

Module 7 : Theories of Reaction Rates

Lecture 34 : PES - I

Objectives

After studying this Lecture you will be able to do the following.

- Distinguish between potential energies and potential energy surfaces (PESs).
- Identify the saddle point, the reactant and product valleys and plateaus on the contour diagram of PESs.
- Distinguish between attractive and repulsive potential energy surfaces.
- Contrast the PESs for the $H_2 + H$ reaction and the $H + CN$ reaction.
- List elementary functional forms for the $H_2 + H$ PES.

34.1 Introduction

In empirical chemical kinetics, the main objective was to obtain appropriate rate laws for chemical reactions. The next step was to justify the rate laws by proposing and verifying the mechanisms proposed for reactions. Approximations such as preequilibrium and the steady state approach greatly simplified the process of relating the rate law for the overall reaction to the rates of the elementary reactions that constitute the reaction mechanism. To rationalize the chemical reactions on a microscopic basis, the collision theory and the transition state theory were used. In these theories, although the molecular nature of the reactants and the energy distribution of molecules were considered, the detailed and specific interactions between the reactants (and the products) as they approach (move away from) one another were not considered. These detailed interactions are explored in this lecture. These interactions are explored through potential energy surfaces (PESs) and we begin by considering the PES for a collinear $H_2 + H$ reaction.

We have studied in the structural chemistry part of this course that the interaction energy between molecules A and B can be calculated by using the Schrodinger equation. When A and B are very far apart, the individual molecules may be expected to occupy their lowest electronic energy levels. At any intermediate separation R_{AB} the energy of the combined system $E_{AB}(R_{AB})$ can be obtained by solving the Schrodinger equation $H \psi(R_{AB}) = E_{AB}(R_{AB}) \psi(R_{AB})$. We have plotted the relative interaction energy between A and B given by $E_{AB}(R_{AB}) - E_A - E_B$ as a function of R_{AB} . This is indeed the relative ground state electronic energy (because it is obtained from the electronic wave functions of A, B and AB) and is commonly referred to as the potential energy. This potential energy has a minimum at the equilibrium bond length and goes to zero at large R_{AB} and for small values of R_{AB} (say, less than $0.529 \overset{\circ}{\text{A}}$ or 1 bohr) it becomes very large. The curve of E_{AB} vs R_{AB} is a two dimensional plot with energy on the y - axis and R_{AB} on the x - axis.

When the interaction between a molecule AB and an atom C is considered, we need to consider not only the distance R_{AB} , but additional variables. These variables are shown in Fig 34.1. For simplicity in presentation, let A, B and C be all hydrogen atoms so that the interaction is between $H_A H_B$ and H_C

Figure 34.1 (a) Collinear and (b) non - collinear collision of $H_2 + H$

Let us consider the collinear motion (collision) between AB and C. The potential energy of A, B and C now depends on two distances R_{AB} and R_{BC} and may be plotted on the z axis with R_{AB} on the x - axis and R_{BC} on the y- axis. This is a three dimensional plot and the PE (plotted against two distances) gives the potential energy surface PES (this is a generalization of the two dimensional plot which gives a curve, to higher dimensions). When C is very far from AB, the situation corresponds closely to the region on the extreme right of Fig 34.2 where a point is marked as 1 in the figure. This region, for a fixed large R_{BC} , looks pretty much like the potential energy of AB plotted against R_{AB}

The maximum point along the path from one minimum to another is called the saddle point. While this point is a maximum along the minimum energy path in the two valleys, this is a minimum point if we traverse a path in a plane perpendicular to the minimum energy path at the saddle point. Such a path starts at large values of R_{AB} and R_{BC} (i.e., at the tip represented by point 3 and goes towards point 4 along a path wherein $R_{AB} = R_{BC}$ throughout. Along this path, we go inward from the plateau, reach the saddle point (the minimum along this path) and rise again to very high values of PE represented by point 4. The path $1 \rightarrow 2$ and $3 \rightarrow 4$ are similar to our treks along mountain passes. The minimum energy path is like the pass from $1 \rightarrow 2$ (one valley to another valley) by passing through the lowest point on the pass between mountains. The path $3 \rightarrow 4$ is a path perpendicular to the $1 \rightarrow 2$ path which corresponds to a passage from the high mountain peak on the left to the high mountain peak on the right by just touching the lowest point on the path (which is the highest point along the pass used by common travellers). The entire PES region near point 4 is a very high PE region. As we go towards $R_{AB} = R_{BC} \rightarrow 0$, we are indeed climbing the steep mountain of the PES.

You may have noticed by now how much explanation is needed to describe a 3 - dimensional figure. The most crucial region is the one that is encountered as we go from point 3 to point 4 in Fig 34.2 hidden from our view. This region is the region containing the activated complex and the transition state (saddle point). This is shown in Fig 34.3. Because of these inconveniences of visualizing 3 - D pictures, contour diagrams have gained prominence.

Figure 34.3 Saddle point. The minimum energy path from points 1 to 2 of Fig 34.2 is also indicated.

34.2 Contour Diagram of PES for H₂ + H

The contour (equipotential energy curve) diagram corresponding to Fig 34.2 is shown in Fig 34.4

Figure 34.4 Contour diagram for the PES of Fig 34.2. The saddle point is denoted by C^{\ddagger} . The points 1, 2, 3, 4 and 5 of Fig 34.2 are also indicated. A few paths on the PES are also shown. A path or a trajectory corresponds to collision process. Path A: R_{AB} is constant as H_C approaches and R_{BC} constant as H_A moves away. Path B: R_{AB} lengthens at an early stage during the approach of H_A . Path C: Along the floor of the potential valley via C^{\ddagger} , the transition state or the saddle point.

On the contour diagrams, each curve represents a constant value of potential energy (i.e., a constant height in Fig 34.2). The curves close to small values of R_{BC} and R_{AB} represent steep heights of Fig (34.2). It is a common practice to keep the difference in energy between adjacent contours to be constant (or very nearly constant). This helps to indicate whether a region in PES is flat or changing sharply. For small values of R_{AB} , notice that there are many lines close to one another. These regions (near point no 4) refer to the steeply rising regions of the PES. Widely spaced contours denote slowly changing regions of PES. Regions near point number 3 are slowly varying. Countours that are "U" shaped indicate a valley.

Each smaller "U" is contained in a larger "U" and is progressively lower in energy. The saddle point corresponds to a contour consisting of a single point (represented by point 5, C^{\ddagger}). From this point, the potential energy is decreasing towards points 1 and 2 and rising towards points 4 and 3. It is rising more slowly towards point 3 than towards point 4. Three paths (which correspond to three different trajectories of collisions between H₂ and H) are indicated on the contour diagram. Along path A, the potential energy rises steeply from the reactant (AB) valley and falls steeply into the product valley. Along this path (and also along all straight lines which are parallel to the axis R_{AB} and R_{BC}) R_{AB} is constant from right to left till it

turns upwards near point 4. Beyond this point and towards point 2 R_{BC} is constant and R_{AB} is changing. Upto near point 4 (from 1) H_C is approaching H_AH_B and beyond point 4, towards point 2, H_A is moving away from a fixed H_BH_C . Along curve B, both R_{AB} and R_{BC} are changing simultaneously. One goes from the "reactant" valley at 1 to the "product" valley at 2 by going over the plateau region. Path C is the minimum energy path. At each point along path C, the potential energy is the smallest possible value, because, if you move along any other direction (other than the forward the direction of path C), the potential energy increase is higher. An important feature associated with contour diagrams here is that two contours never cross one another (can you rationalize this ?).

34.3 Attractive and Repulsive PESs

In an attractive PES, the saddle point lies closer to the reactant valley than the product valley (i.e., it lies at an earlier position on the reaction coordinate). It is the opposite in the case of a repulsive PES wherein the saddle point lies closer to the product valley. Different surfaces have different dynamical (collisional) characteristics and we will take up the dynamics of molecular collisions (which are represented by trajectories) separately in the next lecture. We will next consider a unique PES, which has a deep well in place of the saddle point corresponding to the $H_2 + H$ surface. The contour diagrams for attractive and repulsive PESs are shown in Fig 34.5

Figure 34.5 Attractive and Repulsive PESs

34.4 The HC + N Potential Energy Surface

The HC + N PES is shown in Fig 34.6. You will immediately notice that this is intrinsically very different from the $H_2 + H$ surface. In the region where you may expect a saddle point (which is usually 0.2 to 2 eV higher than the reactant valleys, there is a deep hole of about 10 eV, centered around $R_{CH} = 1 \text{ \AA}$ and $R_{CN} = 1 \text{ \AA}$. This deep hole is due to the formation of a stable HCN molecule (contrast with the point number 5 of earlier figures). The other points which are numbered 1 to 4 have meanings which are similar to those in Fig 34.4.

While " H_3 " is not a stable molecule but a "saddle point" when the R_{HH} values on both sides of the central H atom are about 1 \AA , HCN is a very stable molecule. In the traditional language of valency, both CH and N had an unfilled or incomplete valence shell whereas in $H_2 + H$, H_2 has no unfilled valence shell and can not normally bind covalently to any other molecule. Both the ends of the PES in Fig. 34.6 (points 1 and 2) with $R_{CH} = 1 \text{ \AA}$ and $R_{CN} = 1 \text{ \AA}$ are regions corresponding to negative energies. The CN end (point 2) is lower than the CH end (point 1) because $C \equiv N$ is a much stronger bond than the C-H bond. $H-C \equiv N$ is stabler

than both these ends, and hence the well when both CH and CN distances are small. If you slowly roll a small marble ball on this surface, it will slowly trickle down and settle in the well.

This roll corresponds to H, C and N slowly attaching to one another and forming a stable molecule. If the marble is rolled very rapidly from right to left from point 1, instead of settling down in the well, it may enter the well very briefly, but pop up and go towards point 2. It is akin to a missed put which often happens when you play golf!

Figure 34.6. The HC + N PES. Notice the deep well at point number 5 corresponding to the formation of the HCN molecule and contrast it with the point number 5 of figure 34.4 which corresponds to a transition state of H₃.

We will briefly consider now some empirical / calculated PE functions that describe simple PESs.

34.5 Analytical Potential Energy Functions

In our study of pair potentials between atoms, ions or polar species, we have considered different forms of these functions in module 2. For obtaining the analytic functions (which consist of mainly polynomial and transcendental functions, which can be readily differentiated to obtain the forces between different centers) one either fits the calculated energies (obtained by solving the complete Schrodinger equation) into suitable forms or uses semi-empirical or empirical functions which have been developed for different A + BC systems and other relatively simple cases.

One of the most widely used potential for the A + BC interaction is the LEPS (London - Eyring - Polanyi - Sato) surface. Its origin lies in the valence bond theory. The analytical form for this is:

$$V(R_{AB}, R_{BC}, R_{AC}) = Q_{AB} / (1 + S_{AB}) + Q_{BC} / (1 + S_{BC}) + Q_{CA} / (1 + S_{CA}) - 0.25 [\{ (J_{AB} / (1 + S_{AB}) - J_{BC} / (1 + S_{BC}))^2 + \{ J_{BC} / (1 + S_{BC}) - J_{AC} / (1 + S_{AC}) \}^2 + \{ J_{AC} / (1 + S_{AC}) - J_{AB} / (1 + S_{AB}) \}^2] \quad (34.1)$$

Here, Q and J are the Coulomb and exchange integrals appearing in valence bond theory and Ss are the

overlap integrals. These are obtained from the wave functions of A, B, C and they depend on the separation between A, B and C. The values of Q and J can be obtained from the dissociation energies (D) of AB, BC and CA as follows

$$Q_{AB} + J_{AB} = D_{AB} \{ \exp [-2 \beta_{AB} (R_{AB} - R^0_{AB})] - 2 \exp [- \beta_{AB} (R_{AB} - R^0_{AB})] \} \quad (34.2)$$

$$Q_{AB} - J_{AB} = 0.5 D_{AB} \{ \exp [-2 \beta_{AB} (R_{AB} - R^0_{AB})] + 2 \exp [- \beta_{AB} (R_{AB} - R^0_{AB})] \} \quad (34.3)$$

Here, β s are indicative of how rapidly the potential of a diatomic goes to zero. Although these functions are not as accurate as the ab initio functions (which are obtained by solving the Schrodinger equation without making any approximations), they have provided a very useful qualitative picture.

Another function, which is simpler and more empirical than the LEPS function is the function of Blais and Bunker. This is given by

$$V (R_{AB}, R_{BC}, R_{AC}) = D_{AB} \{ 1 - \exp [-\beta_{AB} (R_{AB} - R^0_{AB})] \}^2 + D_{BC} \{ 1 - \exp [- \beta_{BC} (R_{BC} - R^0_{BC})] \}^2 + D_{BC} \exp [\beta_{BC} (R_{BC} - R^0_{BC})] \{ 1 - \tanh (a R_{AB} + C) \} + D_{AC} \exp [- \beta_{AC} (R_{AC} - R^0_{AC})] \quad (34.4)$$

The first two potentials are the Morse potentials for the AB and BC bonds. The third term includes a switching function, $1 - \tanh (a R_{AB} + C)$, which is zero for large R_{AB} and goes to unity for small R_{AB} . The last term is a repulsive term between A and C. In this and the previous equation, R^0_{AB} is the equilibrium distance between A and B in the AB molecule. You may plot these individual functions and assess their behaviour at small and large interparticle separations (asymptotic).

The experimental determination of these PESs is done through molecular beams and spectroscopic techniques. The anharmonic (not equally spaced) vibrational frequencies yield the potential energy function of the diatomic. The thermal activation energy obtained by using the transition state theory gives the energy difference between the reactants and the saddle point. In the next lecture, the connections between the PESs and the rate constants will be investigated.

Example 34.1

Sketch the $D_2 + F$ potential energy surface and identify the saddle point and the other points (1 to 4) on that surface.

Solution :

The $D_2 + F$ potential energy surface is shown below in Fig. 34.7. Identify the points 1 to 5 by comparing this figure with figures 34.4 and 34.6.

Figure 34.7 The $D_2 + F$ potential energy surface.

34.6 Problems

- 34.1) Draw the contour diagrams for a) Qutub minar, b) Leaning tower of Pisa and c) The Tajmahal.
- 34.2) Rationalize the fact that the activation energy for $AB + C$ reaction very often much lower than the dissociation energy of either AB or BC .
- 34.3) What are the major changes that you would expect in the PES of $H_2 + H$ if the approach of $H - H$ and H is not collinear?
- 34.4) What are the factors that decide whether a reactant valley is shallow or deep?
- 34.5) For a PES, is there a requirement that there is only one saddle point?
- 34.6) Are the PESs for the excited electronic states of reactant(s) identical to the PESs of their ground electronic states? As a hint for your answer, take a look at the energy level diagram for a photophysical process shown in Fig 30.2.

Recap

In this Lecture you have learnt the following

Summary

In this lecture, we have explored the nature of the potential energy surfaces of a few triatomic systems. Potential energy barriers, potential wells and attractive and repulsive PESs have been considered and their representation on a contour diagram has been given. A few empirical forms for these potential energy functions have been given. The location of the saddle point on a minimum potential energy path from reactants to products has been identified. The reaction coordinate, which determines the extent of progress of the reaction has also been defined in the case of the $H_2 + H$ PES as $R_{AB} - R_{BC}$.