\frac{\partial F}{\partial T}\right)_V$

(1997)

9. Using a Carnot cycle, Obtain the Clausius - Clapeyeron equation. At normal pressure the ratio of densities of ice and water is 9 : 10. When 1 kilo - mole of ice is melted, the change in entropy is 22.2×10^3 J/K. If the external pressure is increased by 10^5 N/m^2, what will be the change in the melting point of ice?

(1997)

10. Prove the latent heat equation $\left(\frac{dL}{dT}\right)_{sv} - \frac{L}{T} = Cs - Cp$, Where Cs & Cp are specific heats of saturated vapour and the liquid in contact with it respectively. Given the following values referring to 1gm. Of water at 100°C, L = 539 Cal/gm., $\left(\frac{\partial L}{\partial T}\right)_{sv} = -0.64$ Cal K^{-1} gm^{1} Cp = 1.01 Cal K^{-1} gm^{-1} . Calculate Cs. Explain why the specific heat takes a negative value (1998)

11. Consider the expression $C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial P}{\partial V}\right)_T$

and give reasoning regarding the value of T when $C_p = C_v$ for water. Also, evaluate $C_p - C_v$ for a Van der ~~Wa~~als gas to elaborate that its value is larger for any real gas as compared to an ideal gas.

(2005)

12. Using thermodynamic principles show that the Joule- Thomson coefficient μ can be expressed as

$$\mu = \frac{1}{Cp}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

Calculate the value of μ for an ideal gas and interpret your result physically.

(2006)

13. Establish the relation

$$C_p - C_v = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p.$$

Use it to find out an expression for C_p of one mole of a gas whose internal energy is given by $U = cT - \frac{a}{V}$ and which satisfies the equation of state $\left(P + \frac{a}{V^2}\right)(V - b) = RT$.

Here a, b and c are constants. (2007)

14. Calculate the change in pressure for a change in freezing point of water equal to -0·91 °C. Given, the increase of specific volume when 1 gm of water freezes into ice is 0·091 cc/gm and latent heat of fusion of ice is 80 cal/gm.

(2010)

CLAUSIUS CLAPEYRON

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TUTORIAL SHEET: 23

Special topics

1. Define thermodynamic temperature of a magnetic system. Making use of Gibb's equation, derive an expression for cooling produced due to adiabatic demagnetisation process. Why is the method used only after pre - cooling to a low temperature?

(1993)

2. What is an adiabatic demagnetisation cycle? Discuss the cycle in terms of T-S indicator diagram?

(1994)

3. Define thermodynamic temperature of a magnetic system. Discuss how cooling takes place due to adiabatic demagnetisation. Explain, why cooling due to adiabatic demagnetisation is important at low temperatures.

(1995)

4. Explain how very low temperature can be produced by adiabatic demagnetisation.

(1999)

5. Obtain Vander Waal's equation of state for real gases. What is the value of critical Coefficient for an ideal gas?
Show that the Value of the critical coefficient for Vander Waal's gas is independent of the type of the gas.

(2001)

6. Show that the chemical potential of a system is an intensive quantity and is a function of temperature and pressure only

(2005)

extra

8. (a) What led van der Waals to modify the ideal gas equation? Using the concepts of critical temperature T_c, pressure P_c and volume V_c, show that the critical constant for a real gas is 8/3. 5+15=20

(b) Find out the expressions for van der Waals constants a and b. 20

(c) Calculate the values of van der Waals constants a and b for oxygen with $T_c = 154\cdot 2$ K; $P_c = 49\cdot 7$ atmosphere and $R = 80$ cm^3 atmosphere/K. 20

(2011)

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TUTORIAL SHEET: 24

Specific heat of solids

1. Thermal energy of a solid is given by the relation

$$E = \int_0^{\nu_m} \frac{h\nu\, g(\nu)\, d\nu}{e^{h\nu/K_B T} - 1}$$

where $\nu m = \frac{K_B\theta_D}{h}$ θ_D being the Debye temperature.

Given $g(\nu) = 6Nh^2\nu/(K_B\theta_D)^2$, deduce the expression for E for $T << \theta_D$ and discuss the temperature variation of specific heat for $T << \theta_D$ (Given $\int_0^\infty \frac{x^2 dx}{e^x - 1} = 2.404$)

(1990)

2. Derive the expression for the specific heat of a solid on the Einstein model. Comment on its shortcomings. (1991)

3. Derive an expression for the specific heat of solids in Einstein's model. Explain Einstein temperature (T_E). Find the value of specific heat when

(i) $T >> T_E$ (ii) $T << T_E$ (iii) $T = T_E/2$

(1993)

4. Write the expressions obtained from Einstein's and Debye's theories for the specific heat of solids: What is the basic difference between the two theories? Calculate the heat required to raise the temperature of a solid of mass m from T_1 to T_2 in the low temperature region.

(1995)

θ_D

5. State the basic assumptions of Debye theory of specific heat of solids and write the expression for Cv derived from this theory. Show that this expression yields the famous T^3 law of specific heat at low temperatures. Discuss the extent to which the theory agrees or disagrees with observations on specific heat through the variation of the Debye characteristic temperature θ_D with temperature, in general? (1998)

6. The specific heat of a substance is found to vary with temperature in the following way $C(T) = aT + bT^2$, where C (T) is the specific heat at the temperature T and 'a' and 'b' are constants. Compare the average specific heat of the substance in the temperature range 0 - T to the specific heat at the mid - temperature $\frac{T}{2}$ (1999)

7. Mention the assumptions made by Einstein in explaining the variation of specific heat of solids with temperature. Show how these assumptions were used to derive the formula for the specific heat of solids. How and why Einstein's theory fails at very low temperatures. (1999)

8. Discuss the differences in the assumptions underlying Einstein and Debye theories of specific hear C_v. Give schematic plots of C_v versus reduced temperature for these theories and elucidate the differences therein. Elaborate the meaning of the "law of correspondence states" for these plots. (2005)

9. State Dulong and Petit's law How does it agree with experiment ? Discuss the limitations of the classical theory and success of the quantum theory in explaining the specific heat of solids. (2006)

10. What are the limitations of Einstein's theory of specific heat of solids when compared with experiments at low temperature? Outline the assumptions made in Debye's theory and show that the specific heat at low temperature follows $C_v \propto T^3$ law. What is the significance of Debye's temperature, T_D ? (2009)

⊛ $\text{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-u^2}\,du$

TUTORIAL SHEET : 25

Maxwell- Boltzmann's Statistics

1. A gas possess a Maxwellian velocity distribution function show that the fraction of molecules in a given volume that possesses a velocity (+Vx) in one direction only and whose magnitude is greater than some selected value V_0 is

$$\int_{V_0}^{\infty} f(v_x)\,dV_x = \frac{1}{2}\left[1-\text{erf}\left(\frac{1}{2}\frac{mv_0^2}{KT}\right)^{1/2}\right]$$

symbols have their usual meanings.

(1988)

2. Find the temperature at which r.m.s. velocity of nitrogen molecules in earth's atmosphere equals the velocity of escape from the earth's gravitational field. ~~Mass of~~ N_2 atom = 23. 24 × 10^{-24}gm. Mean radius of earth = 6370 km.

(1988)

3. Calculate the mean free path of helium atoms at NTP, the co-efficient of viscosity being 190×10^{-7} kg $m^{-1}s^{-1}$. Atmospheric pressure = $0.076 \times 13.6 \times 10^3 \times 9.81$ N/m^2.

(1988)

⊛ 76 mm of Hg

4. Explain, using the kinetic model, why peaks in the curves showing Maxwell distribution of molecular speeds move towards higher speed at higher temperature.

(1989)

5. Calculate the mean free path of molecules of H_2 gas at 20^0C at atmospheric pressure. Assume the molecular diameter to be 2.00×10^{-10}m.

(1990)

6. Write down the Maxwell - Boltzmann law for the distribution of speeds C of molecules in a gas. Show the distribution graphically for the temperature T and 2T; also write down the expression for average value of c^3.

(1990)

7. A system is composed of two-level atoms, the excited state 1 being 0.10 eV above the ground state, O. Find the fraction of all atoms which will be in state; 1 if the system is in thermal equilibrium at temperature 300K.

(1990)

8. Write down Maxwell - Boltzmann distribution for the energy of molecules of a gas at temperature T. Find the energy at which this distribution peaks. Compute in eV the mean energy of molecules of a gas at 27^oC.

(1991)

9. Calculate the temperature at which the average speed of H_2 molecules equals that of O_2 molecules at 350K.

(1992)

10. A shower of 6×10^3 molecules, each travelling initially with same velocity, traverses a gas. Estimate the number of molecules which will travel unaffected even after traversing a distance equal to twice the mean free path.

(1992)

$N_{NC} = N_0 e^{-\left(\frac{x}{\lambda}\right)}$

non collision

$$\boxed{\frac{dN}{N} = -\frac{dx}{\lambda}}$$

11. Derive an expression for the pressure exerted by an ideal gas on the walls of the chamber in terms of concentration of molecules 'n', gas temperature T and a universal constant. Specifically discuss how T comes into the picture? (1993)

12. Derive expressions for the Maxwellian distribution of (i) one component of velocities (ii) one component of momenta, in the molecules of an ideal gas. (1994)

13. Calculate the most probable speed Vp, the average speed $\langle V \rangle$ and the root - mean square speed $\langle V^2 \rangle^{1/2}$ for hydrogen molecules at 273 K. (1995)

14. What is Brownian motion? Deduce Einstein's formula for translatory Brownian motion of particles suspended in a liquid and hence determine the Avogadro's number. (1996)

15. State the principle of equipartition of energy. What are its limitations? Show that it is applicable only when the energy is a quadratic function of the associated variable. (1996)

16. how the distribution of velocities for temperatures T_1, T_2 and T_3 ($T_1 > T_2 > T_3$) of gas molecules according to the Maxwell - Boltzman law. Using this law prove that the most probable velocity is $\sqrt{\frac{2}{3}}$ times the root mean square velocity. (1997)

17. Obtain an expression for the mean free path. Mention the correction introduced by Maxwell. Calculate the value of Avogadro's number, if the mean free path of nitrogen molecules at STP is 6.85×10^{-8}m. The molecular diameter is 3.5 A°. (1997)

18. At the NTP the mass of one litre of H_2 is 0.09 gm. Calculate the (i) RMS (ii) Mean (iii) Most probable speed at 27°C. (1999)

19. The RMS speed of Oxygen molecules at 0^0C is 460 m/sec. What would be the RMS speed of Argon molecules (Mol. wt. = 40 gm/mole) at 40^0C and at what temperature this speed would be double that at NTP? (1999)

20. What is the most probable distribution of speeds in a large number of molecules of a gas and indicate the steps for its derivation. (2000)

21. Derive an expression for the Maxwellian distribution of velocities for the molecules of an ideal gas. (2001)

22. 100 particles at a temperature T are distributed among three energy levels, $E_0=0$, $E_1 = KT$ and $E_2 = 2KT$. What is total energy of the system? (2003)

23. State the law of equipartition of energy. Show how this law can be used to calculate specific heat of gases and hence find the ratio $\gamma = C_p / C_v$ for diatomic and triatomic gases. (2008)

24. Consider N independent particles, each of which can be in either of two energy states $+\epsilon$ or $-\epsilon$. Derive expression for entropy of micro canonical ensemble for this system, where $f = \frac{\sum \epsilon_i}{N\epsilon}$ is fixed ~~ε is fixed and~~ ϵ_i is Energy of ith particle

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TUTORIAL SHEET: 26
F-D & B-E Statistics

1. Derive the Bose- Einstein's distribution for an ideal gas. (2002)

2. Disuses the phenomenon of Bose –Einstein's condensation. Obtain the expression for the condensation temperature. Briefly comment on observation of Bose –Einstein's condensate. (2002)

3. Define Fermi energy. For an ideal Fermi gas of N particles at absolute zero temperature, show that the total energy is 3/5 NE_f where E_f is the Fermi energy. (2003)

4. Show that for a distribution of electrons, the number of electron Ni in the energy state Ei are given by

   $$N_i = g_i / A \exp(E_i / kt) + 1$$

   Where g_i represents the no. of quantum stales in the energy level E_i. Further state under what condition this distribution law goes over to Maxwell-boltzmann statistics.

   Show by drawing curves how Fermi –Dirac distribution function varies with the energy at T =0 and also at the other finite temperatures. (2004)

5. Starting from the expression $N = \sum_k \langle n_k \rangle$, where $\langle n_k \rangle$ is the average number of particles in the k^{th} quantum state, derive an expression for the average number of particles in the ground state of an ideal Bose gas. (2005)

6. Utilize the above expression to elaborate the concept of the Bose –Einstein condensation and discuss that the phenomenon explains qualitatively the properties in the low –temperature phase of liquid ^{4}He. (2005)

7. Derive the expression for the Fermi – Dirac distribution function. Represent it graphically for $T = 0$ and $T \neq 0$. (2006)

8. Derive a relation between the total number of Fermions in terms of Fermi momentum and hence obtain te expression for the total energy E of the system at absolute zero Combine this expression with the equation of state $PV = \frac{2}{3}E$ to show that the pressure of an ideal Fermi gas at T = 0 is proportional to $\frac{5}{3}$ power of its number density. (2007)

9. Show that at $T = 0$, the Fermi distribution function has a value 1 for energies less than the Fermi energy ϵ_F and is zero above it. For a system of non-interacting electrons at T = 0, show that the ground state energy of the system of N particles is $\frac{3}{5}NE_F$. (2008)

10. Energy distribution for n_i particles in classical statistical mechanics is given by

    $$n_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

    Where α and β are constants. g_i is the single particle states in the i th level. Using equipartition theorem, show that correct thermodynamic interpretation is

    $$\beta = \frac{1}{kT} \qquad (Use. \int_0^\infty e^{-x} x^{1/2} dx = \frac{\sqrt{\pi}}{2} \text{ and}$$

    $$\int_0^\infty e^{-\beta x} x^{3/2} dx = \frac{3\sqrt{\pi}}{4\beta^{5/2}})$$

    (2009)

11. Calculate the number of different arrangements of 10 indistinguishable particles in 15 cells of equal a priori probability, considering that one cell contains only one particle.

(2010)

12. Consider the following statement:

"The Fermi energy of a given material is the energy of that quantum state which has the probability equal to $\frac{1}{2}$ of being occupied by the conduction electrons."

Is the above statement correct? Give reasons for your answer.

(2010)

Q. Show that Fermi Dirac distⁿ lead to Pauli Exclusion Principle.

या तो g_i को Constant मान के $\langle E\rangle = \frac{1}{2}kT$ Prove करो

या फिर g_i को $Ae^{\frac{1}{2}}$ मान के $\langle E\rangle = \frac{3}{2}kT$ Prove करो