

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

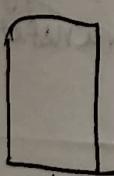
open system

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

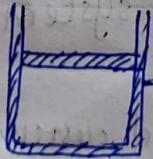
Thermoflask: isolated system

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

electrical properties
colour
optical properties

H.W.

Colour of nanogold.

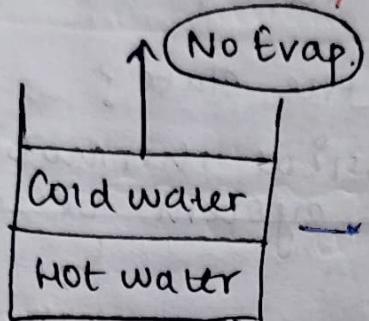
Thermodynamic equilibrium:

no change in state for a period of time.

Types:

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

if a system obeys all these eqbm. independently



attainable when
humidity is 100%.

Egbm.
mech ✓
chem. ✓
phase ✓
thermal ✓

uniform temperature \leftarrow heat transfer in the bucket

hot water \rightarrow
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

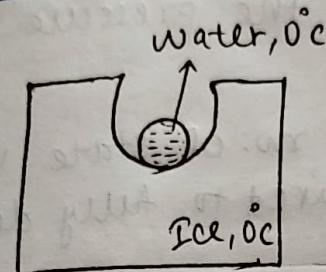
hot water rises &
in the process
facilitates heat
transfer

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.

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

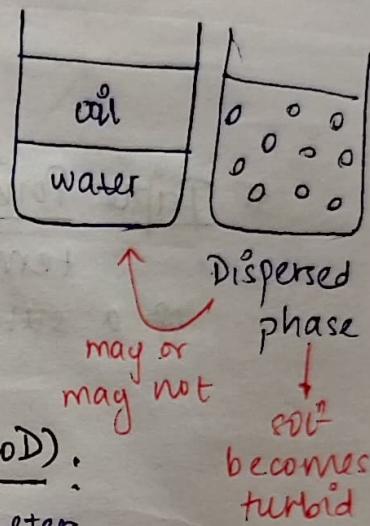
22/8/23

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:

$$F + P - C = 2$$

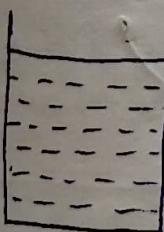
Phase

Degrees of freedom

Components

UV400
cuts off all λ below 400 nm
cheap sunglasses (dark) do not cut off λ 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°C

P has to be 1 atm

Triple Point:

temperature at which all 3 phases of a substance coexist.

$$P = 3$$

$$F + P - C = 2$$

$$F + 3 - 1 = 2$$

$$\boxed{F=0}$$

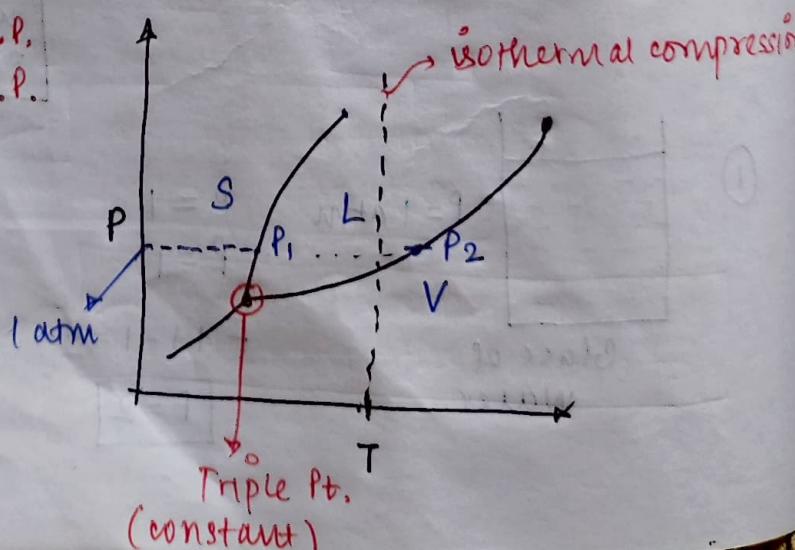
\therefore the system is invariant, i.e., it does not move state

$$Q = S - I + F$$

Phase Diagram [Typical Single Component Phase Diagram].

P_1 - Normal M.P.

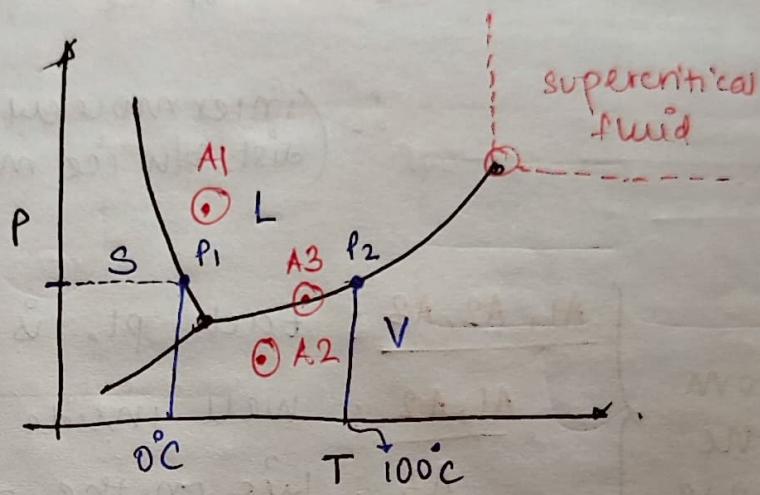
P_2 - Normal B.P.



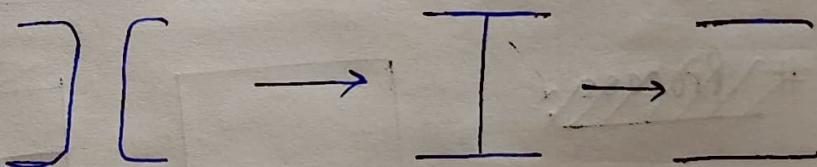
Trend:

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,

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

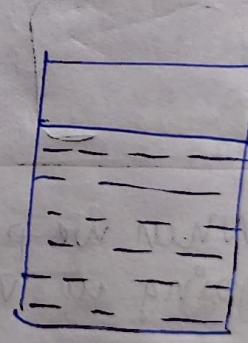
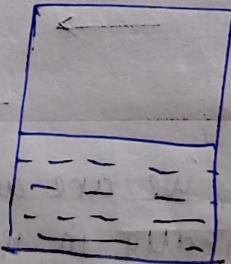
$(\text{no. of molecules})_{\text{of ice}} < (\text{no. of mol.})_{\text{of water}}$

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

form
the
phase
diagram

- A₁, A₂, A₃: Each pt. is a state
- A₁, A₂: well inside a phase
- A₃: 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

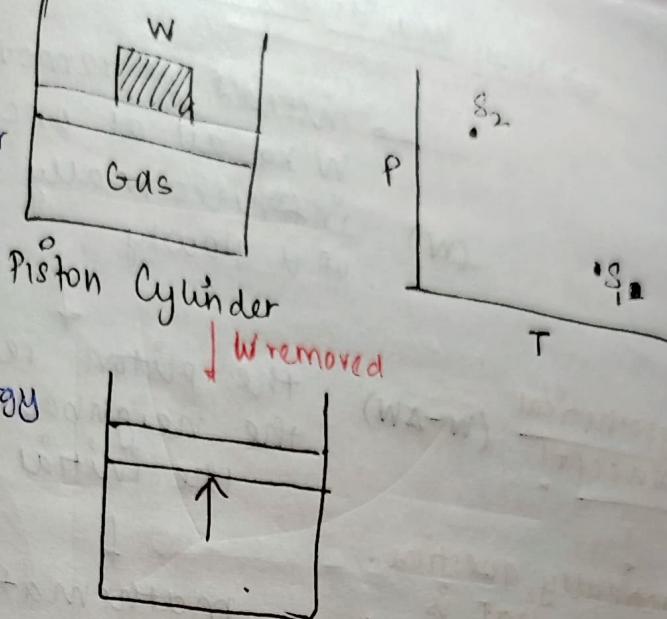
Phase rule does not take into consideration the compositions

$P = 1 \text{ atm}$
↓
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 eqbm

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

29/8/23

$$W \pm Q = U$$

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

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

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

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

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

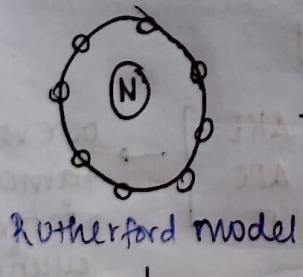
Neglected for
bulk systems

Components of U.

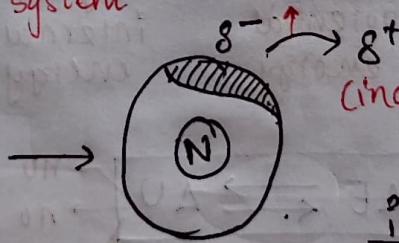
- Internal K.E. $\rightarrow k_B T$ (average translational)
- Internal P.E. \rightarrow vander waals energy
- Rotation, vibration \rightarrow depends on the molecule

we need
neighbouring
molecules

more like a property
of the system



but e^- are not
equally spaced



localization
of e^- cloud.

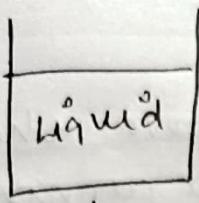
induced dipole-
induced dipole
interaction

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

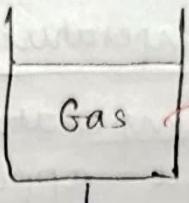
universal
vdw

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

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.

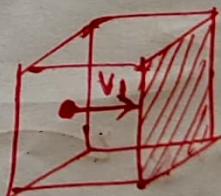
Ideal gas:

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



when a gas molecule
is about to hit the
wall, it experiences
vdw attrⁿ from wall.

↓
not collisions that
are intermolecular

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

} dimensionally related

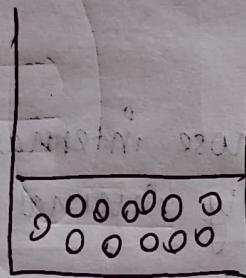
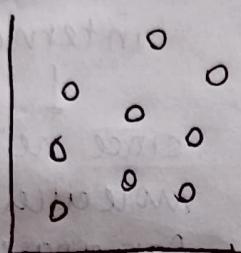
attrⁿ causes v_1 to ↑
 $v_1 + \Delta v_1$

pressure correction : ↑ P_0

Critical Temperature :

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

Liquefaction of Gas :



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

$-A/r^6$

remains almost
constant with T

\uparrow as the
T increase

Critical Temp. \Leftarrow

Thus, there is a T above which the P.F.
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

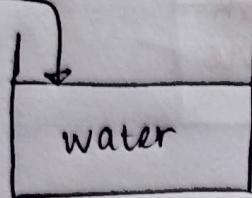
gain of int. energy

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 

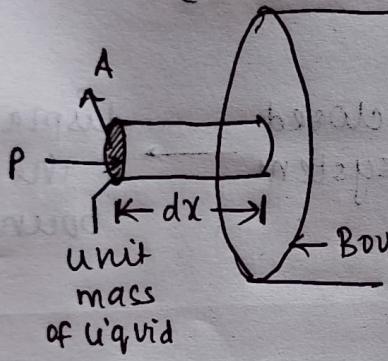
$$(p = \text{constant})$$

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

$$16.9 - = 26.7$$

1 atm 1.0132

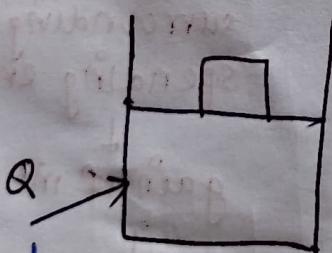
Flow Work



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

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

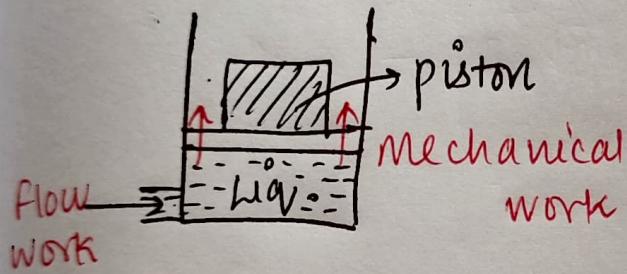
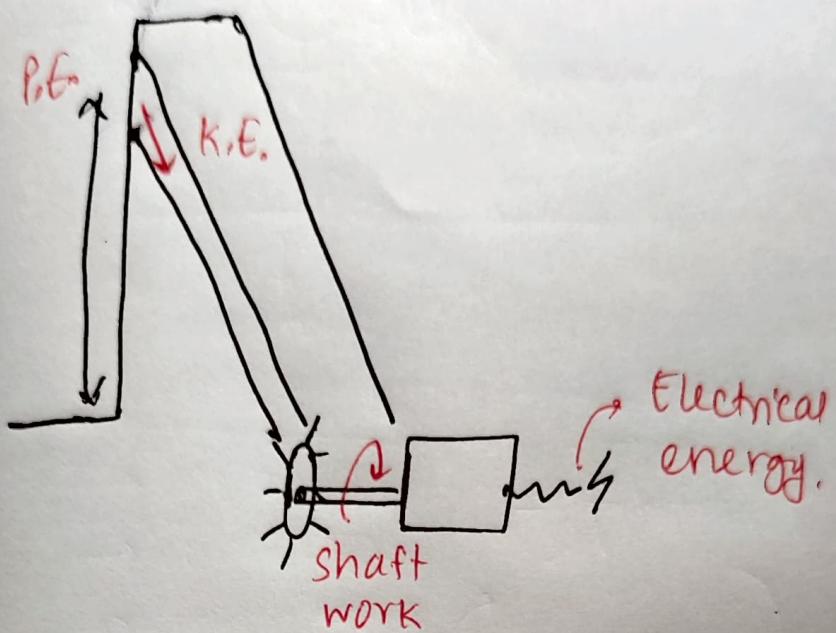
$$= P \frac{dA}{dt}$$



raises the T
raises the V

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

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



5/9/23

$$\delta F = \pm \delta Q \pm \delta W$$

Process → How many types?

↓
Thermodynamically

Ideal

Non-ideal

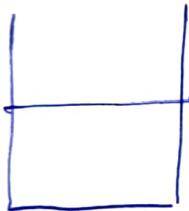
reversible

cyclic

both find
reverse and
processes
follow the
same path

Engineering / practical standpoint

Batch



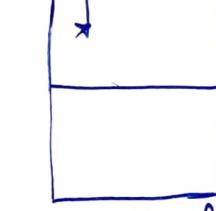
Tank ~~stop~~ of water
(also steady state)

inlet = outlet = 0

NO

liquid level
in the tank

Semi-batch

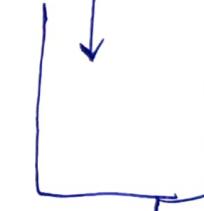


stop of coffee
tank of water

YES

$$h = f(t)$$

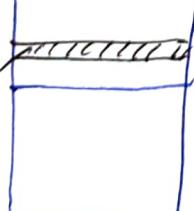
continuous



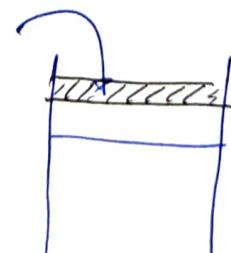
MAY OR

MAY NOT → steady state
(inlet = outlet)

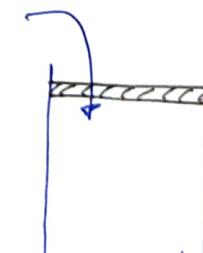
Lid



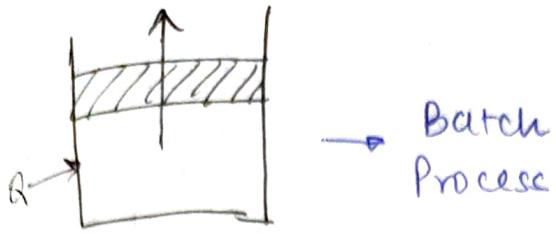
closed system



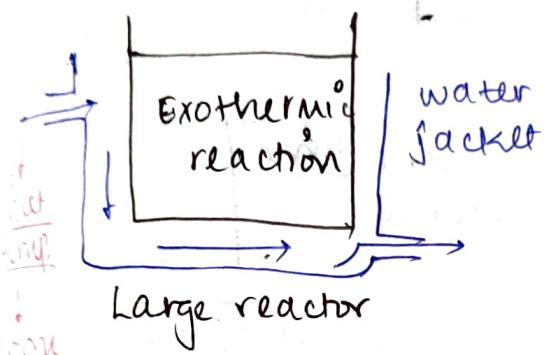
has to be
Open



These arrows
represent
flow of mass



[semi-batch could have been raised but for semi-batch mass needs to added/removed, not energy]



→ Water takes up the heat

maintains the temp. of reactor

This is our objective

we try to make the flow of H_2O in steady state

so we can calculate the flow so that heat is adequately transferred to it

Would we want the outlet be water or steam?

- Water
- As water has a much lesser specific volume than steam. Easier to handle.

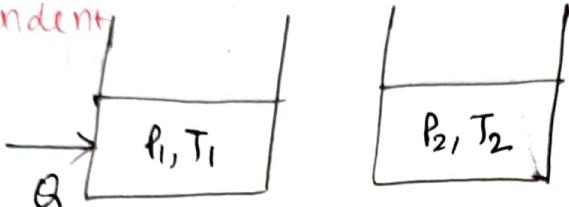
→ Water flow →

Process? Yes
Continuous? Yes.

$$dE = \pm \partial Q \pm \partial W$$

$$U_2 - U_1 = E_2 - E_1 = Q - W$$

Classical form
is independent of time



→ this classical energy
balance did not
tell us how much
time it took us to
re-equilibrate.

↓
that is after E_1 ,
at what time E_2
is considered.

In a continuous system time
must be considered

we take a small time interval $[At \rightarrow 0]$

↓
assumption is the system does
not deviate much from its
eqbm. state [ideal process]

$$\Delta U + \Delta KE + \Delta PE = \delta Q - \delta W$$

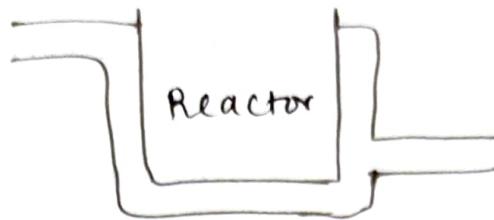
in the rate form

$$\lim_{At \rightarrow 0} \frac{\Delta U}{At} = \lim_{At \rightarrow 0} \left(\pm \frac{\delta Q}{At} \pm \frac{\delta W}{At} \right)$$

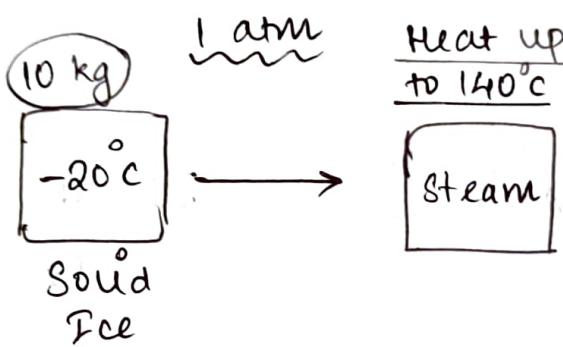
$$\Rightarrow \boxed{\frac{dE}{dt} = \pm \frac{\partial Q}{\partial t} \pm \frac{\partial W}{\partial t} = \pm \dot{Q} \pm \dot{W}}$$

↓
Deviation from Classical Thermodynamics

- we are taking into account time
- we can at max have a dynamic steady state

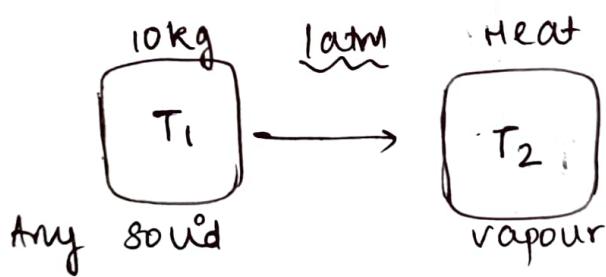


Estimation of Physical Properties



we need 5 parameters

- C_p of water
- C_p of ice
- C_p of steam
- L_iH_v of melting
- L_vH_i of vaporization



we need 7 parameters

- 3 sp. heat
- 2 latent heat
- T_1, T_2

Unit of C_p ? $\frac{\text{Kcal}}{\text{kg} \text{ } ^\circ\text{C}}$

Unit of λ ? $\frac{\text{kcal}}{\text{kg}}$

C_p, C_v : sp. heat capacity at const. pressure & const. volume

Heat Capacity: heat required to raise the temperature of 1 kg (or) 1 m³ of substance by 1 °C

Specific Heat Capacity: ratio of the heat capacity of the substance to the heat capacity of water
 ↓
in calories : 1

C_p, C_v → are actually heat capacities, but are called specific heat capacities (why? no idea!)

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

$$\partial Q = dU + PdV$$

$$U + PV = H$$

const. volume :

$$\hat{C}_v = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right) \Big|_v$$

$$\hat{C}_v = \frac{1}{m} \left(\frac{\partial U}{\partial T} \right)$$

const. pressure:

$$\hat{C}_p = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right) \Big|_p$$

$$= \frac{1}{m} \left(\frac{dU + PdV + Vdp}{\partial T} \right) \Big|_p$$

$$\hat{C}_p = \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)$$

$C_p, C_v = \text{Gas?}$

$$\boxed{\hat{C}_v|_{\substack{\text{ideal} \\ \text{gas}}} = 1.5 R}$$

comes from the
Kinetic Theory
of gases.

$$P = \frac{2}{3} \left\{ \frac{nV}{V} \left(\frac{1}{2} m \bar{u}^2 \right) \right\}$$

no. of molecules Total volume

$$\left(n = \frac{V}{N_A} \right)$$

no. of moles

$$= \frac{2}{3} \frac{n N_A}{V} \left(\frac{1}{2} m \bar{u}^2 \right)$$

$$\boxed{PV = \frac{2}{3} n \hat{U}_T}$$

Molar Translational Kinetic Energy.

from Ideal Gas Law:

$$PV = nRT$$

$\hat{U} \rightarrow$ Molar Internal energy

$$\Rightarrow nRT = \frac{2}{3} n \hat{U}_T$$

for an ideal gas

$$\mu RT = \frac{2}{3} \mu \hat{U}$$

$$\boxed{\hat{U} = \frac{3}{2} RT}$$

$$\boxed{\hat{C}_p|_{\substack{\text{ideal} \\ \text{gas}}} = 2.5 R}$$

$$\rightarrow \boxed{\hat{C}_p = \hat{C}_v + R}$$

$$\boxed{\frac{\hat{C}_p}{\hat{C}_v} = \frac{5}{3} = 1.67}$$

5(6) Parameters

No generic formulae is available $C_p \rightarrow$ Gas, Liq , Solid
 $\lambda \rightarrow \lambda_{\text{S-L}}, \lambda_{\text{L-V}}$ There is an exact ThermoD formula

We have found the sp. heat of gas, now can we find the other 4 parameters?

Pelt & Dulong Law

- The heat capacity of all crystalline solid elements is $= 6.2 \frac{\text{cal}}{\text{gm} \cdot \text{atom} \cdot \text{K}}$

- Atomic wt. $> 40 \rightarrow$ works well

- Exceptions -

<u>solid</u>	C - 1.8	2.8	Liquid
	H - 2.3	4.3	
	B - 2.7	4.7	
	Si - 3.8	:	
	O - 4.0	:	
	P - 5.4	:	

- For liquid - $8.0 \frac{\text{cal}}{\text{gm} \cdot \text{atom} \cdot \text{K}}$

KOPP Rule

The heat capacity of a solid compound is approximately equal to the sum of heat capacities of the constituents.

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_l)}$$

vapour pressure
 tendency of volatility

Molar latent Heat of Vaporiz.
 Molar sp. heat volume of Gas & liquid