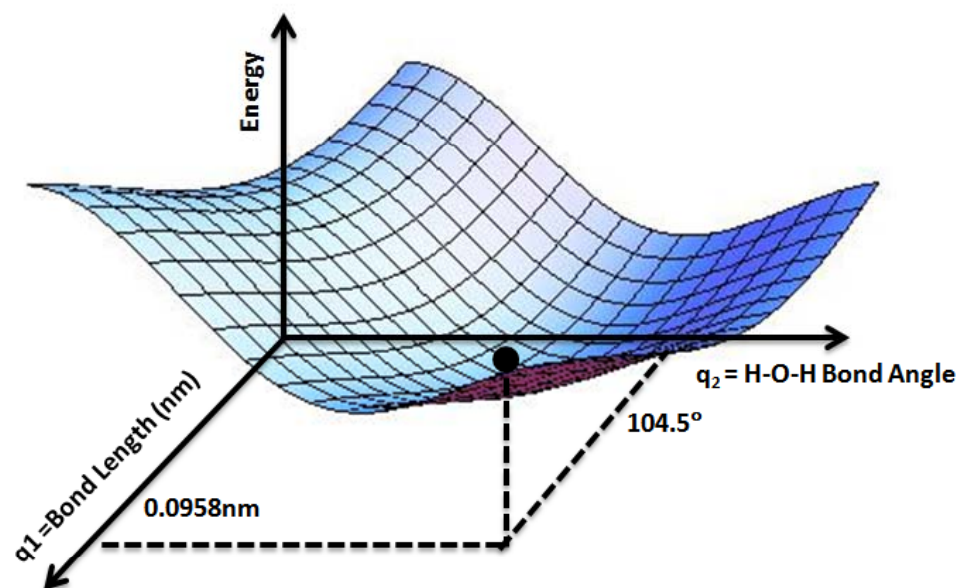
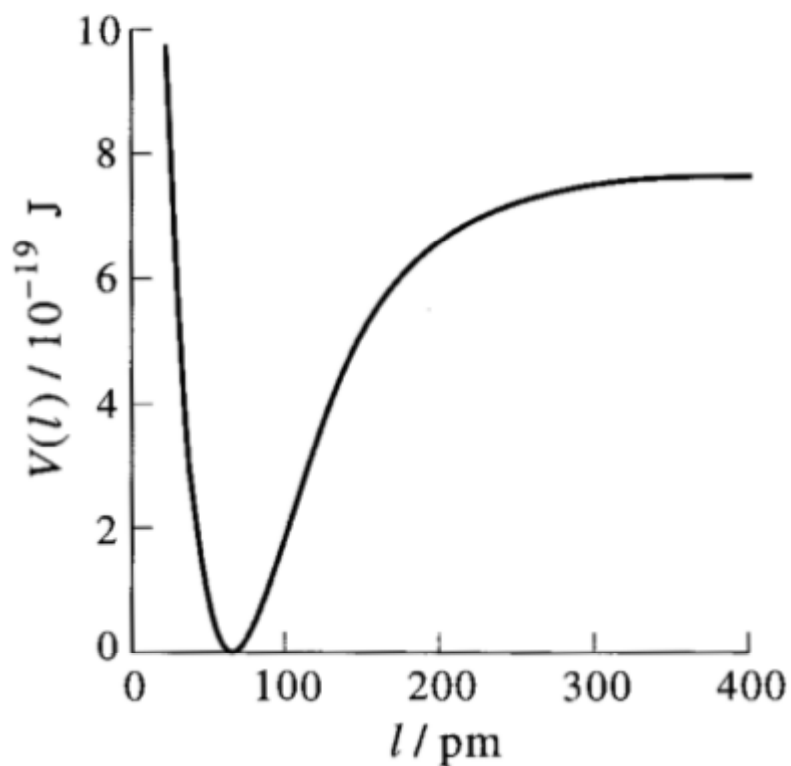


# Potential Energy Surfaces



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## Morse Potential Energy Curve



**FIGURE 5.6**

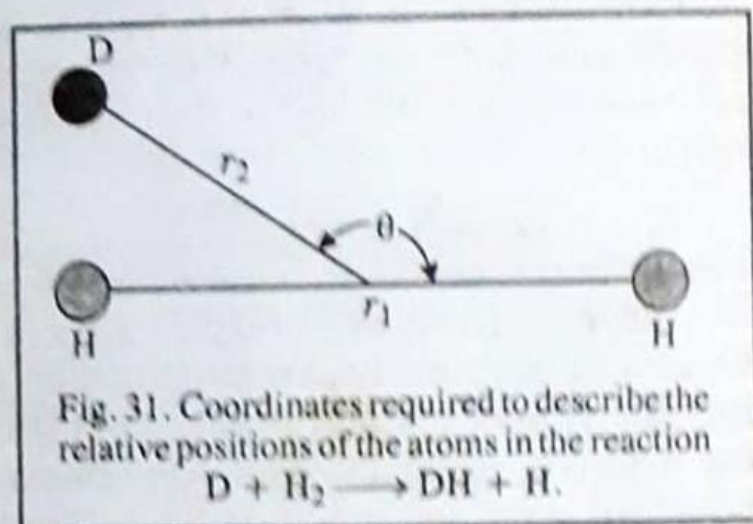
The Morse potential energy curve  $V(l) = D(1 - e^{-\beta(l-l_0)})^2$  plotted against the internuclear displacement  $l$  for H<sub>2</sub>. The values of the parameters for H<sub>2</sub> are  $D = 7.61 \times 10^{-19} \text{ J}$ ,  $\beta = 0.0193 \text{ pm}^{-1}$ , and  $l_0 = 74.1 \text{ pm}$ .

## Potential Energy Surfaces

Consider one of the simplest reactions, viz.,  $D + H_2 \longrightarrow DH + H$ . We need three spatial coordinates to describe the configuration of this reacting system at any point along the reaction path (Fig. 31). These coordinates are : the internuclear distance  $r_1$  between H and H; the distance  $r_2$  of D from the midpoint of the H—H bond and the angle  $\theta$  between the H—H bond and the vector from the midpoint of the bond to D.

It is evident that one particular approach of D to H—H is energetically more favourable than any other. This is, in fact, the path in which D approaches H—H along the line of centres of the three-body system, i.e., the angle  $\theta$  is either  $0^\circ$  or  $180^\circ$ . The reason for this is that when D approaches H—H along the  $\theta = 0^\circ$  direction, the D atom 'feels' appreciable repulsion from any one of the H atoms whereas in an approach from any other direction, the D atom is under the influence of repulsive field from both the H atoms.

Now, as the D atom approaches H—H along the line of centres of the atoms, the potential energy depends only on two coordinates, viz., the distances D—H and H—H. If one distance is plotted against the X-axis and the other along the Y-axis in a plane, the potential energy can be plotted along the Z-axis normal to the plane. In this way the potential energy  $V(x, y)$  of the reacting system can be visualized as a *surface in three dimensions*.



It was R. Marcellin (1885-1914) who, in 1915, had suggested the idea of representing a chemical reaction by such a potential energy surface. However, the first potential energy surface was actually computed in 1931 by H. Eyring and M. Polanyi (1891-1976). Since the computational techniques at that time were not perfect, these researchers were not able to perform a purely theoretical calculation and had to rely on a semi-empirical approach based on spectroscopic data. However,



more accurate calculations performed later showed that the potential energy surface constructed by Eyring and Polanyi by a combination of calculation and intuition was essentially correct. This surface is shown in Fig. 32 in the form of a three-dimensional model.

We can easily trace the path of the reaction over this surface. It is the path from the reactant side to the product side that follows the contour of minimal potential energy. If we consider the side to the product side that follows the contour of minimal potential energy, then the reaction path resembles that of a bobsled sliding on its run. The path traverses a deep valley ( $D+H_2$ ), rises over a hump to a **saddle point** at the activated complex ( $D-H-H$ ) and then passes down the other side of the pass into **point** at the activated complex ( $D-H-H$ ) and then passes down the other side of the pass into another valley ( $DH+H$ ). The reaction path is called the **reaction coordinate**. Fig. 28 shows a contour map of the region of the saddle point. The elevation of the saddle point is 38 kJ which is the activation energy of the reaction. This occurs at the configuration of the activated complex where  $r_1=r_2=93$  pm. This distance is considerably greater than the normal interatomic distance (174 pm) in  $H_2$ .

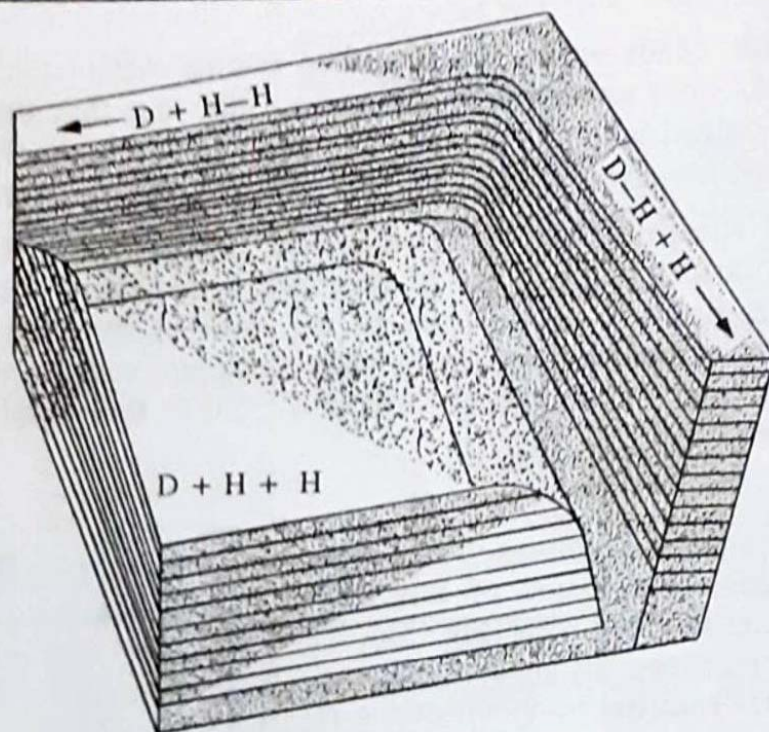


Fig. 32. The Eyring-Polanyi potential energy surface for the  $D + H_2 \longrightarrow DH + H$  reaction.

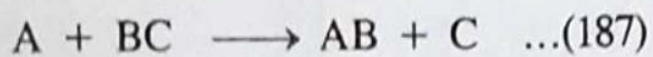


✦ The potential energy surface gives a map of a chemical reaction from beginning to end. In any reaction, there is always a particular configuration at the saddle point. In many respects, the activated complex which results from this configuration of atoms is like an ordinary molecule except that it is not an equilibrium configuration. Thus, we can imagine a reaction to take place in two stages, viz., the formation of the activated complex from the reactants and the decomposition of the activated complex into products. These stages are not sharply defined in any way and from a dynamic point of view the reaction proceeds smoothly and continuously. However, we can designate a transition state as the highest region of potential energy surface along the reaction path.

Though kinetic theory gives us useful information about molecular collisions, it does not deal with changes that take place at the molecular level when reactants are converted into products. When two molecules are very close to each other, they cannot be considered separately because their wave functions overlap. Thus, from the time the reactant molecules are close to each other until the products are well separated, the system is a kind of **supermolecule**. This supermolecule is different from an ordinary molecule because it is in the process of change, but it is a molecule in the sense that its energy and electron distribution can be calculated for each nuclear configuration by using quantum mechanics. According to the Born-Oppenheimer approximation, the electrons move much more rapidly than the nuclei so the molecular electronic energy and wave functions can be calculated

for a given nuclear configuration by using the electronic Schrödinger wave equation. This procedure has been used to calculate the electronic potential energy function so that the Schrödinger wave equation may yield the molecular vibrational energy levels.

For a reaction involving  $N$  nuclei, there are  $3N$  nuclear coordinates, three translational coordinates of the centre of mass and two or three rotational coordinates (about the centre of mass) that do not affect the potential energy. Thus, potential energy is a function of  $3N - 5$  coordinates if the nuclei are constrained to a straight line and  $3N - 6$  coordinates in general. For the simplest type of reaction



where A, B and C are atoms, three coordinates are required. It is not possible to plot the potential energy as a function of three coordinates, but if the angle  $\theta$  of approach of A to BC is fixed, the potential energy can be plotted as a function of  $r_{AB}$  and  $r_{BC}$ , where  $r$  is the intermolecular distance. Such a plot is shown

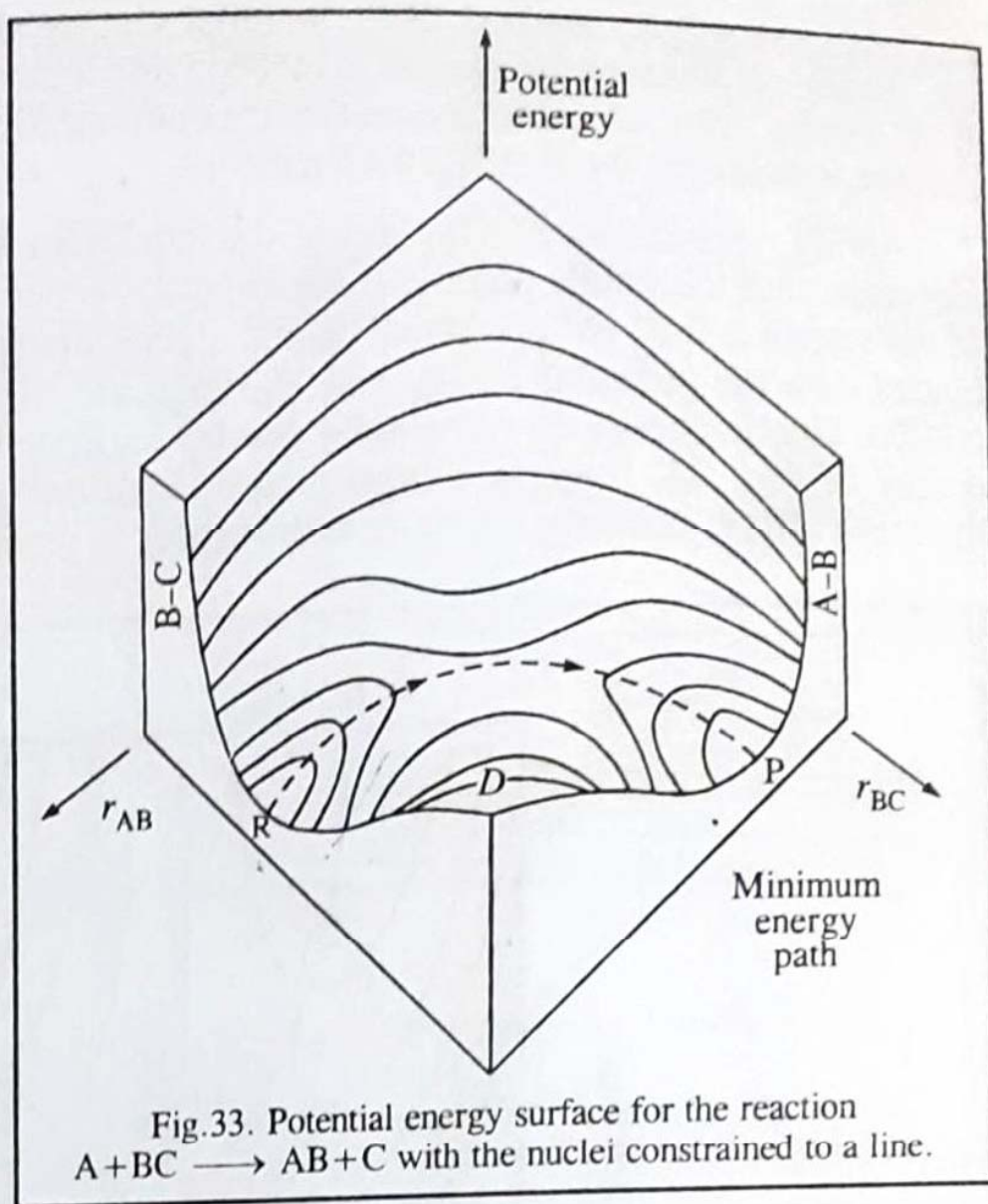


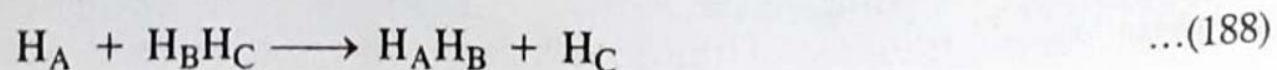
Fig.33. Potential energy surface for the reaction  $A + BC \longrightarrow AB + C$  with the nuclei constrained to a line.



in Fig. 33. If  $r_{AB}$  is rather large, as shown on the left face of the diagram, the potential energy is essentially that of the BC molecule. Similarly, the right face gives the potential energy of the AB molecule. Initially, the  $r_{AB}$  distance is very large. As A approaches BC, the lowest energy path is given by the dashed line from reactants R to products P. This dashed line gives the minimum energy path which is sometimes referred to as the **reaction coordinate**. We will shortly see that the configuration of the system does not actually move along the reaction coordinate in the reaction but the reaction coordinate does help us visualize the surface. The highest point along the reaction coordinate is a saddle point. At the **saddle point**, the potential energy is a maximum along the reaction coordinate but it is a minimum in the direction perpendicular to the reaction coordinate. The reaction system at this point is said to be in the **transition state**. In Fig.33, *D* is a high plateau giving the potential energy of three atoms well separated from each other.

As a simple example, let us consider what happens when A approaches a non-vibrating BC molecule along the internuclear axis. The point representing the configuration of the system moves along the minimum energy path, the dashed line in Fig.33. As  $r_{AB}$  decreases, the kinetic energy is converted into potential energy as the point representing the system of three nuclei moves up the valley from the left. If there is initially enough kinetic energy for the system to go over the saddle point, AB and C are formed and gain energy as the system goes down the valley to the right. If the kinetic energy is too low, the system returns down the valley to the left. This is expressed by saying that the reactants bounce off each other. Fig. 33 applies only when the nuclei are constrained to a line. The potential energy surface will be different if there is a different angle  $\theta$  of approach. It is very difficult to calculate quantum mechanically an accurate potential energy surface for reaction of type (1). In fact, surfaces have been calculated only for a few reactions.

The reaction of a hydrogen atom with a hydrogen molecule





has been extensively studied. The potential energy surface for this reaction for  $\theta = 180^\circ$  is described by means of the contour diagram in Fig. 34. This surface has been calculated by M. Karplus and R.N. Porter using *ab initio* methods with configuration interaction (CI). The error at any point on the surface is less than 0.03 eV (2.9 kJ mol<sup>-1</sup>).

As  $H_A$  approaches  $H_BH_C$ , along the minimum energy path, the potential energy of the system increases until the saddle point is reached at  $\star$ . At this point  $r_{AB} = r_{BC} = 93$  pm and the potential energy of the system is 0.37 eV (42 kJ mol<sup>-1</sup>), the highest along the dashed line. Since the saddle point is 0.37 eV higher than the potential of  $H_A$  and  $H_BH_C$  at an infinite distance, this energy must be supplied from relative kinetic energy or vibrational energy in order for the reaction to occur. In the upper right-hand corner of Fig. 34, there is a high plateau with energy of 432 kJ mol<sup>-1</sup>. This is the energy of three hydrogen atoms infinitely far apart with respect to separated reactants or products.

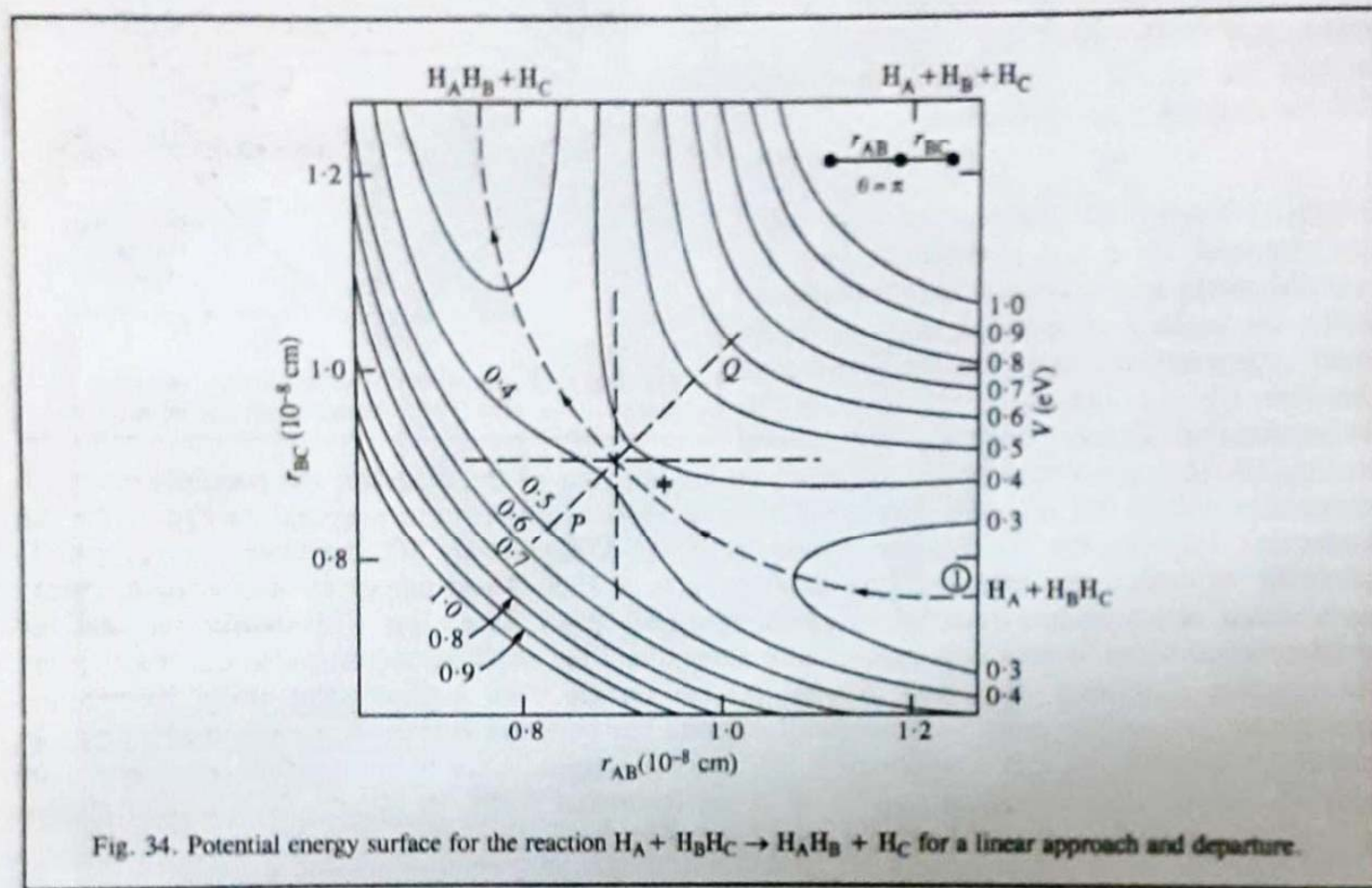


Fig. 34. Potential energy surface for the reaction  $H_A + H_BH_C \rightarrow H_AH_B + H_C$  for a linear approach and departure.



