

8/8/23

- (1) Basic Concepts of Thermodynamics.
- (2) Introduction to Energy Balance without chemical rxn. - Estimation of Parameters
- (3) Energy Balance with chemical rxn. - Steam Tables
- (4) Humidity - Psychometric chart

Steam at

$$3 \text{ atm} \rightarrow 1.5 \text{ atm}$$

450 K

$T = ?$

but, steam is not an ideal gas!

we must be tempted to use the ideal gas eqn.

instead use the  
Steam Table!

surroundings

Nature of the boundary

System

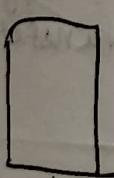
open system

Boundary

closed system

isolated system

Closed system



Nature of the boundary

Permeable vs Non-permeable

open system?

No  
permeable

Yes  
permeable boundary

Balloon:



closed system

(with a flexible membrane)

piercing of a balloon

open system



closed system

rare example of a closed system without a definite boundary

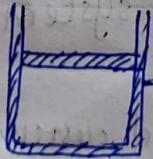
Thermoflask: isolated system

Can the boundary of a closed system be insulated?

Yes. 2 modes of energy transfer:

i) Heat transfer

ii) Work done



insulated but the piston can move up & down, thus doing some work

closed

system

energy

transfer

State:

condition of the system.

1) How to define the state?

2) And, as per classical thermodynamics, when can the state of the system be defined?

minimum no. of independent variables that fully capture the condn. of a state

when the system is in equilibrium

### Nanoscale:

the length scale at which intensive properties become extensive

H.W.  
Colour of nanogold.

electrical properties  
colour  
optical properties

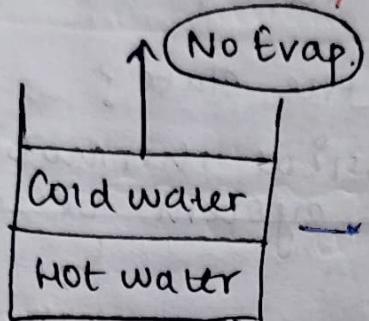
### Thermodynamic equilibrium:

no change in state for a period of time.

#### Types:

if a system obeys all these eqbm. independently

- ① Mechanical Eqbm.
- ② Thermal Eqbm.
- ③ Chemical Eqbm.
- ④ Phase Eqbm.
- ⑤ Radiative Eqbm. (Extra)



attainable when  
humidity is 100%.

Egbm.  
mech ✓  
chem. ✓  
phase ✓  
thermal ✓

uniform temperature in the bucket → heat transfer → hot water moves up due to density diff.

### case 1

hot water over  
cold water

↓  
cold water being  
denser remains  
at the bottom

slower thermal homogenization

## case 2

cold water over  
hot water

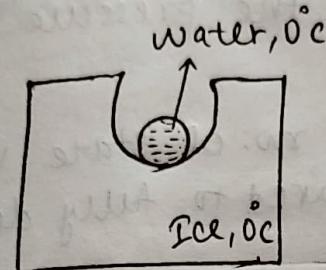
hot water rises &  
in the process  
facilitates heat  
transfer

faster thermal homogenization

as twice

Eabm.:

- no macroscopic flow
- no transfer of heat
- no chemical rxn.
- no mixing



→ actually, nothing  
will happen, neither  
ice melts, nor the  
water droplet freezes.

$(\text{internal energy})$   
 $\text{of water at } 0^\circ\text{C}$ )  $>$   $(\text{internal energy})$   
 $\text{of } \cancel{\text{ice}} \text{ at } 0^\circ\text{C}$ )

Latent Heat

energy transfer →   
water molecule  
ice molecule

∴ an ice molecule takes up energy from the water molecule & melts. At the same time, the water molecule that loses the energy solidifies. Thus ultimately, there is no observable change given  $0^\circ\text{C}$  is maintained.

↓  
the system is in equilibrium }  
but there is molecular-level }  
transfer; no  
macroscopic flow.

Dynamic  
Eabm.

## Defining the State:

minimum no. of independent variables

Eg:  $H_2O$  at  $80^\circ C$

can we say it is water?

thus, P & T need  
to be defined to  
know the state  
of  $H_2O$

No, because we do not know  
if the pressure is 1 atm.

Degrees of freedom: min. no. of state variables  
required to fully define a system

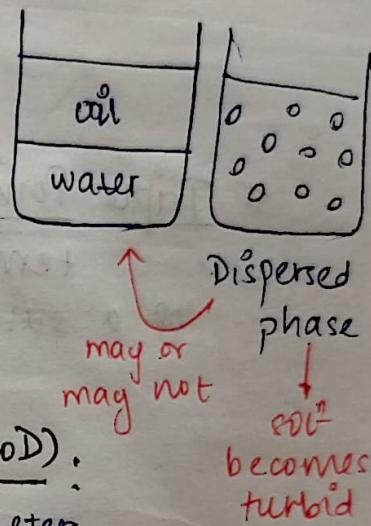
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## # Phase:

part or whole of the system which is:

- Physically distinct
- Macroscopically homogeneous.

Eg: Oil-water system



## # Degrees of freedom (acc. to ThermoD):

minimum no. of parameters you need to independently define for defining the state.

## # Gibbs Phase Rule:

$$F + P - C = 2$$

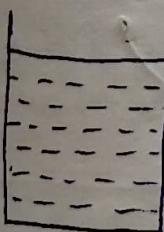
Phase

Degrees of freedom

Components

|   |
|---|
| UV400   |
| cuts off all $\lambda$ below 400 nm   |
| cheap sunglasses (dark) do not cut off $\lambda$ below 400 nm that too with a dilated pupil due to dark |

①



Glass of Water

$$P = 1 \text{ atm}$$

$$C = 1$$

$$P = 1$$

$$F + 1 - 1 = 2$$

$$F = 2$$

Both P & T needs to be defined

(2)



$$C = 1$$

$$P = 2$$

$$F + 2 - 1 = 2$$

$$\boxed{F=1}$$

I have water vapour & liquid water coexisting

at  $P = 1 \text{ atm}$

at  $T = 100^\circ\text{C}$

$T$  has to be  $100^\circ\text{C}$

$P$  has to be  $1 \text{ atm}$

### # Triple Point:

temperature at which all 3 phases of a substance coexist.

$$P = 3$$

$$F + P - C = 2$$

$$F + 3 - 1 = 2$$

$$\boxed{F=0}$$

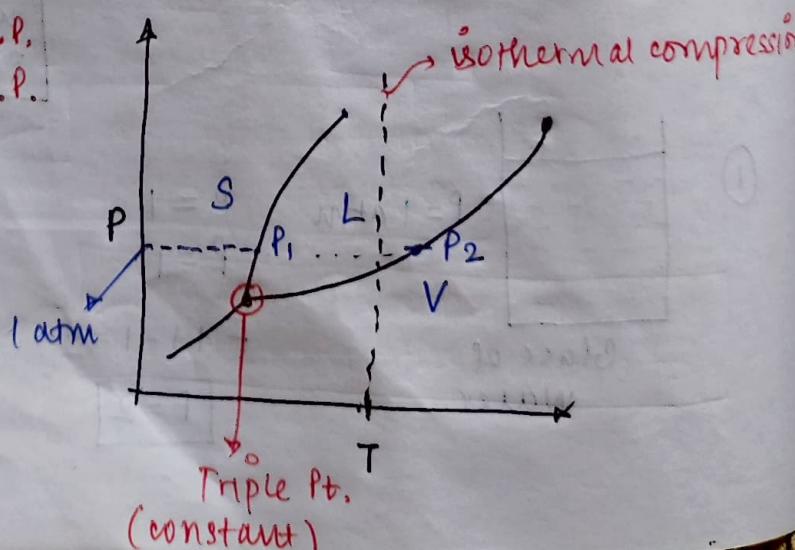
$\therefore$  the system is invariant, i.e., it does not move state

$$Q = S - I + F$$

### # Phase Diagram [Typical Single Component Phase Diagram].

$P_1$  - Normal M.P.

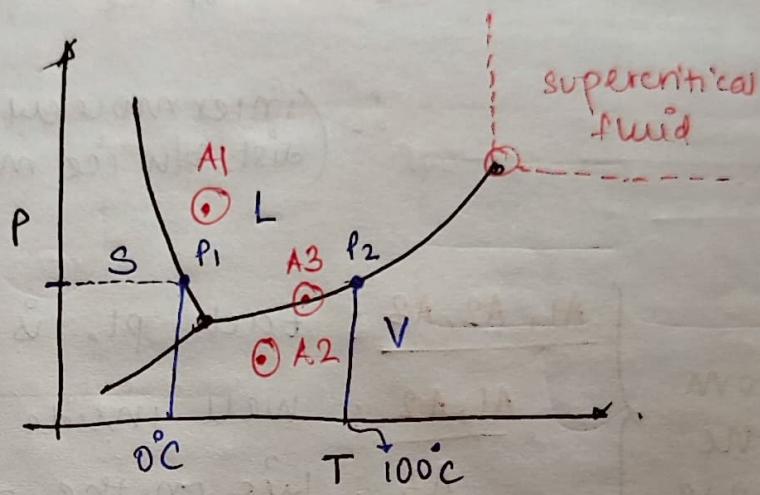
$P_2$  - Normal B.P.



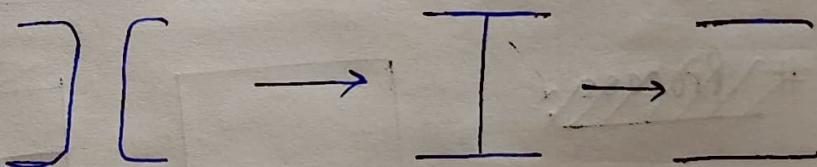
Trend:

If  $P \uparrow$ , both M.P. & B.P.  $\uparrow$

### Phase Diagram of Water.



When we press two blocks of ice, they join



When we press, we are applying  $P$  (we are going up vertically in the phase diagram).

$$S \rightarrow L$$

When we withdraw the pressure,  $P$  drops, this  $L$  again solidifies

thus ice blocks join

Regelation

$(\text{Density of ice}) < (\text{Density of water})$

a. for the same volume,

$(\text{mass of ice}) < (\text{mass of water})$

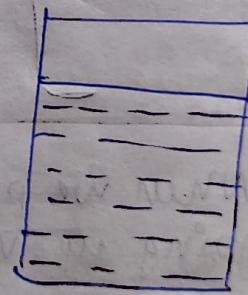
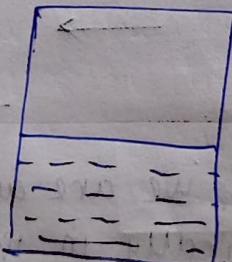
$(\text{no. of molecules})_{\text{of ice}} < (\text{no. of mol.})_{\text{of water}}$

$\therefore (\text{intermolecular dist. b/w ice mol.}) > (\text{b/w water molecules})$

form  
the  
phase  
diagram

- A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>: Each pt. is a state
- A<sub>1</sub>, A<sub>2</sub>: well inside a phase
- A<sub>3</sub>: lies on the phase boundary,  
will have one reduced degree of freedom

# Process:



$$C = 1$$

$$P = 2$$

$$\Rightarrow F = 1$$

50% Liq +  
50% Steam

90% Water + 10% steam

will lie on the same point on the phase diagram

limitations  
of Phase Rule

Phase rule does not take into consideration the compositions

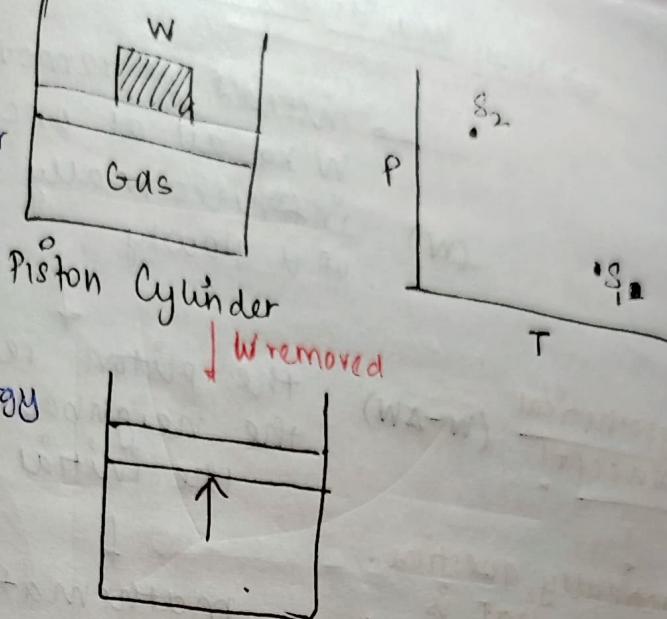
$$P = 1 \text{ atm}$$

↓  
implied  
that  
 $T = 100^\circ\text{C}$

## # Process :

state of a system  
is changing  
from one  
state to another

↓  
always occurs  
when there is  
change in energy  
↓  
given or  
withdrawn



Dissipation: interconversion of friction  
into heat that is lost.

thus, a frictionless piston  
is considered in problems

→ can we join  $S_1$  &  $S_2$  to show the process?

NO, as the intermediate processes/  
states are not in equilibrium

## # Reversible Process :

Any system that goes  
from  $S_1$  to  $S_2$  &  
back to  $S_2$  → Cyclic Process

Necessary condition:  
the forward path  
is known well

↓  
if the same path  
is followed back  
↓  
Reversible Process

↳ Ideal Process

⇒ Now, how do we know the path of a process?

• To instead of removing the entire  $W \text{ kg}$  all at once, if we remove infinitesimally small amounts of it slowly

hypothetical concept!

$(W - \Delta W)$

the piston remains in the neighbourhood of the initial eqbm.

↓  
practically, question arises, what is infinitesimally small?

↓  
mathematically, the system never departed the equilibrium

### Quasi-Equilibrium / Ideal process

"An ideal process may or may not be reversible but a reversible process must be ideal."

### # Energy Balance :

First Law of Thermodynamics : → Energy can neither be created nor destroyed.

$$\Delta E = E_{S2} - E_{S1} = \pm Q \pm W$$

energy at the final state      initial state

possible only when there is a process

except in a nuclear rxn

$$E = mc^2$$

mass defect

$$\Delta U = \pm Q \pm W$$

$$dU = \pm \partial Q \pm \partial W$$

for open system

cannot define a state → no eqm

valid only for a closed system

mass is conserved

$$E = mc^2$$

mass defect → in a nuclear rxn, the atomic mass is not conserved. The difference is mass defect.

mass can be destroyed, but no instances of mass being created

$$mc^2 \rightarrow E$$

energy can be created, but no instances of energy being destroyed

$$E = E_{PE} + E_{KE} + E_U + E_s$$

↑                              ↓                              ↓                              ↓

kinetic energy            potential energy            internal energy            surface energy

$$\Delta E \rightleftharpoons \Delta U$$

no ΔKE  
no ΔPE  
no ΔEs

our very famous piston-cylinder system

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$$W \pm Q = U$$

$$\Delta E = \pm Q \pm W$$

$$\delta E = \pm \delta Q \pm \delta W$$

state  
function

$$E_2 - E_1$$

path  
function

we cannot write

$$Q_2 - Q_1 \text{ (or) } W_2 - W_1$$

macroscopic P.E.  
of the system

$$E = P.E. + K.E. + U + \text{surface energy}$$

$$(mgh) \left(\frac{1}{2}mv^2\right)$$

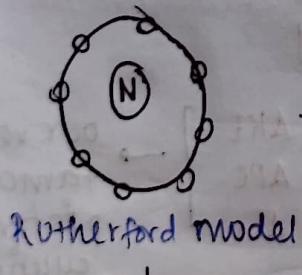
Neglected for  
bulk systems

### Components of U.

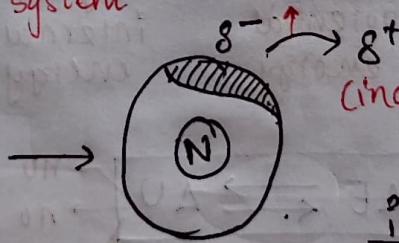
- Internal K.E.  $\rightarrow k_B T$  (average translational)
- Internal P.E.  $\rightarrow$  vander waals energy
- Rotation, Vibration  $\rightarrow$  depends on the molecule

we need  
neighbouring  
molecules

more like a property  
of the system



but  $e^-$  are not  
equally spaced



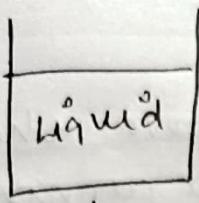
induced dipole-  
induced dipole  
interaction

$$= -\frac{A}{r^6}$$

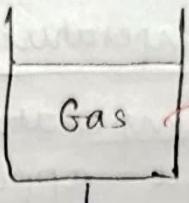
universal  
vdw

$$\begin{cases} I.D. - I.D. \text{ inter}^n \\ P.D. - I.D. \text{ "} \\ P.D. - P.D. \text{ "} \end{cases}$$

increasing  
strength



↓  
internal energy  
is dominated  
by internal P.E.



→ Mean free path  $\propto$   
system where the  
internal energy is  
dominated by  
internal K.E.

↓  
since neighbouring  
molecules are very  
far apart, internal  
P.E. cannot be  
manifested.

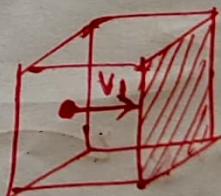
### Ideal gas:

A gas whose internal energy  
comprises of only internal K.E.

van der waals  
eqn. of state

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

exclusion  
volume



\* Gas pressure is a  
manifestation of  
collisions with the  
walls of the container

↓  
not collisions that  
are intermolecular

$$\frac{1}{r^6} = -\frac{A}{(r^3)^2} \propto \frac{1}{v^2}$$

} dimensionally related

when a gas molecule  
is about to hit the  
wall, it experiences  
vdw attr<sup>n</sup> from wall.

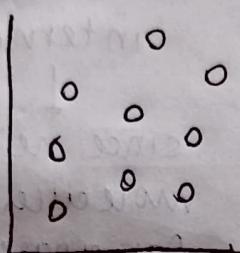
attr<sup>n</sup> causes  $v_1$  to ↑  
 $v_1 + \Delta v_1$

pressure correction : ↑  $P_0$

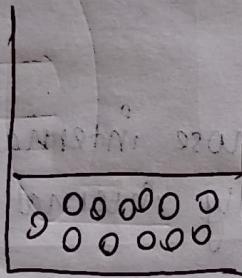
## Critical Temperature :

Temperature above which whatever pressure you apply, you cannot liquefy a gas.

## Liquefaction of Gas :



So far no S.I.  
between



Gas  $\rightarrow$  Int. P.E.  $\rightarrow 0$

↓  
compress

to reduce the  
mean free path

bringing the molecules  
close so that I.D.-I.D.  
or vdw interactions  
can start

$$TA = (v - V) \left( \frac{N}{V} + 1 \right)$$

liquefaction is only  
possible when:

(internal)  
(internal)  
P.E. > K.E.

$-A/r^6$

KBT

remains almost  
constant with T

$\uparrow$  as the  
 $T$  increase

Critical Temp.  $\Leftarrow$

Thus, there is a  $T$  above which the P.E.  
cannot exceed the internal K.E.

$$\Delta E = \pm Q \pm W$$

Heat transfer  
↓  
due to a diff. in T

Work done

- conduction
- convection
- radiation

*Show work*

$$W = - \int_{\text{state 1}}^{\text{state 2}} \vec{F} \cdot d\vec{s} = - \int_{\text{state 1}}^{\text{state 2}} P \cdot dV$$

$$-\int \left(\frac{\vec{F}}{A}\right) \cdot (A d\vec{s})$$

state 2

Mechanical Work → closed system → displacement of the system  
 boundary

Sign Convention:

Work done by the system : - ve  
 Work done on the system : + ve

system is spending some internal energy

loss of its int. energy

hence - ve

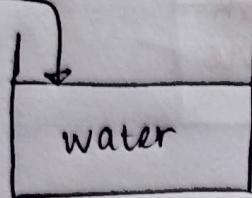
surrounding is spending energy

gain of int. energy  
hence + ve

Electrical Work:  $W = Q \int_a^b \vec{E} \cdot d\vec{r}$

Torque :  $T = Fr$

Shaft Work :  $W_c = F \cdot s = \frac{I}{r} \cdot 2\pi r n$

$Q$ 

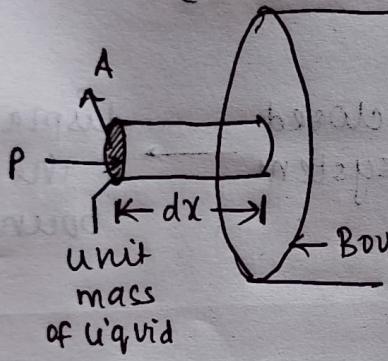
$$(p = \text{constant})$$

$$\text{Mass flow rate} = m = \rho V$$

$$16.9 - = 26.7$$

1 atm                    1.0132

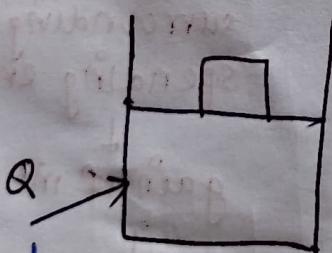
### Flow Work



$$\delta W_{\text{flow,in}} = PA dx$$

$$\frac{\delta W_{\text{flow,in}}}{\delta t} = \frac{PA dx}{dt}$$

$$= P \frac{dA}{dt}$$



raises the T  
raises the V

Flexible wall:  $U \uparrow (PV)_{\text{work}} \uparrow \rightarrow \text{Enthalpy}$

Rigid wall:  $U \uparrow (PV)_{\text{work}} = 0$

