

Chemical Process Calculation

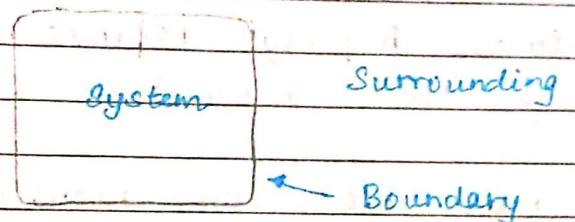
- The conservation equations :
- Conservation of mass
 - Conservation of energy

However, for nuclear rxn, the second one doesn't apply, this follows from the famous eqn:

$$E = mc^2$$



mass
defect



Isolated System

No heat or mass transfer

Boundary - Insulated, Rigid, Non-permeable

Closed System

No mass transfer but heat transfer

Boundary - Non-permeable, Non-rigid

Open System

Both mass and heat transfer

Boundary - permeable, Non-rigid

A system can be described by the following factors, rigidity, permeability and insulated or not.

- Earth is open system for energy, but closed system for matter.
- Isolated system : calorimeter, thermos flask

Property

- Observable and calculative things belonging to something

Intensive Property - Something that doesn't depend on size (Eg: Density)

Extensive Property - Depends on size.
(Eg: Mass, Volume)

- At nano scale, some intensive properties become extensive properties

Note:-

Generally, ratio of two extensive properties is an intensive property
(Eg:- Density = Mass / Volume)

However there are some exceptions like
Volume / Area = length which is again an extensive property.

State

Condition of a system

State

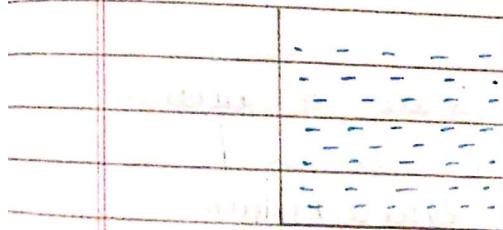
Steady state

(A condition of a system that doesn't change in time broadly)

Unsteady state

(A condition of a system that changes after some time)

Steady state



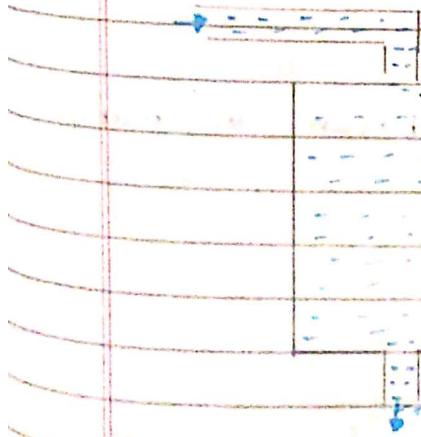
$$\dot{m}_{in} = 0$$

$$\dot{m}_{out} = 0$$

$$\Delta E = 0$$

Static Steady State

State



$$\dot{m}_{in} = \dot{m}_{out}$$

$$\dot{H}_{in} = \dot{H}_{out}$$

$$\Delta E = 0$$

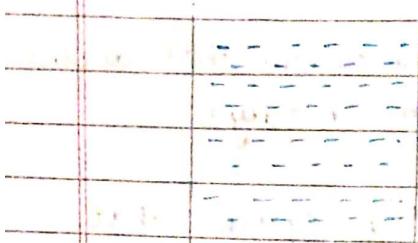
Mass gained by system
is Mass lost to surroundings

Dynamic steady state

State

Unsteady state

- Only possible in dynamic systems



→ Dynamic system

→ Unsteady state

Draining

Equilibrium

→ Equilibrium is sort of state of balance

→ A system itself can be equilibrium

→ A system can be in equilibrium with the surroundings.

→ A system can be in equilibrium in many ways.

→ Thermodynamic eq.

→ Mechanical eq.

→ Chemical eq.

→ Radioactive eq.

A body can be in eq. of particular kind at a time and need not be in other.

Eg:-



The shown system is in mechanical eq., while it's not in thermal eq.

Consider the below situation

~~heat transfer~~

T_1

$Q \rightarrow$

T_2

conduction

T_1

$Q \rightarrow$

T_2

Radiation

In radiation,
 $(T_1 > T_2)$

Second block will transfer
or receive heat depending
on block 1
Second block radiates heat
on its own but also
receives heat from block 1

$$Q = [\text{heat radiated from 1 to 2}] - [\text{heat radiated from 2 to 1}]$$

If $T_1 = T_2$

In conduction, $Q = 0$ (no transfer of energy)

In radiation, $Q = 0$ (no net transfer of energy)

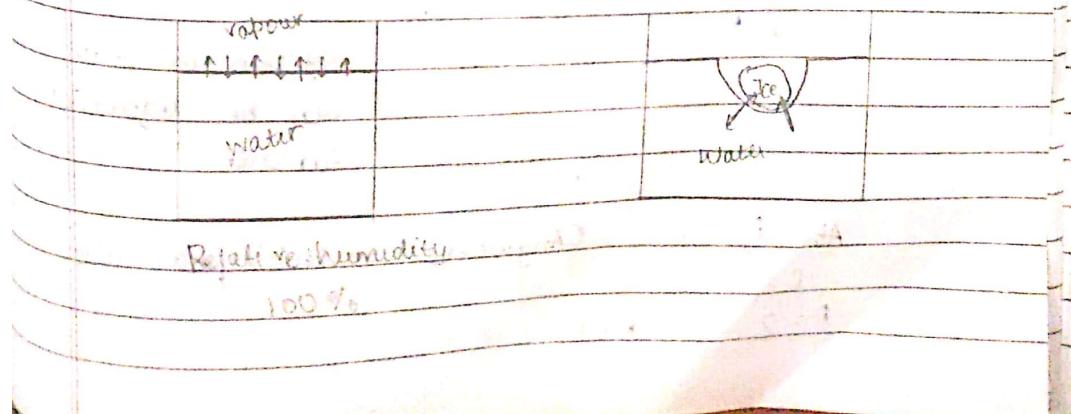
→ Water and ice co-exist at 0°C and are in dynamic equilibrium.

Rate of melting = Rate of solidification

Also, in the below case,

rate of evaporation

= rate of condensation



Phase
 (chemically uniform, physically distinct and mechanically separable (in most case))

If two phases are in eq., all their properties are same.

— No. of phases

$$F + P - C = 2$$

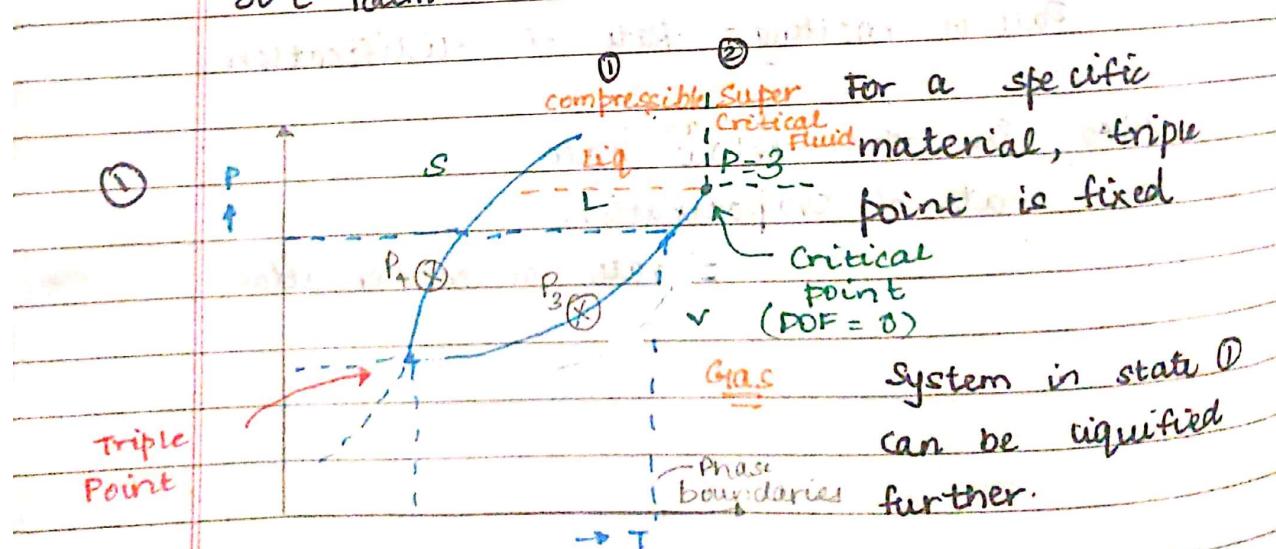
— degree of freedom

— No. of comp.

Water at 50°C isn't a state, as pressure need to be defined

Degree of freedom — No. of independent variables that needs to be specifically mentioned to define a state

Water	:	water	States are diff.
50°C 1atm	:	50°C 2atm	Phases are same



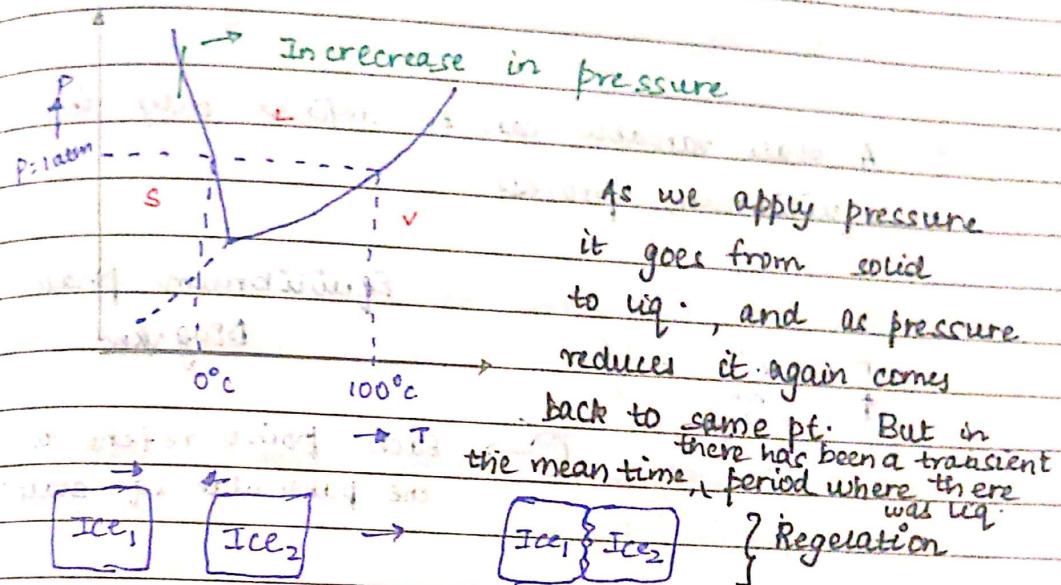
At P_3 $C=1$ (Anywhere in this phase diagram
 $C=1$)

$$P=2 \Rightarrow F=1$$

Scanned with CamScanner

Melting and Boiling points are two points marked on the phase diagram at $P = 1 \text{ atm}$.

The above one won't be the phase diagram for water as density of water \neq density of ice. For water, the slope of S-L phase boundary is negative.



They will fuse

As they are pressed, there is some water formed. Now we have a system, where as the pressure is increasing the system transforms from solid to liq. at const. temp.

Phase diagram ① can't capture phase diagram of water as it can't explain regelation.

- Adiabatic System $Q = 0$
- Isothermal $\Delta T = 0$
- Isobaric System $\Delta P = 0$
- Isochoric system $\Delta V = 0$

State variable:

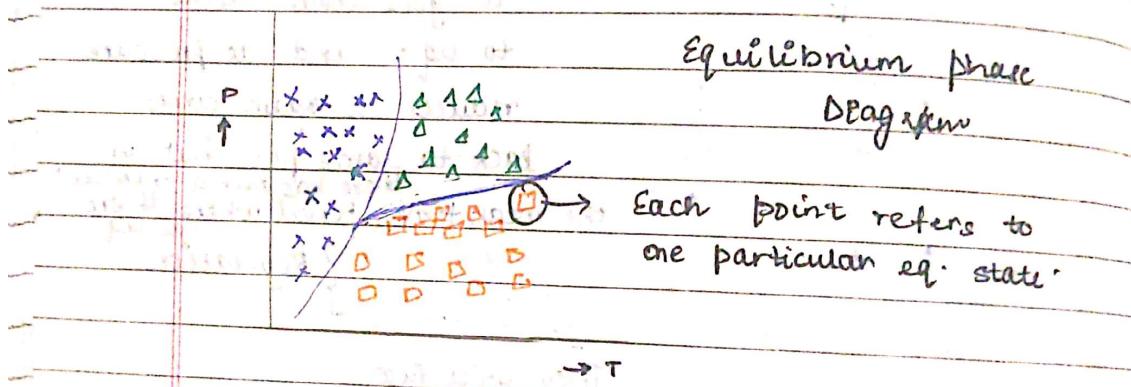
- Variables that depend on state only and not on the history of it.

Created			Overnight	Left
6 hrs before				

$T = 350$ → Temp is

state variable

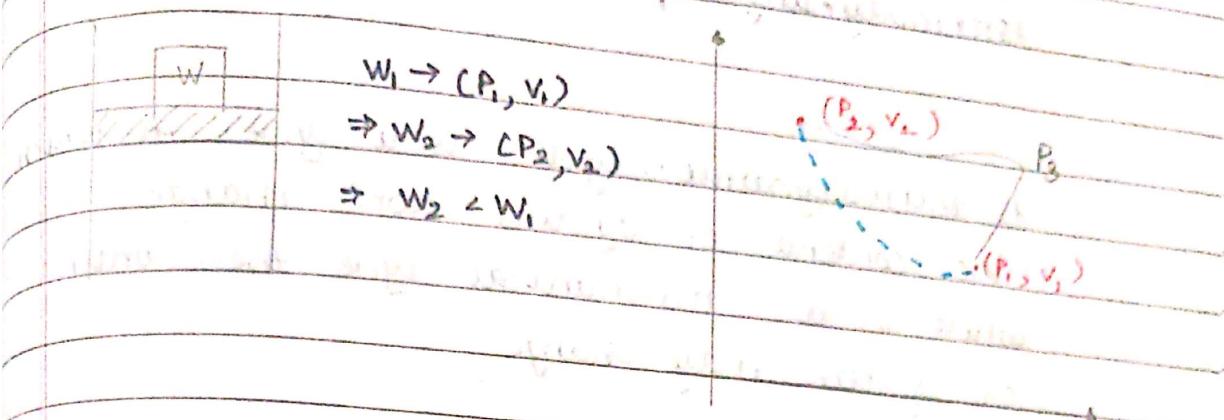
- A state variable can be defined only in equilibrium process



A state variable is something that not only depends on state but also something that can be identified when system is at eq.

process

When one or more state variables of a system changes from one equilibrium state to another equilibrium state



It is clear that can't say about the path in the above process

P_3 is a highly possible, as when W_1 is removed, there is increase in volume, i.e. the piston overshoots.

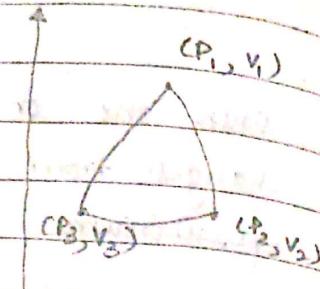
Considering the piston arrangement and equilibrium after each infinitesimal change then we can define the path

We assume system never deviates from equilibrium process

If for a process, the state variables of the path is known, it's an equilibrium process and if they are not known it's a non-equilibrium process

Cyclic process:-

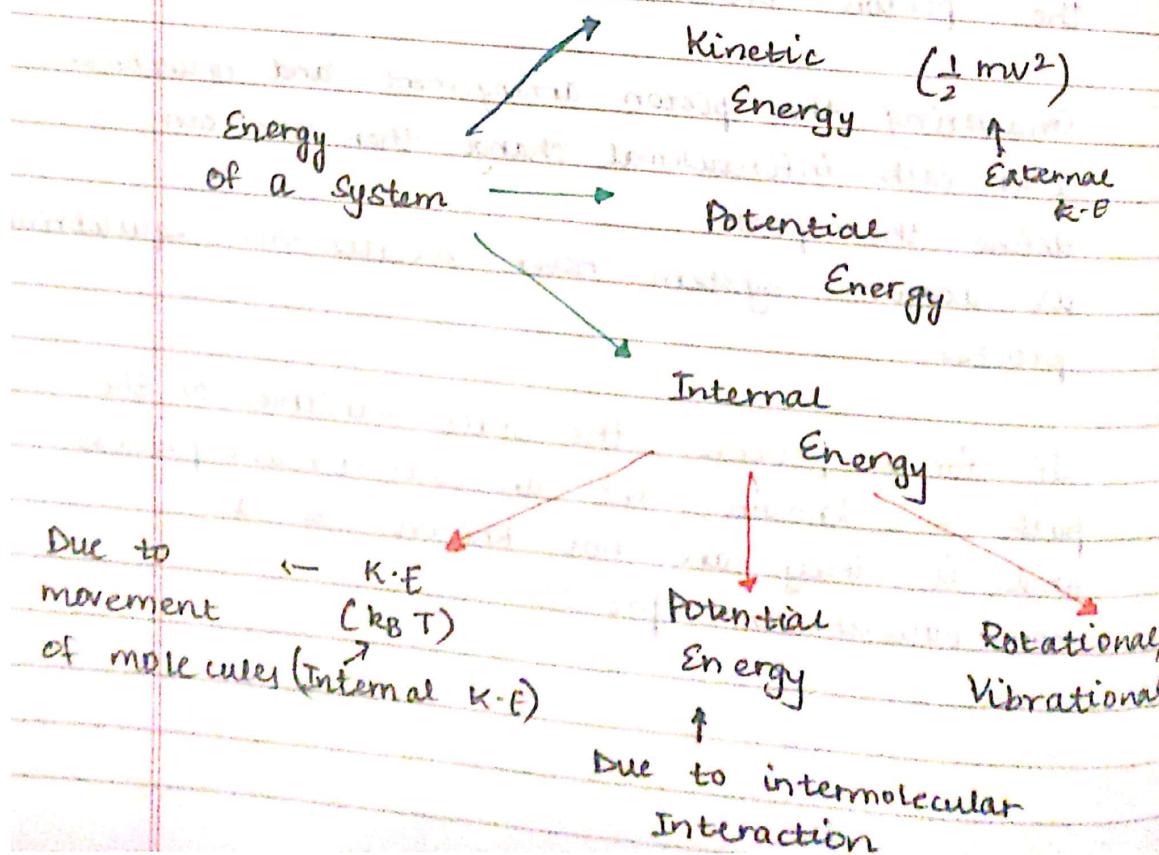
A process in which the system returns to same thermodynamic process



A thermodynamic cycle is a cycle in which the contents of system don't change while in a mechanical cycle the contents of system may change

Cyclic process has nothing to do with eq. or non-eq.

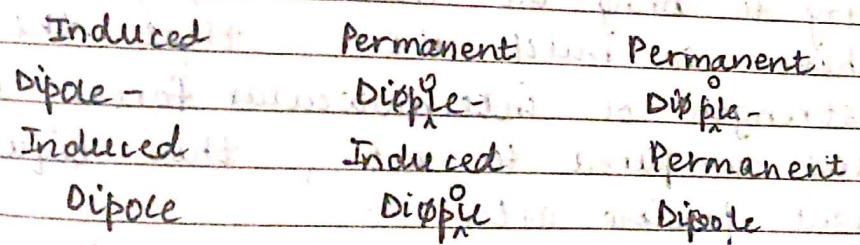
Components of Energy and Energy balance of system



Note :-

- For an ideal gas, the internal energy consists of internal K.E.
- Ideal gases, monatomic gases at low pressure and high pressure, closest to an ideal gas.
- For this course, steam (Water) isn't an ideal gas.
- Intermolecular Interaction \Rightarrow Vander Waal's interaction

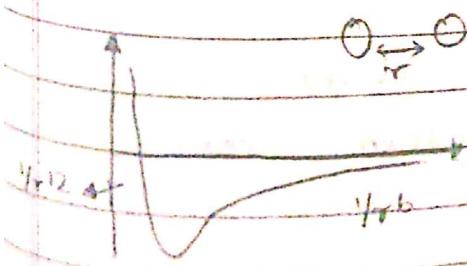
Vander Waal's Interaction



Inst. Localization

of e^- cloud

$$\phi = -\frac{A}{r^6} + \frac{B}{r^{12}}$$



→ By compressing the gas, we are actually bringing the gas molecules close to each other, thereby reducing intermolecular spaces

→ Liquid - Dominated by internal potential energy

→ Gas - Dominated by internal kinetic energy

→ As $T \uparrow$, K.E \uparrow , and has no effect on P.E

After T_c , even how much ever pressure we apply, how much ever close we try to bring the molecules, molecules have so much K.E that the strength of intermolecular forces are less compared to K.E, thus liquification isn't possible after T_c .

Work

O Mechanical work

$$W = - \int_{S_1}^{S_2} \vec{F} \cdot d\vec{s}$$

If system does work (-ve)

If work is done on system (+ve)



$$\Delta E = \dot{F}Q + \dot{W}$$



$$\Delta U + \Delta K + \Delta PE$$



No change
in elevation
system
is stationary
 $= 0$

Thus, $\Delta U = \dot{F}Q + \dot{W}$ Heat Transfer Mode

$*$
diff. comp.

→ Mechanical Work : Physical movement of boundary

$$W = - \int_{S_1}^{S_2} \vec{F} \cdot d\vec{s} \rightarrow W = - \int_{S_1}^{S_2} P dV$$

→ Shaft work :- Special case of mechanical work

$$T = F \cdot r$$

$$\Rightarrow F = \frac{T}{r} \quad w_s = F \cdot s \quad n \rightarrow \text{rotational}$$

$$= \frac{T}{r} \cdot 2\pi r n \quad \text{speed}$$

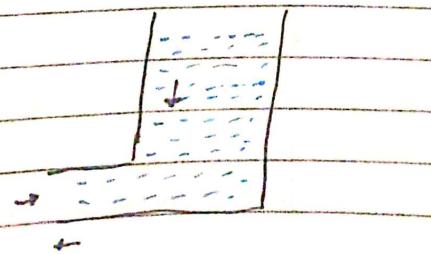
$$= 2\pi T n$$

→ Flow work :- Associated with fluid flow

→ Volumetric flow rate (Q)

→ Mass flow rate (M)

→ Linear velocity



surrounding
is doing work →
unit mass of fluid
is being pushed from surrounding to the system

$$P_{\text{flow,in}} = PA \frac{dx}{dt}$$

Let mass flow rate = m

Volumetric flow rate:

$$m = \rho V$$

$$\frac{f_w}{\delta t} = PA \frac{dx}{dt}$$

$$= P(AV)$$

$$= \rho V \text{ volumetric flow rate}$$



Slanted so as to the pressure is high at bottom

Dissipation depends on friction, viscosity (for a fluid flow), if either of them is zero, dissipation is zero.

For crude oil, viscous dissipation is very high, thus it has to be cooled down

Ans

Energy Balance Eqn:

$$\Delta U = Q + W$$

$$\Delta U = U_2 - U_1 \quad \left. \begin{array}{l} 1 \rightarrow \\ 2 \rightarrow \end{array} \right\} \text{Eq. state}$$

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

The above eqn. isn't applicable for cont. process

$$Q = m C_p \Delta T$$



Energy Balance Eqn. for a flowing system

Rate Form of energy balance eqn:

$$\frac{\Delta U}{\Delta t} + \frac{\Delta K}{\Delta t} + \frac{\Delta P}{\Delta t} = \frac{\delta Q}{\Delta t} - \frac{\delta W}{\Delta t} \rightarrow \text{first law as}$$

$$\frac{\Delta U}{\Delta t} + \frac{\Delta P}{\Delta t} + \frac{\Delta K}{\Delta t} = \frac{\delta Q}{\Delta t} - \frac{\delta W}{\Delta t}$$

Taking $\Delta t \rightarrow 0$

a rate eqn. that
expresses the inst./
avg. rate at which

energy flows through

\Rightarrow If $\frac{\Delta U}{\Delta t} = \frac{dU}{dt}$ and so on "control surface" as
heat, work or flow

$$\therefore \frac{dE}{dt} = \dot{Q} - \dot{W}$$

Rate form of first law

The assumption here is very similar to the
one we took to define ideal process

Here, the change in time is so small that
the system is in eq.

$$Q = m C_p \Delta T$$

$m, \Delta T \rightarrow$ process parameters
 $C_p \rightarrow$ by system

$C_p \rightarrow$ Physical property

$$C_p = a + bT + cT^2$$

a, b, c are constants and only depend on material and not on T

$$Q = \int_{T_1}^{T_2} (C_p dT) m$$

Thus,

$$\Delta E = Q + W \rightarrow \text{Eq. form}$$

$$\frac{\Delta E}{dt} = \dot{Q} + \dot{W} \rightarrow \text{Rate form}$$

$$\Delta E = \underbrace{\Delta K \cdot E}_{\downarrow} + \underbrace{\Delta P \cdot E}_{\downarrow} + \Delta (\text{Internal Energy})$$

Internal $K \cdot E \rightarrow f(T)$

Internal $P \cdot E \neq f(T)$

Internal energy due to rotation, vibration etc.

② (endo)



① (exo) $\rightarrow Q$ (exothermic)

Exothermal $(\Delta U)_{\text{prod}} < (\Delta U)_{\text{reactant}}$

Endothermic $(\Delta U)_{\text{prod}} > (\Delta U)_{\text{reactant}}$

$$Q = \int_{T_1}^{T_2} m C_p dT \leftarrow \begin{array}{l} \text{Implicit Assumptions} \\ \rightarrow C_p \text{ is known} \end{array}$$

If all these 5 are known, then we can properties are known to know, there you can do all the possible thermal calculations.

Heat Capacity of Gasses

Amt. of heat req. to increase the temp. of an object by 1°C

Specific heat: It is the ratio of heat capacity of a body to heat capacity of an equal mass of water.

Heat capacity of any subst quantity of a substance is

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

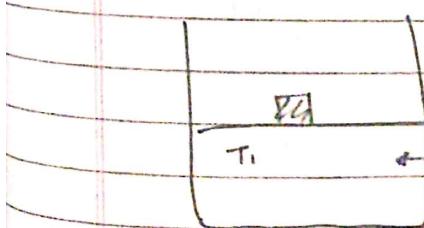
$\partial Q \rightarrow$ Heat added to achieve a temp. ∂T for unit mass.

$$\Rightarrow CV = \left(\frac{\partial Q}{\partial T} \right)_V$$

$$= \frac{\partial U}{\partial T}$$

$$\partial Q = \partial U + \partial W = \underbrace{\partial U}_{dU} + PdV \downarrow dH$$

Enthalpy



\rightarrow State fn.

M_1	$T_2 > T_1$	$V_2 > V_1$	Expansion \rightarrow Work done
T_2			Temp rise \rightarrow Internal energy increase

~~For monoatomic gases~~

$$\dot{c}_v = \frac{3}{2} R, \quad \dot{c}_v + R = \dot{c}_p \Rightarrow \dot{c}_p = \frac{5}{2} R$$

From kinetic Theory of gases,

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

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

v - No. of molecules present

V - Total vol.

m - mass of each molecule

u - Avg. translational velocity of the molecules

n - No. of moles

N_A - Avagadro's Number.

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

$$PV = \frac{2}{3} n U_T$$

U_T = Total molar translational E

$$PV = nRT$$

$$\Rightarrow U_T = \frac{3}{2} RT$$

Thus,

$$\dot{c}_v = \frac{\partial U}{\partial T} = \frac{3}{2} R$$

For a mono atomic gas

$$U_T \approx U$$

$$\therefore U = \frac{3}{2} RT$$

$$\dot{c}_p = \frac{\partial H}{\partial T} = \frac{\partial}{\partial T} (U + PV)$$

$$= \frac{\partial U}{\partial T} + P \frac{\partial V}{\partial T}$$

$$= \frac{BR}{2}$$

For an ideal gas,
 $i_r = i$

$$\text{Molar K.E.} = i = \frac{3}{2} RT$$

$$\delta Q = du + \delta w$$



$$\delta Q = du + PdV + \text{Const. pressure}$$

Only mech. work

$$C_V = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right)_{V,P} = \frac{1}{m} \left. \frac{\partial (U+PdV)}{\partial T} \right|_V \\ = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_P = \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right)_{P,V} = \frac{1}{m} \left. \frac{\partial [U+PdV+vdp]}{\partial T} \right|_P \\ = \frac{1}{m} \left. \frac{\partial (U+PV)}{\partial T} \right|_P \\ = \left(\frac{\partial H}{\partial T} \right)_{P,V}$$

$$\text{For monoatomic } \frac{C_P}{C_V} = \frac{5}{3}$$

- Steam isn't an ideal gas
- Not applicable to gases like O_2, N_2, CO_2

Heat capacity of Solids

Petit and Dulong law :-

Heat capacity of all crystalline solid elements is nearly const. and is equal to 6.2 cal/g-atom

→ Only for 1 mole

→ Works only for elements > 40

$$\hat{C} = 3R$$

$$\hat{C}_p \cdot M = K = 3R$$

KOPP Rule

The heat capacity of a solid compd. is approximately equal to sum of heat capacities of constituent elements.

→ It is applicable for solids as well.

Latent heat of Fusion (Melting) :

No empirical / approximate relation exists

Latent Heat of vapourization (Boiling) :

Directly related by thermodynamic eqn. to vapour pressure

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

↑
Lat. occ.
by unit mass

$$\hat{V}_g \gg \hat{V}_l$$

$p^* \rightarrow$ vapour Pressure

$T \rightarrow$ Temp.

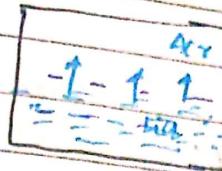
$\Delta H_v \rightarrow$ Molar latent

heat of vapourization

$\hat{V}_g, \hat{V}_l \rightarrow$ Molar vol. of

the gas and liquid.

Vapour pressure - Pressure exerted by a vapour phase in a thermodynamic eqn. with its condensed system in a closed system



closed system.

- Nature of eq: Dynamic
- Measured at 1 atm
- $P^* = f(T) \approx$ Increases with Temp.
- B.P (V.P = atm. pressure)

Weaker interaction, lower B.P, lower surface tension, higher V.P

Volatile liq.

- ↳ liq with high V.P
- ↳ Volatile liq
- ↳ Perfume / deo / Aftershave etc.
- ↳ Organic base

Antoine eqn:

$$\log P^* = A - \frac{B}{C + T} \quad A, B, C \rightarrow \text{Antoine Co-efficients}$$

$$\frac{dP^*}{dT} = \frac{\Delta H}{T(C(\hat{V}_G - \hat{V}_L))}$$

$$\frac{dP^*}{d(\ln T)} = \frac{\Delta H}{T(C(\hat{V}_G - \hat{V}_L))}$$

Clasius - claypeyron Eqn: $(\hat{V}_G \gg \hat{V}_L)$

considering vapour phase to be an ideal gas

$$\hat{V}_G = \frac{RT}{P^*}$$

$$\frac{dP^*}{dT} = \frac{\Delta \hat{H}_v P^*}{RT^2}$$

$$\Rightarrow d(\ln P^*) = \frac{\Delta \hat{H}_v dT}{RT^2}$$

$$\ln \left(\frac{P_1^*}{P_2^*} \right) = \frac{\Delta \hat{H}_v}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\log \left(\frac{P_1^*}{P_2^*} \right) = \frac{\Delta \hat{H}_v}{2.303} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\ln(x) = 2.303 \log_{10}(x)$$

→ Trouton Rule

At its

The ratio of molar heat of vapourization ($\Delta \hat{H}_v$) of a substance to its normal boiling point is const.

$$\frac{\Delta \hat{H}_v}{T_b} = \frac{2.303}{T_b} = k \quad \text{For many material}$$

$$k = 21$$

$$\Delta \hat{H}_v \rightarrow \frac{\text{cal}}{\text{gm mole}}$$

Reference Substance Plot.

$P^* \propto T \leftarrow$ Antoine Eqn.
 $\rightarrow A, B, C ?$

Reference material

$\rightarrow T$ v.s P^* well

Another material

$\rightarrow T \rightarrow (P_i^*)_{\text{Ref.}}$

$$\begin{aligned} P_i^* &\rightarrow T_1 \rightarrow T_{\text{ref}}, \\ T_2 &\rightarrow T_{\text{ref}_2} \\ T_3 &\rightarrow T_{\text{ref}_3} \end{aligned}$$

Some temp., measure

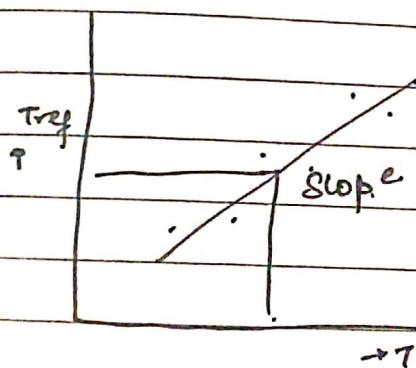
" P (P_i^*) , note

the sample material's
temp. for which we

get P_i^* , find out

at which temp ref

material had P_i^*



$$d(\ln P^*) = \frac{\Delta H}{RT^2} dT$$

$$= \frac{\Delta H}{RT_{\text{ref}}^2} \nu_{\text{ref}} dT_{\text{ref}}$$

$$\frac{\Delta H}{\Delta H_{\text{ref}}} = \left(\frac{T}{T_{\text{ref}}} \right)^2 \frac{dT_{\text{ref}}}{dT} \quad \left. \right\} \text{const. pressure.}$$