## 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 #.

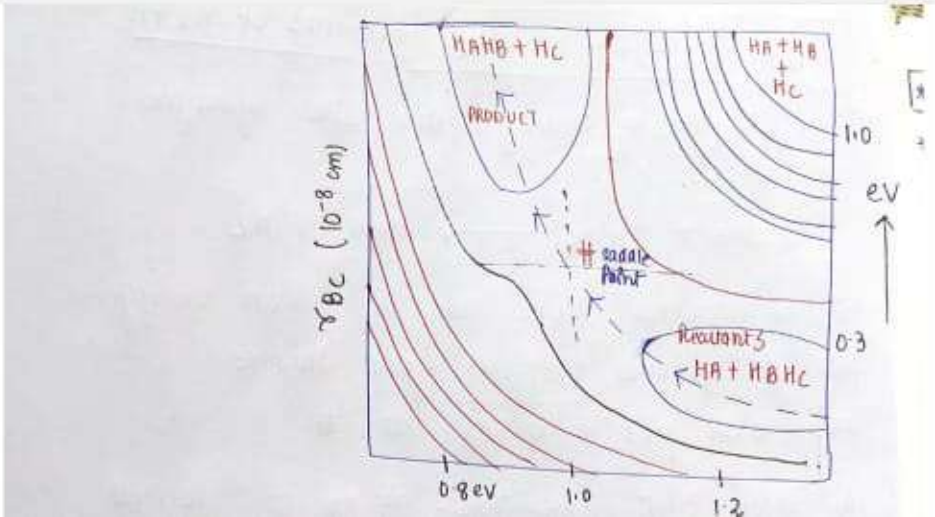
* At saddle point $r_{AB} = r_{BC} = 93$ pm and Potential Energy of system is 0.37 eV (42 KJ mol$^{-1}$) Highest along Dashed line.

* 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).





or Vibrational energy in order for

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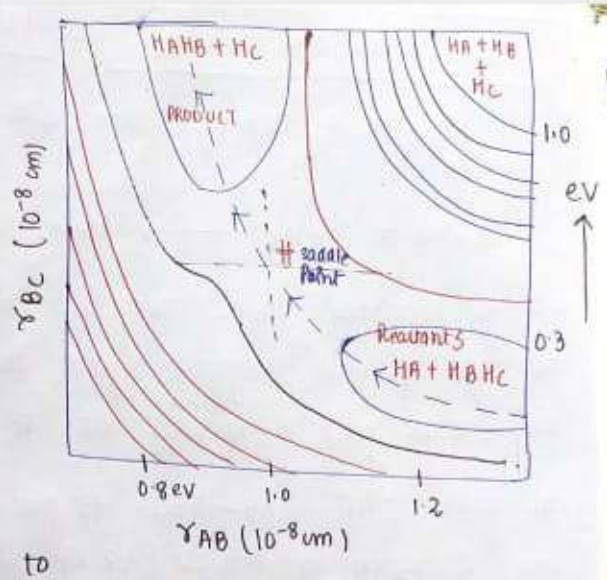



Factors That Led to Product Formation

* 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 $H_A + H_BH_C \rightarrow H_A H_B + H_C$

Barrier energy = 10 Kcal/mol much lesser to break $H_2$ (110 Kcal)

$H_3$ molecule is Not a stable molecule

In terms of valency for $H_2 + H$, $H_2$ has no unfilled valence shell and cannot bind covalently



* PES For HC + N

* The PES for HC + N is shown in Diagram

$$8b = \frac{RTc}{Pc}$$

$$\boxed{b = \frac{RTc}{8Pc}}$$

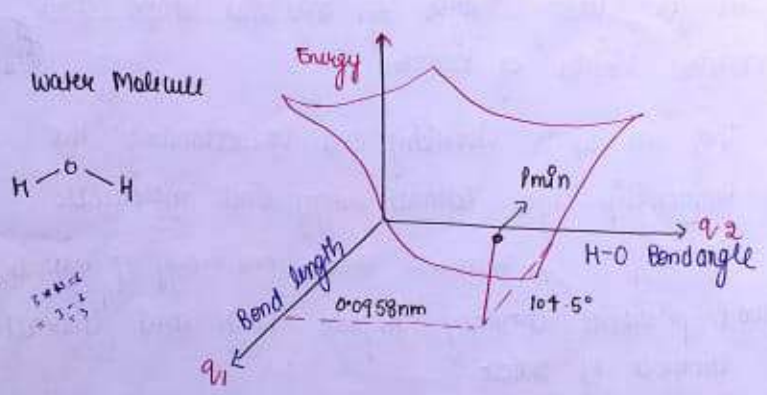


## POTENTIAL ENERGY SURFACE

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




* Pmin correspond to minimum Energy Geometry for Three atoms i.e to the equilibrium 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 structure

molecule

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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 & Suend 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 Geometric 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

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SADDLE POINT

It correspond to transition state, ie The Highest Energy point on Reaction 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

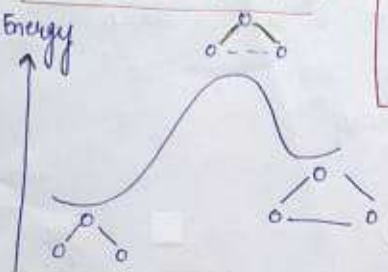
For Transition state

① $\frac{\partial^2 E}{\partial q_2} > 0$ For all q except along the Reaction coordinate and



"STRUCTURE OF INTEREST"

Energy




② $\frac{\partial^2 E}{\partial q_2} < 0$

for along Rea coordinate

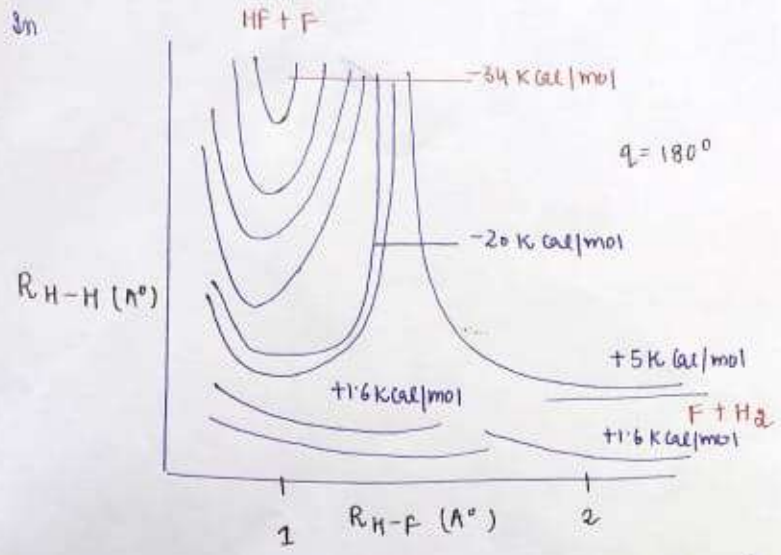
2/5

* 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

$F + H_2 \longrightarrow HF + H$

$\gamma_{H-F}$ 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.