CHAPTER-2

INTERMOLECULAR FORCES & POTENTIAL ENERGY SURFACES

(i) Intermolecular forces → Proposed by Van der Waals → Dutch Physicist

The forces of attraction existing between molecules of substances (Gaseous, liquid or solid) are called Intermolecular forces.

* Forces which exist b/w within the same molecule or a polyatomic ion are called INTRAMOLECULAR FORCES

* Greater the Intermolecular forces Higher is boiling point

Magnitude of Intermolecular forces

Solid > liquid > Gases.

(ii) Types and origin of Intermolecular forces

(a) Dipole-Dipole Interaction
(b) Ion-Dipole Interaction
(c) Ion-Induced Dipole } Debye Forces
(d) Dipole-Induced Dipole
(v) Dispersion Forces
(vi) Hydrogen Bonding

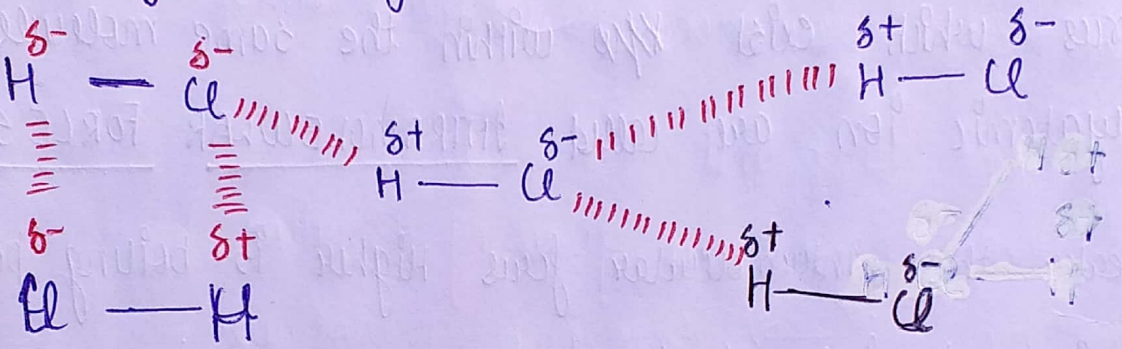
Dipole-Dipole, Dipole-Induced Dipole & Dispersion forces are collectively called Vanderwaal forces

(a) Dipole - Dipole Interactions (Keesom forces)

* These forces exist between Polar molecules like HF, HCl, H_2O, etc.

* Polar molecules have Permanent Dipoles [The positive pole of one molecule is attracted by Negative Pole of other molecule.

* In HCl → Chlorine being electronegative acquires Negative charge & H acquire Positive charge.



Molecules having higher dipole moment are more Polar & have higher Melting & boiling point indicating strong Dipole - Dipole attractions.

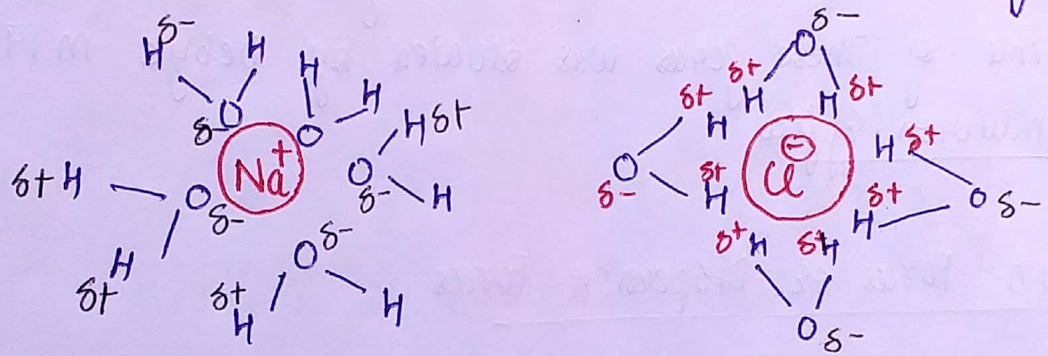
H_2O → 1.8D → Liquid

NH_3 → 1.49D → Gas

(b) Ion-Dipole Interactions

* Attraction between an ion (cation or anion) and a Polar molecule.
* Strength of this interaction depends upon charge and size of ion and magnitude of Dipole moment & size of Polar molecule.

Example ⇒ NaCl dissolved in water. The Polar water molecule attract towards Na^+ & $Cl^\ominus$ ion (Hydration of ions)

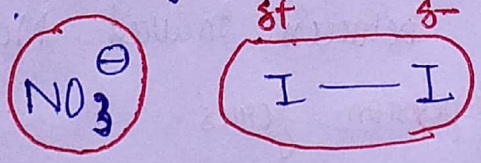


Ion-dipole attraction b/w Na^+ & H_2O molecule & Cl^- & H_2O molecule.

CCl4 being nonpolar & hence NaCl is insoluble in CCl4.

(c) Ion-Induced Dipole

A non polar molecule may be polarized by presence of ion near it. It becomes induced dipole.



NON Polar I_2 get Polarized by NO_3^- ion

Interaction b/w them are called Ion-Induced Dipole Interaction.

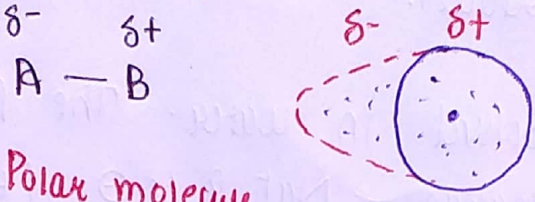
Cation Polarizes by attraction while anion by Repulsion

④ Dipole - Induced Dipole Interaction

* A Non Polar molecule may be polarized by presence of polar molecule (Dipole) near it Thereby making it an Induced dipole.

* Their strength will depend upon strength of dipole & ease of polarisability of Non Polar molecule.

For example



The existence of these forces was studied by Debye in 1920 & called Induction effect

⑤ London Forces or Dispersion Forces

These forces are arise from motion of electron. At any instant of Time e^- cloud of molecule may be distorted so than an Instataneous dipole or momentary dipole is produced in which one part of molecule is slightly more Negative than Rest.

The momentary dipole induces dipole in Neighbouring molecule.

The Forces of Attraction between Induced Momentary Dipole are called London dispersion forces.

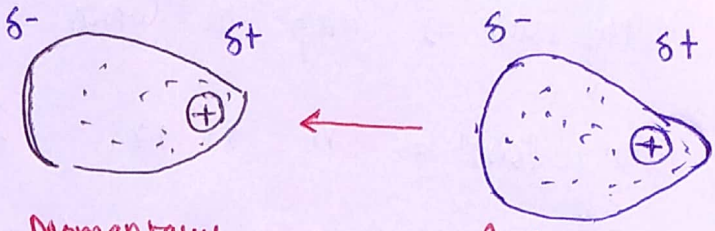
→ operate for very short- distance.

→ Energy of Interaction varies as $1/r^6$.

He atom 1

He atom 2

Before Distortion



Momentary Dipole

Induced Dipole

Formation of momentary Dipole & Induced dipole.

Factors on which Magnitude of London forces depend

* London forces are weakest Intermolecular forces.

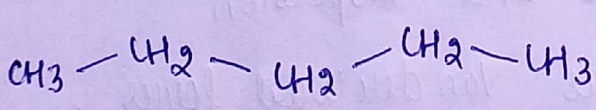
(a) Size / complexity of molecules.

* Larger or more complex are molecules greater is magnitude of London forces. [i.e Large e- cloud get distorted]

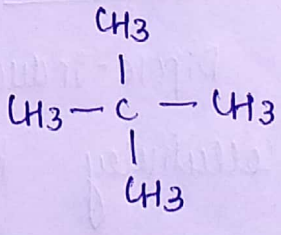
* L.f ↑ with ↑ in molecular mass

$CH_4 < SiH_4 < GeH_4$

(b) Geometry of molecules

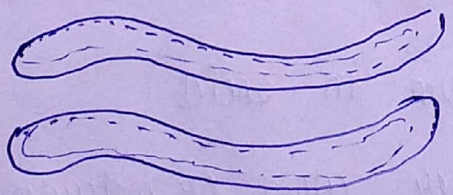


n- pentane
(B.P = 36.2°C)

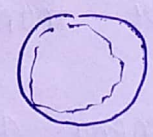


(B.P = 9.5°C)

More sites of attraction



N- pentane



Less sites of attraction

Neo pentane

Melting Point ⇒ Temp. at which solid melt to form a liquid }
Boiling Point ⇒ " " " " liquid changes to vapour. }

M.P and B.P Both depend upon magnitude of Intermolecular forces.

* Ionic compound (constituent Particle are Positively & Negatively Charged)
  → Electrostatic forces of Nature

* Metals
  Constituent Metal atoms are quite strong. (Metallic Bond)

* Covalent compound
  (weak Vanderwaal forces of attraction)
  → Polarity → Geometry of molecule.
  → Size

* VANDER WAALS FORCES

Dipole-Dipole, Dipole-Induced Dipole and Dispersion forces are collectively known as Van der Waal forces.

→ CHARACTERISTIC OF VANDERWAAL FORCES
* Much weaker than Ionic and covalent Bond
* Minimum among gases and maximum in solid
* Not affected by presence of other atom or molecules.

Applications

(i) Physical state

as the magnitude of Vanderwaal forces increases The Physical state changes.

$F_2 < Cl_2 < Br_2 < I_2$

Gas — Liquid

(ii) Melting and Boiling Point

Existence of Vanderwaal force is Responsible for bringing molecule closer.

as Vanderwaal force magnitude increases B.P & M.P Tes.

(iii) Liquefaction of Gases

It take place due to increase in IMF. When gas is cooled to low Temperature & High pressure, molecules come closer leading to increase in vanderwaal forces. & get liquified.

(iv) Deviation of Real gases from Ideal gas Behaviour

Under condition of High Pressure and low Temperature due to presence of V.W.F.

EQUATION OF STATE OF REAL GASES & CRITICAL PHENOMENA

$1\ m^3 = 10^3\ dm^3 = 10^6\ cm^3$

$1\ mL = 1\ cm^3$

$1\ L = 10^3\ cm^3 = 1\ dm^3 = 10^{-3}\ m^3$

1 atm = 76 cm = 760 mm or 760 torr

1 atm = 1·01325 bar or 1 bar = 0·987 atm

1 atm = 101,325 Pa or Nm^{-2}

1 bar = 10^5 Pa or Nm^{-2}

1 bar = 10^2 K Pa

(1) Boyles Law

* Relationship b/w Volume and Pressure of Gas
* Temperature Remaining constant the product of pressure and volume of given mass of Gas is constant

$V \propto \frac{1}{P}$

$PV = \text{const at const Temp}$.

$$P_1V_1 = P_2V_2$$

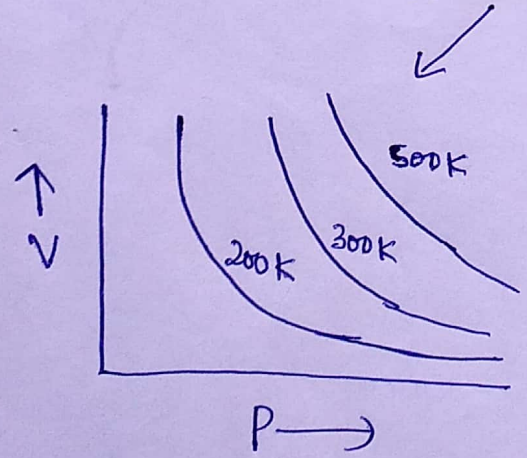
$$\text{density} \propto P$$

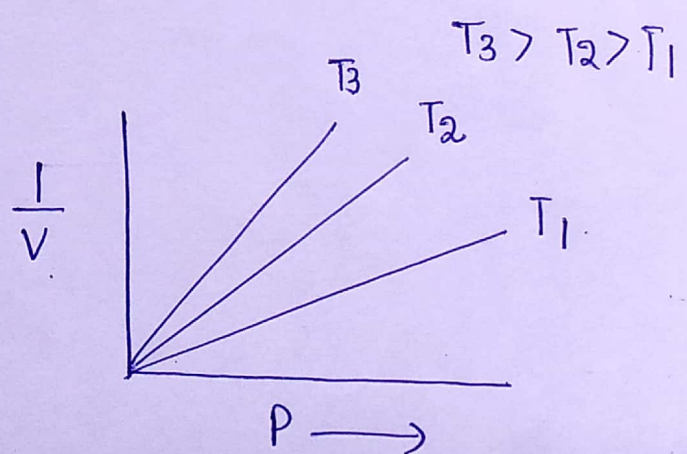
Significanu - At altitude as atmospheric pressure is low air is less dense

→ less oxygen available for breathing cause Headache, Uneasiness

This is called altitude Sickness

Isotherm → P-V Curve at constant Temperature is called Isotherm





CHARLES LAW

* Relationship b/w Temp and Volume of gas
* Pressure Remaining constant, the Volume of given mass of gas is directly proportional to Temprature in degree Kelvin

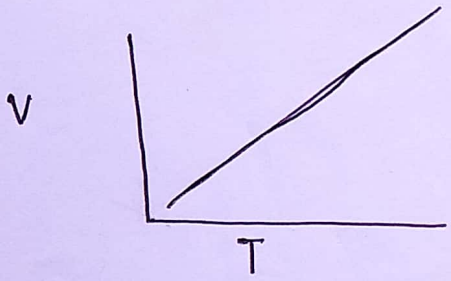
$V \propto T$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V}{T} = \text{constant at const. Pressure}$$

Significance ⇒ Air Expand on Heating and Hence its density decreases. Hot air lighter than atmospheric air.

Filling of Hot air ballons.

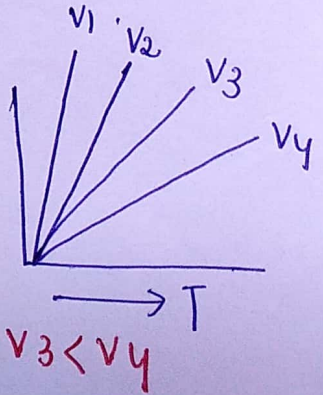


GAY-LUSSAC LAW or Amonton Law

* Press & Temp
* Volume Remaing constant The Pressure of given mass of a gas is directly proportional to its temperature in degrees Kelvin.

$P \propto T$

Isochore → Plot of pressure v/s Temperature



$V_1 < V_2 < V_3 < V_4$

Avagadro law

Equal volume of all gases under same condition of Temperature and Pressure contains equal Number of molecules.

Compressibility Factor

The extent to which a real gas deviates from Ideal behaviour can be conveniently studied in Terms of Quantity "Z" called compressibility factor.

F

$$Z = \frac{PV}{nRT}$$

Z independent of T&P

For Ideal Gas $PV = nRT$ i.e $Z = 1$

FOR REAL Gas $PV \neq nRT$ i.e $Z \neq 1$

(Z is function of both T & P)

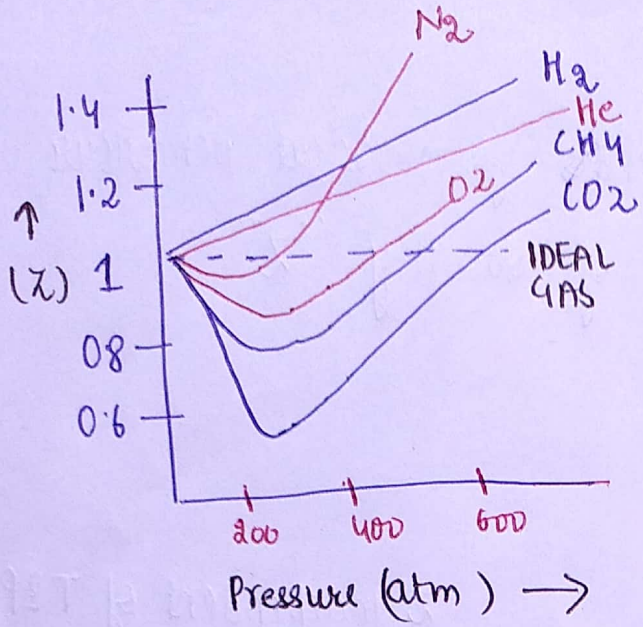
Two cases arises for Real Gases

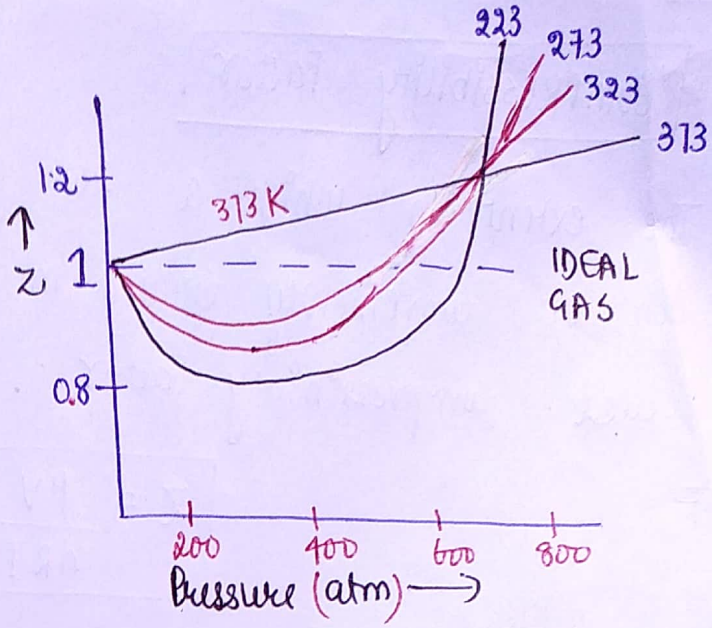
(a) When $Z > 1$ (CH_4, CO_2)

* Gas is said to show Positive Deviation
* Gas is less compressible than expected from Ideal behaviour
* Predominance of strong Repulsive forces among molecule.

(b) When $Z < 1$

* Gas to show Negative deviation
* Gas is more compressible than expected Ideal Behaviour
* Predominance of strong Attractive forces





At same Temperature and Pressure Extent of Deviation depend upon Nature of gas

CO_2 showing larger deviation than H_2 or N_2

* For same gas at Particular Pressure extent of Deviation depend upon Temperature
* as Temp ↑es, the minimum in curve shift upwards
* ultimately a Temp is Reached at which value of z Remains close to 1 over appreciable range of pressure.

BOYLE TEMPERATURE

* The Temperature at which a Real gas behave like an Ideal Gas over appreciable Range of Pressure is called Boyle Temperature or Boyle Point

SIGNIFICANCE OF (Z)

$$Z = \frac{PV_{Real}}{nRT} \quad - (i)$$

If a gas shows Ideal behaviour $PV_{ideal} = nRT$

$$V_{ideal} = \frac{nRT}{P} \quad - (ii)$$

Substituting (ii) in (i)

$$\boxed{Z = \frac{V_{real}}{V_{ideal}}}$$

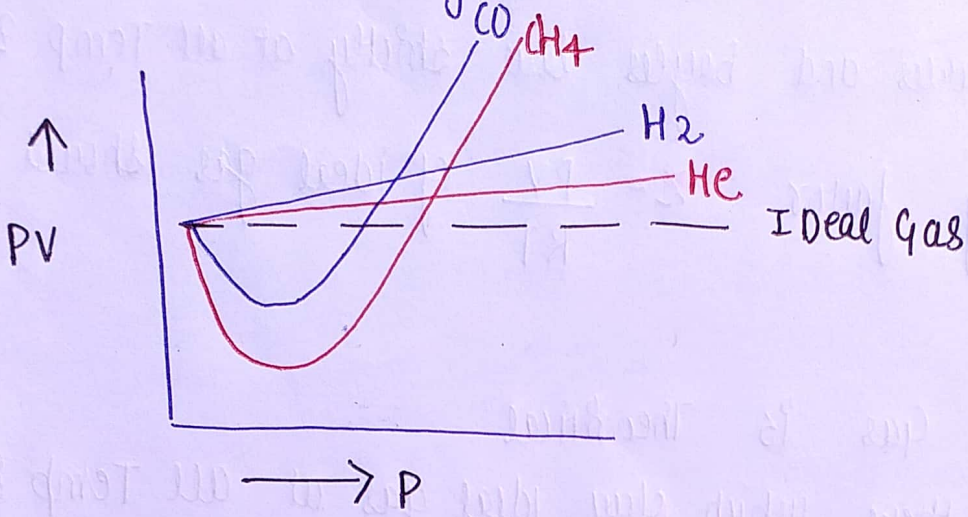
Thus Z is the ratio of actual molar volume of gas (experimentally observed value) to calculated molar value (ideal gas) at same Temperature and same Pressure.

DEVIATIONS OF REAL GASES FROM GAS LAW

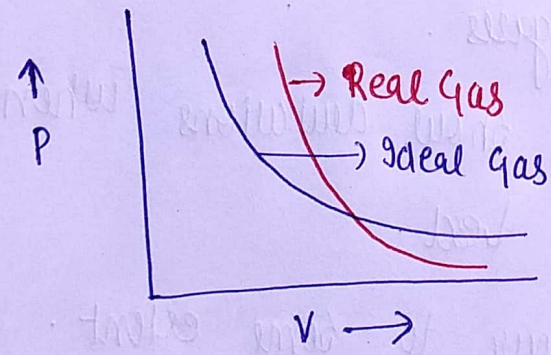
1) BOYLES LAW

According to Boyles Law PV = Constant at Const. Temp.

Plot should be Straight line Parallel to x-axis



* For H_2, He , PV Increases continuously with Increase of Pressure.
* For H_2 and He, PV first decreases and reaches minimum Value and Then Increases continiously with ↑ in pressure.



At Const. Temp

* At High Pressure observed Volume is more than calculated Volume.
* At low Pressure observed and Calculated Volume approach each other

(R)

IDEAL GAS :

→ Gases which obey Ideal Gas Equation $PV = nRT$ under all conditions of Pressure and Temperature is called ideal gas.

→ It obey Charles and Boyles law strictly at all Temp & Pressure

→ Compressibility factor $Z = \frac{PV}{RT}$ of ideal gas should be unity.

* Concept of ideal Gas is Theoritical
* No Gas is there which obey ideal gas at all Temp & Pressure.

REAL GASES

→ Obey gas law fairly well under Low Pressure & High Temperature.

→ Such gases are called Real gases.

→ All Gases are Real but show deviations when P is Tend or T is Tend.

→ Helium shows ideal behaviour to some extent.

Causes of Deviation From Ideal Behaviour

* Ideal Gas Law Obeyed at only Low Pressure and High Temper.
* If P is high or T is low Real Gases make deviation

→ Based on Kinetic Theory of Gases

1* Volume occupied by a gas molecule is Negligible as compared to total Volume of gas.

2* The force of attraction or Repulsion b/w gas molecules are Negligible.

Now If Pressure is High or Temperature is Low Gas ~~Becom~~ molecule come close together.

→ forces of attraction or Repulsion b/w molecules may Not be Negligible

→ Volume occupied by gas may Not be Small

* **EQUATION OF STATE FOR REAL GASES**

OR

* **VAN DER WAAL EQUATION**

J. D Vander waal in 1873 modified Ideal Gas Equation by applying appropriate Corrections

→ Volume of gas molecules & attraction b/w gas molecules was Taken in account.

He put forwarded Modified Equation Known as Van der waal Equation

* For 1 mol of Gas = $\left(P + \frac{a}{V^2}\right)(V-b) = RT$

* For n mole of Gas = $\boxed{\left(P + \frac{an^2}{V^2}\right)(V-nb) = nRT}$

* 'a' and 'b' are called Van der waal constant
* Value of a & b depend upon Nature of Gas.

* DERIVATION OF VAN DER WAAL EQUATION

* Modifying $PV = nRT$ by appling correction for Volume and Pressure

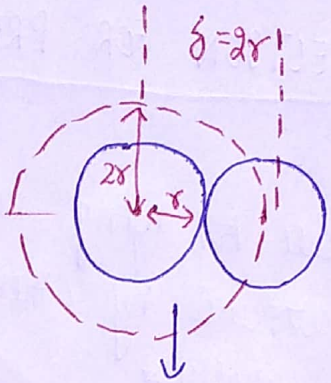
(I) CORRECTION FOR VOLUME

* Low pressure Volume does Not Indules any error
* At High Pressure molecules Came closer

* Two molecules approaching each other

r = radius of molecule

δ = diameter of molecule



Excluded volume

* No volume will be occupied by this pair of molecules within sphere of ($\delta R = 2R$)

$$\text{Excluded Volume} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (2r)^3$$

$$= 8 * \frac{4}{3}\pi r^3$$

$$\text{Excluded volume for single Pair} = \frac{8}{2} * \left(\frac{4}{3}\pi r^3\right) = 4\,V_m$$

* V_m = Volume occupied by single molecule

$$\text{Excluded Volume} = b = 4\left(\frac{4}{3}\pi r^3\right) * n = 4 V_m N$$

N = Avagadro No.

$$b = 4 * \frac{4}{3}$$

$b = 4V_m$ = Excluded or Co-Volume

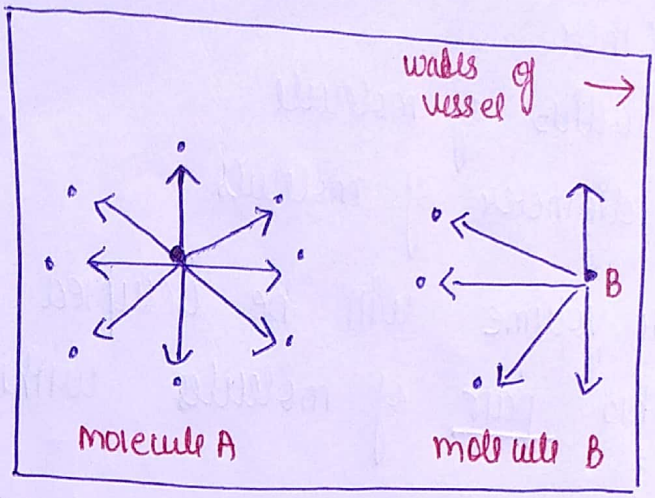
** Corrected Volume = $V - b$ for 1 mole

$= V - nb$ for n mole

(II) CORRECTION FOR PRESSURE

* A molecule (A) lying within vessel attracted by other molecules equally *

* B molecule attracted (Pulled Back) by molecules inside Hence it exerts less pressure



Backword Pull on molecul B by other molecules

Corrected Pressure = $P + p$

$p \propto$ density of gas near wall and density of gas inside

i.e $p \propto (\text{density})^2$ or $p \propto d^2$

But $d \propto \frac{1}{V}$

$p \propto \frac{1}{V^2}$ or $p \propto \frac{n^2}{V^2}$ for n moles

$p = \frac{a}{V^2}$ or $p = \frac{n^2 a}{V^2}$

Corrected Pressure = $\left(P + \frac{a}{V^2}\right)$ For 1 mole

$= \left(P + \frac{an^2}{V^2}\right)$ for n moles

a depend upon Nature of gas

* Units of Vander Waal Constant

a an

→ S.I units of b $V = nb$ $dm^3\ mol^{-1}$ OR Litre mol^{-1}

$$b = \frac{\text{Volume}}{n} =$$

→ S.I unit of a = $p_a = \frac{an^2}{V^2}$ $a = \frac{p_a V^2}{n^2}$

$$a = \frac{\text{Pressure} * (\text{Volume})^2}{(\text{moles})^2}$$

$a =$ atm L^2 mol^{-2} or bar dm^6 mol^{-2}

Significance of Vanderwaal Constant

[*] Greater the value of 'a' stronger will be magnitude of Vanderwaal forces

(ii) Vander Waal Constant 'b'.

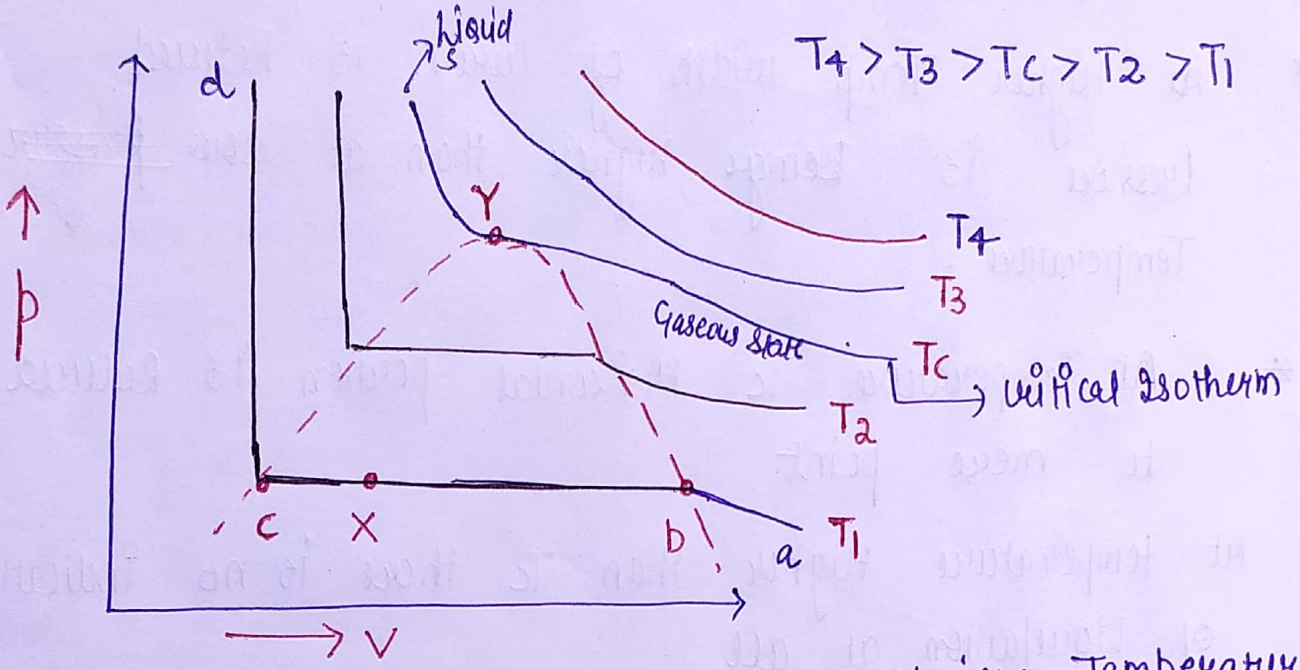
* Its value is a measure of effective size of gas molecules.
* Value of b remains constant over a wide Range of Temp and pressure of gas.
* This shows that gas molecules are Incompressible
* Excluded volume is four times the actual volume
* Higher the value of (b) greater is actual volume of molecules of gas

as Temp ↑es value of a & b diminishes

ANDREW

ISOTHERM OF CO – CRITICAL PHENOMENA

ISOTHERM ⇒ Variation of Volume & Pressure at const Temp.



P-V Relation of CO_2 was measured at various Temperature

(i) At High Temperature T_4 isotherm look like an ideal gas.

(ii) At low Temperature the curves have altogether different appearances.

as P ↑es from a to b Volume decreases

at b liquefaction commences & Volume Decreases Rapidly.

At point c Liquefaction is complete

steepness of line cd is evidence of the fact that Liquid cannot be easily compressed.

ab represent = Gaseous state

bc " liquid & Vapour in equilibrium

Cd = Shows liquid state only.

The Pressure corresponding to line bc is known as vapour pressure of liquid.

* At Higher Temp width of curve is Reduced Pressure is Beings Higher than at low ~~pressure~~ Temperature.

* At Temperature Tc Horizontal portion is Reduced to mere point

At temperature Higher than Tc there is no Indication of Liquefaction at all.

Thus for every gas there is a limit of Temperature above which it cannot be liquefied No matter what pressure is

Y = Critical State ⇒ Liquid & Gas become Indistinguishable. At this point T, P & V have critical values. These three are known as critical Constant.

At Tc = Density, Refractive Index has same values.

Applicability of Vander Waal Equation

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

At Low Pressure

When Pressure is Low Volume is Sufficiently large and $\underline{b}$ can be ignored in comparison to V

$$V \ll b$$

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

$$PV + \frac{a}{V} = RT \quad \text{or} \quad Z = 1 - \frac{a}{RTV}$$

at Low Pressure Region Z is less than 1

on Increasing Pressure V decrease and Z will also decrease

At High Pressure

$P \propto \frac{1}{V}$ Volume will be Small $P \gg\gg \frac{a}{V^2}$

So $\frac{a}{V^2}$ can be Neglected

$$P(V-b) = RT \Rightarrow PV - Pb = RT$$

Dividing by RT

$$\boxed{Z = 1 + \frac{Pb}{RT}}$$

Z is greater than 1 and increases Linearly with P

At High Temp and Low pressure

V = large Thus $\frac{a}{V^2}$ = small

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

$\Rightarrow$ $\boxed{PV = RT}$

Under this condition Equation Reduces to Ideal Gas Equation

DEFINATION OF CRITICAL CONSTANTS

* Critical Temperature (T_c)
* T_c is the maximum temperature at which gas can be liquefied:

i.e Temperature above which liquid cannot exist

* Critical Pressure (P_c)

P_c is the minimum pressure required to cause liquefaction at Temp. T_c.

* Critical Volume (V_c)

Volume occupied by 1 mole of gas at critical Temp T_c and critical Pressure (P_c)

Conditions for Liquefaction of gas

* Temp must be at or below critical Temp.
* A suitable Pressure must be applied equal to critical pressure if Temp is at critical Temp.

Relation b/w Van der Waal constant and critical constant

→ application of critical phenomena.

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

$$PV + \frac{a}{V^2} - Pb - \frac{ab}{V^2} = RT$$

multiplying Throughout by V^2

$$PV^3 + aV - PbV^2 - ab - RTV^2 = 0$$

arranging in descending order

$$PV^3 - PbV^2 - RTV^2 + aV - ab = 0$$

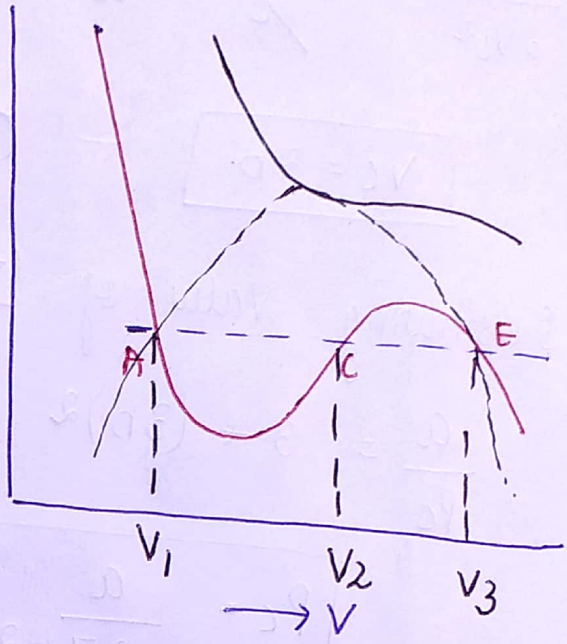
Dividing by P

$$V^3 - bV^2 - \frac{RTV^2}{P} + \frac{aV}{P} - \frac{ab}{P} = 0$$

$$V^3 - V^2 * \left(b + \frac{RT}{P}\right) + \frac{aV}{P} - \frac{ab}{P} = 0 \quad -(II)$$

At critical point The the three Roots of Vanderwaal equation become identical and equal to V_c.

On Increasing the Temp the Three Roots A, C & E become closer and became identical at T_c.



$$(V-V')(V-V'')(V-V''')=0$$

at T_c $\quad V' = V'' = V''' = V_c$

$$(V - V_c)^3 = 0$$

Expanding above expression we obtain

$$V^3 - V_c^3 - 3V_cV^2 + 3V_c^2 V_m = 0 \quad -(II)$$

Under critical conditions $T = T_c$ and $P = P_c$

Substituting above value in Equation 4.4

$$V^3 - V2\left(b + \frac{RT_c}{P_c}\right) + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \quad -(III)$$

Since both Equation (III) and (II) are identical then coffiient of equal power of V must be equated

$$b + \frac{RT_c}{P_c} = 3V_c \quad -(IV)$$

$$\frac{a}{P_c} = 3V_c^2 \quad -(V)$$

$$\frac{ab}{P_c} = V_c^3 \quad -(VI)$$

Dividing equation VI by V

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} * \frac{P_c}{a} \quad \Rightarrow \frac{V_c}{3} = b$$

$$\boxed{V_c = 3b} \quad - \text{(VII)}$$

Substituting value of (VII) in (V)

$$\frac{a}{P_c} = 3 * (3b)^2 = 27b^2$$

$$\boxed{P_c = \frac{a}{27b^2}} \quad - \text{(VIII)}$$

Substituting above value in equation (IV)

$$b + \frac{RT_c}{a} * 27b^2 = 3 * 3b$$

$$9b = b + RT_c * \frac{27b^2}{a}$$

$$8b = RT_c * \frac{27b^2}{a}$$

$$\boxed{T_c = \frac{8a}{27bR}}$$

* Derivation of $P_c V_c = \frac{3}{8} RT_c$ from Vander waal Equation

$$V^3 - V^2\left(b + \frac{RT_c}{P_c}\right) + V\frac{a}{P_c} - \frac{ab}{P_c} = 0$$

From equation ~~(ii)~~ (vii)

$$b = \frac{1}{3} V_c$$

Substituting value of b in equation (iv)

$$b + \frac{RT_c}{P_c} = 3V_c$$

$$\frac{V_c}{3} + \frac{RT_c}{P_c} = 3V_c$$

$$\Rightarrow \quad \frac{RT_c}{P_c} = 3V_c - \frac{V_c}{3} \quad \Rightarrow \quad \frac{RT_c}{P_c} = \frac{9V_c - V_c}{3}$$

$$\frac{9V_c - V_c}{3} = \frac{RT_c}{P_c} \quad \Rightarrow \quad \frac{8}{3} V_c = \frac{RT_c}{P_c}$$

or

$$\boxed{P_c V_c = \frac{3}{8} RT_c}$$

Calculation of van der Waal constant in Terms of T_c & P_c

$$V_c = \frac{3}{8}\frac{RT_c}{P_c}$$

Squaring above we get

$$V_c^2 = \frac{9}{64}\frac{R^2T_c^2}{P_c^2}$$

$$V_c^2 = \frac{a}{3P_c}$$

$$\frac{a}{3P_c} = \frac{9}{64} * \frac{R^2T_c^2}{P_c^2}$$

$$\boxed{a = \frac{27}{64}\frac{R^2T_c^2}{P_c}}$$

Now $$3V_c = b + \frac{RT_c}{P_c}$$ ——(i)

from (IV) $$b = \frac{V_c}{3} \quad \text{or} \quad V_c = 3b$$

$$9b = \frac{RT_c}{P_c} + b$$

$$8b = \frac{RT_c}{P_c}$$

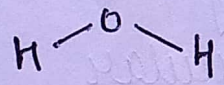
$$\boxed{b = \frac{RT_c}{8P_c}}$$

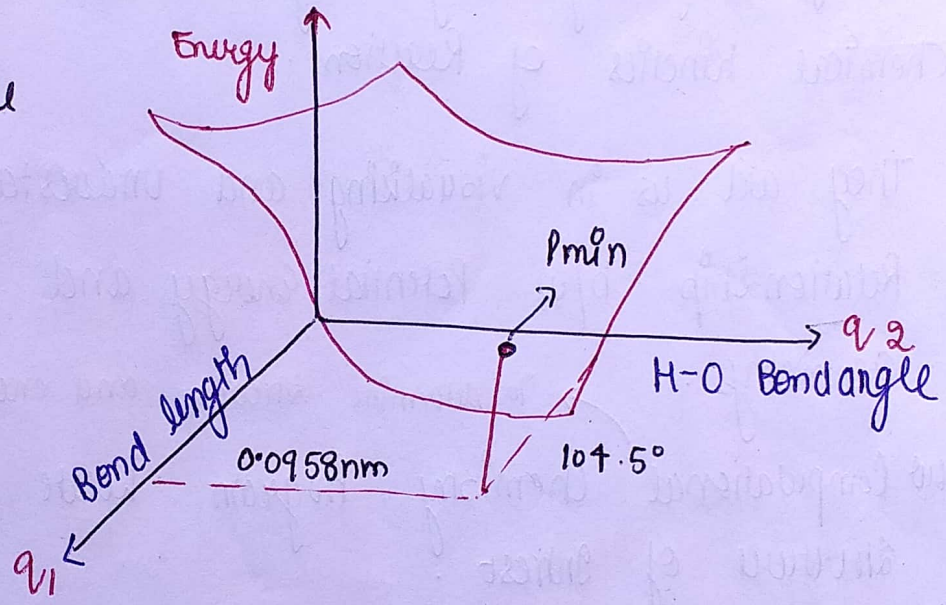
POTENTIAL ENERGY SURFACE

PES describes the energy of system particularly a collection of atoms in terms of position of atoms.

PES defines energy as function of one or more coordinates if only one coordinate taken in account surface is called Potential Energy curve or Energy Profile

PES of water Molecule





3N-5
= 3*3 - 5
= 9-5
= 4

3*N-6
= 3-6
= -3

* Pmin correspond to minimum Energy Geometry for Three atoms i.e to the equilbrium Geometry of water molecule

* Theoritically used to explore properties of structures composed of atoms.
  i.e finding Minimum Energy, Shape of molecules or calculating Rates of chemical Reaction.

In mathematics

Geometry of a set of atoms can be described by vector $\vec{r}$. whose elements Represent the atom position.

$\vec{r}$ = Set of Cartesian coordinates of atom or
Set of Inter-atomic distances or angle.

APPLICATION OF PES

* Tool for finding analysis of molecular shape and Chemical Kinetics of Reaction.
* They aid us in visualizing and understanding the Relationship b/w Potential Energy and molecular Geometry. → To determine structure and energy of molecule.
* How Computational Chemistry Program locate and Characterize structure of Intrest.
* Evaluated Points on PES can be classified according to first Derivative & Second Derivative of Energy with respect to position
* $\frac{\partial E}{\partial q_1}$ or $\frac{\partial \varepsilon}{\partial q_2}$ $\frac{\partial^2 E}{\partial q^2}$

STATIONARY POINTS

i;e correspond to actual molecules for finite life time

* Mathematically a stationary point is one at which first Derivative of Potential Energy with Respect to each Geomemic Parameter is zero

$$\frac{\partial \varepsilon}{\partial q_1} = \frac{\partial \varepsilon}{\partial q_2} = 0$$

zero

So Stationary Points have Physical Meaning (Point with 0 gradient) i;e Energy minima correspond to physically Stable chemical species.

SADDLE POINT

it correspond to transition state, i;e The Highest energy point on Reation coordinate.

Saddle point lies at center of saddled shaped Region

Saddle point is Maximum along the Reaction coordinate and minimum along all other direction.

For minimum

$$\frac{\partial^2 E}{\partial q^2} < 0$$

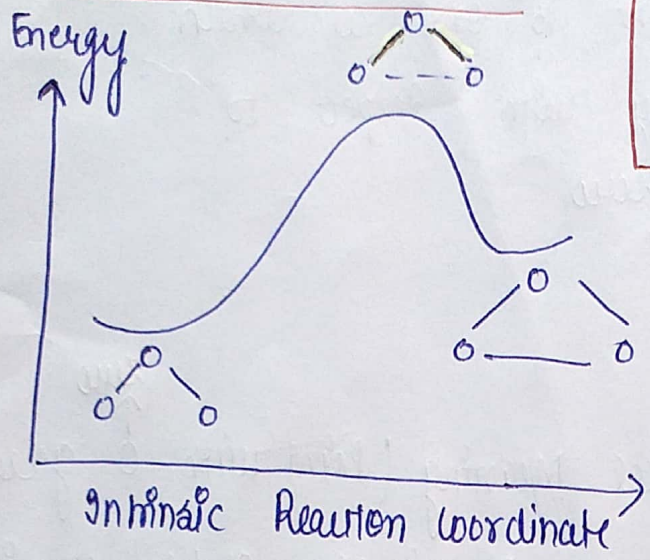
for all q

For Transition state

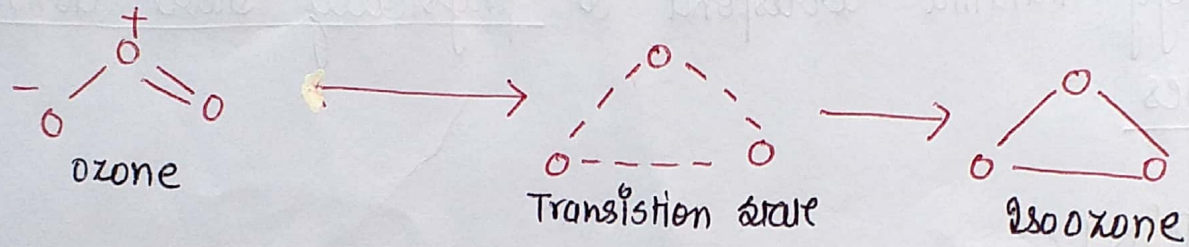
(1) $$\frac{\partial^2 E}{\partial q^2} > 0$$

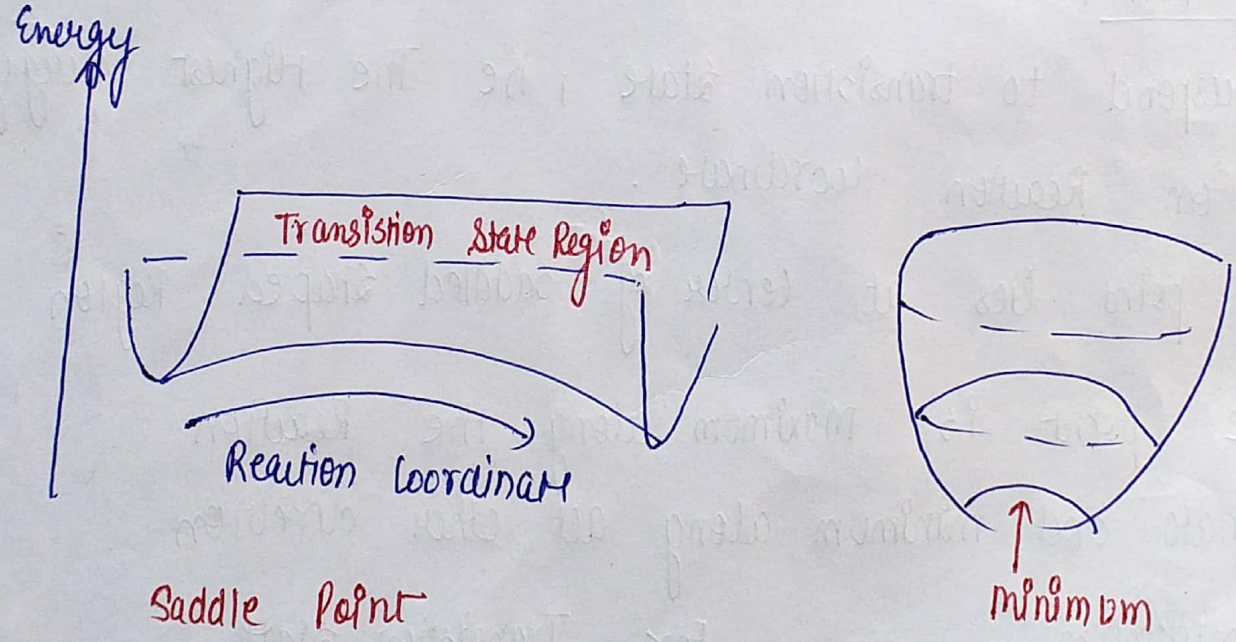
For all q except along the Reation coordinate and

"STRUCTURE OF INTEREST"



② $\frac{\partial^2 E}{\partial q^2} < 0$ for along Reaction Coordinate





at Both Transition state (or saddle Point) & minimum $\frac{\partial E}{\partial q} = 0$ for all geometric coordinates q (along all direction)

at minimum → $\frac{\partial^2 E}{\partial q^2} < 0$ for all q (along all direction)

T.S $\frac{\partial^2 E}{\partial q^2} < 0$ for q = R.C & > 0 for all other q

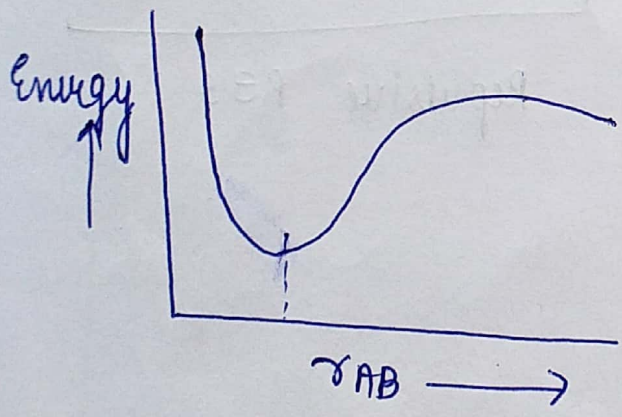
CONTOUR PLOT

* PES is mathematical or Graphical Representation of Relation between energy of molecule & geometry.
* A molecule with n atom is defined by 3n coordinates x, y & z for each atom.
  (3n-6) for Non Linear or (3n-5) coordinates.

* **Diatomic Molecule**

  A–B

* We will have one dimensional PES since there is only one geometric Parameter to vary. r_{A-B}



* **For Triatomic molecule**

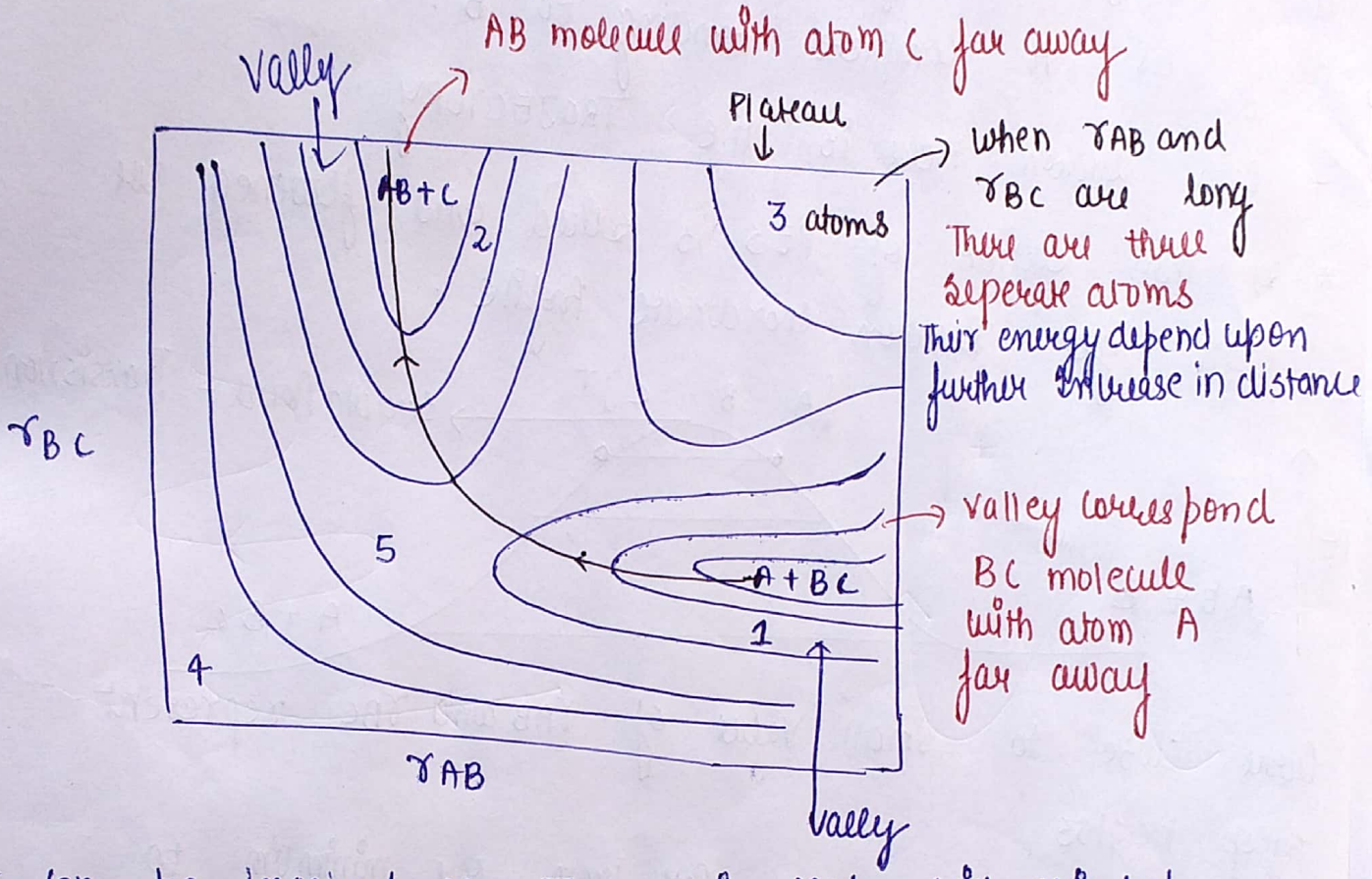
  We can draw Contours

A Contour plot is Graphical Technique for Representing 3D Surface by plotting constant z slices called Contours on 2D format.

A contour for linear Triatomic molecule is

A - B - C

* Two Valleys meeting at pass



* Plot can be imagined as Topographic map with altitude corresponding to potential Energy.

Trajectory

$$A + BC \longrightarrow AB + C$$

A path or Trajectory corresponds to collision process.

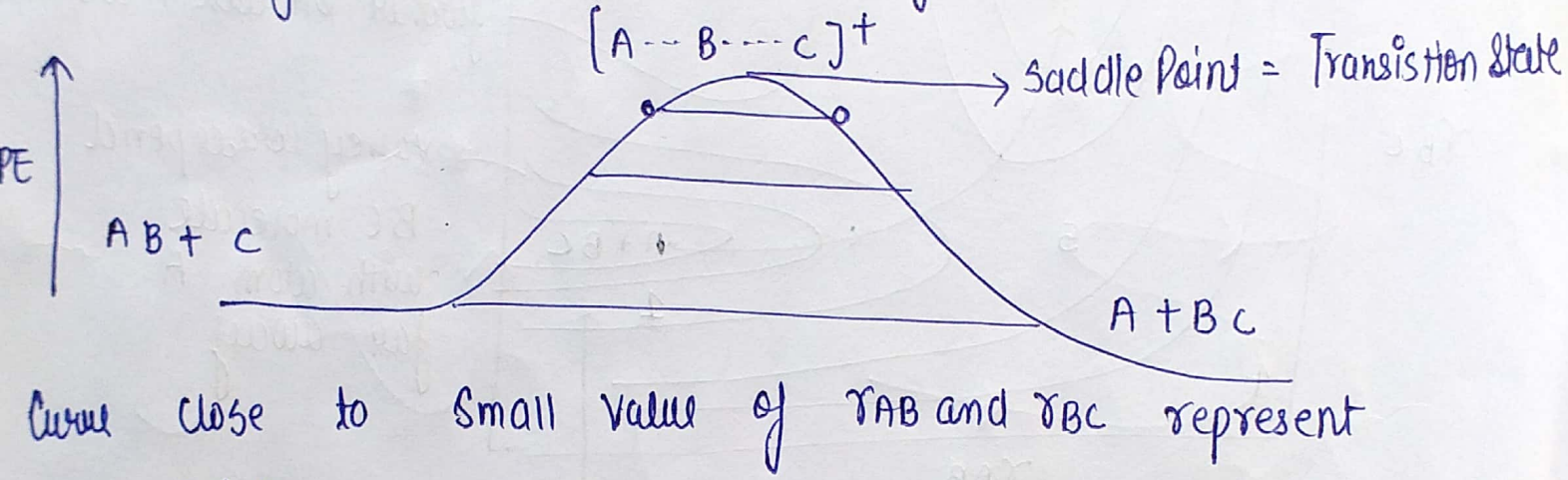
A line is drawn on PES with arrowhead showing approach of ball in prescribed direction.

Atom A is approaching BC (ie r_{AB} shrinks from a large distance where r_{BC} remains in Bonding distance.

As A get close to BC, BC bond began to stretch

until $r_{AB} = r_{BC}$. from this point C atom flies away as A complete Bonding to B.

* Path shown Here is the TRAJECTORY.
* If Thin Section of PES is sliced and flattened we will get Reaction Coordinate Profile.



Curve close to small value of r_{AB} and r_{BC} represent steep heights

* The maximum Point along Path from one minimum to another minimum is called saddle point.
* Eyring and Polanyi Refered to it as T.S

Contour Plot of $H + H_2$ or PES of $H_2 + H$

* The Reaction of hydrogen atom with hydrogen molecule

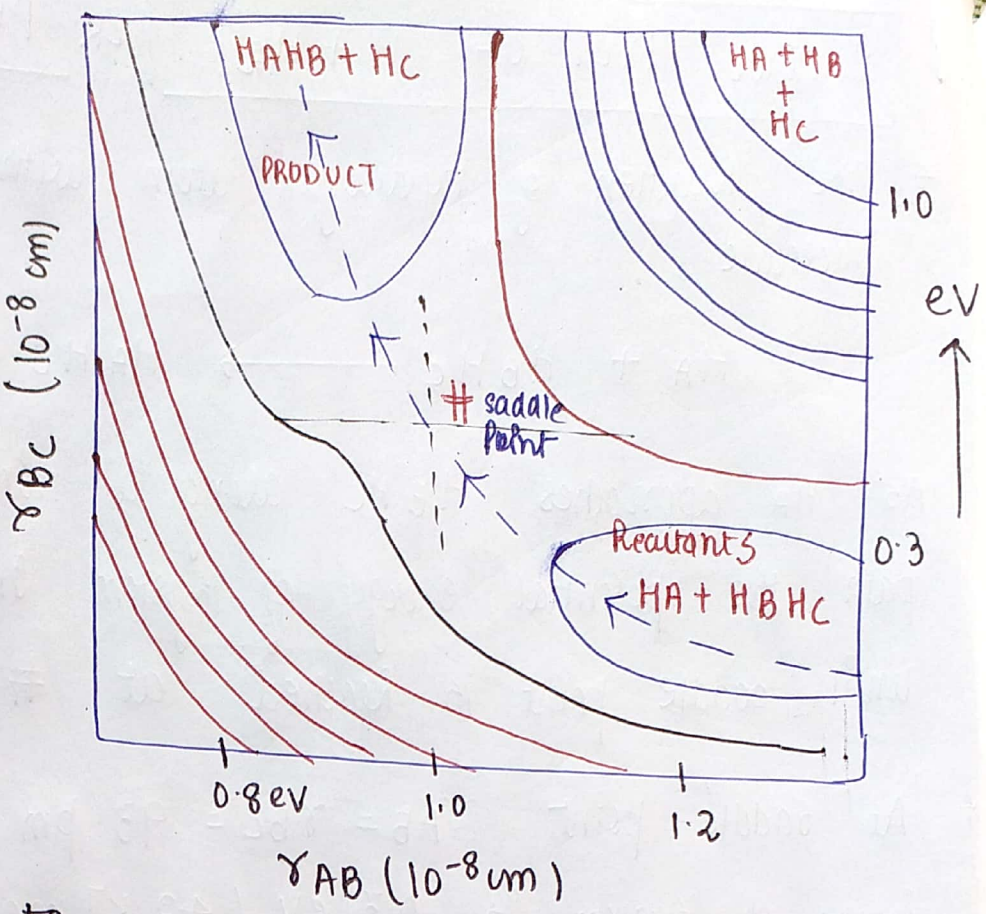
$$H_A + H_B H_C \longrightarrow H_A H_B + H_C$$

* As H_A approaches $H_B H_C$ along a minimum energy path the potential energy of system Increase until saddle point is Reached at #.

* At saddle point $r_{AB} = r_{BC} = 93$ pm and Potential Energy of system is 0.37 eV (42 KJ mol^{-1}) Highest along Dashed line

* Since the saddle point is 0.37 eV higher than Potential of H_A and $H_B H_C$ at an Infinite distance, This energy must be supplied from Relative Kinetic Energy or Vibrational Energy in Order for Reaction To occur.

* In upper Right corner There is High Plateau with Energy of 432 KJ/mol
(This is the energy of 3 Hydrogen atom infinitely far apart with Respect to seprated Reactant or Products).



Factors That Led to Product Formation

* High Translational Energy of Reactants HBHc which is use
* to bind product HAHB.
* High vibrational Energy of HBHc this can be transferred to vibrational energy of HAHB & Translational energy of product Hc.
* High Rotational Energy of HBHc
* In HA + HBHc ⟶ HA HB + Hc

Barrier energy = 10 Kcal/mol much lesser to break H2 (110 Kcal)

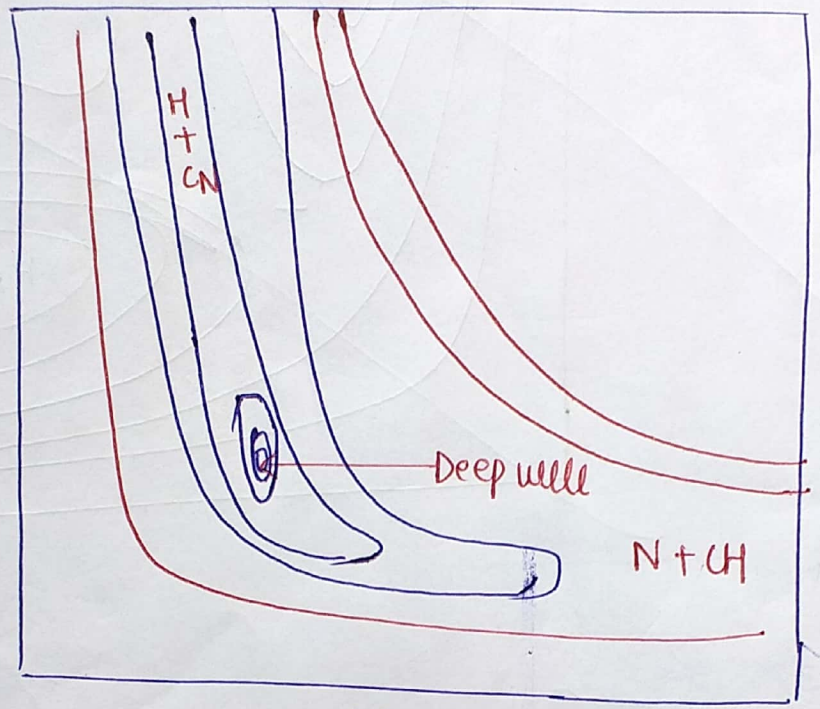
H3 molecule is Not a stable molecule

In terms of valency for H2 + H, H2 has no unfilled valence shell and cannot bind covalently

* PES For HC + N

vv. Imp

* The PES for HC + N is shown in Diagram

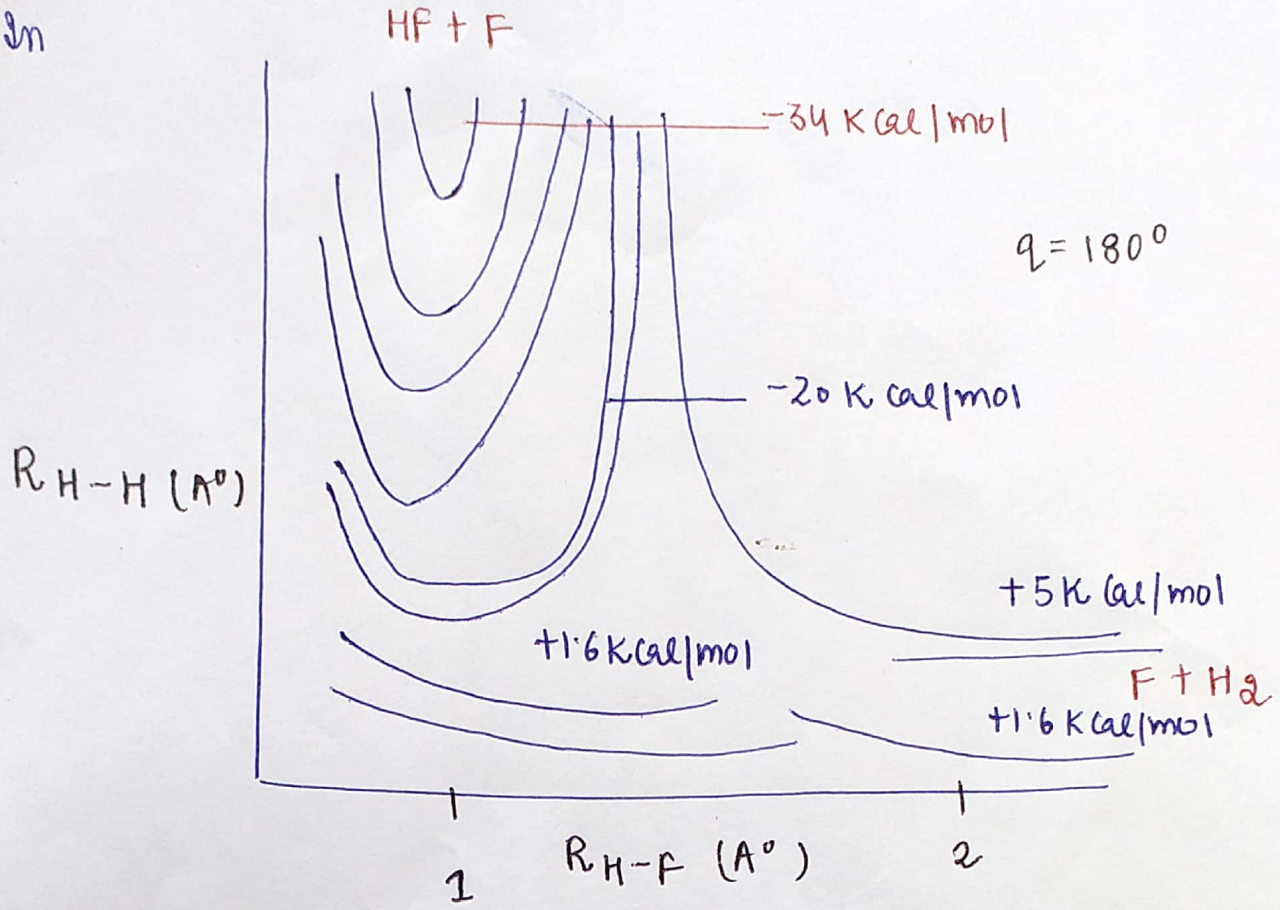


$$H + CN \longrightarrow HCN \longrightarrow HC + N$$

* Deep Hole of about 10 eV centered around γ_{CH} and γ_{CN} equal to $1 A^{\circ}$.
* Deep Hole demonstrate formation of stable HCN molecule
* The Region with γ_{CH} and γ_{CN} of $1 A^{\circ}$ have eqt Negative Energies.
* The CN end is lower in energy in compare to CH end because C≡N is much stronger than C-H Bond

H-C≡N is stable than both CN and CH end and Hence deep Hole or well when both CH and CN distance are small.

POTENTIAL ENERGY SURFACE OF $F + H_2$



In this system

$F + H_2 \longrightarrow HF + H$

γ_{H-F} is 0.93 A°

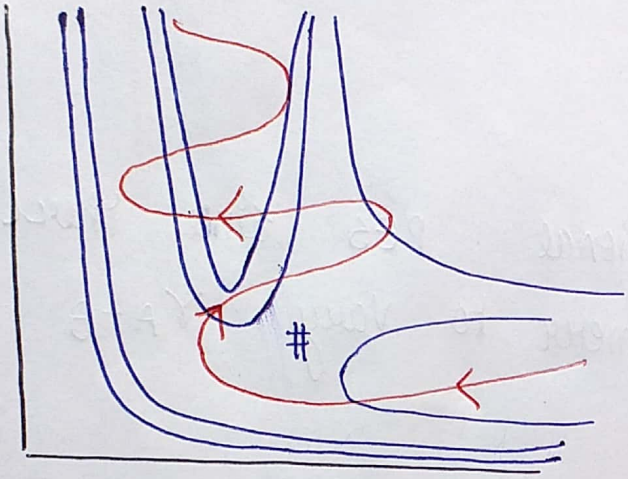
Exoergic Reaction is chemical Reaction where change in free energy is Negative.

* It is a Exoergic Reaction where the barrier is Not High and occurs at early stage of Reaction.
* In such Reaction exoergicity is Realised Primarily along Reaction Path.
* Such a surface having initial Release of exoergicity is called attractive Potential Energy Surface

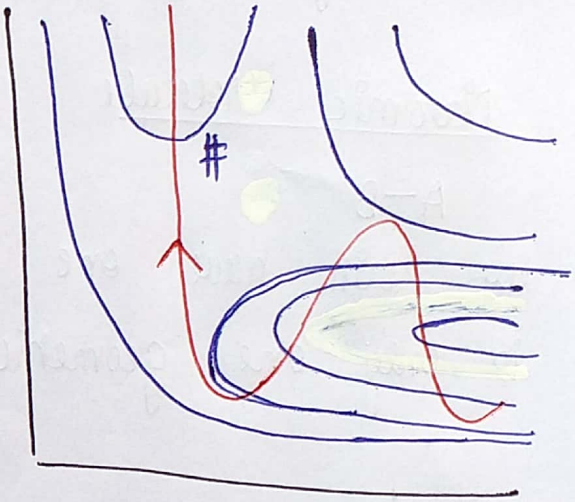
Attractive and Repulsive PES

In attractive PES saddle point lies closer to Reactant valley than Product Valley.
(Lies at an earlier position of Reaction coordinate)

In Repulsive PES saddle Point lies closer to Product valley.



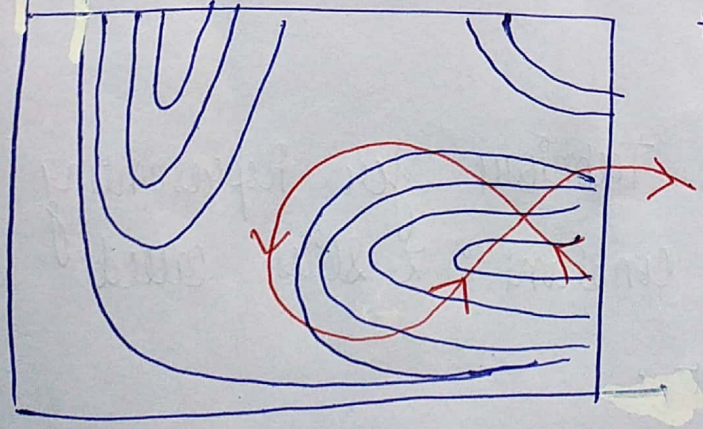
Attractive PES



Repulsive PES

Red line shows Trajectory

NON Reactive PES



* Reaction fails in NON Reactive PES.