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TO MY DAUGHTER

KAREN S. STEIN

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INTRODUCTION

In 1935 Henry Eyring¹ introduced his well known theory for the evaluation of a rate constant of any order. This theory, which is now known as Transition State Theory or Absolute Rate Theory (ART) makes the following assumptions:

1. The reaction shall not involve a jump in the quantum state of electrons. This is known as the adiabatic assumption.
2. Classical mechanics is applicable to the motion of nuclei.
3. There is equilibrium between the reactants and transition state (X^*).
4. The number of systems crossing the activated state are the number of systems which react. This is known as the direct assumption.
5. The interaction potential of the transition state can be approximated by that of independent harmonic oscillators.

It is generally the last two assumptions that are referred to when the validity of ART is discussed. To a large extent, our work will test assumptions 4 and 5 for classical collinear three atom systems.

In ART, the number of systems which cross the activated state are determined partly by a multidimensional dividing surface, whose position on the potential energy surface is fixed for each reaction. It is from the DS that we evaluate the flux of systems which are traveling toward products. It is possible that some of these systems originated from the same point in reactant phase space; i.e. assumption 4 is not valid. If this occurs, the rate constant will be overestimated. ART attempts to correct for this possibility

by multiplying the rate constant by a transmission coefficient, which is the probability that a transition state on the dividing surface originating from reactants will result in a product. In practice however, ART does not provide a way of evaluating the transmission coefficient so it is usually given a value of unity, the value it would have if assumption 4 were valid. Keck² has introduced a variational form of ART which allows us to vary the position and shape of the dividing surface until the least upper bound to the rate is obtained. Koepl³ has shown how to rotate a straight dividing surface about the saddle point, thus enabling us to locate the best straight dividing surface. Koepl, Sverdlik and Pechukas⁴ have shown that the best variational theory dividing surface corresponds to a periodic trajectory which does not necessarily pass through the saddle point.

The average probability that a point in reactant phase space will reach the product region is defined as the mean reaction probability. The procedure for evaluating this quantity using the methods of classical mechanics has been given by Morokuma, Eu and Karplus⁵ for any type of potential, thus providing a test for assumption 5. The mean reaction probability, like the rate constant will be overestimated, and may even exceed unity if assumption 4 is not valid. A quantitative test of assumption 4 had to wait the development of collisional mechanical trajectory theory (CMTT) and the high speed computer. CMTT which allows us to follow the path of a trajectory (a time history of the position and momenta of phase space coordinates), was studied by Karplus, Porter

and Sharma⁶. Trajectories were calculated as early as 1936 by Hirshfelder, Eyring and Topley⁷, but their lack of a high speed computer limited their calculations to a single trajectory. Using CMTT enables us to evaluate Anderson's conversion coefficient⁸, which is similar to the transmission coefficient except that it corrects for transition states which do not contribute to the rate because they originate in the product region of phase space. It is interesting to compare the values of the mean reaction probability calculated using CMTT, the modified form of ART using an accurate interaction potential, and the original form of ART using the harmonic approximation to the potential energy. A comparison of the last two quantities provides a test of assumption 5, a comparison of the first two quantities is a test of assumption 4. Such a comparison was made by Koepl and Karplus⁹ for classical 3-D three atom systems. Morokuma and Karplus¹⁰ have also made a comparison of the trajectory mean reaction probability and the ART mean reaction probability which uses assumption 5. Part of our work will be to make the above comparison for classical collinear three atom systems. We will make this study using thirteen mass combinations on each of three potential energy surfaces. We did not choose our surfaces in an attempt to reproduce experimental results, as does Muckerman¹¹ for example, but rather to test the validity of ART on different types of potential energy surfaces. Besides the calculation of the mean reaction probability, CMTT also enables us to evaluate

the energy distributions for the collision products. Such a calculation was done by Polanyi and Wong¹². In their work however, only brief use was made of the skewed potential energy surfaces. The relationship between the product energy distributions and the features of the potential energy surface will also be discussed.

Recently, Pechukas and McLafferty¹³ have shown that if there are no forces on the skewed potential energy surface which can direct a trajectory with a total energy E back to reactant phase space, then the modified form of ART using the accurate potential energy will be exact at least up to a total energy E . The force affecting the direction of a trajectory on a potential energy surface is given by the negative gradient of the potential energy, and is directed perpendicular to an equipotential contour at a point on it. Only if the line segment in the direction of the force from a contour of energy E intersects the dividing surface is it possible for assumption 4 to be invalid at energy E . We cannot say for sure that assumption 4 is invalid because forces which point in the direction of reactants are not always effective at returning a trajectory to reactants. The work of Pechukas and McLafferty is very useful because it enables us to sit down with a skewed potential energy surface and a ruler and say for sure in some cases, up to what energy the conversion coefficient will be unity.

Outline of Thesis Presentation

Our work begins with a derivation of the CMTT classical collinear rate constant for a three atom system. In section IB we define the CMTT mean reaction probability and show how it is related to the rate constant derived in section IA. From the equation which relates the trajectory mean reaction probability to the CMTT rate constant, the reader will see why it is more convenient to work with mean reaction probabilities and not rate constants. In section IC, the method for choosing the initial conditions for each trajectory is given. In our work, the initial conditions are picked so that all trajectories start out in the reactant region of phase space. The recent work of Porter¹⁴ however suggests that a significant amount of computer time can be saved if the trajectories are originated from the dividing surface. A counting procedure suggested by Anderson^{15,16} prevents trajectories which originate from the same point in reactant phase space from being counted more than once. In section ID, we show how to evaluate the trajectory mean reaction probability using a Monte Carlo approach. Hamilton's equations of motion are introduced as well as a brief description of the numerical integration procedure which evaluate each trajectory. We also include the equation which evaluates the error in the trajectory mean reaction probability. A more complete error analysis is given in appendix I.

In section IIA we derive the ART rate constant calculated using CMTT. Section IIB discusses Keck's variational theory and indicates how it enables us to vary the location

of the dividing surface until the minimum rate is found. As mentioned previously, Koeppl, Sverdlik and Pechukas have found that the best dividing surface corresponds to a periodic trajectory, not necessarily passing through the saddle point. We also show that if the same dividing surface is used, Keck's variational theory gives the same result for the rate constant as ART does; i.e. ART is a special case of Keck's variational theory. Section IID shows how the work of Morokuma, Eu and Karplus⁵ is used to arrive at the expression for the ART mean reaction probability using the interaction potential given by the potential energy surface, and the harmonic oscillator approximation to the potential energy. These expressions for the mean reaction probability will be compared to the trajectory mean reaction probability in chapter three. The method given by Koeppl³ for rotating the ART dividing surface is also described in this section. Of particular interest is the ART dividing surface, the straight dividing surface which corresponds to the minimum mean reaction probability, and the dividing surface perpendicular to the path of steepest descent.

In section IIE, the procedure for the evaluation of the ART mean reaction probability is demonstrated. The evaluation of the Anderson conversion coefficient is given in section IIF. Using a diagram which illustrates some typical trajectories which intersect the dividing surface, we hope to give the reader a clear physical picture of the relationship between the conversion coefficient, the trajectory

mean reaction probability and the ART mean reaction probability. We also show how the conversion coefficient can be factored so that the deviations from assumption 4 can be separated into two parts; deviations from trajectories which originate from reactants (transmission coefficient) and deviations from trajectories which originate from products (product coefficient). As a historical note we compare the transmission coefficient which we use in chapter 3 with the transmission coefficient suggested by Morokuma and Karplus¹⁰ and Anderson⁸ and show why the latter two transmission coefficients have a limited value.

In chapter three, the results of our calculations using CMTT and ART are presented. Our goal in this chapter is to try to explain the trends in the trajectory mean reaction probability, the ART mean reaction probability, the transmission and product coefficients, and the energy distributions of reactive and nonreactive molecules in terms of the features of the potential energy surface. These trends will be observed for reactions on three potential energy surfaces for six series of reactions; e.g. one series corresponds to $X + H-H \rightarrow X-H + H$ where $X = H, D$ and Δ (a hypothetical H atom of mass 10). The series corresponding to the above example is discussed in greater detail than the other series so that the reader may become familiar with the various features of the potential energy surface which are particularly important in effecting the trends of the above quantities. The results of our calculations for the forward and reverse reactions are

given in separate tables. This is done mostly for convenience however, as it will become clear from our discussion that there is a simple relationship between the quantities we calculate for the forward and reverse reactions. On occasion, plots of trajectories on the skewed potential energy surfaces are included to give our discussion more clarity.

Chapter 4 summarizes the results of chapter 3. We show how some trends for a series of reactions are the same on all three potential energy surfaces. In addition, we will generalize the relationship between certain features of the potential energy surface and the trends in a reaction series.

Summarizing the organization of this thesis, we see that it is divided into two parts. The first part consists of chapters one and two which introduces previous works, and the theory on which our work is based. The second part describes the results of our work (chapter 3) and our observations (chapter 4).

I. Collisional Mechanical Trajectory Theory

Introduction

Not since Eyring⁴ wrote his classic paper on Absolute Rate Theory (ART) in 1935 has there been an advancement in reaction kinetics as important as the work by Karplus, Porter, and Sharma⁶ on Collisional Mechanical Trajectory Theory (CMTT). It has become the standard by which all other theoretical studies on reaction kinetics for three atom systems are compared to. In chapter one, we will attempt to introduce some of the main concepts behind CMTT. We will demonstrate the method of calculating trajectories for collinear exchange reactions, and will define the collisional theory mean reaction probability which is the basis for much of our calculations presented in chapter three. We begin chapter one with a derivation of the CMTT rate constant for the collinear three atom system.

IA. The Collinear Collisional Theory Rate Constant

Consider the collinear reaction:



where A, B, and C are atoms and ν is the vibrational quantum number of the diatomic reactant B-C. For a B-C molecule in the vibrational state ν , the differential reaction rate corresponding to relative reactant velocities in the range V_R to $V_R + dV_R$ can be calculated by multiplying the number of collisions in unit time that take place in a unit length (ν), by the probability ($P_r(V_R, \nu)$) a collision will lead to products. To get the overall rate (R), the integration and

sum over the distribution functions for V_R (the relative velocity between A and B-C) and γ is taken. The following derivation of the collinear temperature dependent rate constant ($K(T)$) is the collinear (1-D) analog of the rate constant derived for the three dimensional case by Karplus, Porter, and Sharma⁶.

The number of collisions between A and B-C in state γ per unit volume (i.e. length for the collinear case) during unit time when the velocities of A and B-C are in the differential ranges dV_A and dV_{BC} respectively may be expressed as

$$\gamma V_R dN_A(V_A) dN_{BC}(V_{BC})_{\gamma} \quad (2)$$

where γ is unit length, V_R is the relative velocity between the reactants A and B-C ($V_A - V_{BC}$) and $dN_A(V_A)$ and $dN_{BC}(V_{BC})_{\gamma}$ are the number density distribution functions for A and B-C respectively. The distribution functions are given by the equations

$$dN_A(V_A) = n_A f_A(V_A) dV_A, \quad (3)$$

$$dN_{BC}(V_{BC})_{\gamma} = n_{BC}(\gamma) f_{BC}(V_{BC}) dV_{BC} \quad (4)$$

where $f_A(V_A)$ and $f_{BC}(V_{BC})_{\gamma}$ are the normalized Boltzman velocity distribution functions for A and B-C respectively, n_A is the number of A atoms per unit volume, and $n_{BC}(\gamma)$ is the number of B-C molecules in vibrational state γ per unit volume. Utilizing equations (3) and (4) in (2), we can now express the rate R_{γ} for the vibrational state γ as

$$R_{\gamma} = n_A n_{BC}(\gamma) \int_{-\infty}^{+\infty} dV_A \int_{-\infty}^{+\infty} dV_{BC} f_A(V_A) f_{BC}(V_{BC})_{\gamma} V_R P_r(V_R, \gamma) \quad (5)$$

where $P_r(V_R, \nu)$ is the probability that a collision between A and B-C will lead to products when their relative velocity is between V_R and $V_R + dV_R$ and the reactant B-C is in vibrational state ν . With τ on the right hand side of equation (5), the units for R are molecules sec⁻¹. Using the Boltzmann vibrational distribution function (F_{ν}) for B-C, we may express n_{ν} as

$$n_{\nu} = n_{\text{B-C}} F_{\nu}, \quad (6)$$

where $n_{\text{B-C}}$ is the number of B-C molecules per unit volume.

We can then obtain the overall reaction rate (R) by summing the rates (R_{ν}) for each vibrational state ν . The result is given by the equation

$$R(T) = \sum_{\nu} R_{\nu}(T) = \tau n_A n_{\text{B-C}} \sum_{\nu} k_{\nu}(T) F_{\nu} = \tau n_A n_{\text{B-C}} K(T) \quad (7)$$

where

$$K(T) = \sum_{\nu} F_{\nu} \int_{-\infty}^{+\infty} dV_A \int_{-\infty}^{+\infty} dV_{\text{B-C}} f_A(V_A) f_{\text{B-C}}(V_{\text{B-C}}) V_R P_r(V_R, \nu) \quad (8)$$

and $k_{\nu}(T)$, the rate constant for vibrational state ν is defined by comparison of equations (7) and (8). The distribution functions $f_A(V_A)$ and $f_{\text{B-C}}(V_{\text{B-C}})$ are given by the equations

$$f_A(V_A) = (m_A/2\pi kT)^{1/2} \exp(-m_A V_A^2/2kT),$$

$$f_{\text{B-C}}(V_{\text{B-C}}) = (m_{\text{B-C}}/2\pi kT)^{1/2} \exp(-m_{\text{B-C}} V_{\text{B-C}}^2/2kT) \quad (9)$$

where m_A and $m_{\text{B-C}}$ are the masses of A and B-C respectively. The vibrational distribution function F_{ν} is given by the equation

$$F_{\nu} = f_{\nu} \exp(-E_{\nu}/kT) / Q_{\nu}(T) \quad (10)$$

where $Q_{\nu}(T)$ is the vibrational partition function, f_{ν} is

the degeneracy of state ν , and E_ν is the vibrational energy for state ν . Using equations (9) and (10), equation (8) becomes

$$K(T) = \sum_{\nu} k_{\nu}(T) F_{B_C}(\nu) = Q_{\nu}^{-1}(T) \left[\sum_{\nu} f_{\nu} \exp(-E_{\nu}/kT) \int_{-\infty}^{+\infty} dV \times \int_{-\infty}^{+\infty} dV_{B_C} (m_A/2\pi kT)^{1/2} (m_{B_C}/2\pi kT)^{1/2} \exp(-m_A V_A^2/2kT) \exp(-m_{B_C} V_{B_C}^2/2kT) V_R P_{\nu}(V_R, \nu) \right]. \quad (11)$$

We now make a transformation to the space of V_R and the velocity of the center of mass (V_{CM}) and evaluate the Jacobian (J) defined by the equation

$$dV_R V_{CM} = J dV_A dV_{B_C}. \quad (12)$$

Using the transformation equations

$$V_R = V_A - V_{B_C}, \text{ and}$$

$$V_{CM} = (m_A V_A + m_{B_C} V_{B_C})/M \quad (13)$$

where $M = m_A + m_{B_C}$ we obtain

$$J = \begin{vmatrix} 1 & -1 \\ m_A/M & m_{B_C}/M \end{vmatrix} = 1 \quad (14)$$

The limits of integration are 0 to $+\infty$ for V_R and $-\infty$ to $+\infty$ for V_{CM} . Equation (11) then becomes

$$K(T) = Q_{\nu}^{-1}(T) \left[\sum_{\nu} f_{\nu} \exp(-E_{\nu}/kT) \int_0^{\infty} \exp(-(m_A m_{B_C}/2MkT) V_R^2) \times V_R dV_R \int_{-\infty}^{+\infty} \exp(-(M/2kT) V_{CM}^2) dV_{CM} (m_A/2\pi kT)^{1/2} (m_{B_C}/2\pi kT)^{1/2} \times P_{\nu}(V_R, \nu) \right]. \quad (15)$$

$$\text{Since } \int_{-\infty}^{+\infty} \exp(-ax^2) dx = (\pi/a)^{1/2}, \quad (16)$$

equation (15) may be reduced to

$$K(T) = Q_{\nu}^{-1}(T) \left[\sum_{\nu} f_{\nu} \exp(-E_{\nu}/kT) \int_0^{\infty} \exp(-V_R^2 \mu_{A, B_C}/2kT) \times P_{\nu}(V_R, \nu) V_R dV_R (\mu_{A, B_C}/2\pi kT)^{1/2} \right] \quad (17)$$

where $\mu_{A,BC} = m_A m_{BC} / M$ is the reduced mass for the reactants.

Equation (17) may be expressed in terms of the energy of relative motion (E_R) which is defined by the equation

$$E_R = \frac{1}{2} \mu_{A,BC} V_R^2. \quad (18)$$

Equation (17) then becomes

$$K(T) = (2\pi\mu_{A,BC}kT)^{-\frac{1}{2}} Q_Y^{-1}(T) \left[\sum_Y f_Y \exp(-E_Y/kT) \int_0^\infty \exp(-E_R/kT) P_r(E_R, Y) dE_R \right]. \quad (19)$$

IB Definition of the Collisional Theory Mean Reaction Probability

The classical collinear mean reaction probability ($\bar{P}_r(E)$) has been defined by Morokuma, Eu, and Karplus⁵ by the equation

$$\bar{P}_r(E) = (\xi_I(E))^{-1} \int_0^\infty f_I(E_i) P_r(E-E_i, E_i) dE_i \quad (20)$$

$$\text{where } \xi_I(E) = \int_0^\infty f_I(E_i) H(E-E_i) dE_i \quad (21)$$

is called the reactant density function, E is the total internal energy of the 3 atom system excluding the energy of the center of mass, E_i is the internal energy of the reactant B-C, $f_I(E_i)$ is the classical analog of the quantum mechanical degeneracy, and $H(x)$ is the Heaviside step function

$$\begin{aligned} H(x) &= 1, \text{ for } x > 0, \\ H(x) &= 0, \text{ for } x < 0. \end{aligned} \quad (22)$$

The quantity $E-E_i$ has been defined in section IA as E_R , $E_i = E_Y$, $f_i = f_Y$, $Q_i(T) = Q_Y(T)$, and $E = E_i + E_R$. In equation (20) we require that $P_r(E-E_i, E_i) = 0$ if $E_i > E$ (i.e., $P_r \equiv 0$ for $E_R < 0$). Equation (19) may be re-expressed as

$$K(T) = (2\pi\mu_{A,BC}kT)^{-\frac{1}{2}} Q_Y^{-1}(T) \sum_i \int_0^\infty f_i \exp(-E/kT) P_r(E-E_i, E_i) dE_R \quad (23)$$

We now change the continuous variable from E_R to E and obtain

$$K(T) = (2\pi\mu_{A,B,C}kT)^{-\frac{1}{2}-1} Q_{\pm}(T) \sum_i \int_{E_i}^{\infty} f_i P_r(E-E_i, E_i) \exp(-E/kT) dE \quad (24)$$

Since $P_r = 0$ for $E_i > E$, we may extend the lower limit of integration to zero. If we now treat the B-C vibration classically, we may write

$$K(T) = (2\pi\mu_{A,B,C}kT)^{-\frac{1}{2}-1} Q_{\pm}(T) \int_0^{\infty} dE_i \int_0^{\infty} dE f_{\pm}(E_i) P_r(E-E_i, E_i) \exp(-E/kT) \quad (25)$$

where $Q_{\pm}(T)$ is the classical vibrational partition function for the reactant B-C. Using equation (20), this result may be expressed as

$$K(T) = (2\pi\mu_{A,B,C}kT)^{-\frac{1}{2}-1} Q_{\pm}(T) \int_0^{\infty} \xi_{\pm}(E) \bar{P}_r(E) \exp(-E/kT) dE \quad (26)$$

If $Q_{\pm}$ and $P_{\pm}$ are the B-C vibrational coordinate and conjugate momentum respectively, we may re-express equations (20) and (21) as

$$\bar{P}_r(E) = (\xi_{\pm}(E))^{-1} h \int_{R_{min}}^{R_{max}} \int_{-\infty}^{+\infty} P_r(E-E_i, Q_{\pm}, P_{\pm}) dQ_{\pm} dP_{\pm} \quad (27)$$

$$\xi_{\pm}(E) = h \int_{R_{min}}^{R_{max}} \int_{-\infty}^{+\infty} H(E-E_i) dQ_{\pm} dP_{\pm} \quad (28)$$

where R_{max} and R_{min} are the maximum and minimum values of $Q_{\pm}$ for the total energy E . The integrals of equations (27) and (28) may be evaluated directly by executing classical mechanical trajectories whose initial conditions are chosen using a Monte Carlo Technique.

IC The Selection of Initial Conditions for the Trajectory Determination of $\bar{P}_r(E)$

For the collinear three atom system, four variables must be specified to define the point of origin in phase space of each classical mechanical trajectory. These variables or initial conditions are chosen using a simple Monte Carlo ap-

proach in a way that will produce a classical microcanonical ensemble of trajectories at a given total energy (E). The generalized coordinates and momenta of reference 6 are used to select the initial conditions. The variable Q_1 is the relative cartesian coordinate of atom C with respect to B as the origin, and the variable Q_2 is the relative cartesian coordinate of atom A with respect to the center of mass of the reactant molecule B-C as the origin. The variables P_1 and P_2 are the conjugate momenta for the coordinates Q_1 and Q_2 respectively.

If the atoms A, B, and C with masses m_A , m_B , and m_C respectively have positions on the x axis given by the coordinates x_i ($i = 1, 2, 3$), the coordinates Q_1 and Q_2 are defined by the equations

$$Q_1 = x_3 - x_2, \quad (29)$$

$$Q_2 = x_1 - (m_B x_2 + m_C x_3) / (m_B + m_C). \quad (30)$$

The coordinate of the center of mass is given by the equation

$$Q_3 = (m_A x_1 + m_B x_2 + m_C x_3) / (m_A + m_B + m_C). \quad (31)$$

Since Q_3 plays no role in our study of chemical reactivity, we assign it the value zero.

The total energy of the reactants (E) is the sum of the energy of B-C (E_i) and the kinetic energy of relative motion of atom A with respect to B-C (E_R). The initial value of Q_2 is determined by the requirement that the potential energy of interaction between A and B-C is negligible; the same value is used for all trajectories corresponding to a given reaction system. This distance is referred to as the reaction shell radius. The remaining coordinate and momenta are chosen ran-

domly from the region of classical phase space allowed by E at Q_2 . The initial conditions determined in this way represent a uniform distribution of phase points corresponding to reactants at equilibrium on the reaction shell radius. The nuclear separation of B-C (Q_1) determines the potential energy given by the Morse equation

$$V(Q_1) = D_e (1 - \exp(-\alpha(Q_1 - R_e)))^2 \quad (32)$$

where D_e is the classical dissociation energy, α is a constant, and R_e is the equilibrium internuclear separation. The equation used to calculate the random values of Q_1 has the form

$$Q_1 = R_{min} + X_1 (R_{max} - R_{min}) \quad (33)$$

where X_1 is a pseudo random number distributed uniformly on the range 0 to 1, and R_{max} and R_{min} are the maximum and minimum values of Q_1 respectively (i.e., for which $V(Q_1)$ in equation (32) is equal to E). The values of R_{max} and R_{min} are given by the equations

$$R_{max} = R_e - \ln(1 - (E/D_e)^{1/2}) \quad (34)$$

$$R_{min} = R_e - \ln(1 + (E/D_e)^{1/2}) \quad (35)$$

The vibrational kinetic energy is determined by the specification of P_1 by the equation

$$P_1 = -P_{max} + 2X_2 P_{max} \quad (36)$$

where X_2 is another pseudo random number distributed uniformly on the range 0 to 1. The quantity P_{max} is given by the expression

$$P_{max} = (2\mu_{BC} E)^{1/2} \quad (37)$$

where $\mu_{BC} = m_c m_b / (m_c + m_b)$ is the reduced mass of B-C. At

this point, the total energy of the B-C molecule ($E_i = P_1^2/2\mu_{BC} + V(Q_1)$) is compared to E . If $E_i > E$, the set of initial conditions is rejected and a new set is generated and tested. If $E_i \leq E$, then the relative momentum between atom A and the center of mass of B-C (P_2) is determined by the equation

$$P_2 = (2\mu_{A,BC} (E - E_{BC}))^{1/2}. \quad (38)$$

The Hamiltonian at the initial value of Q_2 can be expressed as

$$H = P_1^2/2\mu_{A,BC} + P_2^2/2\mu_{BC} + V(Q_1), \quad (39)$$

and the value of the Hamiltonian is E for each trajectory.

The trajectories therefore constitute a microcanonical ensemble.

ID Evaluation of Trajectory Mean Reaction Probabilities ($\bar{P}_r^*(E)$)

Trajectories corresponding to the initial conditions determined by equations (33), (36), (38) and the value of Q_2 are calculated to determine the trajectory value of the mean reaction probability defined by equation (27). The trajectories are calculated by obtaining numerical solutions for Hamilton's equations of motion which for the collinear three atom system take the form

$$dQ_1/dt = \dot{Q}_1 = \partial H/\partial P_1 = \mu_{BC} P_1, \quad (40)$$

$$dQ_2/dt = \dot{Q}_2 = \partial H/\partial P_2 = \mu_{A,BC} P_2, \quad (41)$$

$$dP_1/dt = \dot{P}_1 = -\partial H/\partial Q_1 = -\partial V(Q_1, Q_2)/\partial Q_1, \quad (42)$$

$$dP_2/dt = \dot{P}_2 = -\partial H/\partial Q_2 = -\partial V(Q_1, Q_2)/\partial Q_2 \quad (43)$$

where $V(Q_1, Q_2)$ is the potential energy. The derivatives of the potential energy are evaluated by using the "chain rule"

$$\partial V(Q_1, Q_2)/\partial Q_i = \sum_j (\partial V/\partial R_j) (\partial R_j/\partial Q_i) \quad (44)$$

where R ($j = 1, 2$), the A-B and B-C internuclear separations

respectively, are given by the equations

$$R_1 = -(m_c / (m_g + m_c)) Q_1 - Q_2, \quad (45)$$

$$R_2 = Q_1. \quad (46)$$

Since $V \neq f(Q_3, \dot{Q}_3)$ is a constant of the motion and may be assigned the value zero. The four coupled first order differential equations were solved using a fourth order Adams-Moulton "predictor corrector" scheme¹⁸. The size of the integration step (Δt) was adjusted to give accuracy to four significant figures in coordinates and momenta for a random sample of "back integrations" for each reaction system.

The integrals of equation (27) and (28) can be evaluated by using a simple Monte Carlo technique. The approximate number of quantum states in the sampled region of reactant phase space ($\mathcal{V}_r$) is given by the equation

$$\mathcal{V}_r = h^{-1} (\Delta Q_1 \Delta P_1) \quad (47)$$

where ΔQ_1 and ΔP_1 are the ranges in Q_1 and P_1 established by their maximum and minimum values at E . When E is expressed in eV, R_1 in a.u., μ_K in amu and equations (34), (35) and (37) are used to evaluate the ranges, equation (47) provides the result

$$\mathcal{V}_r = 1.3026 (R_{max} - R_{min}) 2P_{max}. \quad (48)$$

The reactant density function may be calculated using the equation

$$\xi_r(E) = (\mathcal{V}_r / N_r) \sum_{j=1}^{N_r} H(E - E_j) \quad (49)$$

where j enumerates the initial condition sets and N_r is the total number of sets of initial conditions examined. The

summation of the step function gives N , the number of sets which pass the test $E > E_i$ (i.e., the number of trajectories which are actually calculated).

The trajectory mean reaction probability may be evaluated using the equation

$$\bar{P}_r^t(E) = (\sum_{j=1}^{N_T} P_{R,j}) H(E - E_i)_j / \xi_I(E) \quad (50)$$

where $P_{R,j}$ is unity for a reactive trajectory and zero for an unreactive one. Equation (49) and (50) may then be combined to give

$$\bar{P}_r^t(E) = \sum_{j=1}^{N_T} P_{R,j} H(E - E_i)_j / \sum_{j=1}^{N_T} H(E - E_i)_j = N_R / N \quad (51)$$

The numerator in this expression is simply the number of reactive trajectories (N_R).

The standard deviations for the numerator (num) and denominator of equation (50) are denoted by S_N and S_D respectively. They are computed using the equations

$$S_N = \sqrt{N_R(N_T - 1)} / N_T, \quad (52)$$

$$\text{and } S_D = \sqrt{N(N_T - 1)} / N_T. \quad (53)$$

The error of the mean for $\xi_I(E)$ at the 95% confidence level is given by the expression¹⁹

$$1.96 S_D / (N_T)^{1/2} \quad (54)$$

The error of the mean for $\bar{P}_r^t(E)$ at the same confidence level is given by the expression²⁰

$$1.96 \bar{P}_r^t(E) \left[(S_N / \text{num})^2 + (S_D / \xi_I(E))^2 \right]^{1/2} / N_T^{1/2} \quad (55)$$

The harmonic oscillator or Small Vibrations Approximation (SVA) result for $\xi_I(E)$ is given by equation (37) of reference 5

$$\xi_I(E) = (h\nu_{Bc})^{-1} / E \quad (56)$$

where ν_{Bc} is the vibrational frequency of B-C.

II. Absolute Rate Theory

Introduction

In chapter one we showed how to evaluate the rate constant and mean reaction probability for collinear reactions using classical collisional theory. In chapter two we will develop expressions for these quantities using Eyring's Absolute Rate Theory (ART) and a more general variational theory of reaction rates. We will explain why these theories are often referred to as phase space theories. We will show how the approximate phase space theories may be used to evaluate mean reaction probabilities which may be compared with the exact values determined by the classical mechanical trajectory theory (CMTT).

IIA. The Formulation of ART

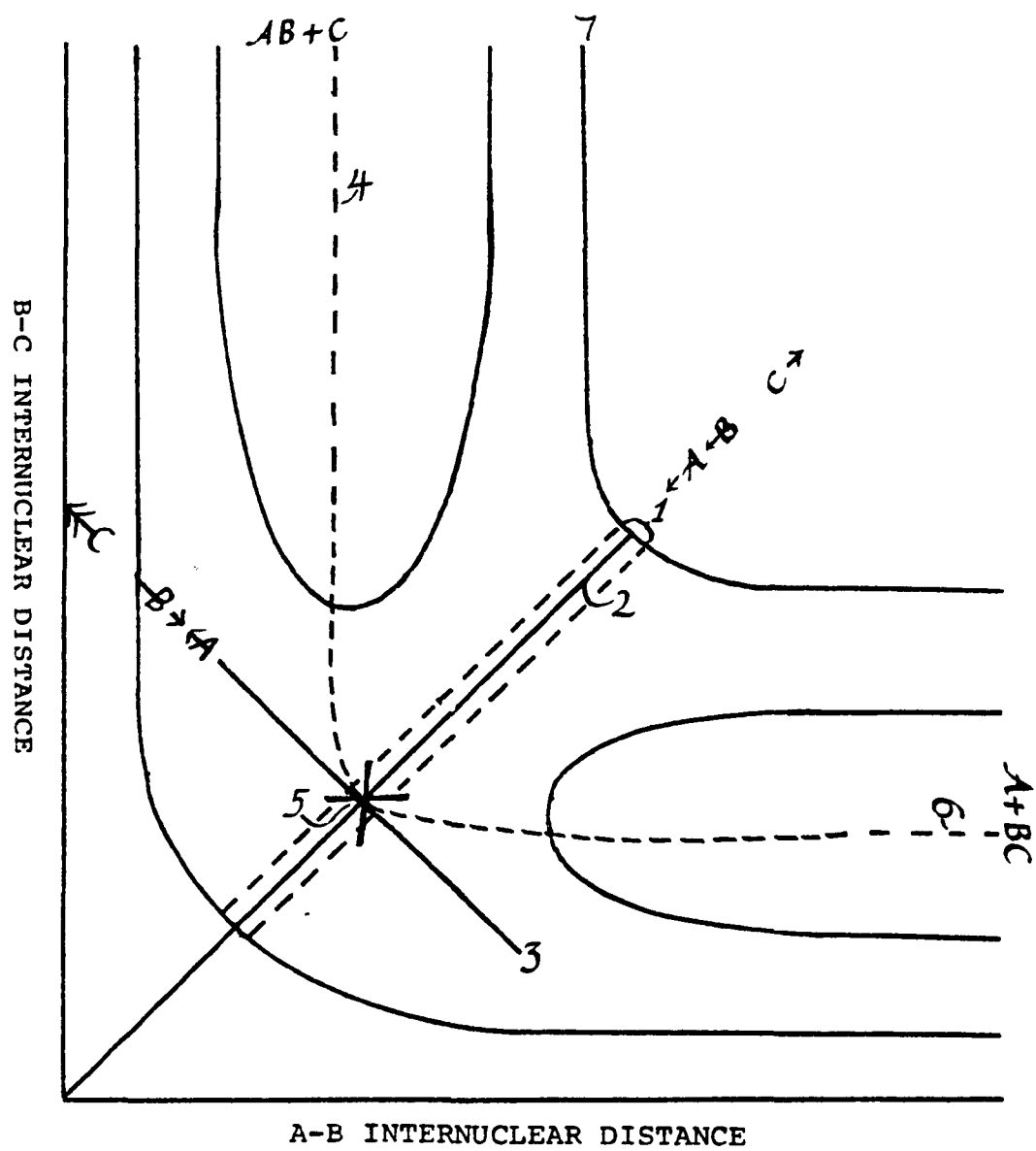
ART was suggested by Marcelin²¹, and developed in a practical way by Eyring¹ in 1935. The CMTT evaluates rate constants by calculating trajectories which span the entire region of phase space between reactants and products. ART is a statistical theory which does not require dynamical calculations and focuses attention on a certain volume of phase space which we call the dividing volume (DV). The DV is a portion of phase space which includes the saddle point and where a certain mass weighted coordinate has a value of approximately zero (see figure 1). A phase point within the DS is called a transition state ($X^\ddagger$). The rate constant is evaluated by multiplying the frequency ($\nu^\ddagger$) with which a transition state crosses the DV at a given location within it, from the re-

QUANTITIES DEFINED ON FIGURE 1

1. Configuration space limits of the dividing volume. The ART transition states are located here.
2. Projection of dividing surface in configuration space; corresponding to the stable normal coordinate.
3. Unstable normal coordinate. This is also called the reaction coordinate.
4. Minimum energy reaction path.
5. Saddle point. Potential energy of X^* is taken as zero here. The classical activation energy is the difference in potential energy between the saddle point and the reactants.
6. Reactants.
7. Potential energy contour which gives the locus of the points of equal energy on the potential energy surface.

FIGURE 1

POTENTIAL ENERGY SURFACE FOR THE REACTION $A + B-C \rightleftharpoons A-B + C$



actant side to the product side, by the value of the equilibrium distribution function for $X^\ddagger$ and the conversion coefficient (ξ) at this location, and integrating the product of these three quantities over the entire DV. The quantity ξ is related to the probability that a $X^\ddagger$ at a given location within the DV will contribute to product formation. There is some confusion in the literature concerning the meaning of this factor in the development of the rate expression. We will take this point up later.

We will now derive an expression for the classical collinear rate constant of ART for the $A + B-C$ reaction. It is modeled after the derivation given by Johnston.²² A less rigorous derivation, but one which gives good insight into the formulation of ART is given by Laidler.²³

It is assumed that the distribution of transition states within the DV is the equilibrium one. This distribution is the one obtained if both reactants and products are present at equilibrium. The relationship between the reactants, products and transition states can be expressed by the equation



The equilibrium distribution function for $X^\ddagger$ (P) on a differential element $d\gamma$ which is within the DV and spans it from the reactant side to the product side is defined by the equation

$$P(q_1, q_2, q_3, p_1, p_2, p_3) = \frac{X^\ddagger(q_1, q_2, q_3, p_1, p_2, p_3)}{[A][B-C]} = \frac{h^{-3} \exp(-\varepsilon/kT) d\gamma}{Q_R(T)} \quad (58)$$

where $d\gamma = \prod_{i=1}^3 dq_i dp_i$, $Q_R(T)$ is the classical reactant partition function per unit length, $\xi(q_1, q_2, q_3, p_1, p_2, p_3)$ is the total

energy of $X^\ddagger$ within $d\tau$, q_i , p_i ($i = 1, 2, 3$) are the coordinates and momenta of phase space for the collinear reaction system, and the brackets denote concentrations for reactant and transition state species. When we multiply the distribution function by the frequency $\nu^\ddagger$ and the conversion coefficient $\mathcal{C}$ and then integrate the product over the entire DV , we obtain the thermal rate constant

$$K(T) = Q_R^{-1}(T) h^{-3} \int \cdots \int \mathcal{C} \nu^\ddagger \exp(-\mathcal{E}/kT) d\tau. \quad (59)$$

Equation (59) provides the exact classical rate constant with units of $\text{cm}^3(\text{molecules sec})^{-1}$ and is equal to the collisional theory result given by equations (19) and (26). The variables $\mathcal{C}$ and $\nu^\ddagger$ do not depend on the center of mass (CM). Since the Hamiltonian gives a separable term for the energy of the CM, we may integrate over its momentum components. We must also integrate over the coordinates of the CM so as to obtain unit volume. The result of these operations factors from the integral of equation (59) as the translational partition function for $X^\ddagger(Q_{CM}^\ddagger(T))$. Equation (59) can now be rewritten as

$$K(T) = Q_R^{-1}(T) Q_{CM}^\ddagger(T) h^{-2} \int \cdots \int \mathcal{C} \nu^\ddagger \exp(-\mathcal{E}'/kT) \prod_{i=1}^3 dq_i dp_i \quad (60)$$

where $\mathcal{E}'$ is the Hamiltonian excluding the contribution due to the CM.

We now assume that $\nu^\ddagger$ and $\mathcal{C}$ depend on a single coordinate and its conjugate momentum (q^*, p^*), and that the energy of the complex is separable in a contribution due to (q^*, p^*) and the remaining coordinate and momentum. We can specify these assumptions symbolically using the equations

$$\begin{aligned}
 V^{\ddagger}(q_1, \dots, p_2) &= V(q^*, p^*), \\
 \mathcal{E}(q_1, \dots, p_2) &= \mathcal{E}(q^*, p^*), \\
 \mathcal{E}' &= \mathcal{E}_t + \mathcal{E}^*(q^*, p^*) .
 \end{aligned}
 \tag{61}$$

As we shall see, the assumptions of equation (61) will enable us to separate the integral in equation (60) into two parts, one of which involves the coordinates q^* and p^* . The coordinates $(q_1, \dots, p_2)$ are the normal vibrational coordinates, q^* is the unstable stretching normal coordinate. The remaining coordinate corresponds to a stable stretching normal coordinate. The stable stretching normal coordinate is presumably perpendicular to the reaction path and therefore a $X^{\ddagger}$ moving along this coordinate would not cross the DV. The value of the stable normal coordinate (q_s) and its conjugate momentum (p_s) determines the concentration of $X^{\ddagger}$ near the corresponding location within the DV. The Hamiltonian $\mathcal{E}'$ may be expressed as

$$= (p^{*2} + p_s^2)/2 + V(q^*, q_s) \tag{62}$$

Equations (60) and (61) enable us to write

$$\begin{aligned}
 K(T)_{\text{ART}} &= Q_R(T) Q_{\text{CM}}^{\ddagger}(T) \int_{-1}^{+1} \int_{-1}^{+1} h^{-1} dq_s dp_s \exp\left[-(p_s^2/2 + V(q^*, q_s))\right] \\
 &\times \int_{-1}^{+1} \int_{-1}^{+1} h^{-1} V^{\ddagger} \mathcal{E} dq^* dp^* \exp(-p^{*2}/2)
 \end{aligned}
 \tag{63}$$

where the integration limits are defined by DV and our model for the evaluation of the rate constant. Those for q^*, p^* will be specified later. Equation (63) can be re-expressed

$$K(T)_{\text{ART}} = \frac{Q_{\ddagger}(T) \exp(-E_c/kT)}{Q_R(T)} h^{-1} \iint V^{\ddagger} \mathcal{E} \exp(-\mathcal{E}^*/kT) dq^* dp^* \tag{64}$$

where E_c is the potential energy of the saddle point when measured from the bottom of the reactant valley (i.e., the

classical activation energy), $Q_{\ddagger}(T)$ is a partition function for $X^{\ddagger}$ evaluated for a phase space which includes that of the CM but is reduced by the requirement $q^* = 0$, $\varepsilon^* = p^{*2}/2$, and the potential energy $V(0, q_s)$ used to evaluate $Q_{\ddagger}(T)$, is measured from the saddle point. The location of the ART DV is fixed by the equation

$$-\delta/2 < q^* < +\delta/2. \quad (65)$$

The frequency ν^* for crossing the DV along q^* may be expressed as $\nu^* = \dot{q}^*/\delta = p^*/\delta$ (66)

since for a normal coordinate $p = \dot{q}$. The integral remaining in equation (64) becomes

$$h \int_{-\delta/2}^{+\delta/2} \frac{dq^*}{\delta} \int_0^{\infty} \mathcal{E} \exp(-p^{*2}/2kT) p^* dp^*.$$

The limits of the integral for p^* are 0 and ∞ because only $X^{\ddagger}$ with positive p^* can finally give products and contribute to the rate. If we now assume that $\mathcal{E} = 1$ for $p^* > 0$, the factor given by expression (67) provides the familiar quantity kT/h of ART. We have assumed that all phase points with $p^* > 0$ within the DV will proceed directly to the product region of phase space. This means for example that no provision is made to account for a $X^{\ddagger}$ which is reflected and returns to the reactant region of phase space after leaving the DV with $p^* > 0$. We will refer to this approximation in the theory as the "direct approximation". We can now write equation (64) as

$$K(T)_{\text{ART}} = (kT/h) \frac{Q_{\ddagger}(T)}{Q_R(T)} \exp(-E_c/kT). \quad (67)$$

Since there are $X^{\ddagger}$ which cross the DV a number of times,

and therefore contribute to the rate more than once, equation (67) gives an upper bound for $K(T)$ given by equation (19).

IIB Keck's Variational Theory of Chemical Reaction Rates

In addition to ART, there are other phase space theories such as Keck's Variational Theory, which permit us to vary the location of the DV and thus find a minimum upper bound for the rate. As we will use the variational approach in our work, and since Keck's Variational Theory is important for a complete understanding of the relationship between the DV and the rate, we introduce it here.

Keck's Variational Theory (KVT) of chemical reaction rates is based on an approach used by Marcelin²¹, and developed later by Wigner²⁴ and Horiuti.²⁵ It considers a partial surface along the boundary of the DV called a Dividing Surface (DS). The constraints which define the DS are

$$DS(q,p) = 0, \quad (68)$$

$$\vec{v} \cdot \vec{n} > 0 \quad (69)$$

where $\vec{v}$ is the generalized velocity of $X^\ddagger$ and $\vec{n}$ is the unit outward normal vector to a differential element ($d\sigma$) on the DS. The ART DS is shown in figure 1. Keck evaluates the rate by multiplying the equilibrium density of $X^\ddagger$ by the velocity perpendicular to the DS at a given location on the DS, and integrating their product over the entire DS. The rate constant can be expressed using the equation

$$K^{VT}(T) = \int_{DS}^{\vec{v} \cdot \vec{n} > 0} \rho(\vec{v}, \vec{n}) d\sigma \quad (70)$$

where ρ is the density distribution function for a given DS.

In principle, the location and shape of the DS is varied until the curve which gives a minimum rate is found. As Horiuti points out, the best DS does not necessarily pass through the saddle point. The only restriction on the selection of the DS is that it cannot have any holes. A DS has holes if there are trajectories which can map from reactants to products without passing through the DS. Keck indicates that equation (70) gives an upper limit for the rate for four reasons. Reactive trajectories originating from reactants may contribute more than once to the rate if they cross the DS more than once. Also, non-reactive trajectories which originate from reactants, and cross the DS also contribute to the rate. These are called reflected trajectories. In addition, the integral over the DS includes those regions of phase space for which $X^\ddagger$ originating from products contribute incorrectly to the rate by crossing the DS more than once. Finally, trajectories which form closed loops in the transition region also contribute incorrectly to the rate.

IIC Comparison of Theories

In sections IIA and IIB we have introduced ART and KVT. Here, we compare both theories and discuss the advantages of KVT.

Equations (67) and (70) are similar in that both the ART and KVT rate constants are evaluated by performing an integration over a region of phase space. In ART, integration is performed over all phase space within a specified definite DV. The variational theory performs the integration over a DS which may be varied. If the DS used in KVT is the same as

the one used in ART, the rate constants evaluated using both theories are the same if the conversion coefficient of ART is unity at all locations within the DV. To show this, equation (70) is re-expressed as¹⁶

$$K(T)_{VT} = \frac{Q_T^*(T)h}{Q_R(T)} \int_{DS} \int \int V_n \beta \exp(-\epsilon/kT) dq_2 dp_1 dp_2 \quad (71)$$

where $Q_T^*(T)$ is the translational partition function for X^* , V_n is the velocity in phase space normal to the DS and β relates the differential surface area to the position and momentum coordinates. If the quantities q_2 and p_2 are the stable stretching normal coordinate and conjugate momenta, and p_1 is the conjugate momenta of the unstable normal coordinate, then $V_n = p_1$ and $\beta = 1$. When the assumptions of equation (47) are utilized, equations (71) and (67) are identical if $\bar{f} = 1$ at all locations of the DV. For the three atom collinear case, the dimensions of the DV and DS are four and three respectively. As mentioned in section IIB, the DS is part of a larger surface which bounds the DV and is subject to the constraints of equations (68) and (69). The DV and DS indicated on figure 1 represent projections in configuration space.

KVT is more flexible than ART because it permits us to vary the shape and position of the DS until the best one is found. The best DS gives a minimum upper bound for the rate. The ART DS gives a minimum for the rate only when the potential energy is given by the small vibrations approximation (SVA). In the work which we present in chapter 3, we only

consider dividing surfaces which are "straight" and which pass through the saddle point.

IID Extraction of SVA and Accurate Mean Reaction Probabilities for Straight Dividing Surfaces

We will now derive an expression for the mean reaction probability of ART ($P_R^{ART}(E)$). A method for the variation of the location of straight dividing surfaces is also discussed here. Of particular interest will be the ART DS, and the DS which is perpendicular to the path of steepest descent on the potential energy surface (PES) at the saddle point ($DS_{\perp}$). The results of our CMTT calculations of $\bar{P}_R^{\dagger}(E)$ will later be compared to $P_R^{ART}(E)$ except when the ART DS has holes (section IIC). If this happens $\bar{P}_R^{\dagger}(E)$ will be compared to the mean reaction probability corresponding to $DS_{\perp}$.

From equation (26) of reference 5, we may write

$$\bar{P}_R(E) = [\xi_I(E)]^{-1} \int_0^{\infty} P_r(E-E_i, E_i) dE_i \quad (72)$$

If we assume that $K(T)_{ART}$ as given by equation (67) gives the result of equation (26), the two equations can be used to find the ART value for the quantity defined by equation (72).

Equating equations (67) and (26) we obtain

$$\int_0^{\infty} \xi_I(E) \bar{P}_R(E) \exp(-E/kT) dE = (kT/h) Q_{\ddagger}(T) \exp(-E_c/kT). \quad (73)$$

The reactant partition functions in equations (26) and (67) cancel since $(2\pi \mu_{A,B} kT)^{1/2} \cdot Q_I(T) = Q_R(T)$. Rewriting equation (73), we obtain

$$\int_0^{\infty} \xi_I(E) \bar{P}_R^{ART}(E) \exp(-E/kT) dE = (kT/h) \int_{DS} \int \exp(-(\epsilon_T + E_c)/kT) \times dq_1 dp_1 \quad (74)$$

where ϵ_T is the internal energy of $X^{\ddagger}$ and q_1 and p_1 are

the coordinate and momenta corresponding to the stable stretching coordinate. Employing the inverse Laplace transform¹⁷ and letting $\beta = (kT)^{-1}$, equation (74) can be expressed as

$$\bar{P}_R^{ART}(E) = \frac{(2\pi i)}{\mathcal{E}_T(E)} \int_{\delta-\infty}^{-1} \int_{\delta+\infty}^{+1} \exp[(E - \mathcal{E}_T - E_c)\beta] d\beta \frac{dq_2 dp_2}{h} \quad (75)$$

$$\text{Since } (2\pi i) \int_{\delta-\infty}^{-1} \int_{\delta+\infty}^{+1} \beta^{-1} \exp[(E - \mathcal{E}_T - E_c)\beta] d\beta = H(E - \mathcal{E}_T - E_c) \quad (76)$$

$$\bar{P}_R^{ART}(E) = \mathcal{E}_\ddagger(E) / \mathcal{E}_T(E) \quad (77)$$

where $\mathcal{E}_\ddagger(E)$ is the transition state energy density function which is defined by the equation

$$\mathcal{E}_\ddagger(E) = h^{-1} \int_{DS} \int H(E - \mathcal{E}_T - E_c) dq_2 dp_2 \quad (78)$$

The small vibrations approximation result for equation (77) is given by the expression

$$\begin{aligned} \bar{P}_R^{ART}(E) &= (\nu_k / \nu_s) (E - E_c / E) & E \geq E_c \\ &= 0 & E < E_c \end{aligned} \quad (79)$$

$$\begin{aligned} \text{where } \mathcal{E}_T(E) &= (h\nu_k) \frac{-1}{-1} E \\ \mathcal{E}_\ddagger(E) &= (h\nu_s) \frac{-1}{-1} (E - E_c), \end{aligned} \quad (80)$$

and ν_s and ν_{kc} are the stable stretching frequency of the transition state and diatomic reactant molecule respectively.

$\mathcal{E}_\ddagger(E)$ can be interpreted as the number of internal states on the ART DS for a total energy less than or equal to E.

From section IIB it is clear that the mean reaction probability may be evaluated for a variety of dividing surfaces. Koepl³ has shown how to do this for a straight DS by carrying out an orthogonal transformation of the normal coordinates. The alternate stable coordinate (q_s') and unstable coordinate (q_u') are defined by the equations

$$q_s' = -\cos(\phi) \cdot q_u + \sin(\phi) \cdot q_s, \quad (81)$$

$$q_u' = \sin(\phi) \cdot q_u + \cos(\phi) \cdot q_s, \quad (82)$$

where ϕ is the transformation angle. Equation (82) may also be expressed as

$$q_u' = \sin(\phi) \cdot (C_1^u \Delta R_1 + C_2^u \Delta R_2) + \cos(\phi) \cdot (C_1^s \Delta R_1 + C_2^s \Delta R_2) \quad (83)$$

where the unstable normal mode coefficients are C_1^u and C_2^u , the stable normal mode coefficients are C_1^s and C_2^s , and ΔR_1 and ΔR_2 are the deviations from the saddle point values of the A-B and B-C bond lengths respectively. We can also write

$$q_u' = C_1^{u'} \Delta R_1 + C_2^{u'} \Delta R_2 \quad (84)$$

$$\text{where } C_1^{u'} = \sin(\phi) \cdot C_1^u + \cos(\phi) \cdot C_1^s, \quad (85)$$

$$C_2^{u'} = \sin(\phi) \cdot C_2^u + \cos(\phi) \cdot C_2^s.$$

From an examination of figure 1 we can see that the orientation of the DS in configuration space can be specified in terms of its slope. Since $q_u' = 0$ on the DS, the slope may be expressed as

$$\Delta R_2 / \Delta R_1 = -C_2^{u'} / C_1^{u'} \quad (86)$$

In order to find ϕ , we express equation (86) as

$$\chi_\phi = - \frac{\tan(\phi) \cdot C_1^u + C_1^s}{\tan(\phi) \cdot C_2^u + C_2^s}. \quad (87)$$

Equation (87) is then rearranged to obtain the expression

$$\phi = \tan^{-1} \left[-(C_1^s + \chi_\phi C_2^s) / (C_1^u + \chi_\phi C_2^u) \right]. \quad (88)$$

Using equation (19) of reference 3, the eigenvalue for the alternate stable coordinate ($\lambda_{u'}$) may be expressed as

$$\lambda_{s'} = \lambda_s \sin^2(\phi) + \lambda_u \cos^2(\phi) \quad (89)$$

where $\lambda_s = 4\pi^2 \nu_s^2$ and $\lambda_u = 4\pi^2 \nu_u^2$ are the eigenvalues for the real and imaginary vibrations and ν_s and ν_u are the corresponding frequencies. Since λ_s and $\lambda_{s'}$ are positive, it fol-

lows that

$$\tan(\phi) \geq (-\lambda_v/\lambda_s)^{\frac{1}{2}} \geq 0 \quad (90)$$

where $\lambda_v < 0$. The variable ϕ is therefore restricted to the range

$$\phi_\infty < \phi \leq \pi/2,$$

$$\text{or } -\pi/2 \leq \phi < -\phi_\infty \quad (91)$$

where $\phi_\infty = \tan^{-1}(-\lambda_v/\lambda_s)^{\frac{1}{2}}$. When $\phi = \pm\phi_\infty$, $v_{\text{eff}} = 0$ and the SVA result for the value of $\bar{F}_R(E)$ given by equation (79) is infinite.

There are two reasons for considering dividing surfaces other than the one given by ART. First, as suggested by Keck, an alternate DS can be used as a trial surface in an attempt to find the minimum upper bound for $\bar{F}_R(E)$. The second reason is that the ART DS has holes in some cases. When this occurs, we must use an alternate DS if the value of $\bar{F}_R(E)$ is to provide an upper bound for $\bar{F}_r^T(E)$. One choice for an appropriate DS is the one perpendicular to the path of steepest descent ($DS_\perp$) on the PES at the saddle point.

IIE Evaluation of Accurate Mean Reaction Probabilities

The method used for the evaluation of the accurate values of the ART and KVT mean reaction probabilities will now be given. The quantity $\varepsilon_T(E)$ is defined by equation (28). It is given as an integral over reactant phase space, and can be evaluated using a simple Monte Carlo technique.²⁷ Pseudo random values of the vibrational coordinate ($Q_\perp$) and conjugate momentum ($P_\perp$) are selected within the limits of the maximum and minimum values of $Q_\perp$ and $P_\perp$ defined by the total energy E .

These limits are given by the equations

$$P_2^{max} = (2\mu_k E)^{\frac{1}{2}}, \quad (92)$$

$$P_1^{min} = -(2\mu_k E)^{\frac{1}{2}}, \quad (93)$$

$$Q_1^{max} = R_e - \ln(1 - (E/D_e)^{\frac{1}{2}}) / \alpha, \quad (94)$$

$$Q_2^{min} = R_e - \ln(1 + (E/D_e)^{\frac{1}{2}}) / \alpha. \quad (95)$$

Equations (94) and (95) were obtained by using the Morse potential energy function which is given by the equation

$$V(Q_1) = E = D_e (1 - \exp(-\alpha(Q_1 - R_e)))^2 \quad (96)$$

where D_e is the dissociation energy of the reactant molecule B-C, R_e is the equilibrium internuclear distance for the B-C molecule, and α is the Morse constant.

If the quantity $\xi_T(E)$ is evaluated using equations (79) and (80), we refer to this result as the accurate value of the reactant energy density function ($\xi_T^A(E)$). The harmonic value of $\xi_T(E)$ corresponds to a potential energy function which is given by the equation

$$V(Q_1) = \frac{1}{2}k(Q_1 - R_e)^2 \quad (97)$$

where k is the harmonic force constant determined by the Morse potential. The quantity k can be expressed by the equation

$$k = \left[\frac{d^2 V}{dQ_1^2} \right]_{Q_1=R_e} = 2D_e \alpha^2. \quad (98)$$

When evaluating equation (28) by the harmonic approximation, equations (94) and (95) are replaced by the equations

$$\begin{aligned} Q_1^{max} &= (2E/k)^{\frac{1}{2}} + R_e \\ Q_2^{min} &= -(2E/k)^{\frac{1}{2}} + R_e. \end{aligned} \quad (99)$$

Random values of Q and P are calculated using the equations

$$\begin{aligned} P_2 &= P_1^{min} + 2X_1 P_2^{max}, \\ Q_2 &= Q_1^{min} + X_2 (Q_1^{max} - Q_1^{min}) \end{aligned} \quad (100)$$

where X_1 and X_2 are decimal pseudo random numbers which are distributed uniformly on the range 0 to 1. The internal energy of the reactant B-C molecule is calculated using the equation

$$E = V(Q_1) + P_1^2 / 2\mu_{BC} \quad (101)$$

where $V(Q_1)$ is given by equation (96) or (97). The quantity

$\xi_{\mathcal{I}}(E)$ can be calculated from the expression

$$\xi_{\mathcal{I}}(E) = 1.3026 \cdot (P_{\max} - P_{\min}) \cdot (Q_{\max} - Q_{\min}) \cdot (N)^{-1} \sum_{i=1}^N H(E - E_i) \quad (102)$$

where N is the number of (Q_1, P_1) pairs chosen from reactant phase space and the factor 1.3026 is the constant defined in chapter I.

The coordinates used for the evaluation of $\xi_{\mathcal{I}}(E)$ are the stable stretching normal coordinate (q_s) and its conjugate momentum (p_s). The limits of p_s are given by the equations

$$\begin{aligned} p_s^{\max} &= (2(E - E_m))^{1/2}, \\ p_s^{\min} &= -(2(E - E_m))^{1/2} \end{aligned} \quad (103)$$

where $E_m = E_c$ for a DS with a positive slope on the PES, and $E_m \leq E_c$ for a DS with a negative slope. In the latter case, the DS extends into the reactant or product valley, and the minimum energy of a $X^\ddagger$ can be less than the activation energy. The quantity $\xi^*(E)$ can be evaluated for a DS with a negative slope using the Monte Carlo procedure, however the result may not be used to calculate an upper bound for $\bar{P}_r^\ddagger(E)$ because the DS has holes.

When evaluating the limits of the stable stretching coordinate ($q_s^{\max}$ and $q_s^{\min}$) from the energy given by the PES, a numerical procedure is used which finds the two values of q_s for a total energy E . The random values of q_s and p_s are then

calculated using the equations

$$q_s = -q_s^{\min} + X_s (q_s^{\max} - q_s^{\min}), \quad (104)$$

$$p_s = -p_s^{\min} + 2X_s (p_s^{\max}). \quad (105)$$

The quantity $\mathcal{E}_{\pm}(E)$ calculated from equations (104) and (105) is referred to as the accurate value of $\mathcal{E}_{\pm}(E)$ ($\mathcal{E}_{\pm}(E)_{acc}$), and the ratio of $\mathcal{E}_{\pm}(E)_{acc}/\mathcal{E}_I^{acc}(E)$ is referred to as the accurate value of the mean reaction probability ($\bar{P}_R(E)_{acc}$). If the SVA value of $\mathcal{E}_{\pm}(E)$ is desired, $q_s^{\max}$ and $q_s^{\min}$ are evaluated using the harmonic potential given by the equation

$$V(q_s) = \frac{1}{2} \lambda_s q_s^2 \quad (106)$$

where λ_s is the eigenvalue for the stable stretching normal coordinate. The values of $q_s^{\max}$ and $q_s^{\min}$ are calculated using the equations

$$\begin{aligned} q_s^{\max} &= (2E/\lambda_s)^{\frac{1}{2}}, \\ q_s^{\min} &= -(2E/\lambda_s)^{\frac{1}{2}}. \end{aligned} \quad (107)$$

In order to evaluate the accurate value of $\mathcal{E}_{\pm}(E)$, the potential energy given by the appropriate PES must be used. The coordinates of the PES are the internuclear distances. The normal coordinates can be transformed to the internuclear coordinates by using the equations

$$\begin{aligned} R_2 &= q_s / (-C_1^s C_2^s / C_1^s + C_2^s) + R_2^a, \\ R_1 &= (-q_s - C_2^s (R_2 - R_2^a)) / C_1^s + R_1^a, \\ R_3 &= R_1 + R_2 \end{aligned} \quad (108)$$

where R_1 is the distance between atoms A and B, R_2 is the distance between atoms B and C, and R_3 is the distance between atoms A and C. The quantities R_1^a and R_2^a are the equilibrium internuclear separations which give the location of the saddle

point on the collinear PES. The internal energy of the $X^\ddagger$ is given by the equations

$$\xi_T^{\text{acc}} = V(R_1, R_2, R_3) + \frac{1}{2} p_s^2, \quad (109)$$

$$\xi_T^{\text{SVA}} = \frac{1}{2} \lambda_s (q_s)^2 + \frac{1}{2} p_s^2 \quad (110)$$

where equation (109) is used to compute $\xi_T^{\text{acc}}(E)$ and equation (110) is used to compute the SVA value of $\xi_T(E)$. The quantity $\xi_+(E)$ may now be evaluated using the equation

$$\xi_+(E) = 1.3026 \cdot (q_s^{\text{max}} - q_s^{\text{min}}) \cdot (p_s^{\text{max}} - p_s^{\text{min}}) (N)^{-1} \sum_{i=1}^N H(E - E_T - E_c). \quad (111)$$

As a check on the Monte Carlo procedure, the value of the SVA results for $\xi_T(E)$ and $\xi_+(E)$ can be compared to the analytical values given by equation (80). Once $\xi_T(E)$ and $\xi_+(E)$ have been evaluated, the mean reaction probability given by equations (77) or (79) can be calculated. The value of N in equation (102) and (111) is 10^4 . We used only 600 trajectories in evaluating $\bar{P}_r^+(E)$ because of the considerably longer time it takes to calculate a trajectory than to examine a point in phase space. The error in $\bar{P}_R(E)_{\text{acc}}$ or $\bar{P}_R(E)_{\text{SVA}}$ corresponding to the 95% confidence limit is therefore much less than the error in $\bar{P}_r^+(E)$.

IIF Evaluation of Conversion, Transmission and Product Coefficients.

Reflected trajectories can be grouped into the following three categories:

1. Reactive trajectories which originate from the reactant region of phase space. These trajectories cross the DS an odd number of times. The minimum number of crossings for traject-

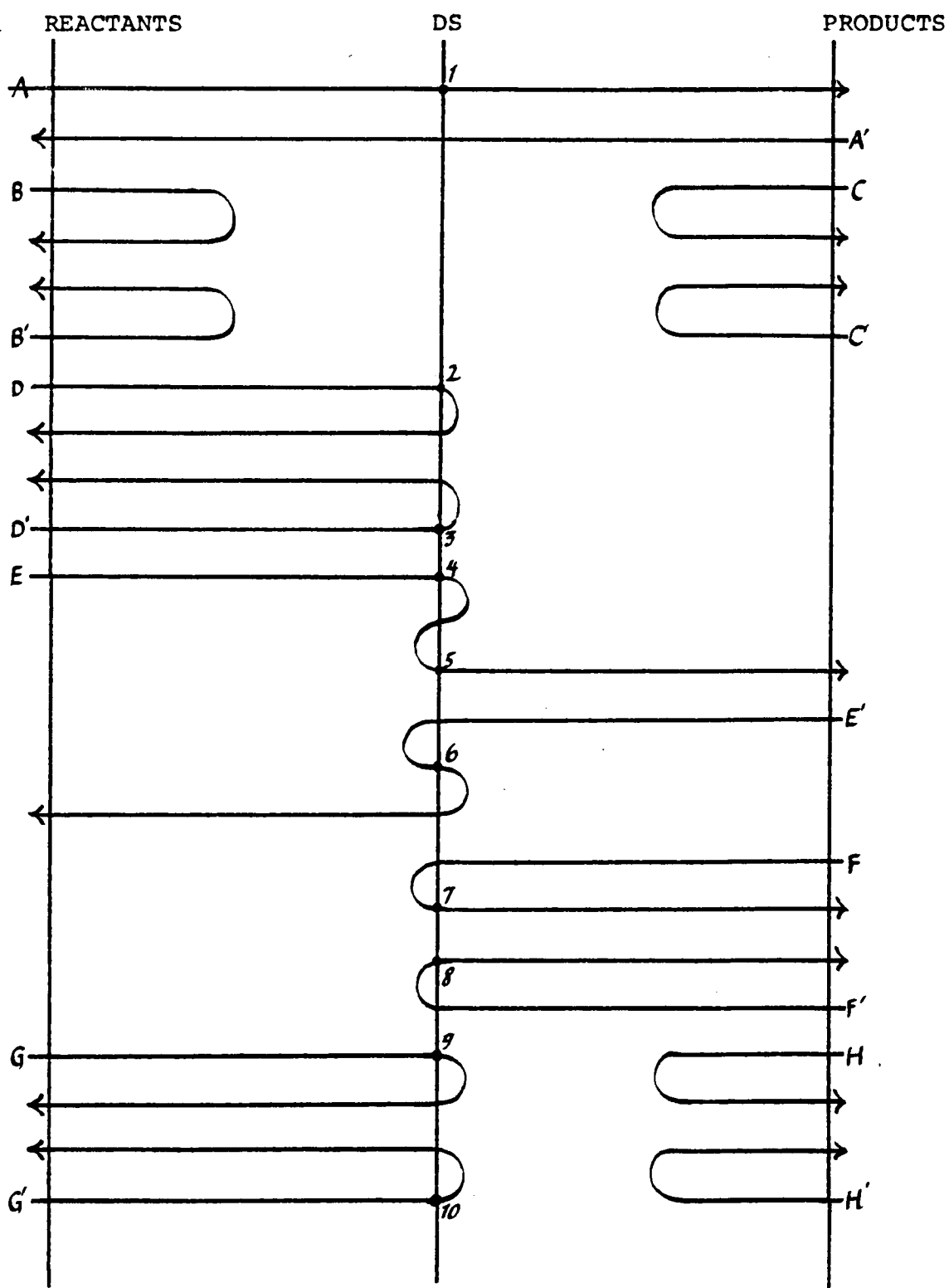
ories of this type is three. Each trajectory contributes once to $\bar{P}_r^{\pm}(E)$, but contributes to $\bar{P}_R(E)_{Acc}$ every time it crosses the DS traveling in the direction of products; e.g. a trajectory which crosses the DS five times will contribute to $\bar{P}_R(E)_{Acc}$ three times i.e. at positions on the DS which correspond to the 1st, 3rd and 5th crossings.

2. Non-reactive trajectories which originate in the reactant region. These trajectories cross the DS an even number of times i.e., at least twice. They do not contribute to $\bar{P}_r^{\pm}(E)$ but contribute to $\bar{P}_R(E)_{Acc}$ at positions on the DS which correspond to the 1st, 3rd, 5th, ... etc. crossings; e.g. a non-reactive trajectory which crosses the DS 4 times contributes twice to $\bar{P}_R(E)_{Acc}$.

3. Trajectories which originate from the product region of phase space. These trajectories do not contribute to $\bar{P}_r^{\pm}(E)$ but contribute to $\bar{P}_R(E)_{Acc}$ each time they cross the DS moving in the direction of products; i.e. on the 2nd, 4th, 6th, ... etc. crossings. For example trajectories of this type which cross the DS four times and five times will both contribute twice to $\bar{P}_R(E)_{Acc}$. For reactants and products at equilibrium, the principle of microscopic reversibility requires that the number of reactive trajectories for a reaction in the forward direction must equal the number of reactive trajectories for the reaction in the reverse direction.

Figure 2 provides an illustration of an equilibrium sample of trajectories. Each trajectory is followed by one which must be present due to the time reversal symmetry of

FIGURE 2



trajectories i.e., each trajectory is followed by one whose presence is required by the principle of microscopic reversibility. A dot indicates positions on the DS where the trajectory is traveling in the direction of products. These dots correspond to transition states which contribute with equal weight to the value of $\bar{P}_R(E)_{ACC}$. Only those transition states which lie on trajectories which originate in the reactant region and proceed directly to products contribute to $\bar{P}_r^t(E)$. Transition state theory assumes that all transition states lie on trajectories which originate in the reactant region and proceed directly to products. Trajectories A and A' are direct trajectories i.e., they cross the DS only once. Trajectories B, B', C, C', and H and H' are non-reactive trajectories which do not cross the DS. Thus they do not contribute to $\bar{P}_r^t(E)$ or $\bar{P}_R(E)_{ACC}$. If only the trajectories A, A', B, B', C, C', H, and H' were present, then $\bar{P}_r^t(E) = \bar{P}_R(E)_{ACC}$. The reflected trajectories in category 1 are E and E', those in category 2 are D, D', G, G', and those in category 3 are E', F and F'. As Anderson⁸ and Mayer²⁸ point out, a uniform or equilibrium distribution of chemical reaction systems in the reactant and product regions of phase space will produce a family of trajectories which give an equilibrium distribution of transition states on the DS. This is a consequence of the Liouville theorem.²⁹

Trajectories traveling in the forward direction in figure 2 are those which originate from reactants. The quantity

$\bar{P}_r^{\pm}(E)$ for the forward reaction given by equation (51) can be written as

$$\bar{P}_r^{\pm}(E) = \sum_{\text{odd } n} T_n^{\pm} / \sum_{n=0} T_n^{\pm} \quad (112)$$

where $T_n^{\pm}$ gives the number of trajectories which originate in the reactant region of phase space and cross the DS n times (e.g. $T_1^{\pm} = 4$). The numerator in equation (112) gives the number of reactive trajectories and the denominator gives the total number of trajectories calculated which originate from reactants. The value of $\bar{P}_r^{\pm}(E)$ for the trajectories shown in figure 2 is 2/8.

The density of trajectories in the reactant region of phase space may be expressed as $\sum_{n=0} T_n^{\pm} / \mathcal{E}_I^{\pm}(E)$ where $\mathcal{E}_I^{\pm}(E)$ is the density function for the reactants. The density of trajectories in the product region of phase space may be expressed as $\sum_{n=0} T_n^{\mp} / \mathcal{E}_I^{\mp}(E)$ where $\mathcal{E}_I^{\mp}(E)$ is the density function for the product region of phase space and the $T_n^{\mp}$ are the number of trajectories which originate from the product region and cross the DS n times. In order to obtain an equilibrium distribution of trajectories at the DS, these trajectory densities must be equal. If we execute a uniform distribution of $\sum_{n=0} T_n^{\pm} = N$ trajectories from the reactant region, we must execute a uniform distribution of $(\mathcal{E}_I^{\mp}(E) / \mathcal{E}_I^{\pm}(E)) \cdot \sum_{n=0} T_n^{\pm}$ trajectories from the product region. The distribution of trajectories on the DS will then be a uniform one with the same density as trajectories originating from the reactant and product regions of phase space.

The quantity $P_R(E)_{acc}$ may be expressed as $N_{\neq}(E)/N$ where $N_{\neq}(E)$ is the total number of transition states which are generated from equilibrium distributions of reactants and products. The contribution to $N_{\neq}(E)$ from trajectories which originate from the reactant region ($N_R^{\neq}(E)$) is given by the expression

$$N_R^{\neq}(E) = T_1^R + T_2^R + 2(T_3^R + T_4^R) + 3(T_5^R + T_6^R) + \dots \quad (113)$$

The contribution to $N_{\neq}(E)$ from trajectories which originate in the product region is given by the equation

$$N_P^{\neq}(E) = T_2^P + T_3^P + 2(T_4^P + T_5^P) + 3(T_6^P + T_7^P) + \dots \quad (114)$$

Thus the total contribution to $\bar{P}_R(E)_{acc}$ on the DS ($N_{\neq}(E)$) is equal to $N_R^{\neq}(E) + N_P^{\neq}(E)$. The values of $N_R^{\neq}(E)$ and $N_P^{\neq}(E)$ from figure 2 are 7 and 3 respectively, and the value of $\bar{P}_R(E)_{acc}$ is 10/8.

The conversion coefficient $\xi(E)$ is defined by the expression

$$\bar{P}_R^{\neq}(E) = \xi(E) \cdot \bar{P}_R(E)_{acc}. \quad (115)$$

It is clear then that $\xi(E)$ is equal to the ratio $\bar{P}_R^{\neq}(E)/\bar{P}_R(E)_{acc}$. Using equation (112) and the relationship for $\bar{P}_R(E)_{acc}$, $\xi(E)$ is given by the expression

$$\xi(E) = \sum_{\text{odd } n} T_n^R / N_{\neq}(E). \quad (116)$$

The quantity $\xi(E)$ in figure 2 has the value of 2/10. Since the numerator and denominator of equation (116) are the same for the forward and reverse reactions, $\xi(E)$ is also the same for both reactions. The quantity $\xi(E)$ can also be written as

$$\xi(E) = \left(\sum_{\text{odd } n} T_n^R / N_R^{\neq}(E) \right) \cdot (N_R^{\neq}(E) / N_{\neq}(E)). \quad (118)$$

The ratios $\sum_{\text{odd } n} T_n^R / N_R^{\neq}(E)$ and $N_R^{\neq}(E) / N_{\neq}(E)$ are called the transmission coefficient ($\chi(E)$) and product coefficient ($\eta(E)$)

respectively. When we multiply $\bar{P}_R(E)_{Acc}$ by $\chi(E)$, we are "correcting" for transition states which arise from reflected trajectories which correspond to categories one and two. These contribute to $\bar{P}_R(E)_{Acc}$ but not to $\bar{P}_r^{\pm}(E)$. The quantity $\eta(E)$ "corrects" for transition states which correspond to reflected trajectories in category three. The values of $\chi(E)$ and $\eta(E)$ corresponding to figure 2 are 2/7 and 7/10 respectively. The evaluation of $\chi(E)$ and $\eta(E)$ for the reverse reaction will be discussed in chapter 3.

Transmission coefficients have also been defined by Morokuma and Karplus¹⁰ ($\chi(E)_m$) and Anderson¹ ($\chi(E)_A$). They are given by the equations

$$\chi(E)_m = \sum_{\text{odd } n} T_n^R / \sum T_{n>0}^R \quad (119)$$

$$\chi(E)_A = (\sum_{\text{odd } n} T_n^R + \sum_{\text{even } n} T_{n>1}^F) / N_{\mp}(E) \quad (120)$$

The values of $\chi(E)_A$ and $\chi(E)_m$ from figure 2 have the values 4/10 and 2/6 respectively. The quantities $\chi(E)_A$ and $\chi(E)_m$ were not used in the way we use our transmission coefficient, but rather as a conversion coefficient; i.e. they were intended to account for all transition states arising from trajectories in categories 1, 2 and 3 which contribute to $\bar{P}_R(E)_{Acc}$ but not to $\bar{P}_r^{\pm}(E)$.

We can see that the difference between equations (116) and (120) is the term $\sum_{\text{even } n} T_{n>1}^F$. Thus $\chi(E)_A = \xi(E)$ if there are no reflected trajectories originating from products and $\chi(E)_A > \xi(E)$ if there are reflected trajectories originating from products. The quantity $\chi(E)_m$ does not recognize the

contribution to $\bar{P}_R(E)_{Acc}$ from trajectories originating from products. It also counts only once the contribution to $\bar{P}_R(E)_{Acc}$ from each trajectory originating from reactants even though a trajectory may have more than one $X^\ddagger$ on the DS moving in the direction of products (e.g. trajectory E in figure 2). Only if there are no reflected trajectories originating from reactants or products will $\chi(E)_m = \xi(E)$, otherwise $\chi(E)_m > \xi(E)$.

III. Trajectory and Phase Space Results

Introduction

In this chapter, the results of our phase space and trajectory calculations for the reactions



will be given. The results are organized in tables 3 - 32 . Each table presents the results for a given set of reactions on a specified PES. The results for each series of reactions are given at two values of the total energy E . The series of reactions studied are $X + H-H$, $H + X-H$, $H + H-X$, $H + X-X$, $X + H-X$, and $X + X-H$ where X corresponds to masses of 1, 2 and 10 amu. The results for the reverse reactions for each series are presented in separate tables. In accordance with the notation of equation (121), the reverse reaction is expressed as $A-B + C \longrightarrow A + B-C$. For example, the results for the reverse of the reaction $X + H-H$ will be found in the table headed by $X-H + H$. Because of the symmetrical nature of the Porter-Karplus (PK) PES, the reaction $H + H-X$ is equivalent to the reaction $X-H + H$. These reactions are not equivalent when the PES is unsymmetrical. No calculations for the reverse reactions for systems with a symmetrical arrangement of masses were performed using the PK PES since the forward reaction is identical to the reverse reaction.

Table 3 contains the trajectory and phase space theory results for the series of reactions $X + H-H \longrightarrow X-H + H$ on the PK PES. The first column in each table indicates the masses for the three atom system. The mass of the attacking atom A is given first. The second and third masses correspond to B

and C respectively; B is always the atom attacked by A. The quantity α is the skew angle for the Eyring representation of the PES. The relationship between the skew angle and the masses is given by the equation

$$\alpha = \cos^{-1} \left[\frac{m_A m_C}{(m_A + m_B)(m_B + m_C)} \right]^{\frac{1}{2}}. \quad (122)$$

Potential energy surfaces are plotted using the skewed coordinates introduced by Eyring. The sloping vertical axis corresponds to $b \cdot R_a$ and the horizontal axis corresponds to $a \cdot R_i$ where $a = \mu_{A,B}^{\frac{1}{2}}$ and $b = \mu_{C,B}^{\frac{1}{2}}$, and the μ 's are reduced masses. The coordinates R_i and R_a are the internuclear separations for A-B and B-C respectively.

The column labeled E gives the total energy for each of the trajectories calculated. As we explained earlier, the trajectories for each reaction form a microcanonical ensemble. The trajectory mean reaction probability ($\bar{P}_r^T(E)$), Anderson's conversion coefficient ($\bar{C}(E)$), the transmission coefficient ($\gamma(E)$), and the product coefficient ($\eta(E)$), are all evaluated from the trajectory information listed at the bottom of each table. The quantity T_n^R gives the number of trajectories of type n which originate in the reactant region where n specifies the number of times the trajectory crosses the DS. The order of the numbers T_n^R is always $T_1^R, T_2^R, T_3^R, \dots$ except for those cases where we indicate n in parenthesis for trajectories which have an unusually large number of transition states. From table 3 for example, we see that the values of T_n^R for the reaction $H + H-H \longrightarrow H-H + H$ at .9ev are 406, 103,

15, and 2; thus $T_1^R = 406$, $T_2^R = 103$, etc. Trajectories of the type T_i^R for the forward and reverse reactions correspond to what we have called direct trajectories. Eyring's ART assumes that all of the trajectories are of this type. The trajectory numbers T_n^P give the number of trajectories of type n which originate from the product region. The set T_n^P has the same meaning for the reverse reaction $A-B+C \rightarrow A + B-C$, as the set T_n^R for the forward reaction.

An equal number of trajectories are calculated for reactions in the forward and reverse direction. The densities for calculated trajectories in the reactant and product regions of phase space are $N/\xi_I^R(E)$ and $N/\xi_I^P(E)$ where N is the number of trajectories calculated and $\xi_I^R(E)$ and $\xi_I^P(E)$ are the density functions for the reactants and products respectively. The values of T_n^R and T_n^P in the tables for both the forward and reverse directions of the reaction $A + B-C \rightarrow A-B + C$ correspond to $N = 600$ trajectories i.e., an equal number of trajectories calculated in both directions. In general $\xi_I^R(E) \neq \xi_I^P(E)$, and the density of calculated trajectories on the reaction shell radius in the reactant and product regions of phase space will be unequal. The distribution of trajectories on a given DS will therefore not be a uniform one. To obtain the uniform distribution of trajectories corresponding to equilibrium, the densities of calculated trajectories in the reactant and product regions must be equal. We obtain a uniform distribution of trajectories at the DS by multiplying the values of T_n^P by the weighting factor $\omega(E) = \xi_I^P(E)/\xi_I^R(E)$.

The set of numbers T_n^P for the forward reaction $A + B \rightarrow C$ is also the set of numbers T_n^R for the reverse reaction $A \rightarrow B + C$. In table 1 we give the reactant density functions for all the reactions studied; in table 2 the weighting factors ($\omega(E)$) for all the reactions are given.

The reader will note that $\sum_n T_n^R = N_R(E)$, and $\sum_n T_n^P$ is the total number of trajectories which reach the DS from the reactant region of phase space. The quantity $\omega(E) \cdot T_{n,1}^P$ is the equilibrium number of trajectories which originate in the product region of phase space which cross the DS more than once and thus contribute to the phase space mean reaction probability. The quantity $N_R^\ddagger(E)$ gives the total number of transition states generated by trajectories which originate from an equilibrium distribution in the reactant region of phase space (i.e. $N_R^\ddagger(E) = T_1^R + T_2^R + 2(T_3^R + T_4^R) + 3(T_5^R + T_6^R) + \dots$). The quantity $N_P^\ddagger(E)$ gives the total number of transition states generated by $\omega(E) \cdot N$ trajectories which originate from an equilibrium distribution in the product region of phase space (i.e. $N_P^\ddagger(E) = \omega(E) \cdot (T_1^P + T_2^P + 2(T_3^P + T_4^P) + 3(T_5^P + T_6^P) + \dots)$). The quantity $N_\ddagger(E)$ is the sum $N_R^\ddagger(E) + N_P^\ddagger(E)$ which gives the total number of transition states which originate from equilibrium densities of reactants and products. The conversion coefficient which we introduced in chapter 2 is given by the ratio $N_R(E)/N_\ddagger(E)$, the transmission coefficient is given by the ratio $N_R(E)/N_R^\ddagger(E)$ and the product coefficient is given by the ratio $N_P^\ddagger(E)/N_\ddagger(E)$. In the tables, we also report the trajectory values for the average fraction of the final vibrational energy ($F_{vib}^{BC}(E)$) for non-

TABLE 1
Reactant Density Functions

Diatomic Molecule	Type of Surface					
	PK-PW $\epsilon_T(.5) *$	PK-PW $\epsilon_x(.9)$	LEPS $\epsilon_x(.25)$	LEPS $\epsilon_x(.5)$	LEPS $\epsilon_x(1.078)$	LEPS $\epsilon_x(1.328)$
H-H	1.879	3.483	1.093	2.231	4.202	5.246
D-H	2.194	4.016	1.267	2.580	4.834	6.058
Δ -H	2.542	4.717	1.481	3.019	5.667	7.049
D-D	2.666	4.920	1.541	3.174	5.954	7.457
Δ - Δ	5.915	11.122	3.466	7.078	13.277	16.659

* Energy is in ev.

TABLE 2

Weighting Factors $\omega(E)$ for the Reverse Reaction

Mass	Surface Type			
	PK-PW $\omega(.5\text{ev})$	PK-PW $\omega(.9\text{ev})$	LEPS $\omega(1.078\text{ev})$	LEPS $\omega(1.328\text{ev})$
H+H-H	1	1	.2601	.4253
D+H-H	1.168	1.153	.3015	.4918
Δ +H-H	1.353	1.354	.3525	.5755
H+D-H	1	1	.2621	.4259
H+ Δ -H	1	1	.2613	.4283
D+H-D	1	1	.2621	.4259
Δ +H- Δ	1	1	.2613	.4283
D+D-H	1.215	1.225	.3188	.5239
Δ + Δ -H	2.327	2.358	.6116	1.004
H+D-D	.823	.817	.2128	.3460
H+ Δ - Δ	.430	.424	.1115	.1812
H+H-D	.856	.867	.2261	.3683
H+H- Δ	.739	.739	.1929	.3165

reactive trajectories, and the average fraction of the final vibrational energy for reactive trajectories ($F_{vib}^{AB}(E)$). The principle of microscopic reversibility requires that the average fraction of the final vibrational energy for the reverse reaction $A-B + C \rightarrow A + B-C$ is also the average initial vibrational energy of reactive trajectories for the forward reaction $A + B-C \rightarrow A-B + C$. Since the final configuration of non-reactive trajectories are as equally likely to be chosen as the initial configuration (with the signs of P_i and P_a reversed), $F_{vib}^{BC}(E)$ is also the average fraction of initial vibrational energy for non-reactive trajectories.

We can also relate the initial average fraction of vibrational energy for the reverse reaction ($F_{vib}^{AB}(E)_p$) to the initial fraction of vibrational energy corresponding to non-reactive trajectories for the forward reaction ($F_{vib}^{BC}(E)_R$). In the microcanonical ensembles used in our trajectory studies, each trajectory has the total energy E . The average vibrational kinetic energy for a harmonic oscillator is $E/2$. Since the kinetic energy corresponding to the motion of the center of mass is zero for each trajectory in the ensemble, the balance of the energy corresponds to the energy of relative motion. A function $F_v(E)$ is defined by the equation

$$F_v(E) = \left[\frac{N - N_R(E)}{N} \right] F_{vib}^{BC}(E)_R + \frac{N_R(E)}{N} F_{vib}^{AB}(E)_p \quad (123)$$

The principle of microscopic reversibility may be invoked to establish that the function $F_v(E)$ must have a value of $\frac{1}{2}$ for a microcanonical ensemble of harmonic oscillators. The

initial value of the average fraction of vibrational energy was calculated for 1000 trajectories using the Morse potential at total energies of .25ev, .5ev, .9ev, 1.078ev, and 1.328ev. These fractions were $.495 \pm .018$, $.499 \pm .018$, $.503 \pm .018$, $.504 \pm .018$, and $.507 \pm .018$ respectively. Using the results in table 3, we find that the values of the function $F_v(E)$ for the reaction $H + H-H$ on the Porter-Karplus PES at .5ev and .9ev are .508 and .520 respectively.

The phase space mean reaction probabilities are also presented in the tables. The superscript ACC indicates that the accurate potential energy given by the potential energy surface was used to calculate this quantity. The SVA superscript indicates that the small vibrations approximation was employed to evaluate the potential energy on the DS. The subscript indicates the type of DS which was used; SD indicates the DS perpendicular to the path of steepest descent at the saddle point in configuration space, and M indicates the straight DS for which the phase space mean reaction probability is a minimum. For all reactions on the Porter-Karplus PES, we used the ART DS and we write $\bar{F}_R(E)_{ART}^{ACC}$ rather than $\bar{F}_R(E)_{PS}^{ACC}$ in the upper part of table 3. For other reactions and surfaces we sometimes use a DS other than that of ART. When we do this we will label the phase space result column $\bar{F}_R(E)_{PS}^{ACC}$ and specify the DS used in an adjacent column. When a DS other than that of ART is used to evaluate the phase space mean reaction probability reported in the upper part of the table, it is also used in the trajectory program to evaluate the trajectory mean reaction probability

and the quantities $\xi(E)$, $\chi(E)$, and $\eta(E)$. In the next three columns, we give the conversion coefficient, the transmission coefficient, and the product coefficient. Next we give the phase space mean reaction probability corresponding to the small vibrations approximation for the Hamiltonian of the reaction system and the specified DS. In the final column, we give the result obtained by multiplying $\xi(E)$ and the Monte Carlo mean reaction probability for the specified DS. A comparison of this quantity with the trajectory mean reaction probability provides a good test for the numerical accuracy of the trajectory and phase space results since by definition $\bar{P}_r^t(E) = \xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$. The ART DS was used for the trajectory determination of $\xi(E)$, $\chi(E)$, $\eta(E)$, and $\bar{P}_r^t(E)$ unless the DS had holes. When holes were present in the ART DS, the SD DS was employed.

The discussion of the results for the reactions $X + H-H \rightleftharpoons X-H + H$ on each of the three potential energy surfaces will be more detailed than the discussion for the remaining series of reactions. The more detailed discussions will help the reader become familiar with the tables. Each series of reactions starts with the reaction $H + H-H \rightleftharpoons H-H + H$ and follows with those for an increasing mass of X. When we speak of a trend in the trajectory mean reaction probability for the series $X + H-H \rightarrow X-H + H$, we are referring to a trend in $\bar{P}_r^t(E)$ for the series of reactions $H + H-H \rightarrow H-H + H$, $D + H-H \rightarrow D-H + H$ and $\Delta + H-H \rightarrow \Delta-H + H$ where Δ corresponds to a fictitious hydrogen atom of mass 10.

Throughout our discussions we will refer to various types of skewed potential energy surfaces (PES) and trajectories. To visualize the different types of trajectories more clearly, the reader will find figures 38 - 43 helpful. A detailed description of each PES that we used is given in Appendix 4 and a brief qualitative description is given below.

The skewed Porter-Karplus (PK) PES is symmetrical for symmetrical mass combinations and unsymmetrical for unsymmetrical mass combinations. It is thermoneutral and has a classical activation energy (E_c) of .396ev.

The skewed Polanyi-Wong (PW) PES is unsymmetrical for all mass combinations we examined. Both the PW and PK PES are thermoneutral and have the same classical activation energy.

The skewed London-Eyring-Polanyi-Sato (LEPS) PES is unsymmetrical for all mass combinations we examined. The forward reaction is endothermic and the reverse reaction is exothermic ($\Delta E = .828\text{ev}$). For the LEPS and PW PES, the location of the energy barrier is in the entrance valley for the forward reaction and the exit valley for the reverse reaction. The classical activation energy for the forward and reverse reactions on the LEPS PES is .904ev and .076ev respectively.

We measure the classical activation energy and the energy of each contour from the bottom of the reactant valley; e.g. the classical activation energy on the PW and PK PES is .396ev above the bottom of the reactant valley.

IIIA Trajectory and Phase Space Analysis for the $X + H-H \rightleftharpoons X-H + H$ Reactions on the Porter-Karplus PES.

The values of the trajectory mean reaction probability for this series of reactions at .5ev are $.425 \pm .062$, $.512 \pm .070$, and $.557 \pm .052$. Since the potential energy at the saddle point is .396ev, trajectories for total energies of .5 and .9ev have energies which lie approximately .1 and .5ev above the saddle point. The trajectory mean reaction probability for the $H + H-H$ reaction calculated by Morokuma and Karplus¹⁰ for trajectories ranging in energy from .1 to .125ev above the saddle point is .436. This value is in good agreement with our result. Since there is some overlap of the error ranges for our results, we cannot say that one value is significantly different from the other. However, since the error ranges at the 95% confidence level are very pessimistic ones, we choose to consider the possibility that the reaction probability increases for this series at .5ev. The number of trajectories which reach the DS (T_i^R) in this series are 255, 307, and 334. We can see that all trajectories that reach the DS go on to form products, i.e. $T_i^R = N_R(E)$. Since none of these reactive trajectories are reflected (i.e., cross the DS more than once), the transmission coefficient ($\chi(.5)$) is one for this series. A trajectory can only be reflected if it encounters forces which direct it to return to the DS after it has first encountered it. The direction of the force at a given point on the skewed PES is that of the perpendicular to the equipotential contour at that point. The

skewed PES for the reaction $H + H-H \rightleftharpoons H-H + H$ is given in figure 3. Trajectories originating from the right valley (i.e., for large values of $a \cdot R_1$ and small values of $b \cdot R_2$) correspond to the species on the left side of equation (121), and trajectories originating from the left valley (i.e., small values of $a \cdot R_1$ and large values of $b \cdot R_2$) correspond to the species on the right side of equation (121). The region along each of the equipotential contours which give forces that could return a trajectory moving from the right toward the left valley on the map to the DS is located between the line segments perpendicular to the contour. It can be seen that there are no forces capable of producing a reflected trajectory at .5ev. The skewed PES for the reaction $D + H-H \rightleftharpoons D-H + H$ is given by figure 4. The reactants $D + H-H$ are located in the right valley on the map. There is a small region between points a and b on the .5ev contour where forces could cause trajectories to be reflected. In figure 5, we see that the region located between points a and b on the .5ev contour for the reaction $\Delta + H-H \rightleftharpoons \Delta-H + H$ is even larger. None of the trajectories calculated for the $D + H-H$ or $\Delta + H-H$ reaction actually reached this region on the contour, if they did they would be reflected back along the same path they took on the way from the reactant valley.

The quantity $\chi(.9)$ for this series has the values .775, .725, and .555. This decrease from the values of $\chi(.5)$ is to be expected since the total regions on contours .5 - .9ev on the product side of the DS capable of directing trajectories back across the DS increases for this series of reactions.

These regions on the .9ev contour lie between points a' and b'. The reader will also note that the number of reflected trajectories which originate from equilibrium distributions in the product region of phase space at .5ev ($\omega(E) \cdot T_{n>1}^p$) for this series are 0, 1, and 83; at .9ev, the corresponding numbers are 120, 256, and 397. The same reasoning used to explain a decreasing trend in the values of the transmission coefficient at .9ev can be used here, i.e. the total region located on contours on the reactant side of the DS with forces which are capable of returning trajectories to the DS increases. A comparison of figures 3 - 5 will make this clear. The regions on the .5 and .9ev contours where forces could return a phase point which originates in the product region to the DS are located between points c and d (.5ev) and c' and d' (.9ev) in figures 4 and 5. By symmetry, there are no forces on the .5ev contour on the reactant side of the DS that are directed toward the DS for the H + H-H reaction. This is clearly not the case for the reactions D + H-H and Δ + H-H; see figures 4 and 5. How effective these forces are at returning trajectories which originate from products to the DS is indicated by the product coefficient ($\gamma(E)$). The product coefficients at .5ev for the series are 1, .997, and .924; at .9ev, the corresponding values are .817, .683, and .590. Thus the product coefficients at both energies decrease in this series; this is consistent with an increase in $\omega(E) \cdot T_{n>1}^p$ in the series and the explanation given above.

At this point it may be helpful to examine the relation-

ship between the product and transmission coefficients. Consider the ratio $(N_R^\ddagger(E) - N_R(E))/N_P^\ddagger(E)$. We note that the numerator corresponds to the number of transition states originating from reactants which do not go directly to products while the denominator is the number of transition states originating from products. From previous discussions we recall that only transition states moving in the direction of products can contribute to the rate and therefore it is implied in all our discussions of transition states that they are moving in the direction of products. It can be shown that if the ratio defined above is smaller than $\chi(E)$ (the fraction of transition states originating from the reactant region which lead directly to products), then $\eta(E) < \chi(E)$. As $\chi(E)$ decreases $N_P^\ddagger(E)$ must increase relative to $N_R^\ddagger(E) - N_R(E)$ in order for $\eta(E) < \chi(E)$. As an example of this consider the reaction $D + H-H$. We note that $(N_R^\ddagger(.9) - N_R(.9))/N_P^\ddagger(.9) = 153/258 = .593$. Since $\chi(.9) = .725$, we are not surprised that $\eta(.9)$ has a value of .683 which is smaller than $\chi(.9)$. If the ratio is larger than $\chi(E)$, then $\chi(E) < \eta(E)$. For the reaction $H + H-H$ $(N_R^\ddagger(.9) - N_R(.9))/N_P^\ddagger(.9) = 122/122 = 1$; since $\chi(.9) = .775$, $\eta(.9) = .817$ which is greater than $\chi(.9)$. Finally, when $(N_R^\ddagger(E) - N_R(E))/N_P^\ddagger(E) = \chi(E)$, $\chi(E) = \eta(E)$.

Now that we have explained the relationship between reflected trajectories and the values of $\chi(E)$ and $\eta(E)$, we return to the trajectory mean reaction probability for the series of reactions at .9ev. We note that while the total number of trajectories reaching the DS from the reactant region $(\sum_{n=1}^N T_n^R)$,

is fairly constant at 526, 542, and 542 for the series, the corresponding trajectory mean reaction probabilities $.702 \pm .087$, $.672 \pm .085$, and $.535 \pm .071$ represent a declining trend. We recall that at .5ev, all trajectories reaching the DS went on to form products. From our earlier discussions and an inspection of figures 3 - 5, we can see that as the energy increases, the region on the contour where forces on the product side of the DS could return trajectories to the reactant side increases. An increase in the number of reflected trajectories which do not contribute to the trajectory mean reaction probability is therefore not surprising.

Table 4 provides the results for the reverse reactions $X-H + H \longrightarrow X + H-H$. The values of the average fraction of final vibrational energy for reactive trajectories ($F_{v,l}^{AB}(E)$) at .5ev are $.240 \pm .020$, $.267 \pm .032$, and $.257 \pm .031$ for the series. At .9ev, the quantity $F_{v,l}^{AB}(.9)$ is $.437 \pm .037$, $.436 \pm .046$, and $.520 \pm .051$. As we noted earlier, the final values of the average fraction of vibrational energy for the reverse reaction $A-B + C \longrightarrow A + B-C$ are equal to the initial values for the forward reaction $A + B-C \longrightarrow A-B + C$. In table 3 we find the values of the average fraction of vibrational energy for the product molecule A-B. At .5ev, the values for the reaction series of the forward reaction are $.240 \pm .020$, $.251 \pm .030$, and $.300 \pm .031$; at .9ev, the corresponding values are $.437 \pm .037$, $.523 \pm .053$, and $.610 \pm .043$. Symmetry of course requires that the values are identical for the forward and reverse directions of the reaction $H + H-H$. The values of $F_{v,l}^{AB}(E)$ for the for-

ward direction of the reaction are larger than those for the reverse direction for the $D + H-H$ reaction at .9ev and for the $\Delta + H-H$ reaction at both .5 and .9ev. For these reaction systems, the initial values of the average fraction of vibrational energy (i.e., the values for the reactants at the reaction shell radius) are therefore smaller than the corresponding final values. In the forward direction for these reaction systems, the translational energy of trajectories in the reactant valley is converted partially to vibrational energy by the time the trajectories reach the product valley. It is interesting to point out that $F_{vib}^{Bc}(E)$ shows an increasing trend at .5ev for the forward reaction and a decreasing trend at .9ev. The average final vibrational energy at the higher energy decreases due to an increase in the number of trajectories which strike the inner wall and return to the reactant region. These trajectories have higher than average amounts of translational energy.

We will now take up the discussion of the results for the phase space mean reaction probability. As mentioned before, the ART DS was used to evaluate $\chi(E)$, $\eta(E)$, and $\xi(E)$ for all reactions involving the Porter-Karplus PES. In our tables, we include the phase space mean reaction probabilities for the DS perpendicular to the path of steepest descent at the saddle point (SD) and the best straight DS for which the phase space mean reaction probability calculated using the accurate Hamiltonian, is a minimum (M), as well as the result for the ART DS. At .5ev, the phase space

mean reaction probabilities for the ART DS are $.418 \pm .013$, $.486 \pm .015$, and $.597 \pm .019$. For this series, these values are in excellent agreement with the trajectory results. We do not expect too much deviation here since the total energy exceeds the barrier height by only .1ev. The values of the conversion coefficient at .5ev which are unity or close to unity tell us that the contribution to the phase space mean reaction probability from reflected trajectories which originate from equilibrium distributions in the reactant and product regions of phase space is almost negligible. The reader may have noticed that the error ranges are smaller for the phase space mean reaction probabilities than for the corresponding trajectory values. This is because 10^4 sets of initial conditions were chosen to calculate each phase space mean reaction probability whereas only 600 trajectories were calculated to determine the corresponding collisional theory result. The values of the phase space mean reaction probability calculated using the SVA Hamiltonian ($\bar{P}_R(.5)_{P_S}^{SVA}$) are .425, .495, and .601 for the series. No errors are given here since the function was evaluated analytically. Again, these values are in excellent agreement with both $\bar{P}_R(.5)_{P_S}^{ACC}$ and $\bar{P}_r^+(.5)$. At .9ev the quantity $\bar{P}_R(.9)_{P_S}^{SVA}$ has the values 1.146, 1.334, and 1.620. These may be compared with the values of $\bar{P}_R(.9)_{P_S}^{ACC}$ which are $1.128 \pm .036$, $1.308 \pm .041$, and $1.619 \pm .051$. While the quantities $\bar{P}_R(.9)_{P_S}^{ACC}$ and $\bar{P}_R(.9)_{P_S}^{SVA}$ are in good agreement with each other, we notice that they deviate somewhat from the traj-

ectory mean reaction probabilities, the deviation becoming more severe as the mass of the attacking atom increases. We note that the conversion coefficient, transmission coefficient, and product coefficient are all decreasing for this series suggesting an increasing number of reflected trajectories from both the reactant and product regions of phase space. As an additional check on our trajectory calculations we can compute the phase space mean reaction probabilities using our trajectory results by noting that the ratios $\xi_{\pm}(E)/\xi_I(E)$ and $N_{\pm}(E)/N$ should give the same result. The values of the phase space mean reaction probability at .9ev calculated using our trajectory results are 1.108, 1.357, and 1.633 for the series. These values are in good agreement with the values of $\bar{P}_R(.9)_{PS}^{ACC}$ given in table 3. It is interesting to note that at .5 and .9ev for this series, there are no significant differences between $\bar{P}_R(E)_{ART}^{ACC}$, and $\bar{P}_R(E)_{SD}^{ACC}$ or $\bar{P}_R(E)_M^{ACC}$ since the position of all three DS's are nearly the same. The results for the reverse reaction $X-H + H \rightleftharpoons X + H-H$ are given in table 4. The discussion of the reverse reaction will center mainly on pointing out to the reader the relationship between the results for the forward and reverse reactions. In fact, there is no information contained in table 4 that can't be obtained from table 3. It will be noticed for example that the numbers T_n^R in table 3 become the numbers T_n^P in table 4. We multiply the T_n^R of table 4 by the weighting factor ($\omega(E) = \xi_I^P(E)/\xi_I^R(E)$). This practice provides an equilibrium distribution of trajectories on the DS and allows us to use the prin-

ciple of microscopic reversibility in a convenient way to check the numerical accuracy of our results. For example, the trajectory mean reaction probability for the forward and reverse reactions are given by the expressions

$$\left[\bar{P}_r^{\pm}(E) \right]_{\text{FOR}} = \sum_{\text{odd } n} T_n^R / N \quad (124)$$

$$\left[\bar{P}_r^{\pm}(E) \right]_{\text{REV}} = \sum_{\text{odd } n} T_n^P / N \quad (125)$$

respectively where the T_n^R and T_n^P for example could be those of table 3. The principle of microscopic reversibility requires that at equilibrium the number of trajectories which map from reactants to products (regardless of the number of times they cross the DS) and are moving in the forward (product) direction at the DS must be equal to the number moving in the reverse direction. The principle of microscopic reversibility therefore requires that $\sum_{\text{odd } n} T_n^R = \xi_I^P(E) / \xi_I^R(E) \cdot \sum_{\text{odd } n} T_n^P$. The trajectory mean reaction probability in the forward and reverse direction of table 3 are therefore related by the equation

$$\left[\bar{P}_r^{\pm}(E) \right]_{\text{REV}} = (\xi_I^R(E) / \xi_I^P(E)) \cdot \left[\bar{P}_r^{\pm}(E) \right]_{\text{FOR}} \quad (126)$$

where R and P correspond to the reactants and products of the forward reaction. The results calculated using equation (126) and the entries in table 3 are .425±.062, .702±.087, .438±.060, .582±.074, .412±.038, and .395±.052. The first two values of $\left[\bar{P}_r^{\pm}(E) \right]_{\text{REV}}$ for the H + H-H reaction are in perfect agreement with those of table 4 since T_n^R and T_n^P are identical (i.e., it was unnecessary to calculate trajectories for both directions due to symmetry). The remaining values are in excellent agreement with the entries of table 4.

In general all of the quantities in table 4 which depend

on the values of T_n^R are weighted (i.e., $N_R(E) = \omega(E) \cdot \sum_{\text{odd } n} T_n^R$, $\sum_n T_n^R$, and $N_R^{\ddagger}(E)$). The quantity $\omega(E) \cdot \sum_{\text{odd } n} T_n^R$ for the reverse reaction is identical to the quantity $\omega(E) \cdot \sum_{\text{odd } n} T_n^P$ where the set of numbers T_n^P correspond to trajectories which originate in the product region for the forward reaction. Therefore, due to the inclusion of this weighting factor for the T_n^R of the reverse reaction, the principle of microscopic reversibility requires that the values of $N_R(E)$ for the forward reaction (table 3) should agree with the values of $N_R(E)$ for the reverse reaction within the limits of statistical error. For the same reason, the values of $N_{\ddagger}(E)$ in the two tables should also agree within the limits of statistical error. The reader should be aware that the reaction probability for the reverse reaction corresponds to $\sum_{\text{odd } n} T_n^P / N$ and not $N_R(E) / N$ where N is the number of trajectories we calculate. In order to calculate $\bar{P}_R^{\ddagger}(E)$ for the reverse reaction using the expression $N_R(E) / N$, we must multiply N by the weighting factor $\omega(E)$. We have used this weighting scheme to facilitate tests involving the principle of microscopic reversibility. It is clear that the values of $N_{\ddagger}(E)$ should be equal for both the forward and reverse directions since at equilibrium, the number of transition states moving from left to right for the forward reaction must be equal to the number moving from right to left for the reverse reaction.

The transmission coefficients and product coefficients for the forward and reverse reactions are related by the expressions

$$\begin{aligned} \left[\chi(E) \right]_{\text{REV}} &= \left[\frac{N_R^*(E)}{N_R^{\text{eq}}(E)} \right]_{\text{REV}} \left[\chi(E) \right]_{\text{FOR}} \quad \text{and,} \\ \left[\eta(E) \right]_{\text{REV}} &= \left[\frac{N_R^{\text{eq}}(E)}{N_R^*(E)} \right]_{\text{REV}} \left[\eta(E) \right]_{\text{FOR}} \end{aligned} \quad (127)$$

When the transmission coefficients for the D + H-H and Δ + H-H reactions of table 3 are used to calculate those for the reverse reaction, the results 1.05, .621, .869, and .451 are found to be in good agreement with the corresponding entries in table 4. When the product coefficients for the D + H-H and Δ + H-H reactions of table 3 are used to calculate those for the reverse reaction, the results .948, .797, 1.06, and .727 are found to be in good agreement with the corresponding entries in table 4. Finally, combining equation (127), we see that $\left[\bar{\epsilon}(E) \right]_{\text{FOR}} = \left[\bar{\epsilon}(E) \right]_{\text{REV}}$. The quantities $F_{\text{vib}}^{\text{BC}}(E)_{\text{REV}}$ and $F_{\text{vib}}^{\text{AB}}(E)_{\text{REV}}$ can both be evaluated by using the values of $F_{\text{vib}}^{\text{BC}}(E)_{\text{FOR}}$ and $F_{\text{vib}}^{\text{AB}}(E)_{\text{FOR}}$ and equation (123) as noted earlier. Within the harmonic oscillator approximation, the right hand side of equation (123) is $\frac{1}{2}$. If the accurate potential energy given by the Morse equation is used, the right hand side of equation (123) is equal to the accurate average fraction of initial vibrational energy for reactive and nonreactive trajectories. These values were given earlier for the four energies used in our study. The equations which relate the average fractions of vibrational energy for the reactants and products of the forward and reverse reactions are

$$\begin{aligned} (F_{\text{vib}}^{\text{AB}}(E))_{\text{REV}} &= \frac{N}{N_r(E)} \left[F_v(E)_{\text{FOR}} - (F_{\text{vib}}^{\text{BC}}(E))_{\text{FOR}} \left(\frac{N - N_r(E)}{N} \right) \right] \\ (F_{\text{vib}}^{\text{BC}}(E))_{\text{REV}} &= \frac{N}{N - \sum_{\text{odd } n} T_n^{\text{P}}} \left[F_v(E)_{\text{REV}} - (F_{\text{vib}}^{\text{AB}}(E))_{\text{FOR}} \left(\frac{\sum_{\text{odd } n} T_n^{\text{P}}}{N} \right) \right] \end{aligned} \quad (128)$$

where the numbers T_n^0 correspond to the forward reaction and $F_V(E)$ is the accurate average fraction of vibrational energy for both reactive and nonreactive trajectories. The quantity $F_V(E)$ has the same value for all mass combinations at the energy E . Equation (128) can be rewritten in the more convenient form

$$\begin{aligned} (F_{vib}^{AB}(E))_{REV} &= (\bar{P}_r^c(E))_{FOR}^{-1} \left[F_V(E)_{FOR} - (F_{vib}^{BC}(E))_{FOR} (1 - \bar{P}_r^c(E))_{FOR} \right] \\ (F_{vib}^{BC}(E))_{REV} &= (1 - \bar{P}_r^c(E)_{FOR} / \omega(E))^{-1} \left[F_V(E)_{REV} - \frac{F_{vib}^{AB}(E)_{FOR} \bar{P}_r^c(E)_{FOR}}{\omega(E)} \right] \end{aligned} \quad (129)$$

where $\omega(E)$ is the weighting factor defined earlier.

Since the phase space mean reaction probabilities for the forward and reverse directions of the reaction of table 3 are given by the equations

$$\begin{aligned} (\bar{P}_R(E)_{PS}) &= \mathcal{E}_\pm(E) / \mathcal{E}_I^R(E) \\ (\bar{P}_R(E)_{PS}) &= \mathcal{E}_\pm(E) / \mathcal{E}_I^L(E), \end{aligned} \quad (130)$$

it follows that they are related by the equation

$$(\bar{P}_R(E)_{PS}) = (\mathcal{E}_I^R(E) / \mathcal{E}_I^L(E)) \cdot (\bar{P}_R(E)_{PS}). \quad (131)$$

When the phase space mean reaction probabilities for the $D + H-H$ and $\Delta + H-H$ reaction of table 3 are used to calculate those for the reverse reaction, the results $.416 \pm .013$, $1.13 \pm .030$, $.441 \pm .014$, and $1.20 \pm .040$ are found to be in good agreement with the corresponding entries in table 4. The agreement is not perfect since different Monte Carlo samples were used to calculate the results in the two tables.

For the reverse reaction $X-H + H \rightleftharpoons X + H-H$, the mass of the end atom varies and the attacking atom is always a light one. At .5ev, trajectory mean reaction probabilities for the three reactions in the series are not significantly

different. The reaction probabilities for the $D-H + H$ and $\Delta-H + H$ reactions are smaller than the values for the forward reactions although there is some overlap of the error ranges. The number of trajectories which reach the DS in our sample (600) for the $D + H-H$ reaction at .5ev is 307; for the reverse reaction $D-H + H$ the corresponding number for a sample of the same size is 250. Fewer trajectories in our samples reach the DS for reaction in the reverse direction. In figure 4, we see that forces perpendicular to the .5ev contour between points b and c point toward the reactant valley and away from the DS for the reverse reaction. Trajectories which originate in the product region could be reflected here before they reach the DS. These forces have no counterpart for reaction in the forward direction. It is tempting therefore to suggest that this interpretation of the effects of forces in the reactant and product valleys explains why fewer reactive trajectories in our sample reach the DS for reaction in the reverse direction. Such an argument would be a fallacious one. Fewer reactive trajectories in our samples reach the DS from the product region than from the reactant region because the density function for the products is larger than the density function for the reactants. One can however correctly use a discussion of forces in the reactant and product valley to account for a difference between the number of reflected trajectories for reaction in the forward and reverse direction.

When we discuss the relationship between the transmission, product, and conversion coefficients and the number of trajectories which reach the DS from the reactant and product

regions, we must compare results for batches of trajectories for reactions in each direction which will generate an equilibrium distribution of trajectories at the DS. We must weight the number of trajectories using the scheme explained earlier to ensure that the densities of our trajectory samples ($N/\omega(E)$) for reaction in each direction are equal. For example, if we calculate 600 trajectories for the reaction $D + H-H$ at .5ev, we find that 307 of them reach the DS. When we calculate 600 for the reverse reaction $D-H + H$, we find that 250 of them reach the DS. The number of trajectories in an equilibrium sample for the reverse reaction is $600 \cdot \omega(.5) = 701$ and the number which reach the DS is therefore $250 \cdot \omega(.5) = 292$. Therefore, in an equilibrium sample of trajectories for the reverse reaction, 292 of them reach the DS. For the $\Delta + H-H$ reaction, the number of trajectories which reach the DS from equilibrium distributions in the reactant and product regions are 334 and 357. It is important that the reader is aware of the distinction we make here between trajectory samples which are always equal for reactions in the forward and reverse directions and equilibrium samples which are unequal if the density function for the reactant and product are unequal. An example of the utility of comparisons involving equilibrium samples is given below.

The transmission coefficients $\chi(.9)$ for the reverse reactions $D-H + H$ and $\Delta-H + H$ are .602 and .420; the corresponding product coefficients are .809 and .732 respectively. The transmission coefficients $\chi(.9)$ for the forward reactions $D + H-H$ and $\Delta + H-H$ are .725 and .555; the corresponding pro-

duct coefficients are .683 and .590. Since more trajectories which originate from equilibrium distributions in the reactant region and reach the DS are reflected for the reactants $X-H + H$ than for the reactants $X + H-H$, we see that $\chi(.9)$ is smaller and $\eta(.9)$ is larger for the former reactions. We conclude our discussion of this series of reactions on the Porter-Karplus PES with some remarks about the product energy distribution for the reverse direction.

For the reverse reaction, the values of $F_{vib}^{bc}(.5)$ are .706, .694 and .608. The values of $F_{vib}^{bc}(.5)$ for the forward reaction show an increasing trend. The difference in the behavior of these results arises due to the presence of nonreactive trajectories which originate in the reactant region for the reverse reaction and are reflected; these trajectories have no counterpart for reaction in the forward direction. As we noted earlier, nonreactive reflected trajectories have more translational energy than nonreactive trajectories which do not reach the DS.

The quantity $F_{vib}^{bc}(.9)$ is .714, .547, .491 for the series; the trend decreasing as in the forward reaction. The quantities $F_{vib}^{ab}(.5)$ are .240, .267 and .257. At .9ev the quantities $F_{vib}^{ab}(.9)$ are .437, .436 and .520. Our earlier discussion of the relationship between the values of $F_{vib}^{bc}(E)$ and $F_{vib}^{ab}(E)$ for the forward and reverse reactions make it clear that for the reaction $D-H + H$ at .9ev and the reaction $\Delta-H + H$ at both .5 and .9ev, the vibrational energy of trajectories in the reactant valley is converted partially to translational energy by the time the trajectories reach the product valley.

IIIB Trajectory and Phase Space Results for the Reaction Series



This section will discuss the above series of reactions using the PW surface and compare the results to the same series of reactions on the PK surface. The reaction $H + H-H \rightleftharpoons H-H + H$ is particularly interesting because it enables us to compare a reaction involving a symmetrical combination of masses using a symmetrical surface (PK surface shown in figure 3) and an unsymmetrical surface (PW surface shown in figure 6), and also because it has been a source of investigation in the past.¹² At .5 and .9ev the trajectory mean reaction probabilities for this reaction are $.366 \pm .057$ and $.607 \pm .078$. The corresponding values on the PK surface are $.425 \pm .062$ and $.702 \pm .087$. At .5ev there are no reflected trajectories (i.e. $\chi(.5) = 1$) on either the PK or PW surface for $X = H$. Therefore the higher trajectory mean reaction probability on the PK surface is due to a greater number of trajectories reaching the DS (220 for the PW and 255 for the PK surface). The number of trajectories in our samples which reach the DS from the reactant and product regions are approximately equal at .5ev for $X = H, D$ and Δ on the PW surface whereas the former exceeds the latter for $X = D$ and Δ on the PK surface. At .9ev the number of trajectories which reach the DS is about the same for the $H + H-H \rightleftharpoons H-H + H$ reaction on both surfaces; 481 for the PW surface and 526 for the PK surface. The corresponding transmission coefficients are .682 for the former and .775 for the latter surface. Thus there are not only less trajectories which reach the DS, but a larger fraction of those trajectories

which reach the DS are reflected on the PW surface. There is also a greater number of nonreactive reflected trajectories on the PW surface (117) than on the PK surface (105).

For an understanding of the trends in the transmission and product coefficients, we can use the same type of reasoning we used in our discussion of the PK surface. At .5ev there are 220 trajectories reaching the DS which originate from reactants (forward reaction) and 231 trajectories that reach the DS and originate from products (reverse reaction). As mentioned before, none of the trajectories which reach the DS in the forward reaction are reflected, but 16 of the trajectories from the reverse reaction have two transition states ($\mathcal{N}(.5) = .932$). The segment of the contour in figure 6 in the product region which has forces perpendicular to it which can direct trajectories to the opposite side of the DS is bounded by arc ab at .5ev and a'b' at .9ev. The corresponding segments on the reactant side of the DS are arcs cd and c'd' respectively. Arc ab, while slightly larger than arc cd is ineffective in returning trajectories to the DS ($\mathcal{N}(.5) = 1$).

For the H + H-H reaction at .9ev, 481 trajectories reach the DS from the reactant side and 429 from the product side. The corresponding numbers are 526 and 526 on the PK surface. The fact that there are more trajectories which reach the DS from the reactant side can be understood by examining arc b'c' in figure 6. This arc can return a trajectory with a large amount of translational energy that originated from products back to products before it reaches the DS. Trajectories originating from reactants with a large

amount of translational energy will reach the DS at least once. In our investigation of the $X + H-H \rightleftharpoons X-H + H$ reactions on the London-Eyring-Polanyi-Sato (LEPS) surfaces, we will see that the greater length of arc bc and $b'c'$ compared to the corresponding arcs on the PW surface results in a much larger difference between the number of trajectories which reach the DS from the reactant and product regions.

Of the 481 trajectories which reach the DS from the reactant region 143 are reflected; the majority returning to reactants (117). There are 111 reflected trajectories originating from products, 87 of which are returned to products. We note that at .9ev there are more reflected trajectories originating from reactants; the reverse of the situation at .5ev. This is because arc $a'b'$ is large compared to arc $c'd'$.

The trajectory mean reaction probability for the $D + H-H$ reaction on the PW surface at .5ev is $.334 \pm .053$ compared to $.512 \pm .070$ for the PK surface. The values of the transmission, product and conversion coefficients at .5ev are .983, .814 and .800 respectively. The corresponding values for the PK surface are 1, .997 and .997. As was the case for the $H + H-H$ reaction, there are no nonreactive reflected trajectories for either surface. Thus the reason the PW trajectory mean reaction probability for the reaction $D + H-H$ at .5ev is smaller than the corresponding value on the PK surface is because less trajectories reach the DS on the PW surface. The number of trajectories which reach the DS for an equilibrium distribution of trajectories in the forward and reverse reactions are 201 and

238 respectively compared to 307 and 292 on the PK surface. Only one trajectory that originated from reactants is reflected while 41 are reflected originating from products. The corresponding values for the $\text{H} + \text{H-H}$ reaction are 0 and 16. From the skewed PES for the $\text{D} + \text{H-H}$ reaction illustrated by figure 7, it can be seen that the length along the arcs ab and cd is larger than the corresponding arcs for the $\text{H} + \text{H-H}$ reaction shown in figure 6. Thus it is not unexpected that there are more reflected trajectories for the $\text{D} + \text{H-H} \rightleftharpoons \text{D-H} + \text{H}$ reaction than for the $\text{H} + \text{H-H} \rightleftharpoons \text{H-H} + \text{H}$ reaction. It is a little unusual that with the DS in the entrance valley (closer to reactants) there are more trajectories that reach the DS originating from products. Since we are discussing equilibrium distributions of trajectories on the DS, we are in effect calculating the results for $\omega(.5) \cdot N$ trajectories for the reverse reaction and only N trajectories for the forward reaction, where $\omega(.5)$ is 1.168 for the $\text{D} + \text{H-H}$ reaction on both the PK and PW surfaces. Since there are more trajectories reaching the DS in an equilibrium distribution in the reverse direction, and the trajectory mean reaction probability is less than that of the forward reaction, it is evident that the former has more nonreactive reflected trajectories than the latter.

The number of trajectories originating from an equilibrium distribution on the DS for the PK surface which are reflected is 0 in the forward reaction and 1 in the reverse reaction. Therefore, arcs ab and cd on the PK surface do

not have forces perpendicular to them which are as effective as the forces perpendicular to the corresponding arcs on the PW surface at returning trajectories to the DS. The nonzero values of T_n^p for the D + H-H reaction at .5ev on the PW surface are 169, 28, 4, and 3; the corresponding nonzero values on the PK surface are 249 and 1. Thus while the number of trajectories which reach the DS are greater on the PK surface, there are more reflected trajectories on the PW surface as was the case for the H + H-H reaction at .5ev. Comparing figures 4 and 7 we notice that the forces perpendicular to arc cd are pointed more in the direction of products in figure 7. The same behavior can be seen by comparing figures 3 and 6, and 5 and 8.

At .9ev the trajectory mean reaction probability for the D + H-H reaction on the PW surface is $.488 \pm .068$ compared to $.671 \pm .085$ for the PK surface. The transmission, product and conversion coefficients for the PW and PK surfaces are .591, .708 and .418, and .725, .683 and .495 respectively. The number of trajectories which reach the DS for this reaction on the PW surface are 477 compared to 542 on the PK surface. Although fewer trajectories reach the DS on the PW surface, more are reflected (200) compared to the PK surface (149). There are 487 trajectories originating from products that form an equilibrium distribution on the DS; 201 of which are reflected. Since the number of reflected trajectories originating from reactants and products are about the same, we can see that the relatively larger size of arc a'b' compared to

c'd' (figure 7) results in a much closer relationship between the number of reflected trajectories in the forward and reverse reactions at .9ev than at .5ev. This was also the case for the H + H-H reaction. The number of trajectories which reach the DS on the PK surface is 542 for the forward reaction and 628 for the reverse reaction. The number of reflected trajectories is 149 originating from reactants and 256 originating from an equilibrium distribution of products. Thus for the PK and PW surfaces the relatively large length of arc a'b' relative to arc c'd' results in a large increase in the number of reflected trajectories originating from reactants compared to the number of reflected trajectories originating from products at .9ev for the D + H-H reaction.

The trajectory mean reaction probability for the reaction $\Delta + \text{H-H}$ on the PW surface at .5ev is $.379 \pm .058$ compared to the corresponding value of $.557 \pm .052$ for the PK surface. The value of the transmission, product and conversion coefficients for the PW surface are .996, .745 and .719. We note that the values of T_n^k are 220, 0 and 8 on the PW surface and 334 on the PK surface. Thus, all trajectories are reactive on both surfaces, however as with all the other reactions in this series more trajectories reach the DS on the PK surface, and there are more reflected trajectories on the PW surface. The number of trajectories originating from reactants and products on the PW surface which form an equilibrium distribution on the DS are 228 and 292 respectively. The number of trajectories which are reflected are 8 and 76 respectively. We note that at .5ev for this series of reac-

tions the number of reflected trajectories from an equilibrium distribution on the DS has increased. Comparing figures 6 - 8, we also notice an increase in the length of arc cd. The number of reflected trajectories originating from reactants for the series at .5ev are 0, 1 and 8. Although small compared to the number of reflected trajectories originating from products, this increase also follows an increase in the length of arc ab shown in figures 6 - 8. At .9ev the trajectory mean reaction probability for the $\Delta + \text{H-H}$ reaction is $.298 \pm .050$ for the PW surface and $.535 \pm .071$ for the PK surface. The values of the transmission, product, and conversion coefficient for the PW surface are .351, .595 and .209 respectively. As is the case at .5ev, we find an increasing number of reflected trajectories originating from reactants and products at .9ev for this series of reactions. The explanation is the same as that given for the series of reactions at .5ev. We notice for the first time that there are more nonreactive reflected trajectories than reactive trajectories for the reaction $\Delta + \text{H-H} \rightleftharpoons \Delta\text{-H} + \text{H}$ at .9ev in the forward and reverse reactions. This accounts for the low trajectory mean reaction probability. The number of trajectories reaching the DS from reactants are 474 on the PW surface and 542 on the PK surface for the above reaction. Thus for the entire series of reactions at .5 and .9ev, more trajectories reached the DS for the forward reaction on the PK surface and in all cases there were fewer reflected trajectories on the PK surface, except for the $\text{H} + \text{H-H}$ reaction at .5ev where there were no reflected

trajectories on both surfaces. As we would expect therefore, the transmission coefficient on the PW surface was less than the corresponding transmission coefficient on the PK surface except for the $H + H-H$ reaction at .5ev where they are both unity. At the same energy, the difference between the transmission coefficient on the PW and PK surfaces for this series increases with the mass of the attacking atom. This indicates that as the DS and barrier are moved into the entrance channel, more trajectories are reflected after reaching the DS. At .5ev the product coefficients on the PW surface are also smaller than on the PK surface for the series; the difference increasing with the mass of the attacking atom. The contribution to the phase space mean reaction probability from trajectories originating from products is therefore greater on the PW surface. Thus the location of the DS and barrier results in the same trend in $\eta(.5)$ and $\chi(.5)$. At .9ev there are fewer reflected trajectories originating from an equilibrium distribution in the product region for the PW surface compared to the PK surface. Therefore $N_P^*(.9)$ is smaller on the PW surface. However, more trajectories originating from reactants reach the DS on the PK surface; $N_A^*(.9)$ is also larger and therefore the values of the product coefficient are similar for the PW and PK surfaces at .9ev. The conversion coefficients are smaller for the series of reactions at .5ev and .9ev on the PW surface.

Summarizing the trends in the trajectory mean reaction probability we can say that at .5ev, the trajectory mean reaction probability and the number of trajectories which reach

the DS (none of which are reflected) increases as the mass of X becomes larger for the PK surface. The trajectory mean reaction probability on the PW surface at .5ev stays about the same for the entire series. Approximately the same number of trajectories reach the DS with a slight increase in the number of reflected trajectories (all reactive) as the mass of the attacking atom increases. At .9ev, both surfaces show a decrease in the trajectory mean reaction probability. For each surface, approximately the same number of trajectories reach the DS for the series at .9ev (ca. 530 on the PK surface and ca. 475 on the PW surface). The decrease in the trajectory mean reaction probability therefore is due to an increase in the number of reflected nonreactive trajectories.

Turning to the vibrational energy distributions, we see that for the PW surface $F_{vib}^{bc}(.5)$ remains about the same as did the trajectory mean reaction probability for the series. The quantity $F_{vib}^{bc}(.5)$ increases on the PK surface as did the trajectory mean reaction probability. As mentioned before, the trajectory mean reaction probability decreases on both the PW and PK surfaces at .9ev. We notice that $F_{vib}^{bc}(.9)$ also decreases. This decrease is due to an increased number of nonreactive reflected trajectories which have more translational energy than nonreactive trajectories not reaching the DS. At .5ev the values of $F_{vib}^{AB}(.5)$ for the forward reaction on the PW surface are .468, .591 and .745. The corresponding values on the PK surface are .240, .251 and .300. The quantity $F_{vib}^{AB}(.5)$ is thus increasing on both surfaces for the series, but it is much

larger on the PW surface. Comparing figures 3 - 5 with figures 6 - 8, we see why this is so. Reactive trajectories on the PW surface meet the barrier early, accelerate, and climb the inner wall in the product valley with a high frequency. We also see that $F_{vib}^{AB}(.5)$ should increase (and does) as the mass of the attacking atom increases because the skew angle decreases. At .9ev the values of $F_{vib}^{AB}(.9)$ are .571, .695 and .782 on the PW surface and .437, .523 and .610 on the PK surface. Thus the trend in $F_{vib}^{AB}(E)$ is increasing for both surfaces at .9 and .5ev, but $F_{vib}^{AB}(.9) > F_{vib}^{AB}(.5)$ for each reaction on the same surface. We also note that $F_{vib}^{AB}(E)$ for the reverse reaction is less than $F_{vib}^{AB}(E)$ for the forward reaction on the PK and PW surfaces. Thus reactive trajectories have more translational energy on the average for the reaction $X + H-H$ on both surfaces. This translational energy is then converted to vibrational energy on the product side of the DS.

IIIC Trajectory and Phase Space Results for the Reaction series

$H + H-X \rightleftharpoons H-H + X$ on the PW surface.

Because of the symmetrical nature of the PK surface the reaction $H + H-X$ was identical to the reaction $X-H + H$. For the PW surface on the other hand, the reaction $H + H-X$ takes place with the barrier and DS in the entrance valley while the reaction $X-H + H$ takes place with the barrier and DS in the exit valley. It is interesting to compare the reactions $H + H-X$ and $X-H + H$ on the PW surface to determine the effect of the shape of the PES on a reaction in which the masses and therefore the skew angle is the same. We are really only studying the reactions $H + H-X$ where $X = D$ and Δ since the reaction $H + H-H$ is the same in the $X + H-H$ and $H + H-X$ series. From table 7, the value of the trajectory mean reaction probabilities at .5ev for the reactions $H + H-X$ are $.367 \pm .057$, $.378 \pm .058$ and $.403 \pm .060$. The corresponding values for the reaction $X-H + H$ are $.358 \pm .055$, $.288 \pm .049$ and $.278 \pm .047$. Clearly the reaction $X-H + H$ where $X = D$ and Δ has a lower trajectory mean reaction probability. The number of trajectories which reach the DS are 220, 227 and 245 for the $H + H-X$ reaction and 231, 204 and 216 for the $X-H + H$ reaction. Since approximately the same number of trajectories reach the DS at .5ev for both reactions, the smaller values in the trajectory mean reaction probability for the $X-H + H$ reaction must be due to a greater number of nonreactive reflected trajectories. The numbers $\sum_{\text{even}} T_{n,0}^k$ for the $H + H-X$ series are 0, 0 and 3; for the $X-H + H$ series the corresponding numbers are

16, 31 and 49. That there are more nonreactive reflected trajectories for the $X-H + H$ series is apparent if the transmission coefficients for the two reactions are compared; the transmission coefficients for the $X-H + H$ reaction at .5ev being smaller. From our previous discussion of the $X + H-H \rightleftharpoons X-H + H$ reaction, we noticed that there is a segment on the .5ev contour (arc cd) in figures 6 - 8 that could return trajectories to the left side of the DS more efficiently than arc ab can return trajectories to the right side of the DS. Therefore, the greater number of nonreactive reflected trajectories for the reaction $X-H + H$ is not surprising. At .9ev however, the trend is reversed. The values of $\sum_{r \neq H} T_{n>c}^R$ are 117, 204 and 263 for the $H + H-X$ reaction and 87, 157 and 235 for the $X-H + H$ reaction. This is due to the greater length of arc a'b' compared to arc c'd'.

At .9ev the values of the trajectory mean reaction probability are $.607 \pm .078$, $.503 \pm .070$ and $.403 \pm .060$ for the $H + H-X$ reaction. Comparing the above numbers to the corresponding results for the $X-H + H$ reaction, we find the values of the trajectory mean reaction probability are larger for the reaction $H + H-X$ at .9ev, than they were at .5ev. The number of trajectories which reach the DS are 481, 506 and 505 for the $H + H-X$ reaction and 423, 422 and 359 (from a sample of 600 trajectories) for the $X-H + H$ reaction. Thus at .9ev there are more trajectories which reach the DS for the reaction $H + H-X$. This is because arcs c'd' in figures 9 and 10 are more effective in helping trajectories reach the DS for the

reaction $H + H-X$ than arcs $a'b'$ (figures 7 and 8) are for the reaction $X-H + H$. There is also the effect of arc $b'c'$ at returning trajectories with a large amount of vibrational energy back to reactants ($X-H + H$) before they reach the DS. We have noticed that at .5ev the number of reflected trajectories originating from reactants are greater for the reaction $X-H + H$ than for the reaction $H + H-X$, and at .9ev the trend is reversed. For the same reasons given above we also note that the number of reflected trajectories originating from products is greater at .5ev for the reaction $H + H-X$ than for the reaction $X-H + H$, with the trend being reversed again at .9ev. It is consistent with this observation then that $\mathcal{N}(.5)$ is smaller for the former reaction and $\mathcal{N}(.9)$ is smaller for the latter reaction. We would expect this trend to be reversed for $\mathcal{N}(E)$. It is, except for the reactions $H + H-\Delta$ and $\Delta-H + H$ at .9ev. This is because a larger fraction of the trajectories which reach the DS for the reaction $H + H-X$ are reactive (although there are also more reflected trajectories).

We have noticed that with the exception of the reactions $H + H-\Delta$ and $\Delta + H-H$ at .9ev, the trajectory mean reaction probabilities for the reactions $X + H-H$ and $H + H-X$ are approximately equal. From the principle of microscopic reversibility we also know that the trajectory mean reaction probability for the reaction $H-H + X$ is greater than the values for the reaction $H + H-X$. Therefore, the trajectory mean reaction probability for the reaction $H-H + X$ is larger than the corresponding values for the reaction $X + H-H$ or $H + H-X$.

It is interesting to compare the energy distributions for the $H + H-X$ and $X-H + H$ reactions. The quantity $F_{vib}^{\delta c}(E)$ for the reaction $X-H + H$ is smaller than $F_{vib}^{\delta c}(E)$ for the reaction $H + H-X$. We expected this in light of our previous discussion of the effects of arc bc and $b'c'$. At .5ev, $F_{vib}^{\delta c}(.5)$ is about the same for the series of reactions $H + H-X$ ca. .673. For the reactions $X-H + H$, the values of $F_{vib}^{\delta c}(.5)$ are similar for $X = D$ and Δ (ca. .452) and slightly larger for $X = H$ (.550). It may seem unusual that there are more nonreactive reflected trajectories (30 more) for the reaction $H + H-H$ than for the reaction $H-H + H$ yet $F_{vib}^{\delta c}(.9)$ is larger for the former reaction. We point out however that the reaction $H-H + H$ has 52 more trajectories that don't reach the DS, many of which are reflected by arc $b'c'$ with relatively large amounts of translational energy. The quantity $F_{vib}^{\delta b}(E)$ like $F_{vib}^{\delta c}(E)$ is less for the $X-H + H$ reaction than for the reaction $H + H-X$ at .5 and .9ev for $X = H, D$ and Δ . This result is expected and was explained in our discussion of the $X + H-H$ reaction. We also find that the reverse reaction ($H-H + X$) has smaller values of $F_{vib}^{\delta c}(E)$ and $F_{vib}^{\delta b}(E)$ at .5 and .9ev than the corresponding values for the reaction $H + H-H$. From the above discussion, this is expected. Since the same relationship for $F_{vib}^{\delta b}(E)$ and $F_{vib}^{\delta c}(E)$ between the forward and reverse reactions for $X + H-H$ were also found, we can say that for the series of reactions $X + H-H \rightleftharpoons X-H + H$ and $H + H-X \rightleftharpoons H-H + X$, translational energy is required in order for a trajectory to be reactive. This translational energy is then converted to vibrational energy on the left side of the DS.

IIID Trajectory and Phase Space Analysis for the $X + H-H \rightleftharpoons$
 $X-H + H$ Reaction on the London-Eyring-Polanyi-Sato (LEPS)
 Surface.

For this and other series of reactions on the LEPS surface the forward reaction is endothermic and the reverse reaction is exothermic ($\Delta E = .828\text{ev}$). Trajectories were run for the forward reactions at a total energy of 1.078 and 1.328ev. Trajectories were run for the reverse reaction at a total energy of .25 and .5ev. The activation energies for the forward and reverse reactions are .904 and .076ev respectively. The saddle point for the LEPS and PW surfaces are both located in the entrance valley for the forward reactions for all series that will be discussed. For both the forward and reverse reactions the differences between the total energy and the activation energy on the LEPS surface are .174 and .424ev compared to the corresponding values of .104 and .504ev on the PW and PK surfaces.

The trajectory mean reaction probabilities for the forward reaction at 1.078ev are $.235 \pm .043$, $.287 \pm .049$ and $.307 \pm .051$. The corresponding number of trajectories to reach the DS are 184, 223 and 259. It is worthwhile to mention that the number of trajectories to reach the DS on the LEPS and PW surfaces are about the same, but less than the number that reaches the DS on the PK surface even though the energy above the saddle point is 1.67 times greater on the LEPS surface. This is easily explained in terms of arc bc shown in figures 11 - 13. As mentioned previously, this arc can return trajectory-

ies to reactants before they reach the DS. The number of non-reactive reflected trajectories (43, 51 and 75) are much larger than the corresponding number at .104ev for the PW or PK surface. It is clear that arc ab in figures 11, 12 and 13 are very effective in returning trajectories back across the DS. It was brought up in our discussions of the PW surface that this arc has forces which are perpendicular to it which point toward reactants in a direct manner. The quantity $\chi(1.078)$ for this series has the values .701, .604 and .535; much smaller than the values of $\chi(.5)$ for either the PK or PW surfaces. We also note that the quantity $\mathcal{N}(1.078)$ is 1 for the series. This is greater than $\mathcal{N}(.5)$ for the same series of reactions on the PW and PK surface except for the H + H-H reaction on the PK surface which also has the value of one for $\mathcal{N}(.5)$. The arc on the LEPS surface at 1.078ev which returns trajectories to the product side of the DS is arc cd. From our discussion of the results of the PW surface we noticed that at .5ev, arc ab was not as effective as arc cd at returning trajectories to the opposite side of the DS. It is therefore consistent with our results on the PW surface that $\mathcal{N}(1.078)$ should be large. For the reverse reaction (X-H + H) we note that $\chi(1.078) > \mathcal{N}(1.078)$ for the series; exactly the opposite of the result we found for the reverse reaction on the PW surface at .5ev. At 1.328ev the trajectory mean reaction probabilities for the series are .437 $\pm$.063, .387 $\pm$.059 and .355 $\pm$.055. Thus, in contrast to the results at 1.078ev, the trajectory mean reaction probabilities appear to be decreasing.

The number of trajectories which reach the DS within the series are 367, 373 and 387. Thus approximately the same number reach the DS at 1.328ev compared to an increasing number within the series at 1.078ev. The decrease in the trajectory mean reaction probability therefore is due to increasing amounts of nonreactive reflected trajectories (105, 141 and 174). This is paralleled by the increasing number of reflected trajectories for the reverse reaction. We remind the reader that nonreactive trajectories for the reverse reaction on the PW surface, and the forward reaction on the LEPS surface are being reflected by a similar type of contour; i.e. arcs cd and ab respectively. The number of trajectories originating from products that are reflected ($T_{n,i}^p$) are 8, 87 and 230. This is readily understandable in terms of the larger length of arc c'd' compared to arc cd. The fact that $\mathcal{N}(1.328)$ decreases within the series is a consequence of the increasing number of reflected trajectories and increasing length of arc c'd'. The quantity $\chi(1.328)$ also decreases due to the increased number of reflected trajectories originating from reactants.

We notice that for the forward reaction $F_{Vib}^{bc}(1.078)$ is ca. .572 and for the reverse reaction $F_{Vib}^{ac}(.25)$ is ca. .944. The explanation for this is the same as we presented in our discussion of the PW surface. For the forward reaction arc bc returns trajectories originally possessing a large amount of translational energy back to reactants with little change in translational energy. Nonreactive trajectories originating from products are returned to products by forces perpendicular to arc cd. These forces are not pointed in the

direction of the DS as directly as those of bc; thus they generally have less translational energy. We also note that $F_{vi6}^{bc}(.25)$ is very large because nearly all the trajectories are reactive ($\bar{P}_r^{\dagger}(.25) = 1$). Thus only the trajectories which have a large amount of vibrational energy are unable to pass over the small barrier. The quantity $F_{vi6}^{bc}(.5)$ for the reverse reaction is also greater than $F_{vi6}^{bc}(1.328)$ for the forward reaction except for the reaction $\Delta + H-H \rightleftharpoons \Delta-H + H$ where they are approximately the same. The quantity $F_{vi6}^{AB}(E)$ is approximately equal within the series at the same energy for the reverse reaction. This is true at 1.078ev in the forward direction but not at 1.328ev. At this energy $F_{vi6}^{AB}(1.328)$ decreases from $X = H$ to $X = D$ and increases from $X = D$ to $X = \Delta$. We can see that translational energy is being converted to vibrational energy at 1.078ev, but at 1.328ev the average vibrational energy of reactive molecules are about the same in the forward and reverse directions.

IIIE Trajectory and Phase Space Analysis for the $H + H-X$

$\rightleftharpoons H-H + X$ Reactions on the LEPS Surface.

The results for the forward and reverse reactions $H + H-X \rightleftharpoons H-H + X$ are given in tables 11 and 12. The skewed LEPS surfaces are shown in figures 11, 14 and 15.

At 1.078ev, the trajectory mean reaction probabilities for the forward reaction for $X = H$ is slightly larger than the value for the other two reactions in the series. The number of trajectories which reach the DS and the number of nonreactive reflected trajectories are approximately the same within the series. We notice that the scale factors (units per inch) in figures 12 and 14 are similar; as they are on figures 13 and 15. Thus arc length bc (and $b'c'$) is significantly longer for the reaction $H + H-X$ than for the reaction $X + H-H$. The fact that less trajectories are reaching the DS for the reaction $H + H-X$ (for $X = D$ and Δ) at both energies is therefore understandable. As for the reaction $X + H-H$ on the LEPS surface at 1.078ev, there are more trajectories being reflected in the forward direction. The reason for this was explained previously. The trajectory mean reaction probability at 1.328ev decreases, as does the number of trajectories which reach the DS. The number of nonreactive reflected trajectories increases for the forward and reverse reactions within this series.

The trajectory mean reaction probability for the reactions $X-H + H$ and $H-H + X$ are all relatively large compared to the forward reactions. There is a larger difference in the traj-

ectory mean reaction probabilities between the reactions $H + H-X$ and $H-H + X$ than between the reactions $X + H-H$ and $X-H + H$ for $X = D$ and Δ . This is because the difference in energy between the reactants and products (.828ev) as well as the mass combinations for each reaction both work to decrease the weighting factor ($\omega(E)$).

The quantity $F_{vib}^{bc}(E)$ is less for the forward reaction compared to the reverse reaction for the same reasons given in the discussion of the LEPS surfaces for the reaction $X + H-H$. It is interesting to note that $F_{vib}^{bc}(E)$ is less for the reaction $H + H-X$ than it is for the reaction $X + H-H$. This is attributable to the longer length of arcs bc and $b'c'$. For the reaction $H + H-D$, $F_{vib}^{ab}(1.328)$ is not significantly different for the forward or reverse reactions. For the reaction $H + H-\Delta$ the values of $F_{vib}^{ab}(E)$ are larger for the reverse reaction at both energies. Thus vibrational energy is being converted to translational energy for this reaction.

IIIF Trajectory and Phase Space Analysis for the $H + X-H \rightleftharpoons H-X + H$ Reactions on the PK Surface

The results for this series of reactions are given in table 13. Since the PK surface is symmetrical, the forward and reverse reactions are identical; i.e. $H + X-H \equiv H-X + H$. Thus T_n^f and T_n^r are the same. The trajectory mean reaction probabilities for this series at .5ev are $.425 \pm .062$, $.358 \pm .056$ and $.305 \pm .050$. The number of trajectories which reach the DS from the reactant region are 255, 215 and 183. All trajectories which reach the DS are reactive ones. The skewed potential energy surfaces shown in figures 3, 16 and 17 have no forces perpendicular to the .5ev contour which could direct trajectories to the opposite side of the DS. We therefore are not surprised that there are no reflected trajectories and that the values of $\chi(.5)$ are unity. Since the reverse reaction is identical to the forward reaction, the values of $\chi(.5)$ are also unity. At .9ev, the trajectory mean reaction probabilities are $.702 \pm .087$, $.778 \pm .094$ and $.852 \pm .100$. Thus at higher energies the trajectory mean reaction probability increases, contrary to the trend at .5ev. We notice that at .9ev, the number of trajectories which reach the DS remains about the same within the series. The reaction probability increases in the series due to a decrease in the number of reflected trajectories.

From table 13 we see that for the reaction $H + \Delta-H$ at .9ev there are no reflected trajectories. To explain this trend, we look at figures 3, 16 and 17. We see that as the mass of the middle atom increases, the skew angle increases

and the forces perpendicular to the arcs which could return trajectories to the DS are not pointed in the direction of reactants in as direct a manner as they are at smaller skew angles. We also notice that as the skew angle increases, the length of arcs ab in this series decreases. Thus the number of reflected trajectories decreases, and $\chi(.9)$ and $n(.9)$ increase for the series.

The quantities $F_{vib}^{\beta c}(.5)$ and $F_{vib}^{A\beta}(.5)$ decrease within this series. Earlier we noticed that in this series the number of trajectories which reach the DS decreases at .5ev. Thus as the skew angle increases, trajectories require more translational energy to reach the DS. At .9ev, $F_{vib}^{A\beta}(.9)$ remains about the same within the series but is higher than $F_{vib}^{A\beta}(.5)$. Therefore, reactive trajectories require less translational energy at .9ev than at .5ev. The increase in the quantity $F_{vib}^{\beta c}(.9)$ with the mass of the middle atom is expected since there is a decrease in the number of nonreactive reflected trajectories, which generally have more translational energy than nonreactive trajectories which do not reach the DS.

IIIG Trajectory and Phase Space Analysis for the $X + H-X \rightleftharpoons X-H + X$ Reactions on the Porter Karplus Surface

Results for this series of reactions are presented in table 14 and the skewed surfaces are given in figures 3, 18 and 19. The trajectory mean reaction probability appears to increase from $X = H$ to $X = D$ and then decrease from $X = D$ to $X = \Delta$. We can explain this trend by examining the number of trajectories which reach the DS and the number of nonreactive reflected trajectories. The values of the former are 255, 278 and 417; the results for the latter are 0, 0 and 192. Thus the number of trajectories which reach the DS in the series increases, and there are reflected trajectories (reactive and nonreactive) only for the reaction $\Delta + H-\Delta$. We do not expect any reflected trajectories for the reaction $H + H-H$ since there are no regions on the .5ev contour on the product side of the DS where forces can return trajectories to the DS. There is a small arc of this type on the .5ev contour for the reaction $D + H-D$, but it is ineffective. However, the skewed surface for the reaction $\Delta + H-\Delta$ given in fig. 19 shows a much larger arc on the .5ev contour which can return trajectories to the DS. We also note that a small region on the .4ev contour which is only .0039ev above the saddle point, can also return trajectories to the DS. Since the skew angle for the $\Delta + H-\Delta$ reaction is 24.62° , the forces perpendicular to this arc point toward the DS in a very direct manner. In fact the forces on a large part of the arc ab are almost perpendicular to the DS. It is therefore not surprising to find that for $X = \Delta$, many trajec-

tories which reach the DS are reflected. Since there are no reflected trajectories for $X = H$ and D , $\chi(.5)$ and $\eta(.5)$ are both unity.

It is interesting to note that for the reactions $X + H-X$ and $H + X-H$ the number of trajectories which reach the DS increases as the skew angle decreases at .5ev. The number of reflected trajectories also follows this trend at .5ev and .9ev for the two series of reactions.

The number of trajectories which reach the DS at .9ev is relatively constant for both series of reactions. As mentioned before, the number of reflected trajectories increases when the skew angle decreases. The trajectory mean reaction probability decreases from $X = H$ to $X = D$ and increases from $X = D$ to $X = \Delta$, the opposite of the trend at .5ev. While the majority of reflected trajectories for the reactions $H + H-H$ and $D + H-D$ are nonreactive, there are comparatively more reactive reflected trajectories for the reaction $\Delta + H-\Delta$. Since the number of reflected trajectories increases in the series, $\chi(.9)$ and $\eta(.9)$ show a decrease in the series.

The quantity $F_{vib}^{8c}(.5)$ remains about the same for $X = H$ and D , and is smaller for $X = \Delta$. The smaller result for $X = \Delta$ is due to the large number of nonreactive reflected trajectories. The trend in $F_{vib}^{A8}(.5)$ follows the trend in the trajectory mean reaction probability as it did for the series $H + X-H$. At .9ev, the quantities $F_{vib}^{A8}(.9)$ show an increasing trend. The quantity $F_{vib}^{8c}(.9)$ decreases from $X = H$ to $X = D$ because there are more nonreactive reflected trajectories for the reaction $D + H-D$ than for the reaction $H + H-H$.

There is an increase in $F_{vib}^{6c}(.9)$ from $X = D$ to $X = \Delta$ because there are fewer reactive reflected trajectories for the reaction $\Delta + H-\Delta$ than for $D + H-D$. Comparing $F_{vib}^{6c}(.9)$ for the reaction $H + H-H$ and $\Delta + H-\Delta$ we see that $F_{vib}^{6c}(.9)$ is smaller for the latter reaction. This is because there are more non-reactive reflected trajectories and less nonreactive trajectories which do not reach the DS for the reaction $\Delta + H-\Delta$.

IIIIH Trajectory and Phase Space Analysis for the $H + X-H \rightleftharpoons H-X + H$ Reaction on the Polanyi-Wong Surface

The results for the forward and reverse reactions for this series are presented in tables 15 and 16. As was the case for the series of reactions $X + H-H \rightleftharpoons X-H + H$, the barrier for the forward reaction is in the entrance valley. The skewed Polanyi-Wong (PW) surfaces for the series are given in figures 6, 20 and 21. The trends for the forward reaction at both values of E are very similar to the trends for the corresponding series of reactions on the PK surface. We note for example that at .5ev, there is a decreasing trend in the trajectory mean reaction probability and the number of trajectories which reach the DS. Thus the relationship between the skew angle and the number of trajectories which reach the DS is the same as it is on the PK surface. The reason there are no reflected trajectories at .5ev is evident from figures 6, 20 and 21. Figure 6 shows a small arc (ab) which could return trajectories to the DS. As we mentioned in our discussion of the $X + H-H$ series for the PW surface, forces perpendicular to arc ab do not return any trajectories in our sample to the DS for $X = H$. The reactions $H + D-H$ and $H + \Delta-H$ do not have an arc of the type ab on the .5ev contour, therefore we expect no reflected trajectories for the forward reaction. The quantity $\gamma(.5)$ is therefore unity, as it was on the PK surface. The results for the reverse reaction given by table 16 show a small number of reflected trajectories (16, 9 and 3) for the series. The reason we

have reflected trajectories for the reverse reaction is because the forces perpendicular to arc cd are pointed more directly toward the DS than arc ab. Due to the small number of reflected trajectories however, $\mathcal{N}(.5)$ is large.

At .9ev the trend in the trajectory mean reaction probability increases for the series, although only slightly from $X = D$ to $X = \Delta$. We also note that the number of trajectories which reach the DS is approximately the same for the series. Thus the trend in the trajectory mean reaction probability and the number of trajectories which the DS is the same as it is on the PK surface. The trend in the number of reflected trajectories for the forward reaction is also the same as it was on the PK surface. As the skew angle increases, the number of reflected trajectories and arc a'b' decreases for the reaction $H + X-H$. The trend in the quantity $\chi(.9)$ is therefore also the same as it is on the PK surface, i.e. it is unity for the reaction $H + \Delta-H$ and decreases as the mass of the middle atom and skew angle decreases. At .9ev, arcs c'd' become larger than arc cd at .5ev. Therefore the number of reflected trajectories for the reaction $H-X + H$ increases. At .9ev, the trend in the number of reflected trajectories originating from reactants and products is the same for the reaction $H + X-H \rightleftharpoons H-X + H$. The quantities $\mathcal{N}(.9)$ and $\chi(.9)$ therefore both have the same trend.

We notice that $F_{vib}^{AB}(.5)$ and $F_{vib}^{\delta C}(.5)$ decrease for the forward reactions on the PK and PW surfaces. There is an increase in $F_{vib}^{\delta C}(.5)$ in the reverse reaction, but $F_{vib}^{\delta C}(.5)$ is still less than the corresponding quantity for the forward reac-

tion. This is due to the decreasing number of nonreactive reflected trajectories for the reactions $H-X + H$ (there are no reflected trajectories from the forward reaction), the lack of forces perpendicular to the .5ev contour on the left side of the DS for $X = H$, and the effect of arc bc discussed previously. The quantity $F_{vib}^{AB}(.5)$ for the reverse reactions are similar to the results for $F_{vib}^{AB}(.5)$ on the PK surface. At .9ev, the trend in $F_{vib}^{BC}(.9)$ is the same as it was on the PK surface; i.e. they both increase for the forward and reverse reactions. The quantity $F_{vib}^{AB}(.9)$ remains about the same for the reverse reaction and decreases for the forward reaction. Summarizing the results for the energy distributions for the forward and reverse reactions on the PW surface, we see that trajectories originating from reactants require a large amount of translational energy in order to react. We also note that this translational energy is converted to vibrational energy on the left side of the DS.

IIII Trajectory and Phase Space Analysis for the $X + H-X \rightleftharpoons X-H + X$ Reactions on the PW Surface

As we noted previously, the trends for the series of reactions $H + X-H$ in the forward direction on the PW surface are similar to the trends for the corresponding series of reactions on the PK surface. The same is true for this series of reactions, the results of which are presented in tables 17 and 18. The trajectory mean reaction probability appears to increase from $X = H$ to $X = D$, then decreases from $X = D$ to $X = \Delta$ on both the PW and PK surfaces at .5ev. The number of trajectories which reach the DS increases slightly as it did on the PK surface for the first two reactions in the series, but increases only slightly again for the second and third reactions compared to a more dramatic increase on the PK surface. The trend in the number of reflected trajectories is the same on both surfaces. The numbers $T_{n>}^R$ are 0, 1 and 241 on the PW surface and 0, 0 and 195 on the PK surface. We can see from figures 6, 22 and 23 that arc ab increases for this series, accounting for the increased number of reflected trajectories. We also note that the region on the .4ev contour for the reaction $\Delta + H-\Delta$ capable of returning trajectories to the DS has a similar counterpart on the PK surface. There are more nonreactive reflected trajectories for the reaction $H-H + H$ and $D-H + H$ than for the corresponding reactions in the forward direction at .5ev because of the greater effectiveness of arc cd in returning trajectories to the DS. The number of reflected trajectories are about the same for $X = \Delta$ for the forward and reverse reactions. This is because of

the relatively large size of arc ab, the region on the .4ev contour capable of returning trajectories to the DS, and the direct manner in which the forces perpendicular to arc ab points toward the DS. The quantity $\chi(.5)$ for $X = H$ and D are 1 and .996, compared to the values 1 and 1 for the corresponding reactions on the PK surface. There is also a decrease in $\chi(.5)$ on the PW and PK surface for the reaction $\Delta + H-\Delta$, but the decrease is more dramatic on the PW surface. The values of $\chi(.5)$ for $X = \Delta$ are .057 for the PW surface and .534 on the PK surface. The quantity $\eta(.5)$ has the values .932, .886 and .528 compared to the values 1, 1 and .682 on the PK surface. Thus the trends in $\eta(.5)$ are also similar for the two surfaces.

At .9ev, the trajectory mean reaction probability decreases from $X = H$ to $X = D$ and increases from $X = D$ to $X = \Delta$. The results are the same on the PK surface. We also note that the number of trajectories which reach the DS are about the same at .9ev; this also being true for the PK surface. The numbers $T_{n>}^k$ are 143, 292 and 438 on the PW surface and 120, 278 and 553 for the corresponding reactions on the PK surface. The quantity $T_{n>}^f$ has the values 111, 225 and 396 for the PW surface and 120, 278 and 553 for the PK surface. It is interesting to note that the largest number of reflected trajectories for the reaction $\Delta + H-\Delta$ are of the type T_3^k on both the PW and PK surfaces at .9ev, and T_2^k at .5ev. We also note that $\chi(.9)$ and $\eta(.9)$ decrease sharply from $X = H$ to $X = \Delta$ and remain about the same for $X = D$ and Δ . The change in these two quantities are larger on the PK surface for $X = D$ and Δ .

The quantity $F_{vib}^{bc}(.5)$ is about the same for the first two reactions in the series, and then decreases for $X = \Delta$. This is also true for the PK surface. The decrease in $F_{vib}^{bc}(.5)$ for the reaction $\Delta + H-\Delta$ on both surfaces is due to the large number of trajectories of the type T_{λ}^R . The values of $F_{vib}^{bc}(.5)$ for the reverse direction are about the same for the first and third reactions and less for the reaction $D + H-D$. The effect of arc bc causes $F_{vib}^{bc}(E)$ to be less at .5 and .9ev for the reverse reaction compared to the forward reaction. The one exception is for the reactions $D + H-D$ and $D-H + D$ at .5ev where $F_{vib}^{bc}(.5)$ is about the same. At .9ev we notice the same trend in $F_{vib}^{bc}(.9)$ for the PK and PW surfaces for the series; i.e. decreasing from $X = H$ to $X = D$, then increasing from $X = D$ to $X = \Delta$. The reason for the increase in the latter on the PW surface is that there are more nonreactive trajectories not reaching the DS than nonreactive reflected trajectories having relatively little vibrational energy. There are less of the former types of trajectories on the PK surface so $F_{vib}^{bc}(.9)$ does not rise as sharply from $X = D$ to $X = \Delta$. The quantities $F_{vib}^{AB}(.5)$ and $F_{vib}^{AB}(.9)$ are less for the reverse reaction than they were for the forward reaction for this series except for the reaction $\Delta + H-\Delta \rightleftharpoons \Delta-H + \Delta$ where they are about the same. This is the same trend we noticed for the series $H + X-H$ on the PW surface, and again reminds us that translational energy is necessary for trajectories to react in the forward reaction and that translational energy is converted to vibrational energy on the left side of the DS.

IIIJ Trajectory and Phase Space Analysis for the $H + X-H \rightleftharpoons H-X + H$ Reactions on the LEPS Surface

The results for the forward and reverse reactions will be found in tables 19 and 20 respectively. The trajectory mean reaction probabilities for this series of reactions decreases at 1.078ev (.174ev above the saddle point). We also note that the number of trajectories which reach the DS and the number of reflected trajectories both decrease. In our discussion of this series of reactions for the PK and PW surfaces at .104ev above the saddle point, we found that the number of trajectories which reach the DS also decreased with increasing skew angle. The decreasing size of arc ab in figures 11, 24 and 25 for the series suggests the reason for the decrease in reflected trajectories. We can see from these three figures that only the reaction $H + H-H$ has an arc cd on the 1.078ev contour. Therefore only the reverse reaction $H-H + H$ is capable of having reflected trajectories at this energy. From table 19 we see that the number of reflected trajectories originating from the reverse reaction is 1, 0 and 0. Since the weighting factor is relatively small (.2601), the one reflected trajectory from the reaction $H-H + H$ is counted as zero and $\chi(1.078)$ is 1 for the series. The quantity $\chi(1.078)$ increases because the number of reflected trajectories originating from the forward reaction decreases.

At 1.328ev (.424ev above the saddle point) the trajectory mean reaction probability does not change significantly for this series in contrast to the increase in this quantity for the same series of reactions on the PW and PK surfaces

at an energy of .504ev above the saddle point. The trend in the number of trajectories which reach the DS and the number of reflected trajectories from the forward reaction is the same as it was at 1.078ev; i.e. both decrease. However, the number of trajectories which reach the DS decreases in approximate proportion to the number of nonreactive reflected trajectories. Therefore there is little change in the trajectory mean reaction probability. Since the trend in the number of reflected trajectories from the forward reaction is the same at both energies, $\chi(1.328)$ and $\chi(1.078)$ both decrease. From figures 11, 24 and 25 we can see that the length of arc c'd' decreases for the series $X = H$ to $X = D$ and is zero for $X = \Delta$. Therefore we expect the number of nonreactive reflected trajectories originating from the reverse reaction to decrease. In fact only the reaction $H-H + H$ at 1.328ev has reflected trajectories. Because of the relatively large skew angle for the reaction $H + D-H$ at 1.328ev (70.53°), the direction of the forces perpendicular to arc c'd' are not pointed toward the DS as directly as on the c'd' arc for the reaction $H + H-H$ shown in figure 11. This explains why there are no reflected trajectories for the reaction $H-D + H$. The 8 reflected trajectories for the reaction $H-H + H$, and zero reflected trajectories for the reaction $H-\Delta + H$, both at 1.328ev, are also understandable from the above discussion. Since only the former reaction has reflected trajectories, $\eta(1.328)$ is less than 1 (.992) only for this reaction.

The quantity $E_{\text{eff}}^{\text{K}}(E)$ is relatively constant for the series at 1.078ev but increases at 1.328ev due to the decrease in

the number of nonreactive reflected trajectories. We also note that the values of $F_{\text{vib}}^{\text{R}}(E)$ are significantly larger for reactions in the reverse direction. At 1.078 eV, $F_{\text{vib}}^{\text{R}}(E)$ remains approximately the same for $X = \text{H}$ and $X = \text{D}$ and appears to decrease slightly from $X = \text{D}$ to $X = \Delta$. At 1.328 eV $F_{\text{vib}}^{\text{R}}(E)$ decreases from $X = \text{H}$ to $X = \text{D}$ and increases from $X = \text{D}$ to $X = \Delta$. Since the values of $F_{\text{vib}}^{\text{F}}(E)$ for the forward reaction are larger than the corresponding values for the reverse direction at both energies, translational energy in the forward reaction is converted to vibrational energy in the reverse reaction.

IIIK Trajectory and Phase Space Analysis for the $X + H-X \rightleftharpoons X-H + X$ Reaction on the LEPS Surface.

From table 21 for the forward reaction we can see that the trend in the trajectory mean reaction probability for this series of reactions at .174ev above the saddle point is the same as it is on the PW and PK surfaces at .104ev above the saddle point. There appears to be an increase in the trajectory mean reaction probability from $X = H$ to $X = D$ and a decrease for $X = D$ to $X = \Delta$. The number of trajectories which reach the DS for this series are 184, 214 and 209, and the number of nonreactive reflected trajectories are 43, 68 and 189. Thus the small value for the trajectory mean reaction probability for the reaction $\Delta + H-\Delta$ is due to the fact that most of the trajectories that reach the DS are nonreactive. In fact there are no direct trajectories at all for this reaction. It is clear from figures 11, 26 and 27 that the reason for the increase in the total number of reflected trajectories is that the length of arc ab increases for this series and as the skew angle decreases the forces perpendicular to these arcs point toward the DS more directly. The result for the reverse reaction given by table 22 shows that T_n^p for the series are 1, 0 and 561. There are less reflected trajectories in the reverse reaction than the forward reaction for $X = H$ and D . This is understandable in light of our previous findings that contour ab is more effective than contour cd at returning trajectories to the DS. It appears that for the reaction $\Delta + H-\Delta$ this trend is reversed. We note however that there are more trajectories which reach the DS from the reverse reaction

than from the forward reaction for the series at both energies (because of the effect of arc bc). As noted previously, there are no direct trajectories from the forward reaction while there are 2 for the reverse reaction. Therefore arc ab is at least as effective in returning trajectories to the DS as arc cd; consistent with the other two reactions in this series. From the above discussion of reflected trajectories for the forward and reverse reactions, it is clear that $\chi(1.078)$ decreases for the series and that $\eta(1.078)$ is unity for $X = H$ and D and relatively small (.576) for $X = \Delta$.

At 1.328ev (.424ev above the saddle point) the trend in the trajectory mean reaction probability is again similar to the trend for the same series of reactions on the PW and PK surfaces at an energy of .504ev above the saddle point. We see that from $X = H$ to $X = D$, the trajectory mean reaction probability decreases, and then increases from $X = D$ to $X = \Delta$. We also note that the number of trajectories which reach the DS remains about the same, and the number of reflected trajectories increases within the series as it did with the PW and PK surface. For the reaction $H + H-H$ and $D + H-D$, the majority of reflected trajectories are nonreactive but for the reaction $\Delta + H-\Delta$ the largest value of T_n^R is T_3^R (174). Thus there are more reflected trajectories for the reaction $\Delta + H-\Delta$ than for the other two reactions, but most of them are reactive. It is interesting to note that for the LEPS, PW and PK surfaces the largest value of T_n^L for the low energy trajectories is T_λ^L , and the largest value of T_n^L for high energy

trajectories is T_3^K . The number of reflected trajectories for the reverse reaction follows approximately the same trend as the number of reflected trajectories in the forward reaction for the series at 1.328ev. Therefore $\chi(1.328)$ and $\eta(1.328)$ both decrease.

We note that $F_{vib}^{\beta C}(E)$ seems to decrease. We can explain this by noting the increase in the number of nonreactive reflected trajectories for the series at both energies except from $X = D$ to $X = \Delta$ at 1.328 where the number of nonreactive reflected trajectories decreases. We also see that $F_{vib}^{\beta C}(E)$ is greater for the reverse reaction than for the forward reaction except for the reaction $D + H-D$ at 1.328ev. This can be explained by noting that there are more nonreactive reflected trajectories for the forward reaction except for the reaction $D + H-D$ at 1.328ev. The quantity $F_{vib}^{\alpha B}(1.078)$ remains about the same for $X = H$ and $X = D$ and increases from $X = D$ to $X = \Delta$. At 1.328ev the value of $F_{vib}^{\alpha B}(E)$ remains approximately constant for the series. It is interesting to note that for the first three entries of $F_{vib}^{\alpha B}(E)$ in table 18 are larger than the corresponding values in table 19. This trend is reversed for the latter three entries. Thus it appears that as the mass of X becomes larger, vibrational energy becomes more important for reacting systems for symmetrical masses of the type $X + H-X \rightleftharpoons X-H + X$.

IIIL Trajectory and Phase Space Analysis for the $X + X-H \rightleftharpoons X-X + H$ Reactions on the PK Surface

The results for the forward and reverse series of reactions are given by tables 23 and 24 respectively. Because of the symmetry of the PK surface, the results for the reactions $H + X-X$ and $X-X + H$ given by table 24 are equivalent. The trajectory mean reaction probabilities for the series of reactions at .5ev are $.425 \pm .062$, $.412 \pm .061$ and $.477 \pm .067$. The number of trajectories which reach the DS for this series at .5ev are 255, 247 and 286. Since all of these trajectories are reactive, the trend in the trajectory mean reaction probability at .5ev is determined by the number of trajectories which reach the DS. The skewed surfaces given by figures 3, 28 and 29 show that there is no portion of the .5ev contour on the product side of the DS capable of returning trajectories to the reactant region; consistent with the fact that there are no reflected trajectories. At .9ev, the number of trajectories which reach the DS are 526, 525 and 517. The values of T_{FVEU}^R are 105, 42 and 0. Thus the trajectory mean reaction probability appears to increase at .9ev because the number of nonreactive reflected trajectories decrease while the number of trajectories which reach the DS are about the same for the series. We can explain the decrease in the number of nonreactive reflected trajectories by noting that the forces perpendicular to arc $a'b'$ in figures 28 and 29 are not pointed in the direction of reactants in as direct a manner as the corresponding arc for the $H + H-H$ reaction shown in figure 3. From the above discussion it is also

clear that $\chi(.5)$ is unity, and $\chi(.9)$ increases for the series.

At both energies the number of trajectories which reach the DS for the reactions $X-X + H$ decreases for the series except for $X = H$ and D at .9ev where $T_{00D_{\Delta I}}^P + T_{E_{\text{VEN}_{\Delta I}}^P}$ are about the same. The most dramatic decrease at .5 and .9ev occurs from $X = D$ to $X = \Delta$. The reason for this is apparent when we look at figure 29. The relatively large length of arc $b'c'$ can return more trajectories to reactants ($\Delta - \Delta + H$) than can arc $b'c'$ in figure 28. The length of arc $b'c'$ in figure 3 is zero. We also note that the forces perpendicular to arcs cd and $c'd'$ in figures 28 and 29 are pointed toward the DS more directly than are the forces on the corresponding arc in figure 3. The length of arc cd increases from $X = D$ to $X = \Delta$ and is zero for the corresponding arc in figure 3. Thus we are not surprised that the number of reflected trajectories (most of which are nonreactive) increases for the reactions $X-X + H$ at both energies. From our discussions of the series of reactions $X + H-H \rightleftharpoons X-H + H$ on the PK surface, we can also understand why there are more reflected trajectories for the reverse reaction than for the forward reaction for $X = D$ and Δ .

The quantity $F_{v_b}^{bc}(.5)$ is approximately constant for the reactions $X + X-H$. At .9ev, $F_{v_b}^{bc}(.9)$ increases. This increase is due to the decrease in the number of nonreactive reflected trajectories. We also note that $F_{v_b}^{bc}(E)$ is greater for the forward reaction than the corresponding values for the reverse reaction at both energies for $X = D$ and Δ . This is

consistent with the finding that there are more nonreactive reflected trajectories for the reverse reaction than for the forward reaction. At .5 and .9ev, the values of $F_{vl}^{AB}(E)$ for the forward reaction are very similar to the corresponding quantities for the reverse reaction. Thus the average vibrational energy of a reactant molecule originating in reactant phase space is approximately carried over into product phase space. For both the forward and reverse reactions, the values of $F_{vl}^{AB}(E)$ at .5 and .9ev are about the same within the series except at .5ev where $F_{vl}^{AB}(.5)$ appears to increase from $X = D$ to $X = \Delta$.

IIIM Trajectory and Phase Space Results for the $X + X-H \rightleftharpoons X-X + H$ Reactions on the PW Surface.

The results for the forward and reverse series of reactions are given in tables 25 and 26 respectively. The trajectory mean reaction probability for this series of reactions at .5ev appears to decrease from $X = H$ to $X = D$ and remains about the same for $X = D$ and $X = \Delta$. The corresponding values of the trajectory mean reaction probability on the PK surface were approximately the same for $X = H$ and $X = D$ and appeared to increase for $X = \Delta$. While the trend in the trajectory mean reaction probability at .5ev on the PK and PW surfaces are not the same, a comparison of tables 23 and 24 will show that on both surfaces there are no reflected trajectories at .5ev; i.e. the trajectory mean reaction probabilities are determined by the number of trajectories which reach the DS. The skewed surfaces for this series of reactions are given by figures 6, 30 and 34. We can see that the length of arc ab on the latter two figures is zero. Arc ab is present in figure 6, however as we have already explained in our discussion of the series of reactions $X + H-H$ on the PW surface, this arc is ineffective at returning trajectories to the DS. The lack of reflected trajectories at .5ev thus conforms to the above discussion. The trend in the trajectory mean reaction probability at .9ev on the PW and PK surfaces are the same; i.e. they both appear to increase. There are also other similarities; e.g. the number of trajectories which reach the DS are about the same for this series

on the PW surface, as it was on the PK surface, and the number of reflected trajectories decreases as the mass of X increases on both the PW and PK surface. We can see from figures 6, 30 and 31 that the length of arc $a'b'$ decreases for the series; thus the decrease in the number of reflected trajectories. Since the number of trajectories which reach the DS are about the same for this series at .9ev, the increase in the trajectory mean reaction probability for this series is due to a decrease in the number of nonreactive reflected trajectories, as was the case for the corresponding reactions on the PK surface. We also note that the number of reflected trajectories for the reverse reaction ($T_{n>1}^P$) decreases at .5 and .9ev (except for $X = D$ and $X = \Delta$ at .5ev where $T_{n>1}^P$ remains about the same). The explanation for this is that the lengths of arcs cd and $c'd'$ decrease for the series. From the above discussion, it is clear that $\chi(.5)$ is unity and $\chi(.9)$ increases for the series; the same trend we noticed on the PK surface. The quantity $\eta(.5)$ also behaves similarly on both surfaces; i.e. it remains about the same for $X = H$ and $X = D$ and appears to decrease for $X = \Delta$. At .9ev, $\eta(.9)$ for the PW surface stays about the same for $X = H$ and $X = D$ and decreases from $X = D$ to $X = \Delta$. For the corresponding reactions on the PK surface, we observe the same trend.

The quantity $F_{vis}^{8c}(.5)$ is approximately constant on the PW surface, as it was for the PK surface. We also note that $F_{vis}^{8c}(.9)$ increases, due to the decrease in the number of reflected trajectories for the series. The same is also true

for the corresponding reactions on the PK surface. Comparing tables 25 and 26 we can see that $F_{vib}^{bc}(E)$ is less for the reverse reaction than for the forward reaction at both energies. This is due to the effect of arcs bc and $b'c'$. We noticed a similar effect on the PK surface for $X = D$ and Δ . We can see that $F_{vib}^{ab}(E)$ is greater for the forward reaction than the reverse reaction at both energies. Thus translational energy on the reactant side of the DS is converted to vibrational energy on the product side of the DS. The vibrational energy distribution for reactant trajectories were about the same on both sides of the DS for the PK surface.

IIIN Trajectory and Phase Space Analysis for the $H + X-X \rightleftharpoons H-X + X$ Reactions on the PW surface.

The results for the forward and reverse reactions for this series are given in tables 27 and 28 respectively. At .5ev the trajectory mean reaction probability appears to decrease for this series, as it did for the corresponding reactions on the PK surface. All of the trajectories which reach the DS are direct at .5ev except for the one nonreactive reflected trajectory for $X = \Delta$. We can understand the trend in reflected trajectories by looking at the skewed surfaces given in figures 6, 32 and 33. As we mentioned previously, arc ab for the reaction $H + H-H$ is ineffective at returning trajectories to the DS. Arc ab is not present in figure 32 so we expect no reflected trajectories for the reaction $H + D-D$. Although the length of arc ab is very small in figure 33, the forces perpendicular to it point toward the DS more directly than do the forces perpendicular to arc ab in figure 6. Thus we see one reflected trajectory for $X = \Delta$ at .5ev because arc ab in figure 33 is more effective in returning trajectories to the DS than arc ab in figure 6. At .9ev the trajectory mean reaction probability is about the same for $X = H$ and $X = D$ but drops from $X = D$ to $X = \Delta$. From table 24 we can see a similar trend at .9ev on the PK surface. The numbers $T_{n>1}^R$ for the PW surface at .9ev decrease from $X = H$ to $X = D$ and increase from $X = D$ to $X = \Delta$. The explanation for this is the same as we gave for the reflected trajectories at .5ev except that the length of arc a'b' is much larger than the length of arc ab for this series.

The number of reflected trajectories originating from products decreases at both energies for the series due to the decreasing size of arcs cd and $c'd'$. Thus $\mathcal{N}(.5)$ and $\mathcal{N}(.9)$ decrease. When we compare the values of $\mathcal{N}(E)$ on the PW and PK surface we can see that they are approximately the same. From our previous discussion we realize that $\chi(.5)$ is unity for $X = H$ and $X = D$ and relatively large (.994) for $X = \Delta$. There is approximately the same trend on the PK surface where the values of $\chi(.5)$ are 1, .990 and .833 for the corresponding reactions. The quantity $\chi(.9)$ increases from $X = H$ to $X = D$ and decreases (for the reasons mentioned above) from $X = D$ to $X = \Delta$. On the PK surface $\chi(.9)$ is about the same for the first two reactions in the series and decreases for the reaction $H + \Delta \rightarrow \Delta$.

The quantity $F_{vb}^{8c}(.5)$ decreases for the series on the PK surface but is approximately the same on the PW surface. At .9ev $F_{vb}^{8c}(.9)$ appears to increase on the PW surface from $X = H$ to $X = D$ and decreases from $X = D$ to $X = \Delta$. There is a decreasing trend in $F_{vb}^{8c}(.9)$ for the corresponding reactions on the PK surface. We note that $F_{vb}^{8c}(E)$ for the reverse reaction is less than the corresponding values for the forward reaction for $X = H$ and $X = D$, but the trend is reversed for $X = \Delta$. This can be explained by noting that arcs bc and $b'c'$ which appears on the left side of the DS for the first two reactions in the series, is on the right side of the DS for the reaction $H + \Delta \rightarrow \Delta$. Thus arcs bc and $b'c'$ for the latter reaction is ineffective at returning nonreactive trajectories with relatively large amounts of translational energy to the

reactant region ($H-\Delta + \Delta$). The quantity $F_{vib}^{\delta c}(E)$ was less for the forward reaction than it was for the reverse reaction on the PK surface. Comparing $F_{vib}^{\delta b}(E)$ at both energies on the two surfaces we note that for the forward reaction $F_{vib}^{\delta b}(E)$ is less on the PK surface than the PW surface for the series; the trend being reversed for the reverse reaction. We also note that $F_{vib}^{\delta b}(E)$ is less for the reverse reaction on the PW surface than for the forward reaction as was the case for the series $X + X-H \rightleftharpoons X-X + H$. Thus reactive trajectories possess relatively large amounts of translational energy in the reactant region which is converted to vibrational energy in the product region.

IIIO Trajectory and Phase Space Results for the $X + X-H \rightleftharpoons$
 $X-X + H$ Reactions on the LEPS Surface.

The results for the forward and reverse reactions are given in tables 29 and 30. The trajectory mean reaction probability at 1.078 and 1.328ev increases for this series. We can see from table 29 that the number of trajectories which reach the DS increases and the number of reflected trajectories decreases as the mass of X increases. The skewed surfaces given by figures 11, 34 and 35 show a decrease in the lengths of arcs ab and a'b'. We also note a decrease in the lengths of arcs bc and b'c' (they are zero for the reaction $\Delta + \Delta-H$). From our previous discussions, a decrease in the lengths of arcs ab and a'b' suggest to us that we should expect a decrease in the number of reflected trajectories; which in fact occurs. We also realize that nonreactive trajectories which are reflected by arcs bc and b'c' tend to lower the average amount of vibrational energy present in nonreactive trajectories returning to reactants ($X + X-H$). Thus the decrease in the lengths of arcs bc and b'c' and the decrease in the number of reflected trajectories for the series at both energies is consistent with the corresponding increase in $F_{vib}^{BC}(E)$. It is informative to note that there are a larger number of reflected trajectories at both energies for the reaction $\Delta-\Delta + H$ compared to the other two reactions than one would expect by comparing the lengths of arcs cd and c'd' in figures 11, 34 and 35. A similar occurrence was present for the reaction $H + X-X$ on the PW surface. We recall that since

the lengths of arcs bc and b'/c' are zero in figure 35, trajectories which are reflected from arcs cd and $c'd'$ travel towards the DS more directly than trajectories reflected from the corresponding arcs in figures 11 and 34. The increase in $\chi(E)$ for the series at both energies, and the lower values of $\eta(E)$ for the reaction $\Delta + \Delta-H$ than for the other two reactions follow from the above discussion.

The quantity $F_{\text{vib}}^{\delta c}(E)$ for the forward reaction increases for the series at both energies for the reasons given previously. At 1.078 and 1.328 eV $F_{\text{vib}}^{A\delta}(E)$ is greater for the forward reaction than the reverse reaction. Thus, as we noticed on the PW surface for the same series of reactions, translational energy in the reactant region is converted to vibrational energy in the product region by reactive trajectories.

IIIP Trajectory and Phase Space Results for the $H + X-X \rightleftharpoons H-X + X$ Reactions on the LEPS Surface.

The results for the forward and reverse series of reactions are given in tables 31 and 32. The trajectory mean reaction probabilities and the number of trajectories which reach the DS decrease for the series at 1.078 and 1.328ev. We recall that this trend was reversed for the reactions $X + X-H \rightleftharpoons X-X + H$ on the LEPS surface. The number of reflected trajectories also decreases at both energies for this series except for $X = D$ and $X = \Delta$ at 1.078ev where they are about the same. It is interesting to compare the number of reflected trajectories for the reactions $H + \Delta-\Delta$ and $\Delta + \Delta-H$ at 1.078ev. There are 20 reflected trajectories for the former reaction and none for the latter reaction. This is because the length of arc ab is zero in figure 35. Another interesting result is that the number of trajectories which reach the DS is larger for the reaction $X + X-H$ than for the reaction $H + X-X$ for $X = D$ and Δ at both energies. This can be explained by looking at the skewed surfaces for the series given by figures 11, 36 and 37 and noting that the lengths of arcs bc and $b'c'$ decreases for the series $X + X-H$ and increases for the series $H + X-X$. Also the lengths of arcs ab and $a'b'$ which can direct trajectories originating from reactants to the DS decreases drastically for the latter reaction. The number of reflected trajectories for the reverse reaction decreases from $X = H$ to $X = D$ at both energies. The decrease in the lengths of arcs ab and $a'b'$ are also

responsible for this occurrence. It is interesting that there are reflected trajectories for the reaction $H + \Delta - \Delta$ at both energies even though the lengths of arcs ab and $a'b'$ are zero in figure 37. We can still use the ideas of Pechukas to explain these reflected trajectories if we note arcs ef and $e'f'$ in figure 37. Since all trajectories which are reflected from these arcs are reactive (T_3^R), it is clear that these trajectories are first reflected by arcs ef and $e'f'$, and are sent in the direction of products by arcs cd and $c'd'$ (see figure 40). Since the number of reflected trajectories originating from products and the weighting factors ($\omega(E)$) are relatively small, the values of $\mathcal{N}(E)$ are relatively large for this series at both energies. We also note that the values of $\mathcal{N}(E)$ are similar to the corresponding values for the reactions $X + X-H$ except for $X = \Delta$ at 1.328ev. The quantity $\chi(1.078)$ increases from $X = H$ to $X = D$ and decreases from $X = D$ to $X = \Delta$. The reason for the former is that there are less reflected trajectories while the reason for the latter is that there are less trajectories which reach the DS for $X = \Delta$ than for $X = D$ while the number of reflected trajectories is almost the same. The quantity $\chi(1.328)$ is approximately the same for $X = H$ and $X = D$ and appears to be less for $X = \Delta$. It is clear from looking at the numbers T_n^R in table 31 that both the number of reflected trajectories and the number of reactive trajectories decrease in approximately the same proportion for the series at 1.328ev. However the value of T_4^R is 9 for the reaction $H + \Delta - \Delta$. This increases the number of transition states on the DS originating from reactants

and results in a lower value of χ (1.328).

The values of $F_{vib}^{bc}(E)$ appear to be decreasing for this series at both energies. These values of $F_{vib}^{bc}(E)$ are less than the corresponding values for the reverse reaction. As we mentioned before, the lower values of $F_{vib}^{bc}(E)$ for the forward reactions are due to the relatively large lengths of arcs bc and $b'c'$ and the greater number of nonreactive reflected trajectories for the forward reaction. We also note that the values of $F_{vib}^{bc}(E)$ for the reactions $H + X-X$ are less than the corresponding values for the reaction $X + X-H$ for $X = D$ and $X = \Delta$ at both energies. As we mentioned before the lengths of arcs bc and $b'c'$ increases for the series of reactions $H + X-X$ and decreases for the series $X + X-H$. Thus we are not surprised at these results. The quantity $F_{vib}^{ab}(E)$ is greater for the forward reaction than for the reverse reaction (only slightly larger for $X = \Delta$) at both energies. Thus for the reactions $H + X-X \rightleftharpoons H-X + X$ and $X + X-H \rightleftharpoons X-X + H$ on the LEPS and PW surfaces translational energy of reactant trajectories is converted partially to vibrational energy on the product side of the DS. On the PK surface however the energy distributions were about the same for the forward and reverse reactions.

TABLE 3
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+HH \rightleftharpoons XH+H$
for the THERMONEUTRAL PORTER-KARPLUS SURFACE

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$			
H+H-H	60.00	.5	.425 $^{+}_{-}$.062	ART	.418 $^{+}_{-}$.013	1	1	1	.425	.418 $^{+}_{-}$.013			
		.9	.702 $^{+}_{-}$.087		1.128 $^{+}_{-}$.036	.633 $^{+}_{-}$.026	.775	.817	1.146	.714 $^{+}_{-}$.037			
D+H-H	54.74	.5	.512 $^{+}_{-}$.070	ART	.486 $^{+}_{-}$.015	.997 $^{+}_{-}$.078	1	.997	.495	.485 $^{+}_{-}$.041			
		.9	.672 $^{+}_{-}$.085		1.308 $^{+}_{-}$.041	.495 $^{+}_{-}$.019	.725	.683	1.334	.647 $^{+}_{-}$.032			
Δ +H-H	47.61	.5	.557 $^{+}_{-}$.052	ART	.597 $^{+}_{-}$.019	.925 $^{+}_{-}$.068	1	.925	.601	.552 $^{+}_{-}$.044			
		.9	.535 $^{+}_{-}$.071		1.619 $^{+}_{-}$.051	.328 $^{+}_{-}$.013	.555	.590	1.620	.531 $^{+}_{-}$.027			
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{jk}^{BC}(E)$	$F_{jk}^{AB}(E)$				
H+H-H	.5	.418 $^{+}_{-}$.013	.425	.418 $^{+}_{-}$.013	.425	.418 $^{+}_{-}$.013	.425	.706	.240 $^{+}_{-}$.020				
	.9	1.128 $^{+}_{-}$.036	1.146	1.128 $^{+}_{-}$.036	1.146	1.128 $^{+}_{-}$.036	1.146	.714	.437 $^{+}_{-}$.037				
D+H-H	.5	.486 $^{+}_{-}$.015	.495	.492 $^{+}_{-}$.015	.499	.482 $^{+}_{-}$.015	.495	.733	.251 $^{+}_{-}$.030				
	.9	1.308 $^{+}_{-}$.041	1.334	1.322 $^{+}_{-}$.042	1.343	1.312 $^{+}_{-}$.041	1.336	.643	.523 $^{+}_{-}$.053				
Δ +H-H	.5	.597 $^{+}_{-}$.019	.601	.614 $^{+}_{-}$.019	.620	.585 $^{+}_{-}$.018	.602	.778	.300 $^{+}_{-}$.031				
	.9	1.619 $^{+}_{-}$.051	1.620	1.633 $^{+}_{-}$.051	1.670	1.614 $^{+}_{-}$.051	1.631	.595	.610 $^{+}_{-}$.043				
	E	T_n^R			$T_n^P \cdot \omega(E)$			$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>}^P$	$N_R^+(E)$	$\omega(E) \cdot N_R^+(E)$	$N_{\neq}(E)$
H+H-H	.5	255			255X1			255	255	0	255	0	255
	.9	406,103,15,2			406,103,15,2X1			421	526	120	543	122	665
D+H-H	.5	307			249,1X1.168			307	307	1	307	1	308
	.9	393,135,10,4			323,204,16,2X1.153			403	542	256	556	258	814
Δ +H-H	.5	334			264,20X1.353			334	334	27	334	27	361
	.9	300,212,17,7,4,2			205,278,12,1,1,1X1.354			321	542	397	578	402	980

* BASED on a SAMPLE of 1800 TRAJECTORIES

TABLE 4
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XH+H \rightleftharpoons X+HH$
for the THERMONEUTRAL PORTER-KARPLUS SURFACE

Masses	α (deg.)	E (ev)	$\bar{P}_r^{\tau}(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{vib}^{acc}(E)$	$F_{vib}^{th}(E)$		
H+H-H	60.00	.5	.425 ⁺ .062	ART	.418 ⁺ .013	1	1	1	.418 ⁺ .013	.706	.240 ⁺ .020		
		.9	.702 ⁺ .087		1.128 ⁺ .036	.633 ⁺ .026	.775	.817	.714 ⁺ .037	.714	.437 ⁺ .037		
H+H-D	54.74	.5	.415 ⁺ .061	ART	.420 ⁺ .013	.997 ⁺ .078	.997	1	.419 ⁺ .035	.694	.267 ⁺ .032		
		.9	.565 ⁺ .075		1.141 ⁺ .036	.488 ⁺ .019	.602	.809	.557 ⁺ .028	.547	.436 ⁺ .046		
H+H- Δ	47.61	.5	.439 ⁺ .045	ART	.434 ⁺ .014	.930 ⁺ .068	.930	1	.404 ⁺ .033	.608	.257 ⁺ .031		
		.9	.363 ⁺ .057		1.208 ⁺ .038	.309 ⁺ .012	.423	.731	.373 ⁺ .020	.491	.520 ⁺ .051		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>},$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.5	255			255			255	255	0	255	0	255
	.9	406,103,15,2			406,103,15,2			421	526	120	543	122	665
H+H-D	.5	249,1X1.168			307			291	292	0	292	0	292
	.9	323,204,16,2X1.153			393,135,10,4			391	628	149	649	153	802
H+H- Δ	*.5	264,20X1.353			334			357	384	0	384	0	384
	.9	205,278,12,1,1,1X1.354			300,212,17,7,4,2			295	674	242	697	257	954

* BASED on a SAMPLE of 1800 TRAJECTORIES

TABLE 5
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+HH \rightleftharpoons XH+H$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_r(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_r(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_r(E)_{PS}^{ACC}$			
H+H-H	60.00	.5	.367 ⁺ .057	ART	.375 ⁺ .015	.932 ⁺ .096	1	.932	.368	.350 ⁺ .039			
		.9	.607 ⁺ .078		1.100 ⁺ .038	.577 ⁺ .028	.682	.817	.990	.613 ⁺ .038			
D+H-H	54.74	.5	.335 ⁺ .053	SD	.436 ⁺ .017	.817 ⁺ .090	.995	.821	.435	.356 ⁺ .042			
		.9	.488 ⁺ .068		1.152 ⁺ .039	.420 ⁺ .021	.591	.712	1.171	.484 ⁺ .029			
Δ +H-H	47.61	.5	.380 ⁺ .058	SD	.512 ⁺ .020	.719 ⁺ .073	.966	.744	.521	.368 ⁺ .040			
		.9	.298 ⁺ .050		1.395 ⁺ .047	.208 ⁺ .010	.351	.592	1.402	.290 ⁺ .017			
	E	$\bar{P}_r(E)_{ART}^{ACC}$	$\bar{P}_r(E)_{ART}^{SVA}$	$\bar{P}_r(E)_{SD}^{ACC}$	$\bar{P}_r(E)_{SD}^{SVA}$	$\bar{P}_r(E)_M^{ACC}$	$\bar{P}_r(E)_M^{SVA}$	$F_{Vib}^{BC}(E)$	$F_{Vib}^{AB}(E)$				
H+H-H	.5	.375 ⁺ .015	.368	.381 ⁺ .015	.385	.366 ⁺ .015	.369	.669	.468 ⁺ .027				
	.9	1.100 ⁺ .038	.990	1.040 ⁺ .035	1.036	1.020 ⁺ .032	1.012	.702	.571 ⁺ .036				
D+H-H	.5	*.402 ⁺ .016	.391	.436 ⁺ .017	.435	.394 ⁺ .016	.395	.690	.591 ⁺ .034				
	.9	*19.34 ⁺ .611	1.051	1.152 ⁺ .039	1.171	1.118 ⁺ .035	1.110	.641	.695 ⁺ .039				
Δ +H-H	.5	*.464 ⁺ .019	.416	.512 ⁺ .020	.521	.436 ⁺ .014	.436	.688	.745 ⁺ .030				
	.9	*6.448 ⁺ .202	1.120	1.395 ⁺ .047	1.402	1.300 ⁺ .041	1.237	.515	.782 ⁺ .025				
	E	T_n^R			$T_n^P \cdot \omega(E)$			$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>1}^P$	$N_R^{\neq}(E)$	$N_P^{\neq}(E)$	$N_{\neq}(E)$
H+H-H	.5	220			215,16X1			220	220	16	220	16	236
	.9	338,94,23,22,3,1			318,83,19,4,5X1			364	481	111	534	120	654
D+H-H	.5	200,0,1			169,28,4,3X1.168			201	201	41	202	44	246
	.9	277,181,16,3			248,153,17,4X1.153			293	477	201	496	201	697
Δ +H-H	.5	220,0,8			160,45,7,4X1.353			228	228	76	236	81	317
	.9	156,285,21,9,2,1			105,234,17,0,1,1,1X1.354			179	474	344	510	351	861

* DS has a NEGATIVE SLOPE

TABLE 6
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XH+H \rightleftharpoons X+HH$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{\chi}^{acc}(E)$	$F_{\eta}^{acc}(E)$		
H+H-H	60.00	.5	$.358^{+.055}_{-.055}$	ART	$.375^{+.015}_{-.015}$	$.931^{+.096}_{-.096}$	.931	1	$.349^{+.039}_{-.039}$	.550	$.174^{+.014}_{-.014}$		
		.9	$.570^{+.073}_{-.073}$		$1.100^{+.038}_{-.038}$	$.541^{+.028}_{-.028}$	.740	.731	$.595^{+.038}_{-.038}$	.512	$.364^{+.018}_{-.018}$		
H+H-D	54.74	.5	$.288^{+.049}_{-.049}$	SD	$.373^{+.015}_{-.015}$	$.818^{+.090}_{-.090}$	.821	.996	$.305^{+.049}_{-.049}$	.464	$.174^{+.021}_{-.021}$		
		.9	$.442^{+.064}_{-.064}$		$.999^{+.034}_{-.034}$	$.429^{+.021}_{-.021}$	.599	.716	$.429^{+.033}_{-.033}$	.410	$.400^{+.044}_{-.044}$		
H+H- Δ	47.61	.5	$.278^{+.047}_{-.047}$	SD	$.378^{+.015}_{-.015}$	$.717^{+.073}_{-.073}$	.736	.975	$.271^{+.054}_{-.054}$	.440	$.196^{+.022}_{-.022}$		
		.9	$.207^{+.040}_{-.040}$		$1.031^{+.035}_{-.035}$	$.198^{+.011}_{-.011}$	.324	.611	$.204^{+.023}_{-.023}$	.440	$.499^{+.039}_{-.039}$		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.5	215,16X1			220X1			215	231	0	231	0	231
	.9	318,83,19,4,5X1			338,94,23,22,3,1			342	429	143	462	170	632
H+H-D	.5	169,28,4,3X1.168			200,0,1			202	238	1	246	1	247
	.9	248,153,17,4X1.153			277,181,16,3			306	487	200	511	203	714
H+H- Δ	.5	160,45,7,4X1.353			220,0,8			226	292	8	307	8	315
	.9	105,234,17,0,1,1,1X1.354			156,285,21,9,2,1			168	486	318	519	331	850

TABLE 7
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $H+HX \rightleftharpoons HH+X$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$			
H+H-H	60.00	.5	.367 ⁺ .057	ART	.375 ⁺ .015	.932 ⁺ .096	1	.932	.368	.350 ⁺ .039			
		.9	.607 ⁺ .078		1.100 ⁺ .038	.577 ⁺ .028	.682	.817	.990	.613 ⁺ .038			
H+H-D	54.74	.5	.378 ⁺ .058	SD	.393 ⁺ .012	.904 ⁺ .090	1	.904	.402	.355 ⁺ .037			
		.9	.503 ⁺ .070		1.075 ⁺ .034	.462 ⁺ .019	.579	.798	1.081	.497 ⁺ .026			
H+H- Δ	47.61	.5	.403 ⁺ .060	SD	.427 ⁺ .013	.903 ⁺ .085	.980	.922	.438	.386 ⁺ .038			
		.9	.403 ⁺ .060		1.158 ⁺ .036	.334 ⁺ .013	.456	.732	1.179	.387 ⁺ .019			
	E	$\bar{P}_R(E)_{ART}^{ACC}$		$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$		$\bar{P}_R(E)_M^{SVA}$	$F_{vic}^{BC}(E)$	$F_{vic}^{AB}(E)$		
H+H-H	.5	.375 ⁺ .015		.368	.381 ⁺ .015	.385	.366 ⁺ .015		.369	.669	.468 ⁺ .027		
	.9	1.100 ⁺ .038		.990	1.040 ⁺ .035	1.036	1.020 ⁺ .032		1.012	.702	.571 ⁺ .036		
H+H-D	.5	*.386 ⁺ .012		.390	.393 ⁺ .012	.402	.380 ⁺ .012		.391	.664	.446 ⁺ .046		
	.9	*.146 ⁺ .037		1.049	1.075 ⁺ .034	1.081	1.082 ⁺ .034		1.077	.580	.614 ⁺ .054		
H+H- Δ	.5	*.424 ⁺ .013		.431	.427 ⁺ .013	.438	.424 ⁺ .013		.432	.686	.531 ⁺ .043		
	.9	*.1238 ⁺ .039		1.159	1.158 ⁺ .036	1.179	1.151 ⁺ .036		1.183	.551	.636 ⁺ .048		
	E	T_n^R			$T_n^P \cdot \omega(E)$			$N_r(E)$	$\sum_n T_n^R$	$T_{n>1}^P$	$N_R^+(E)$	$N_R^+(E) \cdot \omega(E)$	$N_{\neq}(E)$
H+H-H	.5	220			215, 16X1			220	220	16	220	16	236
	.9	338, 94, 23, 22, 3, 1			318, 83, 19, 4, 5X1			364	481	111	534	120	654
H+H-D	.5	227			238, 28X.856			227	227	24	227	24	251
	.9	292, 199, 10, 4, 0, 1			339, 128, 16, 4X.867			302	506	128	522	132	654
H+H- Δ	.5	240, 3, 2			329, 28X.739			242	245	21	247	21	268
	.9	226, 254, 15, 9, 1			255, 225, 22, 7, 1X.739			242	505	188	531	194	725

* DS has a NEGATIVE SLOPE

TABLE 8
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $\text{HH}+\text{X} \rightleftharpoons \text{H}+\text{HX}$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^{\pm}(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{VR}^{acc}(E)$	$F_{VR}^{acc}(E)$		
H+H-H	60.00	.5	.358 $^{+}$.055	ART	.375 $^{+}$.015	.931 $^{+}$.096	.931	1	.350 $^{+}$.039	.550	.174 $^{+}$.014		
		.9	.570 $^{+}$.073		1.100 $^{+}$.038	.541 $^{+}$.027	.740	.731	.613 $^{+}$.038	.512	.364 $^{+}$.018		
D+H-H	54.74	.5	.397 $^{+}$.059	SD	.459 $^{+}$.014	.895 $^{+}$.089	.895	1	.411 $^{+}$.032	.523	.199 $^{+}$.021		
		.9	.592 $^{+}$.078		1.239 $^{+}$.039	.467 $^{+}$.019	.700	.667	.579 $^{+}$.031	.385	.402 $^{+}$.052		
Δ +H-H	47.61	.5	.548 $^{+}$.071	SD	.578 $^{+}$.018	.903 $^{+}$.085	.920	.981	.522 $^{+}$.028	.544	.175 $^{+}$.022		
		.9	.463 $^{+}$.066		1.568 $^{+}$.049	.298 $^{+}$.012	.513	.581	.467 $^{+}$.014	.427	.458 $^{+}$.046		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>},$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.5	215, 16 X1			220			215	231	0	231	0	231
	.9	318, 83, 19, 4, 5X1			338, 94, 23, 22, 3, 1			342	429	143	462	170	632
D+H-H	.5	238, 28X.856			227			204	228	0	228	0	228
	.9	339, 128, 16, 4X.867			292, 199, 10, 3, 0, 1			308	422	214	440	220	660
Δ +H-H	.5	329, 28X.739			240, 3, 2			243	264	5	264	5	269
	.9	255, 225, 22, 7, 1X.739			226, 254, 15, 9, 1			205	377	279	400	289	689

TABLE 9
TRAJECTORY and PHASE SPACE RESULTS for the REACTION $X+HH \rightleftharpoons XH+H$
for the ENDOTHERMIC LEPS SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_r(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_r(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_r(E)_{PS}^{ACC}$			
H+H-H	60.00	1.078	.235 ⁺ .043	SD	.300 ⁺ .009	.766 ⁺ .092	.766	1	.317	.230 ⁺ .029			
		1.328	.437 ⁺ .063		.606 ⁺ .019	.695 ⁺ .045	.701	.992	.627	.421 ⁺ .030			
D+H-H	54.74	1.078	.287 ⁺ .049	SD	.363 ⁺ .011	.771 ⁺ .080	.771	1	.384	.280 ⁺ .030			
		1.328	.387 ⁺ .059		.735 ⁺ .023	.542 ⁺ .033	.604	.897	.759	.398 ⁺ .028			
Δ +H-H	47.61	1.078	.307 ⁺ .051	SD	.479 ⁺ .015	.708 ⁺ .065	.708	1	.491	.339 ⁺ .033			
		1.328	.355 ⁺ .055		.943 ⁺ .030	.399 ⁺ .022	.535	.745	.971	.376 ⁺ .035			
	E	$\bar{P}_r(E)_{ART}^{ACC}$	$\bar{P}_r(E)_{ART}^{SVA}$	$\bar{P}_r(E)_{SO}^{ACC}$	$\bar{P}_r(E)_{SO}^{SVA}$	$\bar{P}_r(E)_M^{ACC}$	$\bar{P}_r(E)_M^{SVA}$	$F_{\omega, \xi}^B(E)$	$F_{\omega, \xi}^{AB}(E)$				
H+H-H	1.078	*.297 ⁺ .009	.294	.300 ⁺ .009	.317	.290 ⁺ .009	.290	.584	.464 ⁺ .047				
	1.328	*12.064 ⁺ .385	.582	.606 ⁺ .019	.627	.597 ⁺ .019	.607	.572	.539 ⁺ .048				
D+H-H	1.078	*.375 ⁺ .012	.360	.363 ⁺ .011	.384	.357 ⁺ .011	.367	.583	.478 ⁺ .047				
	1.328	*10.749 ⁺ .343	.712	.735 ⁺ .023	.759	.726 ⁺ .023	.744	.539	.416 ⁺ .056				
Δ +H-H	1.078	*.505 ⁺ .016	.463	.479 ⁺ .015	.491	.475 ⁺ .014	.474	.550	.480 ⁺ .050				
	1.328	*9.649 ⁺ .309	.916	.943 ⁺ .030	.971	.928 ⁺ .029	.965	.536	.475 ⁺ .055				
	E	T_n^R			$T_n^P \cdot \omega(E)$			$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_n^P$	$N_R^+(E)$	$N_P^+(E)$	$N_{\neq}(E)$
H+H-H	1.078	141, 43			545, 0, 1X .2601			141	184	0	184	0	184
	1.328	260, 100, 2, 5			587, 2, 6X.4253			262	367	3	374	3	377
D+H-H	1.078	172, 51			556 X.3015			172	223	0	223	0	223
	1.328	223, 139, 9, 2			509, 63, 21, 2, 1X.4918			232	373	43	384	44	428
Δ +H-H	1.078	184, 74, 0, 1			569 X.3525			184	259	0	260	0	260
	1.328	206, 170, 7, 4			370, 204, 19, 3, 4X.5755			213	387	132	398	136	534

* DS has a NEGATIVE SLOPE

TABLE 10
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XH+H \rightleftharpoons X+HH$
for the EXOTHERMIC LEPS SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^{\tau}(E)$	DS Type	$\bar{P}_R(E)^{\Delta c}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{\Delta c}$	$F_{VM}^{\Delta c}(E)$	$F_{VM}^{\Delta c}(E)$		
H+H-H	60.00	.25	.910 ⁺ .105	SD	1.158 ⁺ .036	.768 ⁺ .092	1	.768	.889 ⁺ .111	.945	.354 ⁺ .031		
		.5	.988 ⁺ .112		1.447 ⁺ .046	.685 ⁺ .044	.984	.696	.991 ⁺ .071	.851	.473 ⁺ .045		
H+H-D	54.74	.25	.927 ⁺ .107	SD	1.221 ⁺ .038	.767 ⁺ .080	1	.767	.937 ⁺ .100	.946	.347 ⁺ .032		
		.5	.885 ⁺ .103		1.475 ⁺ .047	.571 ⁺ .035	.856	.667	.842 ⁺ .057	.724	.466 ⁺ .046		
H+H- Δ	47.61	.25	.948 ⁺ .109	SD	1.319 ⁺ .041	.726 ⁺ .067	1	.726	.958 ⁺ .094	.942	.344 ⁺ .033		
		.5	.655 ⁺ .083		1.653 ⁺ .052	.412 ⁺ .023	.623	.662	.681 ⁺ .061	.491	.486 ⁺ .049		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.25	545, 0, 1X.2601			141, 43			142	142	43	142	43	185
	.5	587, 2, 6X.4253			260, 100, 2, 5			252	253	107	256	112	368
H+H-D	.25	556, X.3015			172, 51			168	168	51	168	51	219
	.5	509, 63, 21, 2, 1X.4918			223, 139, 9, 2			261	293	150	305	152	457
H+H- Δ	.25	569 X.3525			184, 74, 0, 1			201	201	75	201	76	277
	.5	370, 204, 19, 3, 4 X.5755			206, 170, 7, 4			226	345	181	363	185	548

TABLE 11
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $H+HX \rightleftharpoons HH+X$
for the ENDOTHERMIC LEPS SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\mathcal{E}(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\mathcal{E}(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$	
H+H-H	60.00	1.078	.235 ⁺ .043	SD	.300 ⁺ .009	.766 ⁺ .092	.766	1	.317	.230 ⁺ .029	
		1.328	.437 ⁺ .063		.606 ⁺ .019	.695 ⁺ .045	.701	.992	.627	.421 ⁺ .030	
H+H-D	54.74	1.078	.190 ⁺ .038	SD	.293 ⁺ .009	.687 ⁺ .091	.691	.994	.307	.201 ⁺ .027	
		1.328	.360 ⁺ .056		.581 ⁺ .018	.615 ⁺ .045	.641	.960	.607	.357 ⁺ .028	
H+H- Δ	47.61	1.078	.187 ⁺ .038	SD	.299 ⁺ .009	.605 ⁺ .079	.612	.989	.311	.181 ⁺ .024	
		1.328	.227 ⁺ .042		.596 ⁺ .019	.373 ⁺ .028	.437	.852	.615	.222 ⁺ .018	
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_{M}^{ACC}$	$\bar{P}_R(E)_{M}^{SVA}$	$F_{\nu\bar{\nu}}^{BC}(E)$	$F_{\nu\bar{\nu}}^{AB}(E)$		
H+H-H	1.078	* .297 ⁺ .009	.294	.300 ⁺ .009	.317	.290 ⁺ .009	.290	.584	.464 ⁺ .047		
	1.328	* 12.064 ⁺ .385	.582	.606 ⁺ .019	.627	.597 ⁺ .019	.607	.572	.539 ⁺ .048		
H+H-D	1.078	* 4.439 ⁺ .146	.263	.293 ⁺ .009	.307	.270 ⁺ .009	.272	.532	.490 ⁺ .051		
	1.328	* 4.693 ⁺ .150	.521	.581 ⁺ .018	.607	.564 ⁺ .018	.568	.468	.516 ⁺ .051		
H+H- Δ	1.078	* 2.509 ⁺ .082	.232	.299 ⁺ .009	.311	.257 ⁺ .008	.259	.511	.424 ⁺ .047		
	1.328	* 2.607 ⁺ .084	.460	.596 ⁺ .019	.615	.540 ⁺ .017	.533	.501	.477 ⁺ .058		
	E	T_n^R	$T_n^P \cdot \omega(E)$			$N_r(E)$	$\sum_n T_n^A$	$\omega(E) \cdot T_{n>}^P$	$N_R^{\neq}(E)$	$\omega(E) \cdot N_R^{\neq}(E)$	$N_{\neq}(E)$
H+H-H	1.078	141, 43	545, 0, 1X.2601			141	184	0	184	0	184
	1.328	260, 100, 2, 5	587, 2, 6X.4253			262	367	3	374	3	377
H+H-D	1.078	114, 47, 0, 2	543, 0, 3X.2261			114	163	1	165	1	166
	1.328	214, 105, 2, 7	561, 23, 14, 1X.3683			216	328	14	337	14	351
H+H- Δ	1.078	111, 50, 1, 10	541, 0, 10X.1929			112	172	2	183	2	185
	1.328	130, 153, 5, 6, 1, 1	433, 124, 31, 6, 2X.3165			136	296	52	311	54	365

* DS has a negative slope

TABLE 12
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $\text{HH}+\text{X} \rightleftharpoons \text{H}+\text{HX}$
for the EXOTHERMIC LEPS SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^f(E)$	DS Type	$\bar{P}_r(E)^{\text{acc}}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_r(E)^{\text{acc}}$	$F_{\text{vib}}^{\text{acc}}(E)$	$F_{\text{rot}}^{\text{acc}}(E)$		
H+H-H	60.00	.25	.910 ⁺ .105	SD	1.158 ⁺ .036	.768 ⁺ .092	1	.768	.889 ⁺ .111	.945	.354 ⁺ .031		
		.5	.988 ⁺ .112		1.447 ⁺ .046	.685 ⁺ .044	.984	.696	.991 ⁺ .071	.851	.473 ⁺ .045		
D+H-H	54.74	.25	.910 ⁺ .105	SD	1.296 ⁺ .041	.703 ⁺ .093	.992	.709	.911 ⁺ .119	.940	.424 ⁺ .028		
		.5	.958 ⁺ .110		1.589 ⁺ .050	.611 ⁺ .045	.938	.651	.971 ⁺ .076	.773	.536 ⁺ .042		
Δ +H-H	47.61	.25	.918 ⁺ .106	SD	1.528 ⁺ .048	.592 ⁺ .077	.981	.603	.905 ⁺ .124	.936	.533 ⁺ .026		
		.5	.777 ⁺ .094		1.879 ⁺ .060	.390 ⁺ .029	.728	.536	.733 ⁺ .057	.614	.653 ⁺ .032		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>}$	$\omega(E) \cdot N_R^+(E)$	$N_P^+(E)$	$N_{\pm}(E)$
H+H-H	.25	545,0,1X.2601			141,43			142	142	43	142	43	185
	.5	587,2,6X.4253			260,100,2,5			252	253	107	256	112	368
D+H-H	.25	543,0,3X.2261			114,47,0,2			123	123	49	124	51	175
	.5	561,23,14,1X.3683			214,105,2,7			212	221	114	226	121	347
Δ +H-H	.25	541,0,10X.1929			111,50,1,10			106	106	61	108	71	179
	.5	433,124,31,6,2X.3165			130,153,5,6,1,1			147	189	166	202	175	377

TABLE 13
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $H+XH \rightleftharpoons HX+H$
for the THERMONEUTRAL, PORTER-KARPLUS SURFACE

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\mathcal{G}(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\mathcal{G}(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$	
H+H-H	60.00	.5	.425 ⁺ .062	ART	.418 ⁺ .013	1	1	1	.425	.418 ⁺ .013	
		.9	.702 ⁺ .087		1.128 ⁺ .036	.633 ⁺ .026	.775	.817	1.146	.714 ⁺ .037	
H+D-H	70.53	.5	.358 ⁺ .056	ART	.360 ⁺ .011	1	1	1	.368	.360 ⁺ .011	
		.9	.778 ⁺ .094		.970 ⁺ .030	.778 ⁺ .033	.875	.890	.992	.775 ⁺ .041	
H+ Δ -H	84.78	.5	.305 ⁺ .050	ART	.310 ⁺ .010	1	1	1	.315	.310 ⁺ .010	
		.9	.852 ⁺ .100		.841 ⁺ .026	1	1	1	.850	.841 ⁺ .026	
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{\omega_k}^{SC}(E)$	$F_{\omega_k}^{AB}(E)$		
H+H-H	.5	.418 ⁺ .013	.425	.418 ⁺ .013	.425	.418 ⁺ .013	.425	.706	.240 ⁺ .020		
	.9	1.128 ⁺ .036	1.146	1.128 ⁺ .036	1.146	1.128 ⁺ .036	1.146	.714	.437 ⁺ .037		
H+D-H	.5	.360 ⁺ .011	.368	.360 ⁺ .011	.368	.360 ⁺ .011	.368	.685	.196 ⁺ .026		
	.9	.970 ⁺ .030	.992	.970 ⁺ .030	.992	.970 ⁺ .030	.992	.839	.407 ⁺ .045		
H+ Δ -H	.5	.310 ⁺ .010	.315	.310 ⁺ .010	.315	.310 ⁺ .010	.315	.648	.152 ⁺ .021		
	.9	.841 ⁺ .026	.850	.841 ⁺ .026	.850	.841 ⁺ .026	.850	.911	.437 ⁺ .050		
	E	T_n^R		$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_n^P$	$N_R^+(E)$	$N_P^+(E)$	$N_{\neq}(E)$
H+H-H	.5	255		255X1		255	255	0	255	0	255
	.9	406,103,15,2		406,103,15,2X1		421	526	120	543	122	665
H+D-H	.5	215		215X1		215	215	0	215	0	215
	.9	452,50,15,1		452,50,15,1X1		467	518	66	534	66	600
H+ Δ -H	.5	183		183X1		183	183	0	183	0	183
	.9	511		511X1		511	511	0	511	0	511

TABLE 14
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+HX \rightleftharpoons XH+X$
for the THERMONEUTRAL PORTER-KARPLUS SURFACE

Masses	α (deg)	E (ev)	$\bar{P}_R^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\mathcal{E}(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\mathcal{E}(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$			
H+H-H	60.00	.5	.425 $\pm$.062	ART	.418 $\pm$.013	1	1	1	.425	.418 $\pm$.013			
		.9	.702 $\pm$.087		1.128 $\pm$.036	.633 $\pm$.026	.775	.817	1.146	.714 $\pm$.037			
D+H-D	48.19	.5	.463 $\pm$.066	ART	.510 $\pm$.016	1	1	1	.520	.510 $\pm$.016			
		.9	.465 $\pm$.065		1.385 $\pm$.044	.333 $\pm$.012	.500	.667	1.403	.461 $\pm$.022			
Δ +H- Δ	24.62	.5	.375 $\pm$.057	ART	.968 $\pm$.030	.365 $\pm$.019	.534	.682	.997	.353 $\pm$.021			
		.9	.718 $\pm$.087		2.690 $\pm$.085	.266 $\pm$.009	.420	.633	2.687	.716 $\pm$.034			
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{vic}^B(E)$	$F_{vic}^B(E)$				
H+H-H	.5	.418 $\pm$.013	.425	.418 $\pm$.013	.425	.418 $\pm$.013	.425	.706	.240 $\pm$.020				
	.9	1.128 $\pm$.036	1.146	1.128 $\pm$.036	1.146	1.128 $\pm$.036	1.146	.714	.437 $\pm$.037				
D+H-D	.5	.510 $\pm$.016	.520	.510 $\pm$.016	.520	.510 $\pm$.016	.520	.745	.292 $\pm$.031				
	.9	1.385 $\pm$.044	1.403	1.385 $\pm$.044	1.403	1.385 $\pm$.044	1.403	.539	.461 $\pm$.051				
Δ +H- Δ	.5	.968 $\pm$.030	.997	.968 $\pm$.030	.997	.968 $\pm$.030	.997	.599	.273 $\pm$.043				
	.9	2.690 $\pm$.085	2.687	2.690 $\pm$.085	2.687	2.690 $\pm$.085	2.687	.572	.519 $\pm$.047				
	E	T_n^R			$T_n^P \cdot \omega(E)$			$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>1}^P$	$N_R^{\neq}(E)$	$\omega(E) \cdot N_R^{\neq}(E)$	$N_{\neq}(E)$
H+H-H	.5	255			255X1			255	255	0	255	0	255
	.9	406, 103, 15, 2			406, 103, 15, 2X1			421	526	120	543	122	665
D+H-D	.5	278			278X1			278	278	0	278	0	278
	.9	265, 263, 14, 1			265, 263, 14, 1X1			279	543	278	558	279	837
Δ +H- Δ	.5	222, 191, 3, 1			222, 191, 3, 1X1			225	417	195	421	196	617
	.9	0, 117, 427, 0, 1, 2, 1, 1, 0, 0, 0, 1, 0, 0, 1, 1, (21), 1, (24), 1, 1			0, 117, 427, 0, 1, 2, 1, 1, 0, 0, 0, 1, 0, 0, 1, 1, (21), 1, (24), 1, 1			431	553	553	1025	594	1619

TABLE 15
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $H+XH \rightleftharpoons HX+H$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\mathcal{E}(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\mathcal{E}(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$		
H+H-H	60.00	.5	.367 $^{+}_{-.057}$	ART	.375 $^{+}_{-.015}$	.932 $^{+}_{-.096}$	1	.932	.368	.350 $^{+}_{-.039}$		
		.9	.607 $^{+}_{-.078}$		1.100 $^{+}_{-.038}$	.557 $^{+}_{-.028}$	.682	.817	.990	.613 $^{+}_{-.038}$		
H+D-H	70.53	.5	.323 $^{+}_{-.052}$	ART	.326 $^{+}_{-.013}$	.956 $^{+}_{-.100}$	1	.956	.331	.312 $^{+}_{-.039}$		
		.9	.723 $^{+}_{-.088}$		.913 $^{+}_{-.031}$	.767 $^{+}_{-.037}$	.884	.867	.890	.700 $^{+}_{-.041}$		
H+ Δ -H	84.78	.5	.282 $^{+}_{-.048}$	ART	.293 $^{+}_{-.012}$	.983 $^{+}_{-.125}$	1	.983	.294	.288 $^{+}_{-.039}$		
		.9	.733 $^{+}_{-.090}$		.790 $^{+}_{-.027}$	.936 $^{+}_{-.047}$	1	.936	.792	.739 $^{+}_{-.045}$		
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SO}^{ACC}$	$\bar{P}_R(E)_{SO}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{vib}^{BC}(E)$	$F_{vib}^{AB}(E)$			
H+H-H	.5	.375 $^{+}_{-.015}$	.368	.381 $^{+}_{-.015}$	.385	.366 $^{+}_{-.015}$	.369	.669	.468 $^{+}_{-.027}$			
	.9	1.100 $^{+}_{-.038}$	.990	1.040 $^{+}_{-.035}$	1.036	1.020 $^{+}_{-.032}$	1.012	.702	.571 $^{+}_{-.036}$			
H+D-H	.5	.326 $^{+}_{-.013}$	.331	.332 $^{+}_{-.013}$	.337	.328 $^{+}_{-.010}$	.331	.641	.338 $^{+}_{-.033}$			
	.9	.913 $^{+}_{-.031}$	.890	.910 $^{+}_{-.031}$	.907	.887 $^{+}_{-.028}$	.901	.866	.536 $^{+}_{-.057}$			
H+ Δ -H	.5	.293 $^{+}_{-.012}$	.294	.291 $^{+}_{-.012}$	.295	.288 $^{+}_{-.009}$	.294	.621	.234 $^{+}_{-.030}$			
	.9	.790 $^{+}_{-.027}$	.792	.787 $^{+}_{-.027}$	.793	.792 $^{+}_{-.025}$	.795	.872	.484 $^{+}_{-.053}$			
	E	T_n^R			$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>1}^P$	$N_R^{\neq}(E)$	$\omega(E) \cdot N_R^{\neq}(E)$	$N_{\neq}(E)$
H+H-H	.5	220			215, 16X1		220	220	16	220	16	236
	.9	338, 94, 23, 22, 3, 1			318, 83, 19, 4, 5X1		364	481	111	534	120	654
H+D-H	.5	194			190, 9X1		194	194	9	194	9	203
	.9	421, 39, 13, 1, 0, 1			420, 53, 16, 3X1		434	475	72	491	75	566
H+ Δ -H	.5	169			168, 3X1		169	169	3	169	3	172
	.9	440			453, 30X1		440	440	30	440	30	470

TABLE 16
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $HX+H \rightleftharpoons H+XH$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{vib}^{acc}(E)$	$F_{rot}^{acc}(E)$		
H+H-H	60.00	.5	$.358^{+}_{-}.055$	ART	$.375^{+}_{-}.015$	$.931^{+}_{-}.096$	.931	1	$.350^{+}_{-}.039$	.550	$.174^{+}_{-}.014$		
		.9	$.570^{+}_{-}.073$		$1.100^{+}_{-}.038$	$.541^{+}_{-}.027$	.740	.731	$.613^{+}_{-}.038$	.512	$.364^{+}_{-}.018$		
H+D-H	70.53	.5	$.317^{+}_{-}.052$	ART	$.326^{+}_{-}.013$	$.955^{+}_{-}.109$	.955	1	$.311^{+}_{-}.039$	.560	$.158^{+}_{-}.018$		
		.9	$.727^{+}_{-}.088$		$.913^{+}_{-}.031$	$.768^{+}_{-}.037$	.853	.900	$.701^{+}_{-}.041$	.527	$.335^{+}_{-}.045$		
H+ Δ -H	84.78	.5	$.280^{+}_{-}.048$	ART	$.293^{+}_{-}.012$	$.982^{+}_{-}.125$	.982	1	$.288^{+}_{-}.039$	.614	$.156^{+}_{-}.018$		
		.9	$.755^{+}_{-}.090$		$.790^{+}_{-}.027$	$.938^{+}_{-}.047$	.938	1	$.766^{+}_{-}.045$	.717	$.355^{+}_{-}.041$		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^+(E)$	$N_P^+(E)$	$N_{\pm}(E)$
H+H-H	.5	215,16X1			220			215	231	0	231	0	231
	.9	318,83,19,4,5X1			338,94,23,22,3,1			342	429	143	462	170	632
H+D-H	.5	190,9X1			194			190	199	0	199	0	199
	.9	420,53,16,3X1			421,39,13,1,0,1			436	492	54	511	57	568
H+ Δ -H	.5	168,3X1			169			168	171	0	171	0	171
	.9	453,30X1			440			453	483	0	483	0	483

TABLE 17

TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+HX \rightleftharpoons XH+X$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_R^c(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$		
H+H-H	60.00	.5	.367 $^{+}_{-}$.057	ART	.375 $^{+}_{-}$.015	.932 $^{+}_{-}$.096	1	.932	.368	.350 $^{+}_{-}$.039		
		.9	.607 $^{+}_{-}$.078		1.100 $^{+}_{-}$.038	.557 $^{+}_{-}$.028	.682	.817	.990	.613 $^{+}_{-}$.038		
D+H-D	48.19	.5	.398 $^{+}_{-}$.060	SD	.448 $^{+}_{-}$.018	.882 $^{+}_{-}$.085	.996	.886	.468	.395 $^{+}_{-}$.041		
		.9	.372 $^{+}_{-}$.056		1.262 $^{+}_{-}$.043	.295 $^{+}_{-}$.013	.425	.694	1.258	.372 $^{+}_{-}$.021		
Δ +H- Δ	24.62	.5	.027 $^{+}_{-}$.015	SD	.888 $^{+}_{-}$.035	.030 $^{+}_{-}$.035	.057	.528	.886	.027 $^{+}_{-}$.004		
		.9	.700 $^{+}_{-}$.087		2.344 $^{+}_{-}$.080	.298 $^{+}_{-}$.014	.419	.711	2.385	.699 $^{+}_{-}$.040		
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{\nu_6}^{SC}(E)$	$F_{\nu_6}^{AB}(E)$			
H+H-H	.5	.375 $^{+}_{-}$.015	.368	.381 $^{+}_{-}$.015	.385	.366 $^{+}_{-}$.015	.369	.669	.468 $^{+}_{-}$.027			
	.9	1.100 $^{+}_{-}$.038	.990	1.040 $^{+}_{-}$.035	1.036	1.020 $^{+}_{-}$.032	1.012	.702	.571 $^{+}_{-}$.036			
D+H-D	.5	*.447 $^{+}_{-}$.018	.427	.448 $^{+}_{-}$.018	.468	.431 $^{+}_{-}$.014	.433	.691	.581 $^{+}_{-}$.037			
	.9	*15.433 $^{+}_{-}$.486	1.150	1.262 $^{+}_{-}$.043	1.258	1.222 $^{+}_{-}$.039	1.216	.587	.719 $^{+}_{-}$.041			
Δ +H- Δ	.5	*4.199 $^{+}_{-}$.138	.699	.888 $^{+}_{-}$.035	.886	.781 $^{+}_{-}$.025	.777	.531	.938 $^{+}_{-}$.013			
	.9	*4.237 $^{+}_{-}$.133	1.854	2.344 $^{+}_{-}$.080	2.385	2.288 $^{+}_{-}$.073	2.236	.824	.597 $^{+}_{-}$.047			
	E	T_n^R			$T_n^r \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^A$	$T_{n>}^{\omega(E)}$	$N_R^{\neq}(E)$	$N_R^{\neq \omega(E)}$	$N_{\neq}(E)$
H+H-H	.5	220			215,16X1		220	220	16	220	16	236
	.9	338,94,23,22,3,1			318,83,19,4,5X1		364	481	111	534	120	654
D+H-D	.5	238,0,1			227,29,2X1		239	239	31	240	31	271
	.9	200,262,21,6,2,1			202,211,9,4,0,1X1		223	492	225	525	231	756
Δ +H- Δ	.5	5,216,9,9,2,4,0,1			6,223,8,4,1,0,1,0,0,0,1X1		16	246	238	279	249	528
	.9	64,34,354,6,1,28,0,5,1,1,0,2,0,2,(08)/(ap)3,(24)/			54,18,377,(25)1X1		420	502	396	1002	407	1409

* DS has a NEGATIVE SLOPE

TABLE 18
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XH+X \rightleftharpoons X+HX$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{vib}^{acc}(E)$	$F_{vib}^{th}(E)$		
H+H-H	60.00	.5	.358 ⁺ .055	ART	.375 ⁺ .015	.931 ⁺ .096	.931	1	.350 ⁺ .039	.550	.174 ⁺ .014		
		.9	.570 ⁺ .073		1.100 ⁺ .038	.541 ⁺ .027	.740	.731	.613 ⁺ .038	.512	.364 ⁺ .018		
D+H-D	48.19	.5	.382 ⁺ .058	SD	.448 ⁺ .018	.877 ⁺ .085	.881	.996	.393 ⁺ .041	.419	.181 ⁺ .020		
		.9	.352 ⁺ .054		1.262 ⁺ .043	.284 ⁺ .013	.477	.594	.358 ⁺ .021	.446	.447 ⁺ .045		
Δ +H- Δ	24.62	.5	.028 ⁺ .015	SD	.888 ⁺ .035	.032 ⁺ .004	.064	.503	.028 ⁺ .004	.533	.392 ⁺ .028		
		.9	.720 ⁺ .088		2.344 ⁺ .080	.304 ⁺ .014	.515	.590	.713 ⁺ .040	.327	.390 ⁺ .046		
		E	$T_n^R \cdot \omega(E)$		T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.5	215, 16x1		220			215	231	0	231	0	231	
	.9	318, 83, 19, 4, 5x1		338, 94, 23, 22, 3, 1			342	429	143	462	170	632	
D+H-D	.5	227, 29, 2x1		238, 0, 1			229	258	1	260	1	261	
	.9	202, 211, 9, 4, 0, 1x1		200, 262, 21, 6, 2, 1			211	427	292	442	302	744	
Δ +H- Δ	.5	6, 223, 8, 4, 1, 0, 1, 0, 0, 0, 1x1		5, 216, 9, 9, 2, 4, 0, 1			17	244	241	266	263	529	
	.9	54, 18, 377, (25)1x1		64, 34, 354, 6, 1, 28, 0, 5, 1, 1, 0, 2, 0, 2, (18)1, (20)2, (24)1			432	450	438	839	582	1421	

TABLE 19
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $H+XH \rightleftharpoons HX+H$
for the ENDOTHERMIC LEPS SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$		
H+H-H	60.00	1.078	.235 ⁺ .043	SD	.300 ⁺ .009	.766 ⁺ .092	.766	1	.317	.230 ⁺ .029		
		1.328	.437 ⁺ .063			.606 ⁺ .019	.695 ⁺ .045	.701	.922	.627	.421 ⁺ .030	
H+D-H	70.53	1.078	.200 ⁺ .039	ART	.265 ⁺ .008	.902 ⁺ .136	.902	1	.271	.239 ⁺ .037		
		1.328	.417 ⁺ .061			.547 ⁺ .017	.779 ⁺ .058	.779	1	.535	.426 ⁺ .034	
H+ Δ -H	84.78	1.078	.190 ⁺ .038	ART	.237 ⁺ .007	.927 ⁺ .147	.927	1	.246	.220 ⁺ .035		
		1.328	.412 ⁺ .061			.474 ⁺ .015	.855 ⁺ .071	.855	1	.487	.405 ⁺ .036	
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{vis}^{BC}(E)$	$F_{vis}^{AB}(E)$			
H+H-H	1.078	*.297 ⁺ .009	.294	.300 ⁺ .009	.317	.290 ⁺ .009	.299	.584	.464 ⁺ .047			
	1.328	*.2.064 ⁺ .385	.582	.606 ⁺ .019	.627	.597 ⁺ .019	.607	.572	.539 ⁺ .048			
H+D-H	1.078	.265 ⁺ .008	.271	.268 ⁺ .008	.279	.261 ⁺ .008	.272	.590	.487 ⁺ .049			
	1.328	.547 ⁺ .017	.535	.534 ⁺ .017	.552	.530 ⁺ .017	.545	.617	.425 ⁺ .055			
H+ Δ -H	1.078	.237 ⁺ .007	.246	.234 ⁺ .007	.246	.235 ⁺ .007	.246	.584	.426 ⁺ .049			
	1.328	.474 ⁺ .015	.487	.474 ⁺ .015	.488	.472 ⁺ .015	.488	.656	.503 ⁺ .055			
	E	T_n^R			$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_n^P$	$N_R^{\neq}(E)$	$\omega(E) \cdot N_R^{\neq}(E)$	$N_{\neq}(E)$
H+H-H	1.078	141, 43			545, 0, 1X.2601		141	184	0	184	0	184
	1.328	260, 100, 2, 5			587, 2, 6X.4253		262	367	3	374	3	377
H+D-H	1.078	120, 13			542X.2621		120	133	0	133	0	133
	1.328	250, 71			597X.4259		250	321	0	321	0	321
H+ Δ -H	1.078	114, 9			518X.2613		114	123	0	123	0	123
	1.328	247, 42			565X.4283		247	289	0	289	0	289

* DS has a negative slope

TABLE 20
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $HX+H \rightleftharpoons H+XH$
for the EXOTHERMIC LEPS SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{vib}^{acc}(E)$	$F_{rot}^{acc}(E)$		
H+H-H	60.00	.25	$.910^{+}_{-}.105$	SD	$1.158^{+}_{-}.036$	$.767^{+}_{-}.092$	.998	.768	$.888^{+}_{-}.111$	.945	$.354^{+}_{-}.031$		
		.5	$.988^{+}_{-}.112$		$1.447^{+}_{-}.046$	$.686^{+}_{-}.044$	.987	.696	$.993^{+}_{-}.071$	.851	$.473^{+}_{-}.045$		
H+D-H	70.53	.25	$.903^{+}_{-}.105$	ART	$1.016^{+}_{-}.032$	$.916^{+}_{-}.138$	1	.916	$.931^{+}_{-}.141$	.930	$.243^{+}_{-}.028$		
		.5	$.995^{+}_{-}.113$		$1.299^{+}_{-}.041$	$.781^{+}_{-}.058$	1	.781	$1.015^{+}_{-}.080$	.748	$.347^{+}_{-}.042$		
H+ Δ -H	84.78	.25	$.863^{+}_{-}.101$	ART	$.900^{+}_{-}.028$	$.938^{+}_{-}.149$	1	.938	$.844^{+}_{-}.134$	.920	$.192^{+}_{-}.025$		
		.5	$.942^{+}_{-}.108$		$1.113^{+}_{-}.035$	$.852^{+}_{-}.071$	1	.852	$.948^{+}_{-}.084$	.943	$.276^{+}_{-}.036$		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.25	545,0,1X.2601			141,43			142	142	43	142	43	185
	.5	587,2,6X.4253			260,100,2,5			252	253	107	256	112	368
H+D-H	.25	542X.2621			120,13			142	142	13	142	13	155
	.5	597X.4259			250,71			254	254	71	254	71	325
H+ Δ -H	.25	518X.2613			114,9			135	135	9	135	9	144
	.5	565X.4283			247,42			242	242	42	242	42	284

TABLE 21
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+HX \rightleftharpoons XII+X$
for the ENDOTHERMIC LEPS SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_R^c(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$		
H+H-H	60.00	1.078	$.235^{+}_{-}.043$	SD	$.300^{+}_{-}.009$	$.766^{+}_{-}.092$	.766	1	.317	$.230^{+}_{-}.029$		
		1.328	$.437^{+}_{-}.063$		$.606^{+}_{-}.019$	$.695^{+}_{-}.045$	.701	.992	.627	$.421^{+}_{-}.030$		
D+H-D	48.19	1.078	$.243^{+}_{-}.044$	SD	$.368^{+}_{-}.012$	$.676^{+}_{-}.073$	.676	1	.383	$.249^{+}_{-}.028$		
		1.328	$.327^{+}_{-}.053$		$.737^{+}_{-}.023$	$.441^{+}_{-}.028$	.528	.836	.758	$.325^{+}_{-}.023$		
Δ +H- Δ	24.62	1.078	$.033^{+}_{-}.015$	SD	$.685^{+}_{-}.022$	$.049^{+}_{-}.004$	.085	.576	.722	$.034^{+}_{-}.003$		
		1.328	$.352^{+}_{-}.055$		$1.398^{+}_{-}.044$	$.259^{+}_{-}.016$	.380	.681	1.428	$.362^{+}_{-}.025$		
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{vib}^B(E)$	$F_{vib}^B(E)$			
H+H-H	1.078	* $.297^{+}_{-}.009$	.294	$.300^{+}_{-}.009$	.317	$.290^{+}_{-}.009$	.299	.584	$.464^{+}_{-}.047$			
	1.328	* $12.064^{+}_{-}.385$	.582	$.606^{+}_{-}.019$	.627	$.597^{+}_{-}.019$	.607	.572	$.539^{+}_{-}.048$			
D+H-D	1.078	* $3.863^{+}_{-}.127$	.328	$.368^{+}_{-}.012$	.383	$.339^{+}_{-}.011$	.344	.533	$.485^{+}_{-}.057$			
	1.328	* $3.951^{+}_{-}.126$	.649	$.737^{+}_{-}.023$	.758	$.719^{+}_{-}.023$	.713	.507	$.490^{+}_{-}.060$			
Δ +H- Δ	1.078	* $1.486^{+}_{-}.049$	.433	$.685^{+}_{-}.022$	.722	$.614^{+}_{-}.019$	.623	.512	$.650^{+}_{-}.071$			
	1.328	* $1.675^{+}_{-}.054$	.856	$1.398^{+}_{-}.044$	1.428	$1.291^{+}_{-}.041$	1.289	.466	$.501^{+}_{-}.056$			
	E	T_n^R			$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n+1}^P$	$N_R^{\pm}(E)$	$N_F^{\pm}(E)$	$N_{\neq}(E)$
H+H-H	1.078	141,43			545,0,1X2601		141	184	0	184	0	184
	1.328	260,100,2,5			587,2,6X.4253		262	367	3	374	3	377
D+H-D	1.078	146,66,0,2			563X.2621		146	214	0	216	0	216
	1.328	184,155,11,3,0,0,1			430,140,25,3X.4259		196	354	72	371	73	444
Δ +H- Δ	1.078	0,188,18,1,0,0,1,0,0,0,1			2,443,59,41,1,0,4,2,2,3,0,0,1(21)X.2613		20	209	147	236	174	410
	1.328	34,108,174,2,1,9,0,1,2,1,0,2			66,56,432,18,9,3,1,0,3,11,0,0,0,1,2,1X.4283		211	334	226	555	260	815

* DS has a NEGATIVE SLOPE

TABLE 22
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XH+X \rightleftharpoons X+HX$
for the EXOTHERMIC LEPS SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{vib}^{acc}(E)$	$F_{rot}^{acc}(E)$		
H+H-H	60.00	.25	$.910^{+}_{-}.105$	SD	$1.158^{+}_{-}.036$	$.767^{+}_{-}.092$	.998	.768	$.888^{+}_{-}.111$	.945	$.354^{+}_{-}.031$		
		.5	$.988^{+}_{-}.112$		$1.447^{+}_{-}.046$	$.686^{+}_{-}.044$	.987	.696	$.993^{+}_{-}.071$	.851	$.473^{+}_{-}.045$		
D+H-D	48.19	.25	$.938^{+}_{-}.108$	SD	$1.393^{+}_{-}.044$	$.678^{+}_{-}.073$	1	.678	$.944^{+}_{-}.107$	.936	$.450^{+}_{-}.033$		
		.5	$.758^{+}_{-}.092$		$1.712^{+}_{-}.054$	$.439^{+}_{-}.028$	.727	.604	$.752^{+}_{-}.054$	.565	$.530^{+}_{-}.045$		
Δ +H- Δ	24.62	.25	$.113^{+}_{-}.028$	SD	$2.618^{+}_{-}.082$	$.044^{+}_{-}.004$	.093	.470	$.115^{+}_{-}.011$	.480	$.728^{+}_{-}.014$		
		.5	$.857^{+}_{-}.101$		$3.244^{+}_{-}.102$	$.267^{+}_{-}.016$	.459	.583	$.866^{+}_{-}.058$	.682	$.621^{+}_{-}.031$		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^+(E)$	$N_P^+(E)$	$N_{\pm}(E)$
H+H-H	.25	545,0,1X.2601			141,43			142	142	43	142	43	185
	.5	587,2,6X.4253			260,100,2,5			252	253	107	256	112	368
D+H-D	.25	563X.2621			146,66,0,2			148	148	68	148	70	218
	.5	430,140,25,3X.4259			184,155,11,3,(7)1			194	255	170	267	175	442
Δ +H- Δ	.25	2,443,59,41,14,0,4,2,2,3,(14)1,(21)1 x.2613			0,188,18,1,(7)1,(11)1			18	147	209	191	216	407
	.5	66,56,432,18,9,3,1,0,3,1,1,0,0,0,1,2,1 x.4213			34,108,174,2,1,9,0,1,2,1,0,2			220	254	300	480	344	824

TABLE 23
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+XH \rightleftharpoons XX+H$
for the THERMONEUTRAL PORTER-KARPLUS SURFACE

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{sva}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{acc}$		
H+H-H	60.00	.5	.425 ⁺ .062	ART	.418 ⁺ .013	1	1	1	.425	.418 ⁺ .013		
		.9	.702 ⁺ .087		1.128 ⁺ .036	.633 ⁺ .026	.775	.817	1.146	.714 ⁺ .037		
D+D-H	65.91	.5	.412 ⁺ .061	ART	.420 ⁺ .013	.992 ⁺ .095	1	.992	.430	.417 ⁺ .042		
		.9	.805 ⁺ .096		1.133 ⁺ .036	.697 ⁺ .095	.896	.778	1.158	.790 ⁺ .111		
$\Delta+\Delta$ -H	77.69	.5	.477 ⁺ .067	ART	.470 ⁺ .015	.859 ⁺ .056	1	.859	.468	.404 ⁺ .040		
		.9	.862 ⁺ .101		1.438 ⁺ .046	.597 ⁺ .036	1	.597	1.261	.858 ⁺ .058		
	E	$\bar{P}_R(E)_{ART}^{acc}$	$\bar{P}_R(E)_{ART}^{sva}$	$\bar{P}_R(E)_{SD}^{acc}$	$\bar{P}_R(E)_{SD}^{sva}$	$\bar{P}_R(E)_M^{acc}$	$\bar{P}_R(E)_M^{sva}$	$F_{vib}^B(E)$	$F_{vib}^B(E)$			
H+H-H	.5	.418 ⁺ .013	.425	.418 ⁺ .013	.425	.418 ⁺ .013	.425	.706	.240 ⁺ .020			
	.9	1.128 ⁺ .036	1.146	1.128 ⁺ .036	1.146	1.128 ⁺ .036	1.146	.714	.437 ⁺ .037			
D+D-H	.5	.420 ⁺ .013	.430	.425 ⁺ .013	.436	.425 ⁺ .013	.430	.695	.222 ⁺ .026			
	.9	1.133 ⁺ .036	1.158	1.152 ⁺ .036	1.174	1.141 ⁺ .036	1.159	.847	.457 ⁺ .049			
$\Delta+\Delta$ -H	.5	.470 ⁺ .015	.468	.585 ⁺ .018	.596	.470 ⁺ .015	.472	.715	.285 ⁺ .028			
	.9	1.438 ⁺ .046	1.261	1.562 ⁺ .049	1.605	1.359 ⁺ .043	1.299	.918	.433 ⁺ .044			
	E	T_n^R			$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>1}^P$	$N_R^{\neq}(E)$	$\omega(E) \cdot N_P^{\neq}(E)$	$N_{\neq}(E)$
H+H-H	.5	255			255X1		255	255	0	255	0	255
	.9	406,103,15,2			406,103,15,2X1		421	526	120	543	122	665
D+D-H	.5	247			202,2X1.215		247	247	2	247	2	249
	.9	472,39,11,3			396,114,12X1.225		483	525	154	539	154	693
$\Delta+\Delta$ -H	.5	286			100,20X2.327		286	286	47	286	47	333
	.9	517			218,148X2.358		517	517	349	517	349	866

TABLE 24
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XX+H \rightleftharpoons X+XH$
for the THERMONEUTRAL PORTER-KARPLUS SURFACE

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_a(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_a(E)^{acc}$	$F_{\text{acc}}^R(E)$	$F_{\text{acc}}^D(E)$
H+H-H	60.00	.5	.425 ⁺ .062	ART	.418 ⁺ .013	1	1	1	.418 ⁺ .013	.706	.240 ⁺ .020
		.9	.702 ⁺ .087		1.128 ⁺ .036	.633 ⁺ .026	.775	.817	.714 ⁺ .037	.714	.437 ⁺ .037
H+D-D	65.91	.5	.337 ⁺ .054	ART	.345 ⁺ .011	.988 ⁺ .111	.988	1	.341 ⁺ .040	.648	.216 ⁺ .023
		.9	.680 ⁺ .085		.927 ⁺ .029	.704 ⁺ .027	.765	.921	.653 ⁺ .032	.665	.482 ⁺ .048
H+Δ-Δ	77.69	.5	.167 ⁺ .035	ART	.205 ⁺ .006	.835 ⁺ .134	.835	1	.171 ⁺ .028	.538	.286 ⁺ .037
		.9	.363 ⁺ .056		.608 ⁺ .019	.596 ⁺ .038	.596	1	.362 ⁺ .025	.540	.458 ⁺ .048
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\frac{\omega(E) \cdot N_r(E)}{\sum_n T_n^R}$	$T_{n>1}^P$	$\frac{\omega(E) \cdot N_R^+(E)}{N_P^+(E)}$	$N_{\pm}^+(E)$
H+H-H	.5	255X1			255			255	255	0	255
	.9	406,103,15,2X1			406,103,15,2			421	526	120	665
H+D-D	.5	202,2X1.215			247			245	248	0	248
	.9	396,114,12X1.225			472,39,11,3			500	639	53	710
H+Δ-Δ	.5	100,20,X2.327			286			233	279	0	279
	.9	218,148X2.358			517			514	863	0	863

TABLE 25
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+XH \rightleftharpoons XX+H$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$	
H+H-H	60.00	.5	$.367^{+}_{-.057}$	ART	$.375^{+}_{-.015}$	$.932^{+}_{-.096}$	1	.932	.368	$.350^{+}_{-.039}$	
		.9	$.607^{+}_{-.078}$		$1.100^{+}_{-.038}$	$.557^{+}_{-.028}$	.682	.817	.990	$.613^{+}_{-.038}$	
D+D-H	65.91	.5	$.290^{+}_{-.049}$	ART	$.355^{+}_{-.014}$	$.946^{+}_{-.117}$	1	.946	.350	$.336^{+}_{-.044}$	
		.9	$.688^{+}_{-.084}$		$1.075^{+}_{-.037}$	$.630^{+}_{-.022}$	.776	.811	.941	$.677^{+}_{-.033}$	
$\Delta+\Delta$ -H	77.69	.5	$.312^{+}_{-.051}$	ART	$.321^{+}_{-.013}$	$.899^{+}_{-.113}$	1	.899	.327	$.289^{+}_{-.038}$	
		.9	$.752^{+}_{-.092}$		$1.090^{+}_{-.038}$	$.705^{+}_{-.053}$	1	.705	.880	$.768^{+}_{-.064}$	
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{Vib}^{B,C}(E)$	$F_{Vib}^{A,B}(E)$		
H+H-H	.5	$.375^{+}_{-.015}$	.368	$.381^{+}_{-.015}$	.385	$.366^{+}_{-.015}$	.369	.669	$.468^{+}_{-.027}$		
	.9	$1.100^{+}_{-.038}$	.990	$1.040^{+}_{-.035}$	1.036	$1.020^{+}_{-.032}$	1.012	.702	$.571^{+}_{-.036}$		
D+D-H	.5	$.355^{+}_{-.014}$	.350	$.370^{+}_{-.015}$	.377	$.341^{+}_{-.011}$	.351	.661	$.436^{+}_{-.034}$		
	.9	$1.075^{+}_{-.037}$	.941	$1.015^{+}_{-.035}$	1.014	$.970^{+}_{-.031}$	.972	.823	$.534^{+}_{-.050}$		
$\Delta+\Delta$ -H	.5	$.321^{+}_{-.013}$	.327	$.422^{+}_{-.017}$	.429	$.327^{+}_{-.010}$	.328	.651	$.476^{+}_{-.027}$		
	.9	$1.090^{+}_{-.038}$	.880	$1.124^{+}_{-.038}$	1.153	$.970^{+}_{-.031}$	.913	.881	$.593^{+}_{-.041}$		
	E	T_n^R		$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_n^P$	$N_R^+(E)$	$\omega(E) \cdot N_R^+$	$N_R^+(E)$
H+H-H	.5	220		215, 16X1		220	220	16	220	16	236
	.9	338, 94, 23, 22, 3, 1		318, 83, 19, 4, 5X1		364	481	111	534	120	654
D+D-H	.5	174		148, 8X1, 215		174	174	10	174	10	184
	.9	392, 36, 15, 23, 5, 3, 1		331, 68, 19, 4, 3X1, 225		413	475	115	532	124	656
$\Delta+\Delta$ -H	.5	187		77, 9X2, 327		187	187	21	187	21	208
	.9	451		191, 73, 0, 2, 0, 1X2, 358		451	451	179	451	189	640

TABLE 26
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XX+H \rightleftharpoons X+XH$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^r(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{VR}^{acc}(E)$	$F_{V0}^{acc}(E)$		
H+H-H	60.00	.5	.358 $^{+}_{-.055}$	ART	.375 $^{+}_{-.015}$	.931 $^{+}_{-.096}$	.931	1	.349 $^{+}_{-.039}$	.550	.174 $^{+}_{-.014}$		
		.9	.570 $^{+}_{-.073}$		1.100 $^{+}_{-.038}$	.541 $^{+}_{-.027}$	.740	.731	.595 $^{+}_{-.038}$	.512	.364 $^{+}_{-.018}$		
H+D-D	65.91	.5	.247 $^{+}_{-.044}$	ART	.292 $^{+}_{-.012}$	.947 $^{+}_{-.117}$	.947	1	.277 $^{+}_{-.036}$	.523	.171 $^{+}_{-.020}$		
		.9	.588 $^{+}_{-.077}$		.878 $^{+}_{-.030}$	.640 $^{+}_{-.022}$	.777	.824	.562 $^{+}_{-.027}$	.554	.384 $^{+}_{-.043}$		
H+ $\triangle$ - $\triangle$	77.69	.5	.128 $^{+}_{-.030}$	ART	.138 $^{+}_{-.006}$	.895 $^{+}_{-.112}$	.895	1	.124 $^{+}_{-.016}$	.515	.150 $^{+}_{-.021}$		
		.9	.318 $^{+}_{-.052}$		.462 $^{+}_{-.016}$	.704 $^{+}_{-.052}$	.704	1	.325 $^{+}_{-.027}$	.549	.377 $^{+}_{-.043}$		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_{\rho}^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.5	215,16X1			220			215	231	0	231	0	231
	.9	318,83,19,4,5X1			338,94,23,22,3,1			342	429	143	462	170	632
H+D-D	.5	148,8X1.215			174			180	190	0	190	0	190
	.9	331,68,19,4,3X1.225			392,36,15,23,5,3,1			432	521	83	556	119	675
H+ $\triangle$ - $\triangle$	.5	77,9X2.327			187			179	200	0	200	0	200
	.9	191,73,0,2,0,1X2.358			451			450	630	0	639	0	639

TABLE 27
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $H+XX \rightleftharpoons HX+X$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$	
H+H-H	60.00	.5	.367 ⁺ _{-.057}	ART	.375 ⁺ _{-.015}	.932 ⁺ _{-.096}	1	.932	.368	.350 ⁺ _{-.039}	
		.9	.607 ⁺ _{-.078}		1.100 ⁺ _{-.038}	.557 ⁺ _{-.028}	.682	.817	.990	.613 ⁺ _{-.038}	
H+D-D	65.91	.5	.327 ⁺ _{-.053}	ART	.331 ⁺ _{-.010}	.966 ⁺ _{-.109}	1	.966	.338	.320 ⁺ _{-.038}	
		.9	.642 ⁺ _{-.081}		.919 ⁺ _{-.029}	.692 ⁺ _{-.032}	.791	.876	.910	.636 ⁺ _{-.036}	
H+ Δ - Δ	77.69	.5	.273 ⁺ _{-.047}	ART	.246 ⁺ _{-.008}	.994 ⁺ _{-.129}	.994	1	.255	.245 ⁺ _{-.033}	
		.9	.443 ⁺ _{-.064}		.682 ⁺ _{-.021}	.650 ⁺ _{-.036}	.650	1	.685	.443 ⁺ _{-.028}	
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_{M}^{ACC}$	$\bar{P}_R(E)_{M}^{SVA}$	$F_{\nu\bar{\nu}}^B(E)$	$F_{\nu\bar{\nu}}^{AB}(E)$		
H+H-H	.5	.375 ⁺ _{-.015}	.368	.381 ⁺ _{-.015}	.385	.366 ⁺ _{-.015}	.369	.669	.468 ⁺ _{-.027}		
	.9	1.100 ⁺ _{-.038}	.990	1.040 ⁺ _{-.035}	1.036	1.020 ⁺ _{-.032}	1.012	.702	.571 ⁺ _{-.036}		
H+D-D	.5	.331 ⁺ _{-.010}	.338	.334 ⁺ _{-.013}	.340	.333 ⁺ _{-.010}	.339	.662	.359 ⁺ _{-.040}		
	.9	.919 ⁺ _{-.029}	.910	.915 ⁺ _{-.029}	.914	.911 ⁺ _{-.029}	.918	.778	.498 ⁺ _{-.059}		
H+ Δ - Δ	.5	.246 ⁺ _{-.008}	.255	.273 ⁺ _{-.011}	.279	.246 ⁺ _{-.008}	.255	.626	.290 ⁺ _{-.036}		
	.9	.682 ⁺ _{-.021}	.685	.748 ⁺ _{-.024}	.751	.674 ⁺ _{-.021}	.686	.669	.529 ⁺ _{-.054}		
	E	T_n^R		$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>}^P$	$N_R^+(E)$	$\omega(E) \cdot N_F^+(E)$	$N_{\neq}(E)$
H+H-H	.5	220		215,16X1		220	220	16	220	16	236
	.9	338,94,23,22,3,1		318,83,19,4,5X1		364	481	111	534	120	654
H+D-D	.5	196		230,8X,823		196	196	7	196	7	203
	.9	376,83,9,5		419,58,18,4X,817		385	473	65	487	69	556
H+ Δ - Δ	.5	164,1		347X,430		164	165	0	165	0	165
	.9	266,143		560X,424		266	409	0	409	0	409

TABLE 28
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $HX+X \rightleftharpoons H+XX$
for the THERMONEUTRAL POLANYI-WONG SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{vib}^{acc}(E)$	$F_{rot}^0(E)$		
H+H-H	60.00	.5	.358 $^{+}$ -.055	ARY	.375 $^{+}$ -.015	.931 $^{+}$ -.096	.931	1	.350 $^{+}$ -.039	.550	.174 $^{+}$ -.014		
		.9	.570 $^{+}$ -.073		1.100 $^{+}$ -.038	.541 $^{+}$ -.029	.740	.731	.613 $^{+}$ -.038	.512	.364 $^{+}$ -.018		
D+D-H	65.91	.5	.383 $^{+}$ -.058	ART	.402 $^{+}$ -.012	.964 $^{+}$ -.109	.964	1	.388 $^{+}$ -.046	.604	.164 $^{+}$ -.020		
		.9	.728 $^{+}$ -.088		1.126 $^{+}$ -.036	.676 $^{+}$ -.031	.838	.807	.761 $^{+}$ -.044	.573	.393 $^{+}$ -.046		
$\Delta+\Delta$ -H	77.69	.5	.578 $^{+}$ -.076	ART	.572 $^{+}$ -.019	.993 $^{+}$ -.129	1	.993	.568 $^{+}$ -.077	.790	.147 $^{+}$ -.021		
		.9	.933 $^{+}$ -.107		1.608 $^{+}$ -.050	.624 $^{+}$ -.035	1	.624	1.003 $^{+}$ -.066	.939	.287 $^{+}$ -.038		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.5	215, 16X1			220			215	231	0	231	0	231
	.9	318, 83, 19, 4, 5X1			338, 94, 23, 22, 3, 1			342	420	143	462	170	632
D+D-H	.5	230, 8X, 823			196			189	196	0	196	0	196
	.9	419, 58, 18, 4X, 817			376, 83, 9, 5			357	408	97	426	102	428
$\Delta+\Delta$ -H	.5	347X, 430			164, 1			149	149	1	149	1	150
	.9	560X, 424			266, 143			237	237	143	237	143	380

TABLE 29
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $X+XH \rightleftharpoons XX+H$
for the ENDOTHERMIC LEPS SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\xi(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$			
H+H-H	60.00	1.078	$.235^{+.043}_{-.043}$	SD	$.300^{+.009}_{-.009}$	$.766^{+.092}_{-.092}$	.766	1	.317	$.230^{+.029}_{-.029}$			
		1.328	$.437^{+.063}_{-.063}$		$.606^{+.019}_{-.019}$	$.695^{+.045}_{-.045}$	.701	.992	.627	$.421^{+.030}_{-.030}$			
D+D-H	65.91	1.078	$.285^{+.048}_{-.048}$	ART	$.333^{+.010}_{-.010}$	$.877^{+.101}_{-.101}$	.877	1	.342	$.292^{+.035}_{-.035}$			
		1.328	$.498^{+.069}_{-.069}$		$.702^{+.022}_{-.022}$	$.729^{+.045}_{-.045}$	.729	1	.676	$.512^{+.035}_{-.035}$			
$\Delta+\Delta$ -H	77.69	1.078	$.462^{+.066}_{-.066}$	ART	$.499^{+.016}_{-.016}$	$.969^{+.084}_{-.084}$	1	.969	.524	$.484^{+.044}_{-.044}$			
		1.328	$.765^{+.093}_{-.093}$		$.995^{+.031}_{-.031}$	$.793^{+.040}_{-.040}$	.998	.794	1.038	$.789^{+.047}_{-.047}$			
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{vib}^{BC}(E)$	$F_{vib}^{AB}(E)$				
H+H-H	1.078	* $.297^{+.009}_{-.009}$	.294	$.300^{+.009}_{-.009}$	.317	$.290^{+.009}_{-.009}$	.290	.584	$.464^{+.047}_{-.047}$				
	1.328	* $12.064^{+.385}_{-.385}$	.582	$.606^{+.019}_{-.019}$	.627	$.597^{+.019}_{-.019}$	.607	.572	$.539^{+.048}_{-.048}$				
D+D-H	1.078	$.333^{+.010}_{-.010}$	.342	$.330^{+.010}_{-.010}$	.347	$.330^{+.010}_{-.010}$	.344	.614	$.449^{+.053}_{-.053}$				
	1.328	$.702^{+.022}_{-.022}$	.676	$.663^{+.021}_{-.021}$	.687	$.670^{+.021}_{-.021}$	.687	.618	$.514^{+.059}_{-.059}$				
$\Delta+\Delta$ -H	1.078	$.499^{+.016}_{-.016}$	.524	$.539^{+.017}_{-.017}$	.562	$.496^{+.016}_{-.016}$	.525	.755	$.370^{+.041}_{-.041}$				
	1.328	$.995^{+.031}_{-.031}$	1.038	$1.089^{+.035}_{-.035}$	1.111	$.971^{+.031}_{-.031}$	1.038	.891	$.457^{+.060}_{-.060}$				
	E	T_n^R			$T_n^P \cdot \omega(E)$			$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>1}^P$	$N_R^+(E)$	$\omega(E) \cdot N_P^+(E)$	$N_{\neq}(E)$
H+H-H	1.078	141, 43			545, 0.1X.2601			141	184	0	184	0	184
	1.328	260, 100, 2, 5			587, 2.6X.4253			262	367	3	374	3	377
D+D-H	1.078	171, 24			539X.3188			171	195	0	195	0	195
	1.328	299, 89, 0, 5, 0, 4			593X5239			299	397	0	410	0	410
$\Delta+\Delta$ -H	1.078	277			468, 14X.6116			277	277	9	277	9	286
	1.328	458, 0, 1			473, 107, 0.6X1.004			459	459	113	460	119	579

* DS has a NEGATIVE SLOPE

TABLE 30
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $XX+H \longrightarrow X+XH$
for the EXOTHERMIC LEPS SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^t(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\xi(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{\omega}^{acc}(E)$	$F_{\omega}^{acc}(E)$		
H+H-H	60.00	.25	.910 ⁺ .105	SD	1.158 ⁺ .036	.768 ⁺ .092	1	.768	.889 ⁺ .111	.945	.354 ⁺ .031		
		.5	.988 ⁺ .112		1.447 ⁺ .046	.685 ⁺ .044	.984	.696	.991 ⁺ .071	.851	.473 ⁺ .045		
H+D-D	65.91	.25	.898 ⁺ .104	ART	1.040 ⁺ .033	.878 ⁺ .101	1	.878	.913 ⁺ .110	.947	.279 ⁺ .031		
		.5	.988 ⁺ .112		1.329 ⁺ .042	.737 ⁺ .045	1	.737	.979 ⁺ .067	.556	.365 ⁺ .044		
H+ Δ - Δ	77.69	.25	.780 ⁺ .094	ART	.820 ⁺ .026	.969 ⁺ .084	.969	1	.795 ⁺ .072	.877	.217 ⁺ .029		
		.5	.788 ⁺ .095		.985 ⁺ .031	.798 ⁺ .040	.800	.998	.786 ⁺ .047	.511	.423 ⁺ .047		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_{\rho}^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.25	545,0,1X,2601			141,43			142	142	43	142	43	185
	.5	587,2,6X,4253			260,100,2,5			252	253	107	256	112	368
H+D-D	.25	539X,3188			171,24			172	172	24	172	24	196
	.5	593X,5239			299,89,0,5,0,4			311	311	98	311	111	422
H+ Δ - Δ	.25	468,14X,6116			277			286	295	0	295	0	295
	.5	473,107,0,6X1,004			458,0,1			475	588	1	594	1	595

TABLE 31
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $H+XX \rightleftharpoons HX+X$
for the ENDOTHERMIC LEPS SURFACE with the BARRIER in the ENTRANCE VALLEY

Masses	α (deg)	E (ev)	$\bar{P}_r^+(E)$	DS Type	$\bar{P}_R(E)_{PS}^{ACC}$	$\bar{\phi}(E)$	$\chi(E)$	$\eta(E)$	$\bar{P}_R(E)_{PS}^{SVA}$	$\bar{\phi}(E) \cdot \bar{P}_R(E)_{PS}^{ACC}$		
H+H-H	60.00	1.078	.235 ⁺ .043	SD	.300 ⁺ .009	.766 ⁺ .092	.766	1	.317	.230 ⁺ .029		
		1.328	.437 ⁺ .063		.606 ⁺ .019	.695 ⁺ .045	.701	.992	.627	.421 ⁺ .030		
H+D-D	65.91	1.078	.182 ⁺ .037	SD	.239 ⁺ .008	.845 ⁺ .140	.845	1	.251	.202 ⁺ .034		
		1.328	.347 ⁺ .055		.478 ⁺ .015	.707 ⁺ .071	.707	1	.496	.338 ⁺ .036		
H+ $\triangle$ - $\triangle$	77.69	1.078	.099 ⁺ .019	SD	.135 ⁺ .004	.659 ⁺ .150	.667	.989	.142	.089 ⁺ .020		
		1.328	.175 ⁺ .036		.268 ⁺ .008	.640 ⁺ .105	.644	.994	.281	.172 ⁺ .029		
	E	$\bar{P}_R(E)_{ART}^{ACC}$	$\bar{P}_R(E)_{ART}^{SVA}$	$\bar{P}_R(E)_{SD}^{ACC}$	$\bar{P}_R(E)_{SD}^{SVA}$	$\bar{P}_R(E)_M^{ACC}$	$\bar{P}_R(E)_M^{SVA}$	$F_{\nu/6}^{SC}(E)$	$F_{\nu/6}^{AB}(E)$			
H+H-H	1.078	*.297 ⁺ .009	.294	.300 ⁺ .009	.317	.290 ⁺ .009	.290	.584	.464 ⁺ .047			
	1.328	*12.064 ⁺ .385	.582	.606 ⁺ .019	.627	.597 ⁺ .019	.607	.572	.539 ⁺ .048			
H+D-D	1.078	*.233 ⁺ .007	.228	.239 ⁺ .008	.251	.226 ⁺ .007	.231	.562	.478 ⁺ .053			
	1.328	*14.554 ⁺ .466	.452	.478 ⁺ .015	.496	.465 ⁺ .015	.469	.556	.484 ⁺ .057			
H+ $\triangle$ - $\triangle$	1.078	*.112 ⁺ .004	.112	.135 ⁺ .004	.142	.109 ⁺ .003	.112	.543	.446 ⁺ .064			
	1.328	*.246 ⁺ .008	.221	.268 ⁺ .008	.281	.237 ⁺ .008	.229	.511	.515 ⁺ .056			
	E	T_n^R			$T_n^P \cdot \omega(E)$		$N_r(E)$	$\sum_n T_n^R$	$\omega(E) \cdot T_{n>},$	$N_R^+(E)$	$N_P^+(E)$	$N_{\neq}(E)$
H+H-H	1.078	141, 43			545, 0, 1X.2601		141	184	0	184	0	184
	1.328	260, 100, 2, 5			587, 2, 6X.4253		262	367	3	374	3	377
H+D-D	1.078	109, 18, 0, 1			548X.2128		109	128	0	129	0	129
	1.328	208, 82, 0, 2			595X.3460		208	292	0	294	0	294
H+ $\triangle$ - $\triangle$	1.078	59, 11, 1, 6, 0, 2			504, 0, 12X.1115		60	79	1	90	1	91
	1.328	101, 27, 4, 9, 0, 3			587, 0, 5X.1812		105	144	1	163	1	164

* DS has a negative slope

**Based on a sample of 1800 trajectories

TABLE 32
TRAJECTORY and PHASE SPACE RESULTS for the REACTION SERIES $HX+X \rightleftharpoons H+XX$
for the EXOTHERMIC LEPS SURFACE with the BARRIER in the EXIT VALLEY

Masses	α (deg.)	E (ev)	$\bar{P}_r^{\pm}(E)$	DS Type	$\bar{P}_R(E)^{acc}$	$\bar{Q}(E)$	$\chi(E)$	$\eta(E)$	$\xi(E)\bar{P}_R(E)^{acc}$	$F_{vib}^{acc}(E)$	$F_{vib}^{obs}(E)$		
H+H-H	60.00	.25	.910 $^{+}$.105	SD	1.158 $^{+}$.036	.768 $^{+}$.092	1	.768	.889 $^{+}$.111	.945	354 $^{+}$.031		
		.5	.988 $^{+}$.112		1.447 $^{+}$.046	.685 $^{+}$.044	.984	.696	.991 $^{+}$.071	.851	473 $^{+}$.045		
D+D-H	65.91	.25	.913 $^{+}$.106	SD	1.129 $^{+}$.035	.854 $^{+}$.141	1	.854	.964 $^{+}$.160	.942	324 $^{+}$.027		
		.5	.992 $^{+}$.112		1.383 $^{+}$.044	.705 $^{+}$.071	1	.705	.975 $^{+}$.104	.823	420 $^{+}$.037		
$\Delta+\Delta$ -H	77.69	.25	.858 $^{+}$.072	SD	1.217 $^{+}$.038	.652 $^{+}$.148	.983	.633	.793 $^{+}$.179	.926	440 $^{+}$.023		
		.5	.987 $^{+}$.112		1.487 $^{+}$.047	.645 $^{+}$.106	.991	.651	.959 $^{+}$.160	.881	487 $^{+}$.032		
	E	$T_n^R \cdot \omega(E)$			T_n^P			$\omega(E) \cdot N_r(E)$	$\omega(E) \cdot \sum_n T_n^R$	$T_{n>1}^P$	$\omega(E) \cdot N_R^{\pm}(E)$	$N_P^{\pm}(E)$	$N_{\pm}(E)$
H+H-H	.25	545,0,1X.2601			141,43			142	142	43	142	43	185
	.5	587,2,6X.4253			260,100,2,5			252	253	107	256	112	368
D+D-H	.25	548X.2128			109,18,0,1			117	117	19	117	20	137
	.5	595X.3460			208,82,0,2			206	206	84	206	86	292
$\Delta+\Delta$ -H	** .25	504,0,12X.1115			59,11,1,6,0,2			58	58	20	59	30	89
	.5	587,0,5X.1812			101,27,4,9,0,3			107	107	43	108	58	166

** BASED on a SAMPLE of 1800 TRAJECTORIES

FIGURE 3

SKewed PK PES FOR THE REACTION $H + H-H \rightleftharpoons H-H + H$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

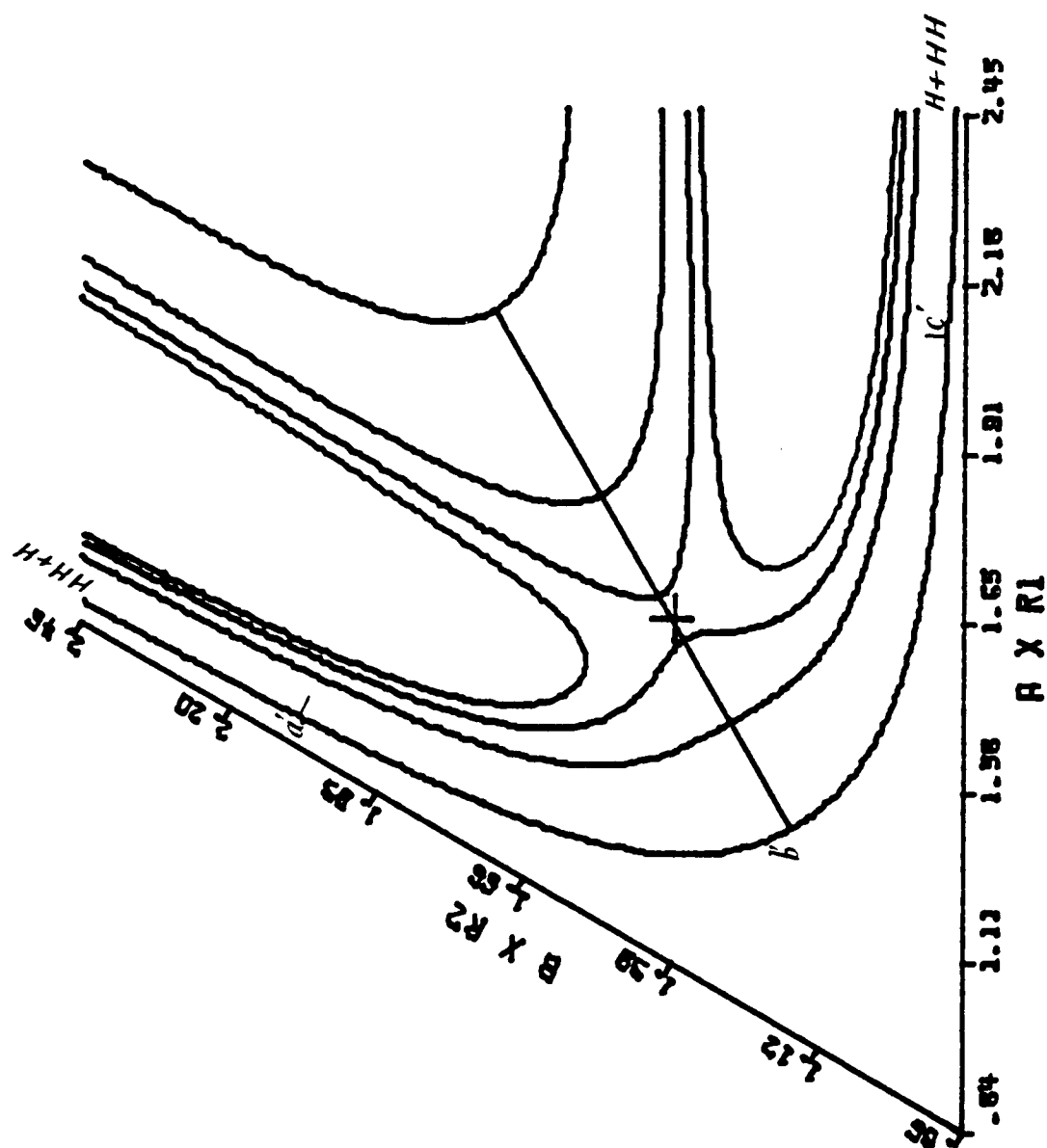


FIGURE 4

SKEWED PK PES FOR THE REACTION $D + H-H \rightleftharpoons D-H + H$
 ENERGY OF CONTOURS = .9, .5, .4, .35ev

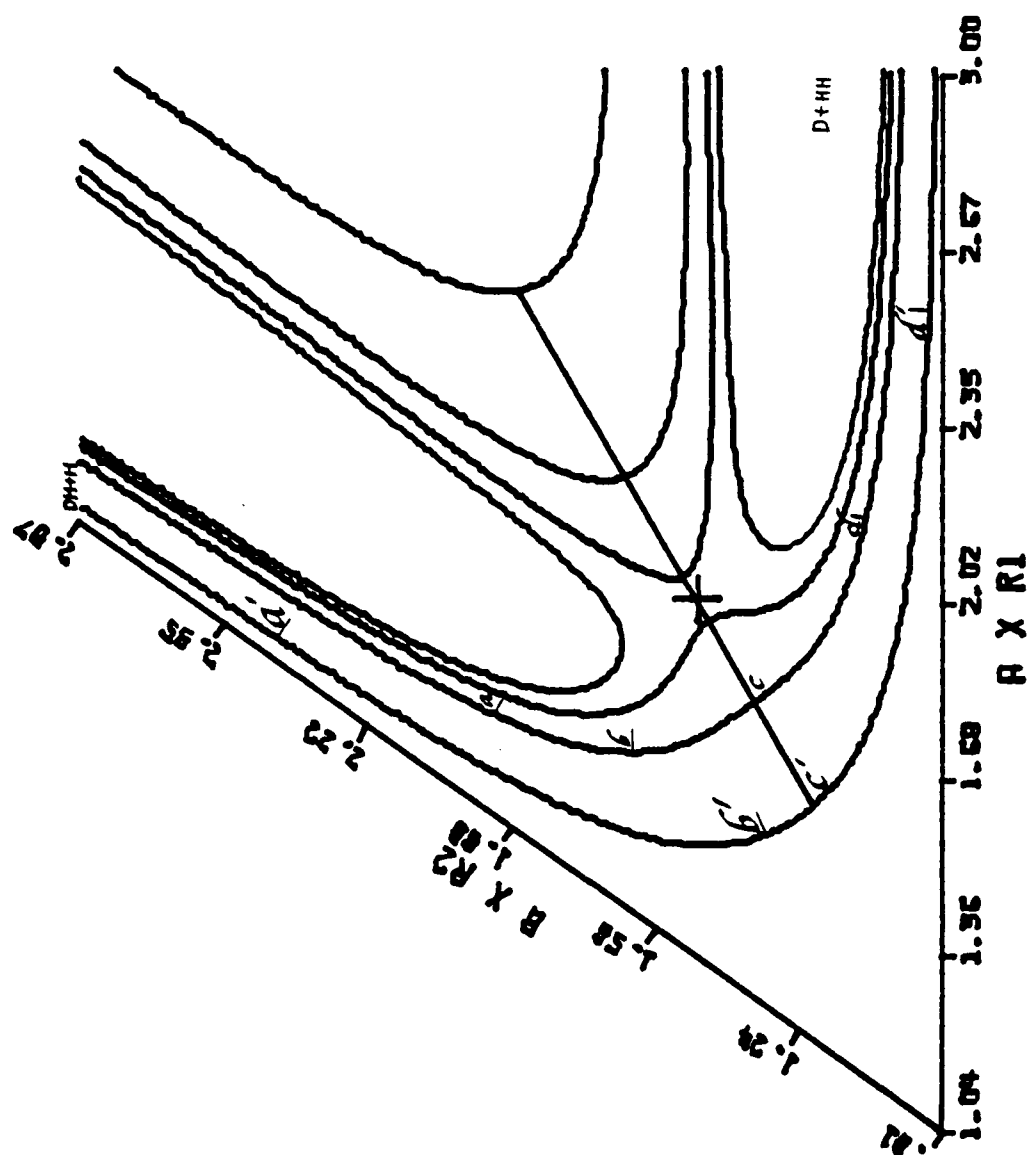


FIGURE 5

SKEWED PK PES FOR THE REACTION $\Delta + \text{H-H} \rightleftharpoons \Delta\text{-H} + \text{H}$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

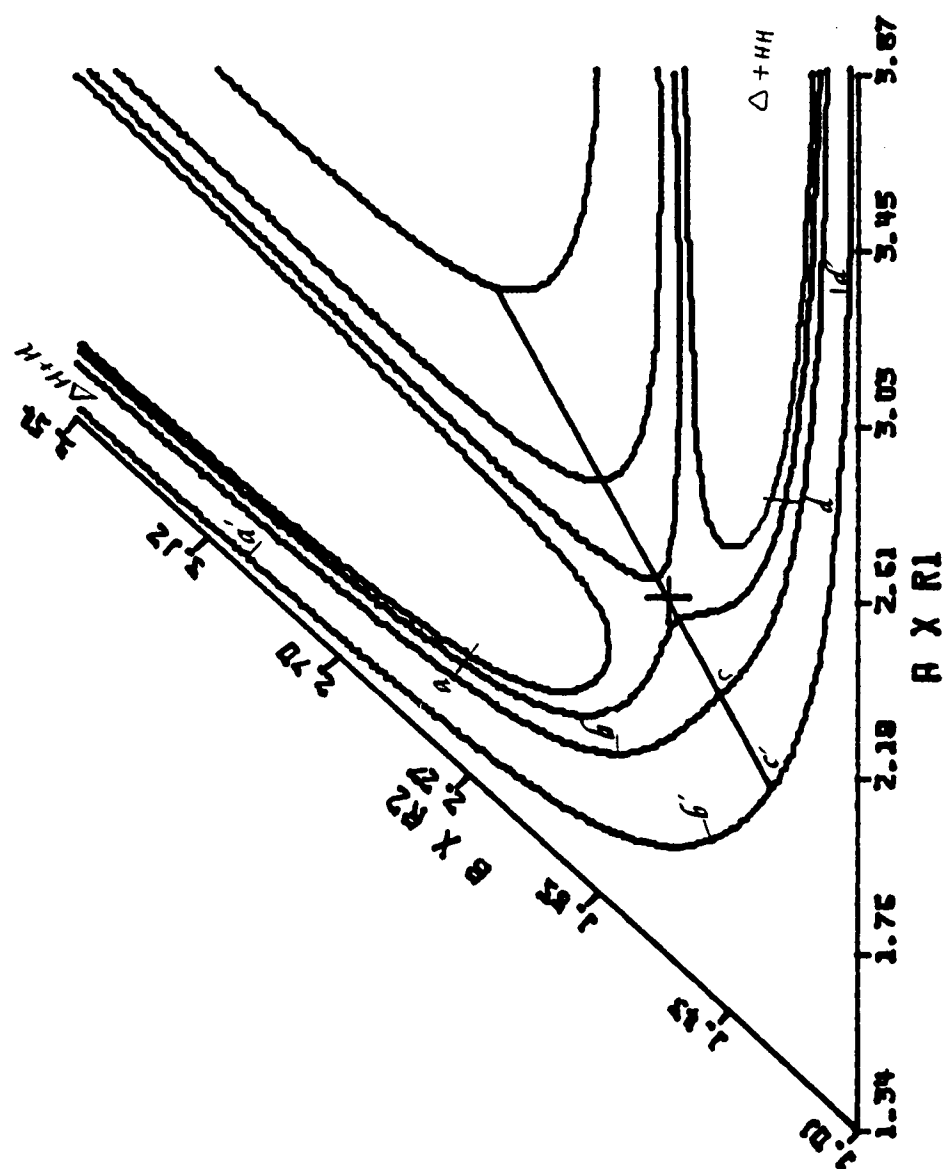


FIGURE 6

SKEWED PW PES FOR THE REACTION $\text{H} + \text{H}-\text{H} \rightleftharpoons \text{H}-\text{H} + \text{H}$
 ENERGY OF CONTOURS = .9, .5, .4, .35ev

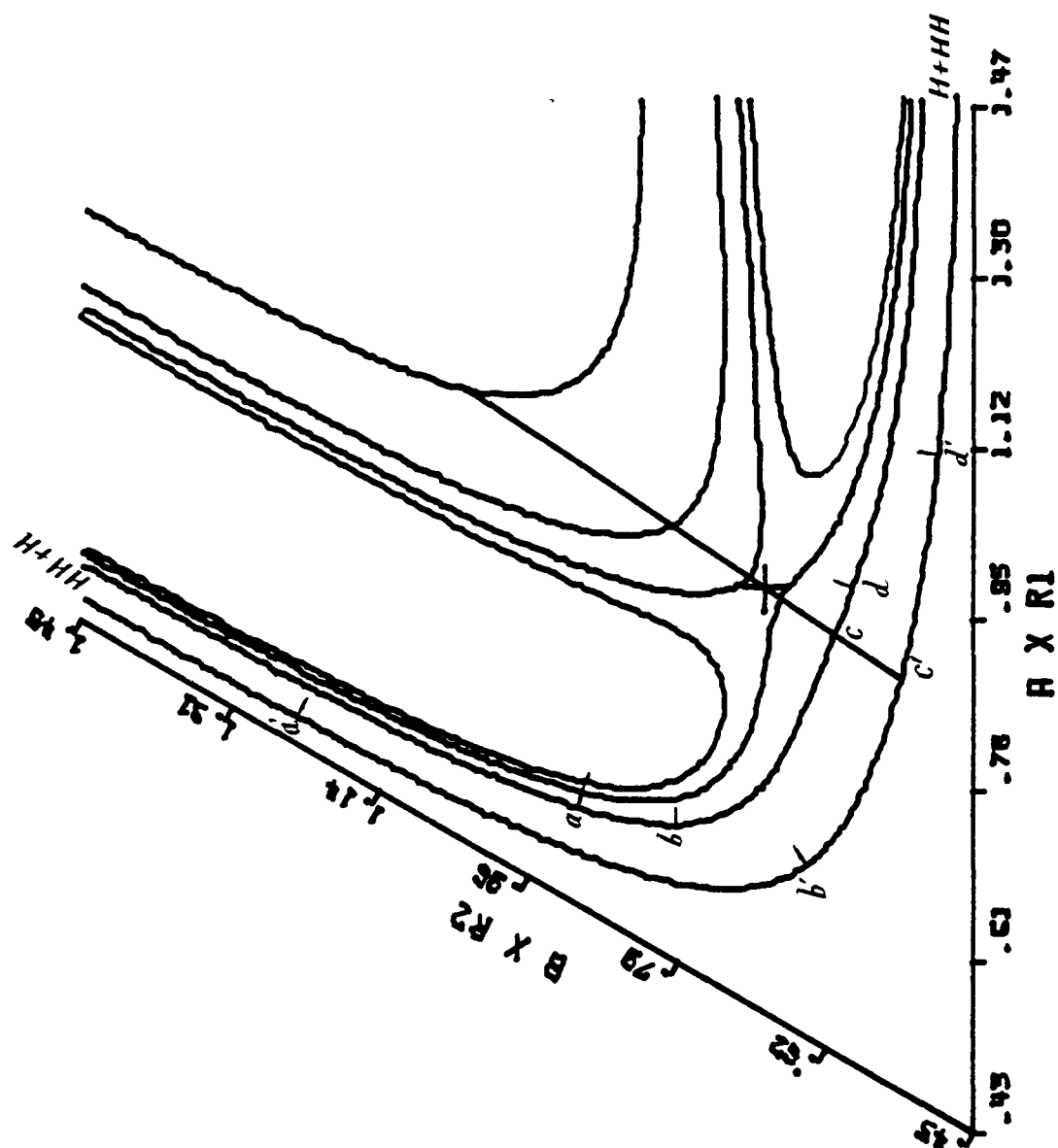


FIGURE 7

SKewed PW PES FOR THE REACTION $D + H-H \rightleftharpoons D-H + H$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

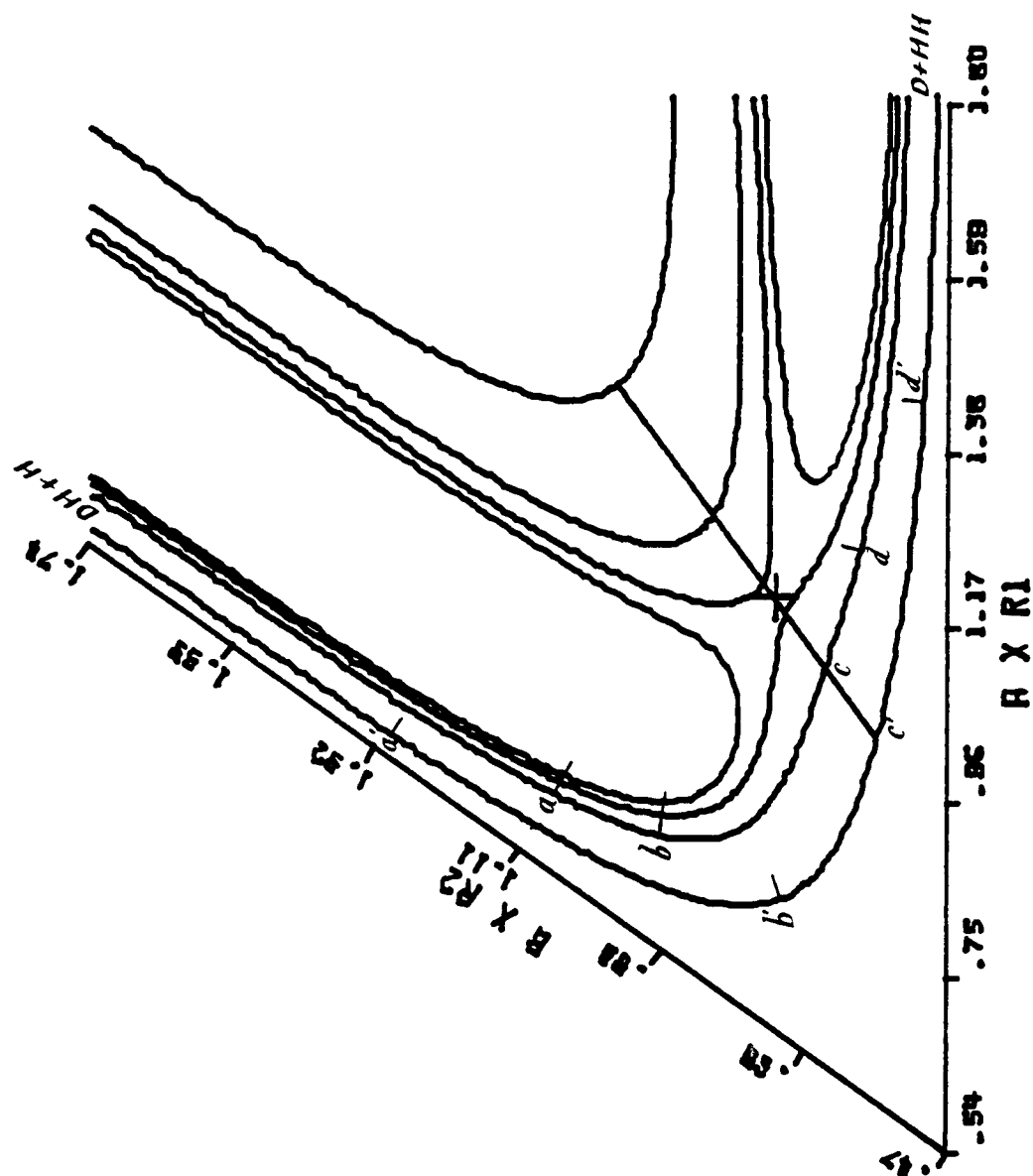


FIGURE 8

SKEWED PW PES FOR THE REACTION $\Delta + \text{H-H} \rightleftharpoons \Delta\text{-H} + \text{H}$
 ENERGY OF CONTOURS = .9, .5, .4, .35ev

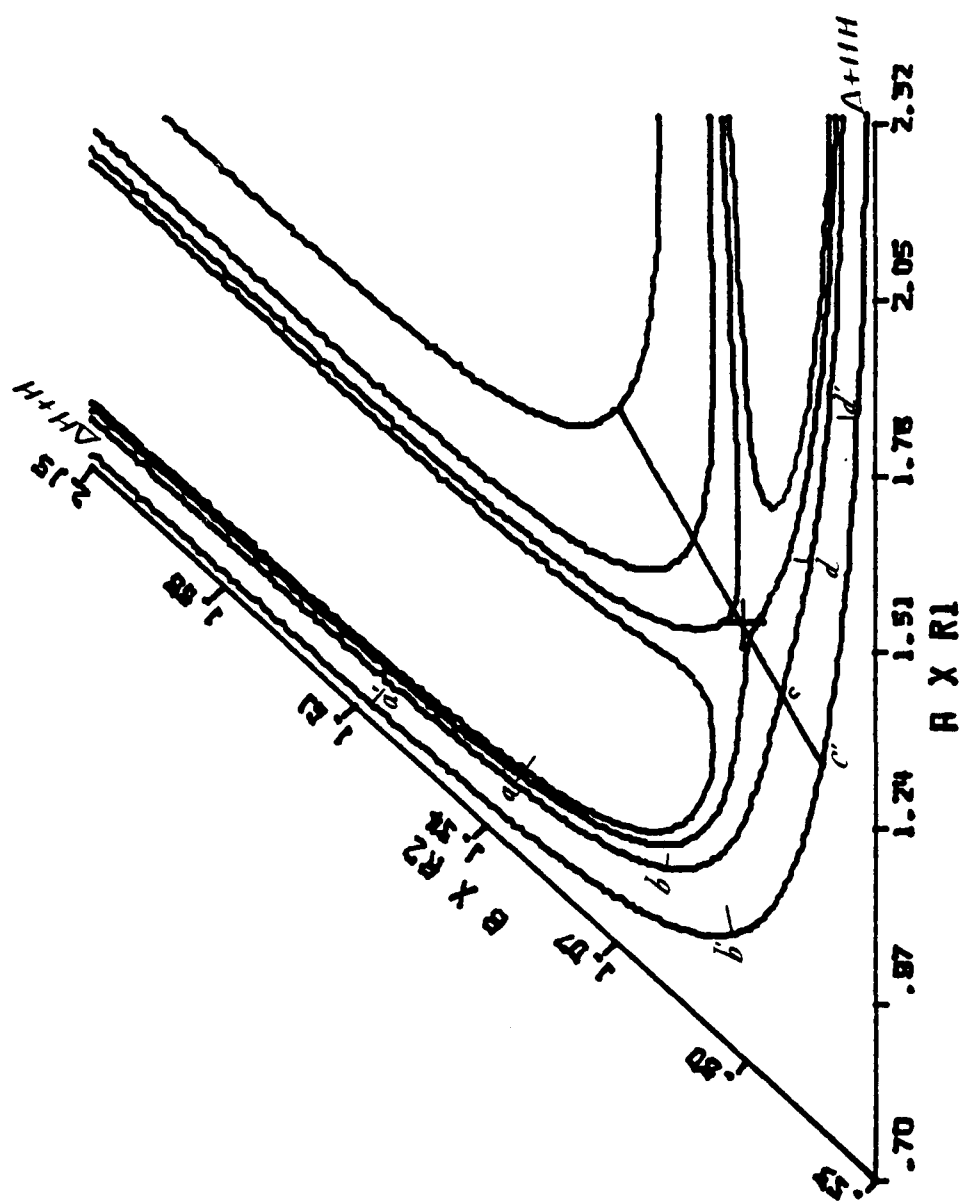


FIGURE 9

SKEWED PW PES FOR THE REACTION $\text{H} + \text{H-D} \rightleftharpoons \text{H-H} + \text{D}$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

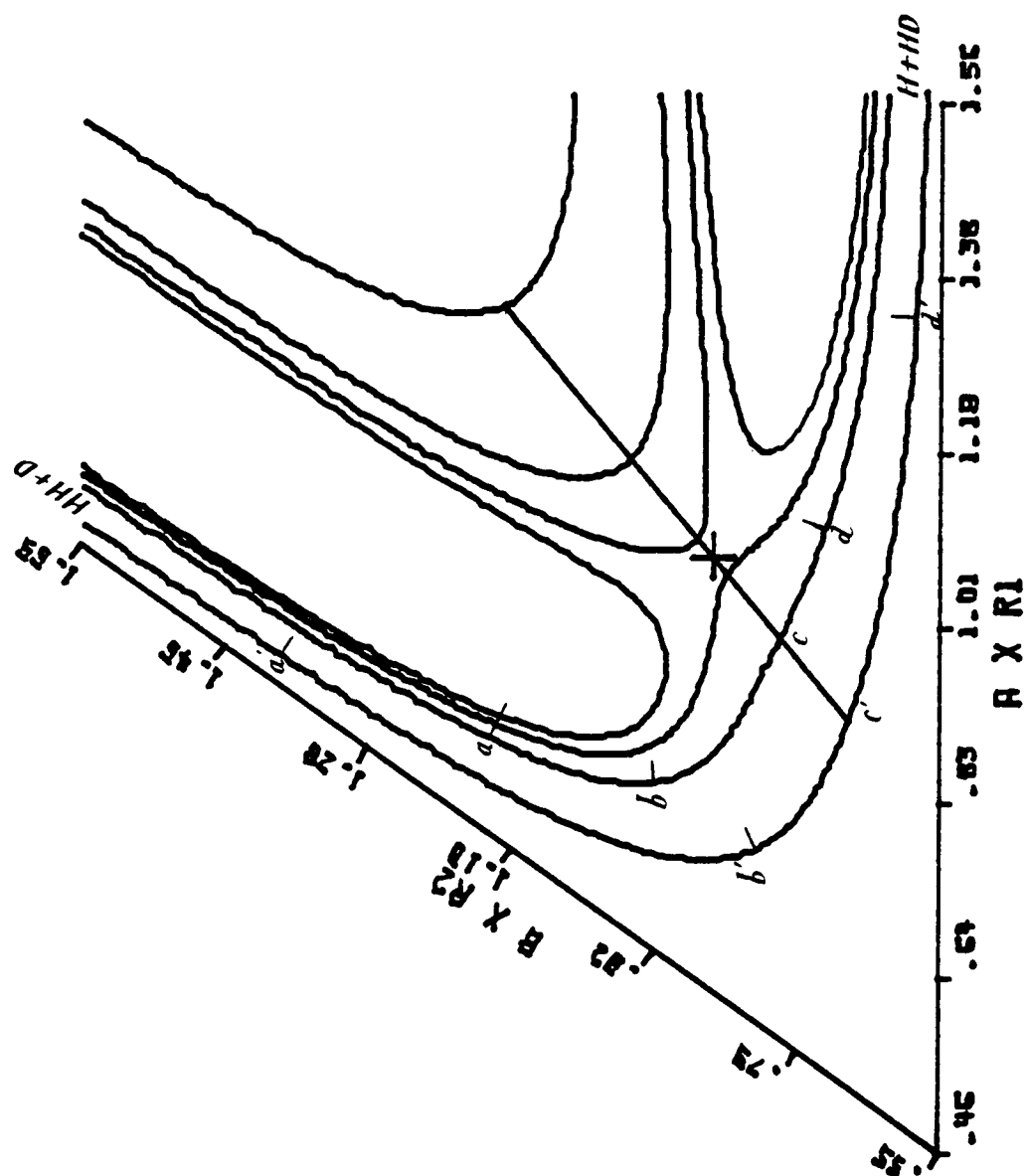


FIGURE 10

SKEWED PW PES FOR THE REACTION $\text{H} + \text{H}-\Delta \rightleftharpoons \text{H}-\text{H} + \Delta$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

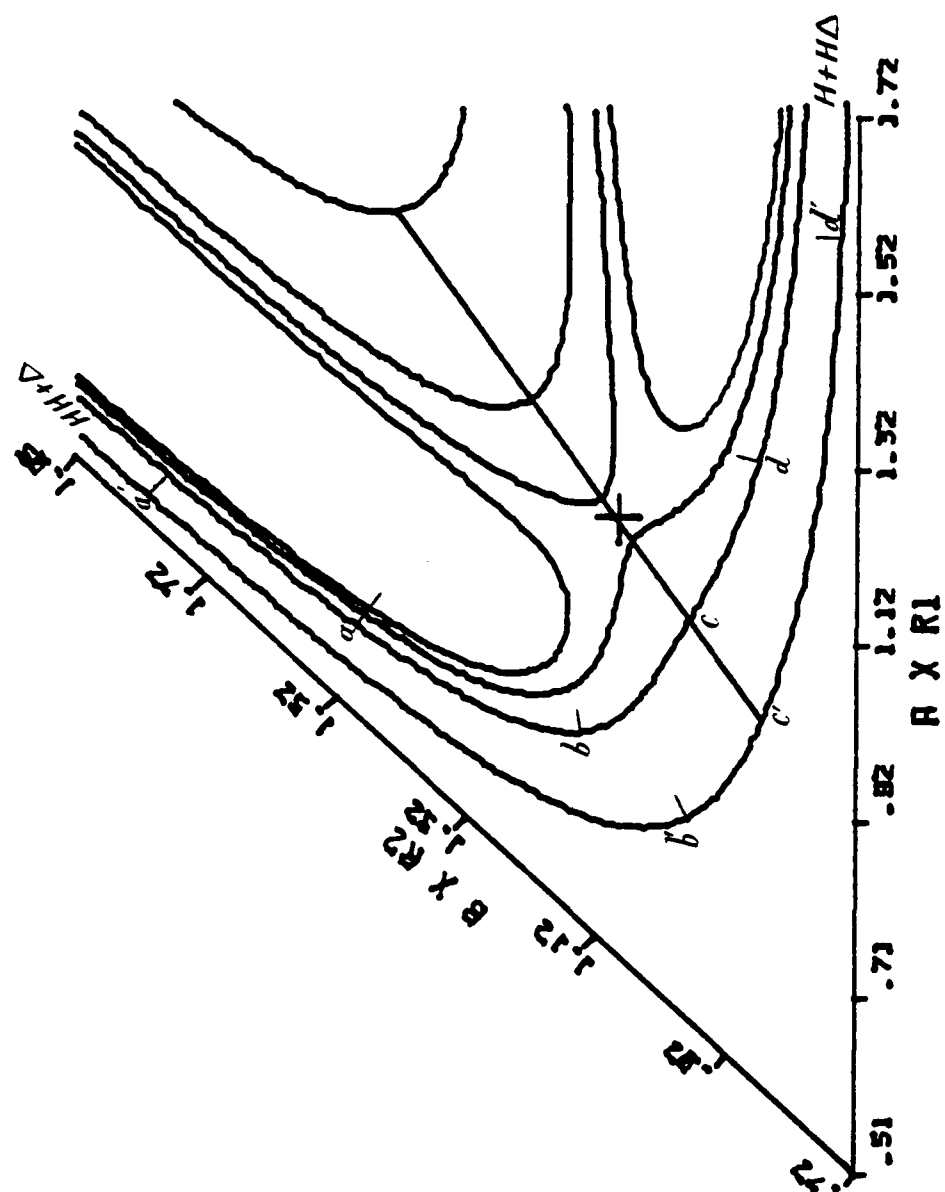


FIGURE 11

SKEWED LEPS PES FOR THE REACTION $\text{H} + \text{H}-\text{H} \rightleftharpoons \text{H}-\text{H} + \text{H}$

$E - E_c = .424, .174, .074, -.002\text{ev}$

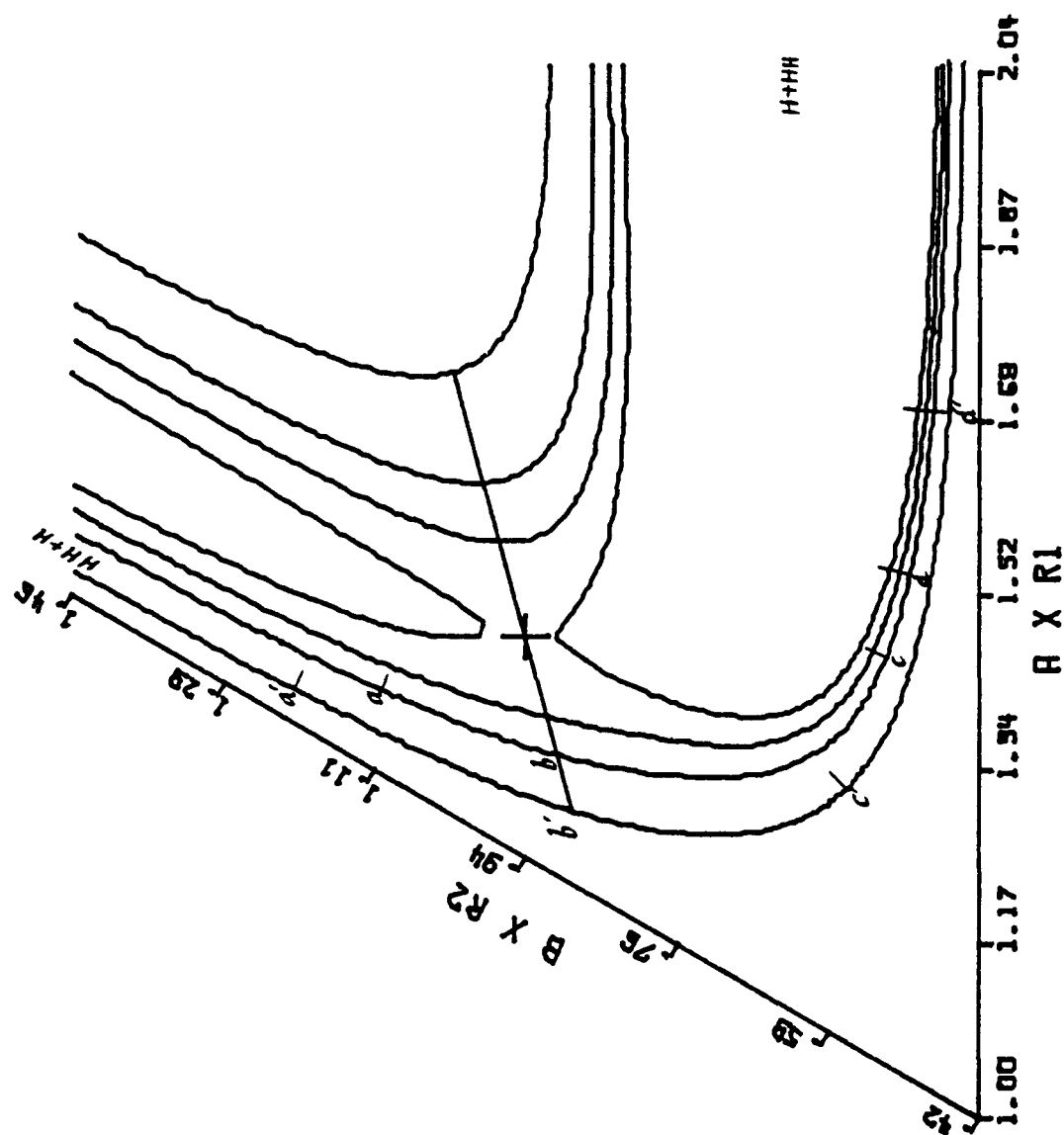


FIGURE 12

SKEWED LEPS PES FOR THE REACTION $D + H-H \rightleftharpoons D-H + H$

$E - E_c = .424, .174, .074, -.002\text{ev}$

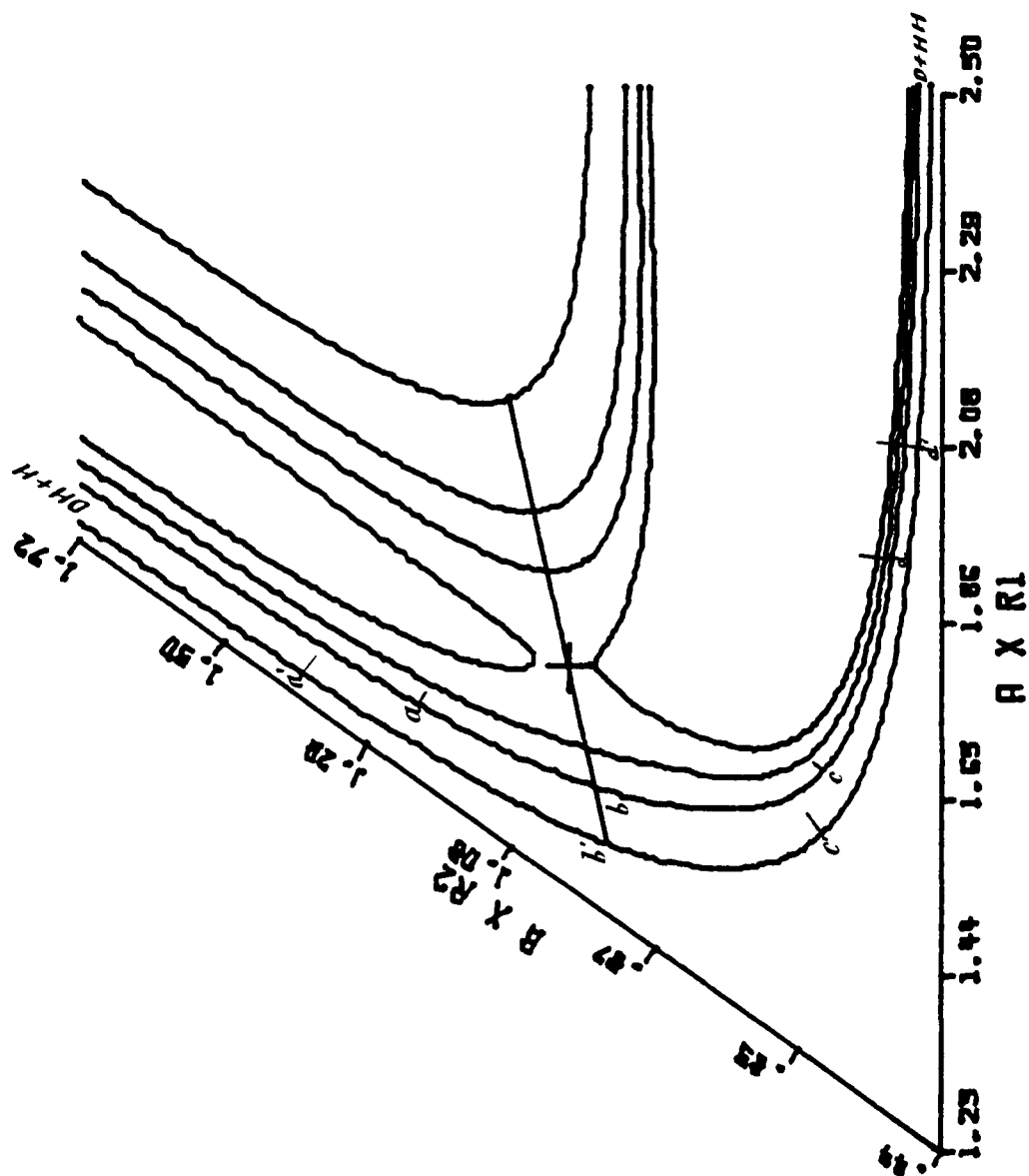


FIGURE 13

SKewed LEPS PES FOR THE REACTION $\Delta + \text{H-H} \rightleftharpoons \Delta\text{-H} + \text{H}$

$E - E_c = .424, .174, .074, -.002\text{ev}$

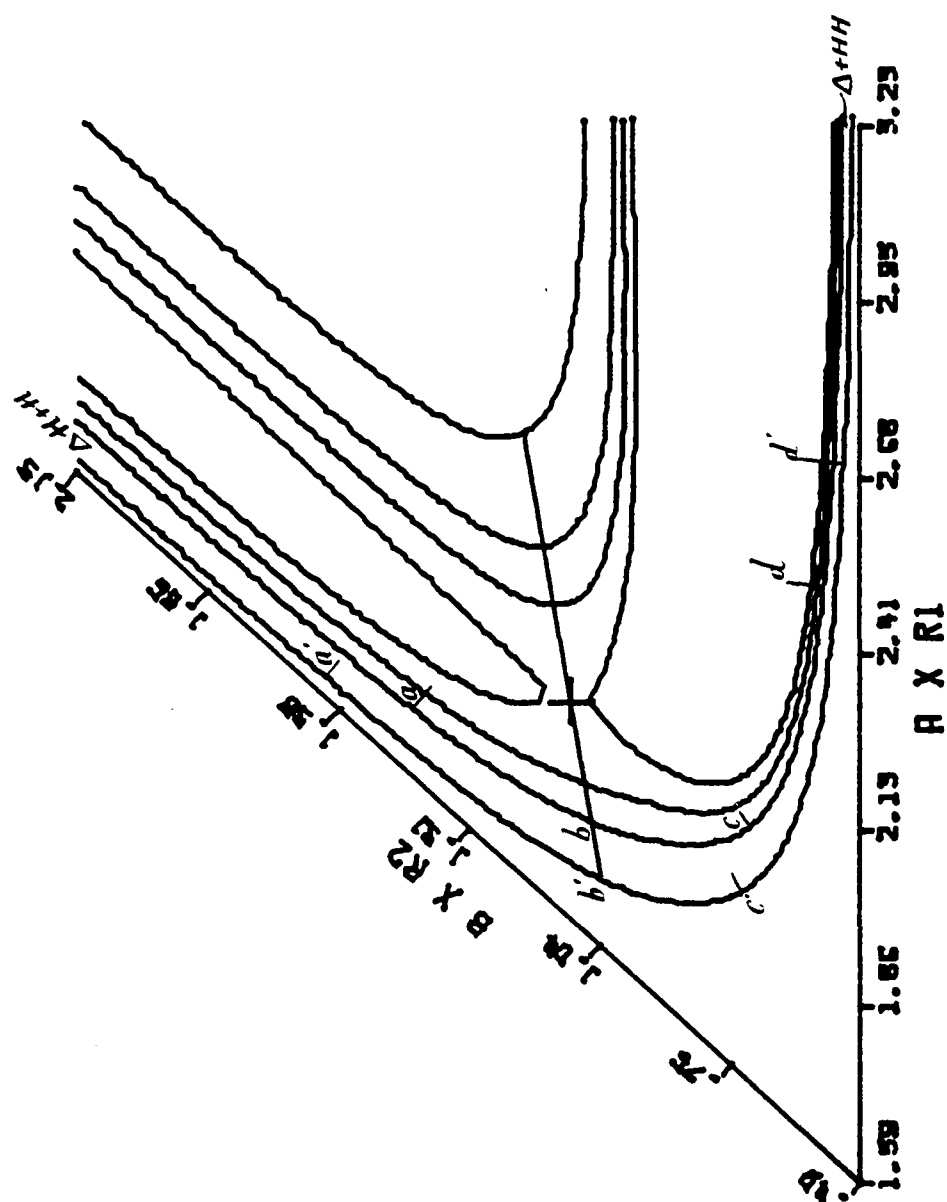


FIGURE 14

SKEWED LEPS PES FOR THE REACTION $\text{H} + \text{H-D} \rightleftharpoons \text{H-H} + \text{D}$

$E - E_c = .424, .174, .074, -.002\text{ev}$

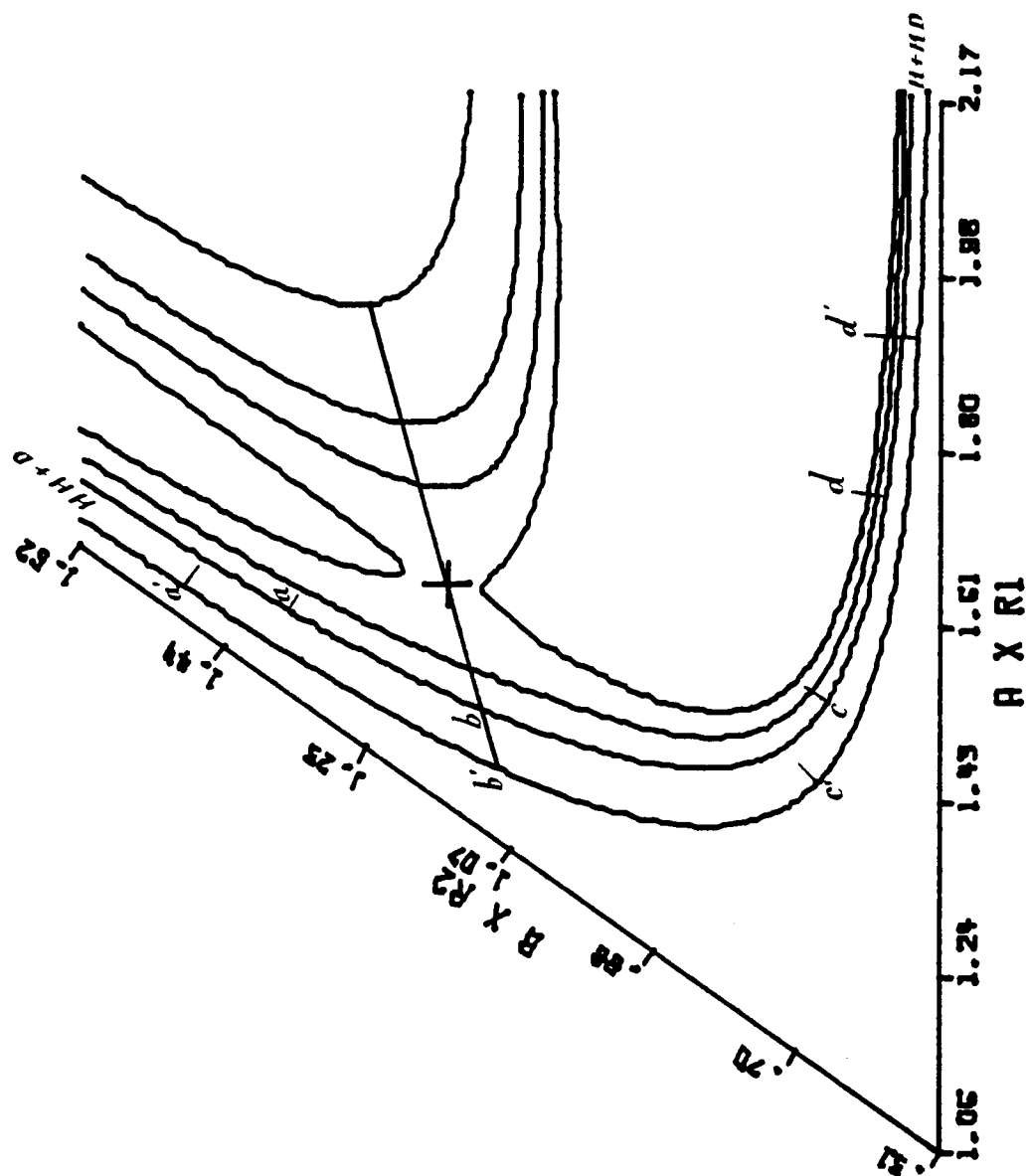


FIGURE 15

SKEWED LEPS PES FOR THE REACTION $H + H-\Delta \rightleftharpoons H-H + \Delta$

$E - E_c = .424, .174, .074, -.002\text{ev}$

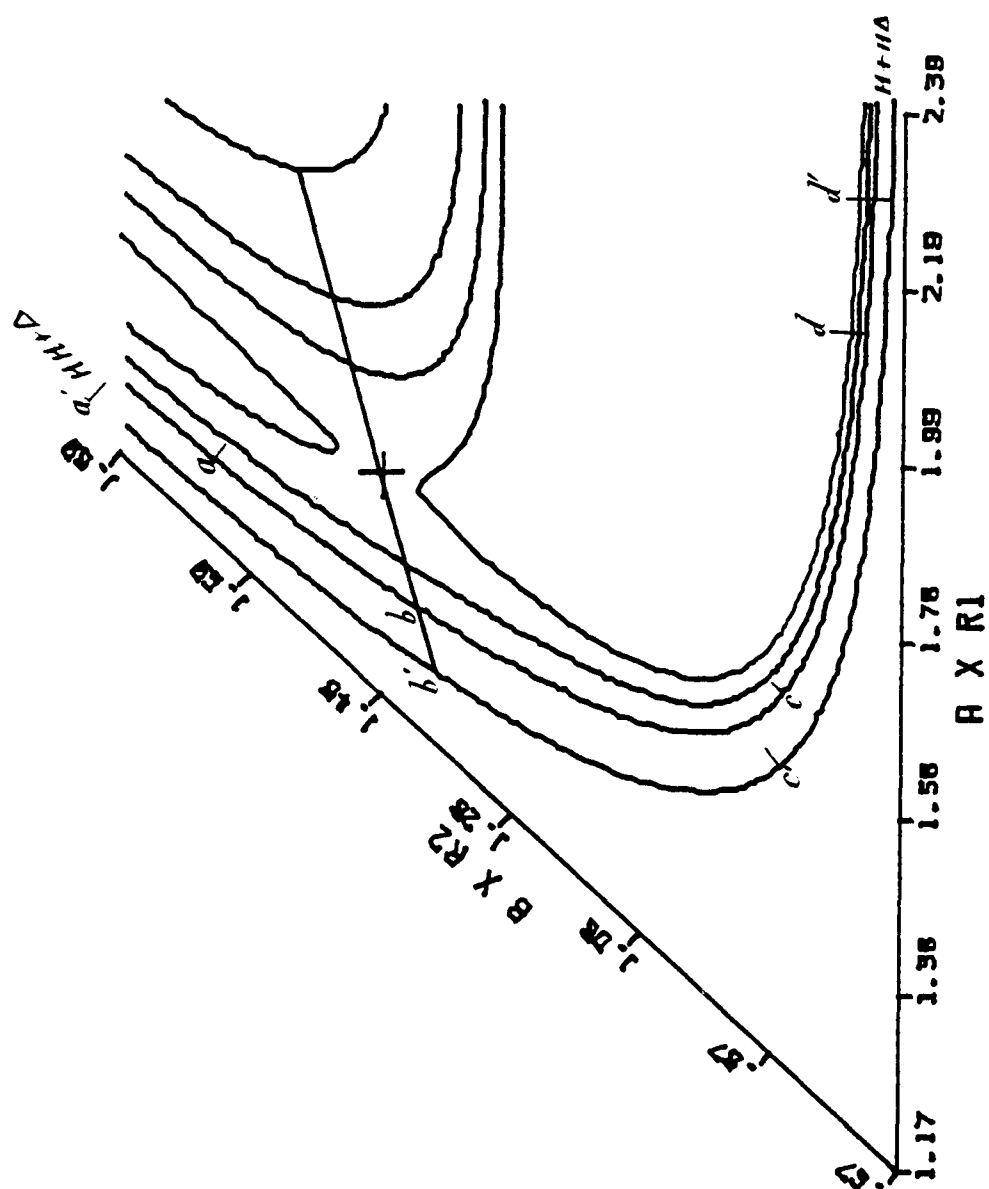


FIGURE 16

SKEWED PK PES FOR THE REACTION $\text{H} + \text{D-H} \rightleftharpoons \text{H-D} + \text{H}$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

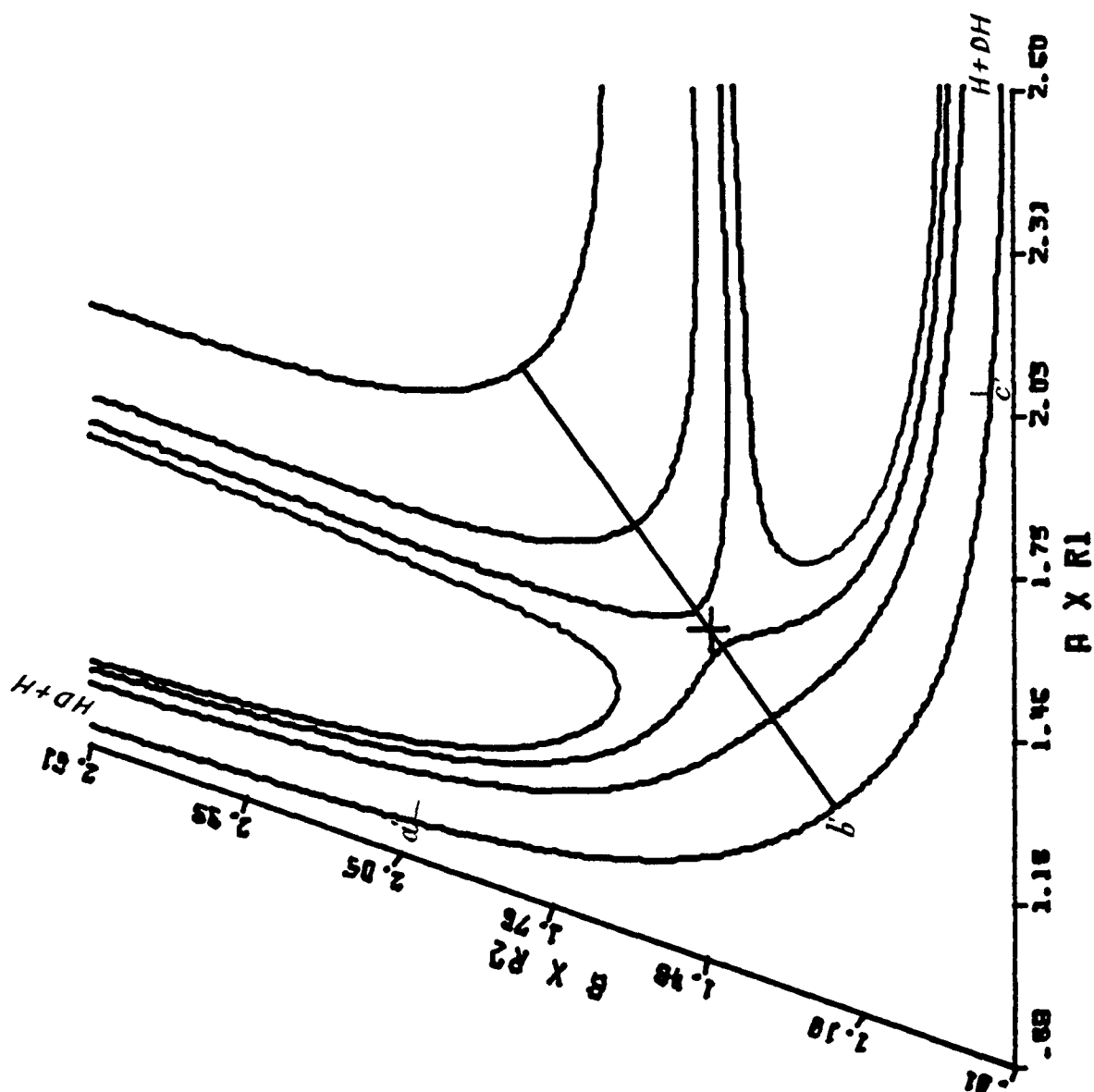


FIGURE 17

SKEWED PK PES FOR THE REACTION $\text{H} + \Delta\text{-H} \rightleftharpoons \text{H-}\Delta + \text{H}$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

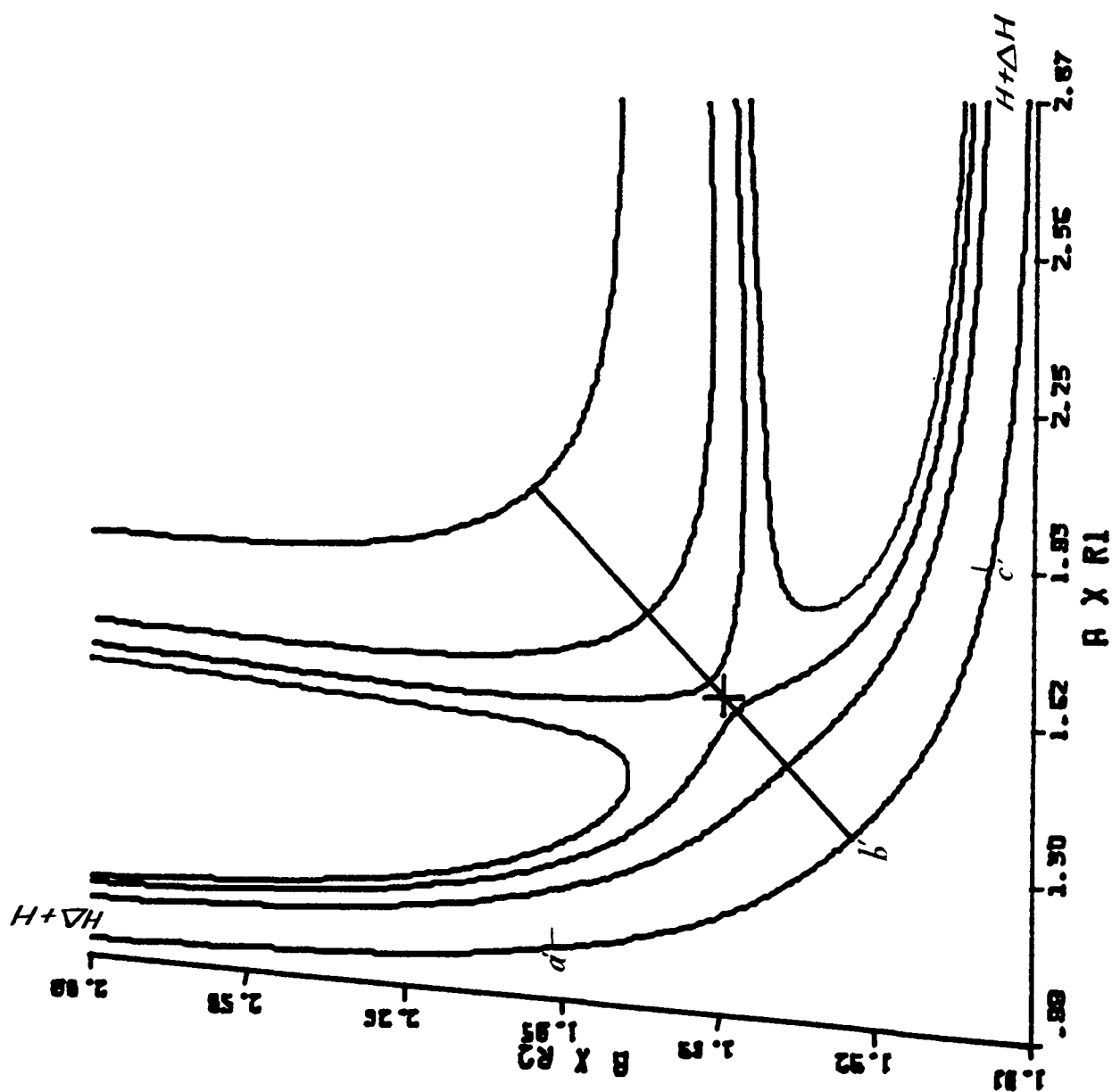


FIGURE 18

SKEWED PK PES FOR THE REACTION $D + H-D \rightleftharpoons D-H + D$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

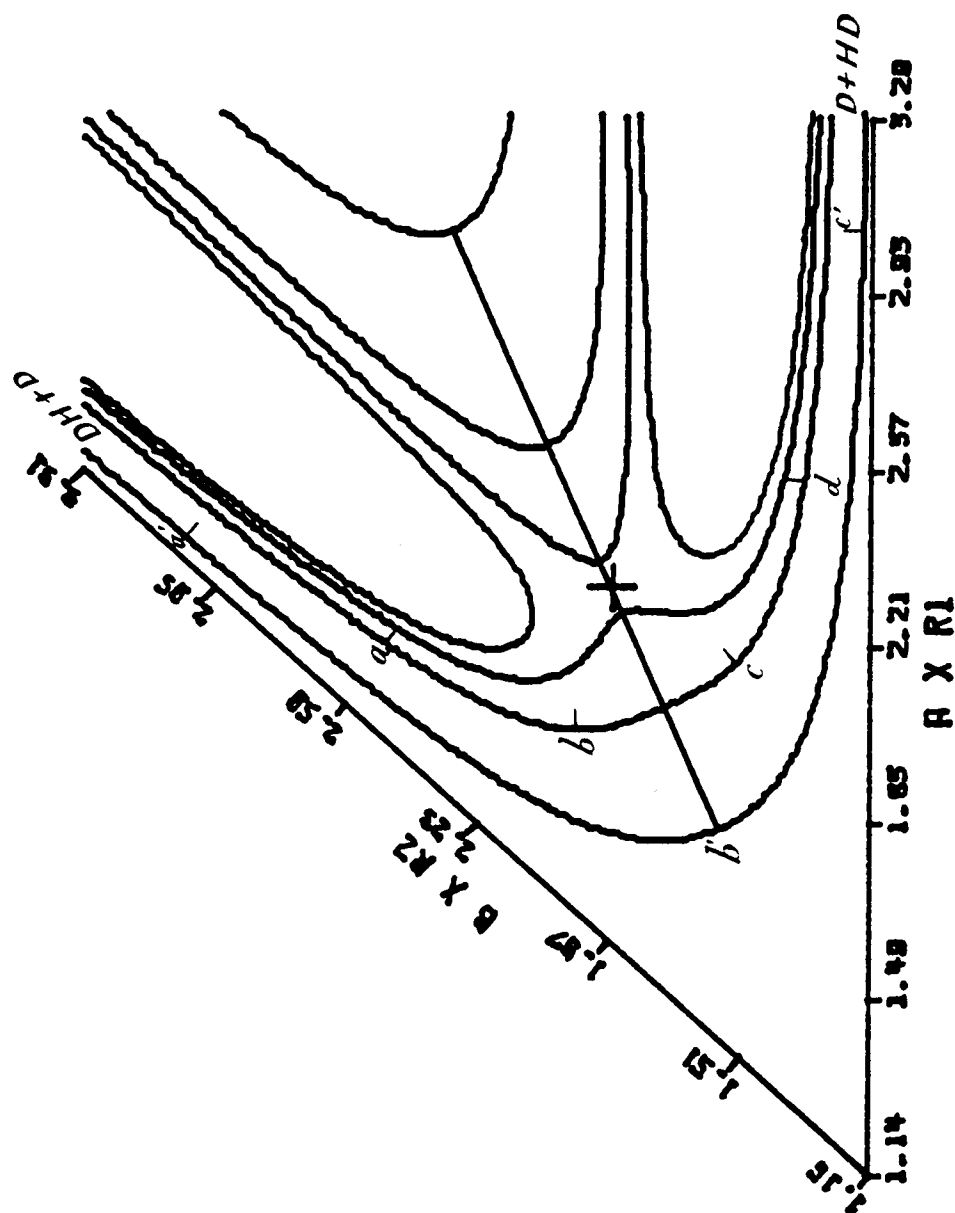


FIGURE 19

SKEWED PK PES FOR THE REACTION $\Delta + \text{H}-\Delta \rightleftharpoons \Delta-\text{H} + \Delta$
 ENERGY OF CONTOURS = .9, .5, .4, .35ev

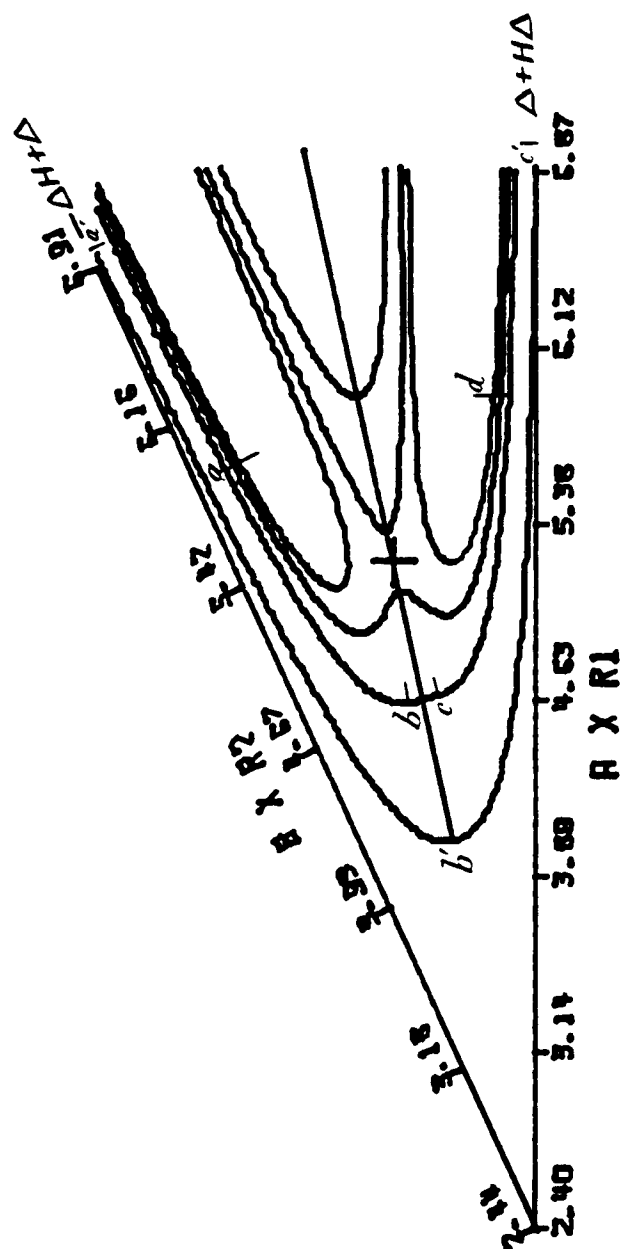


FIGURE 20

SKEWED PW PES FOR THE REACTION $\text{H} + \text{D-H} \rightleftharpoons \text{H-D} + \text{H}$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

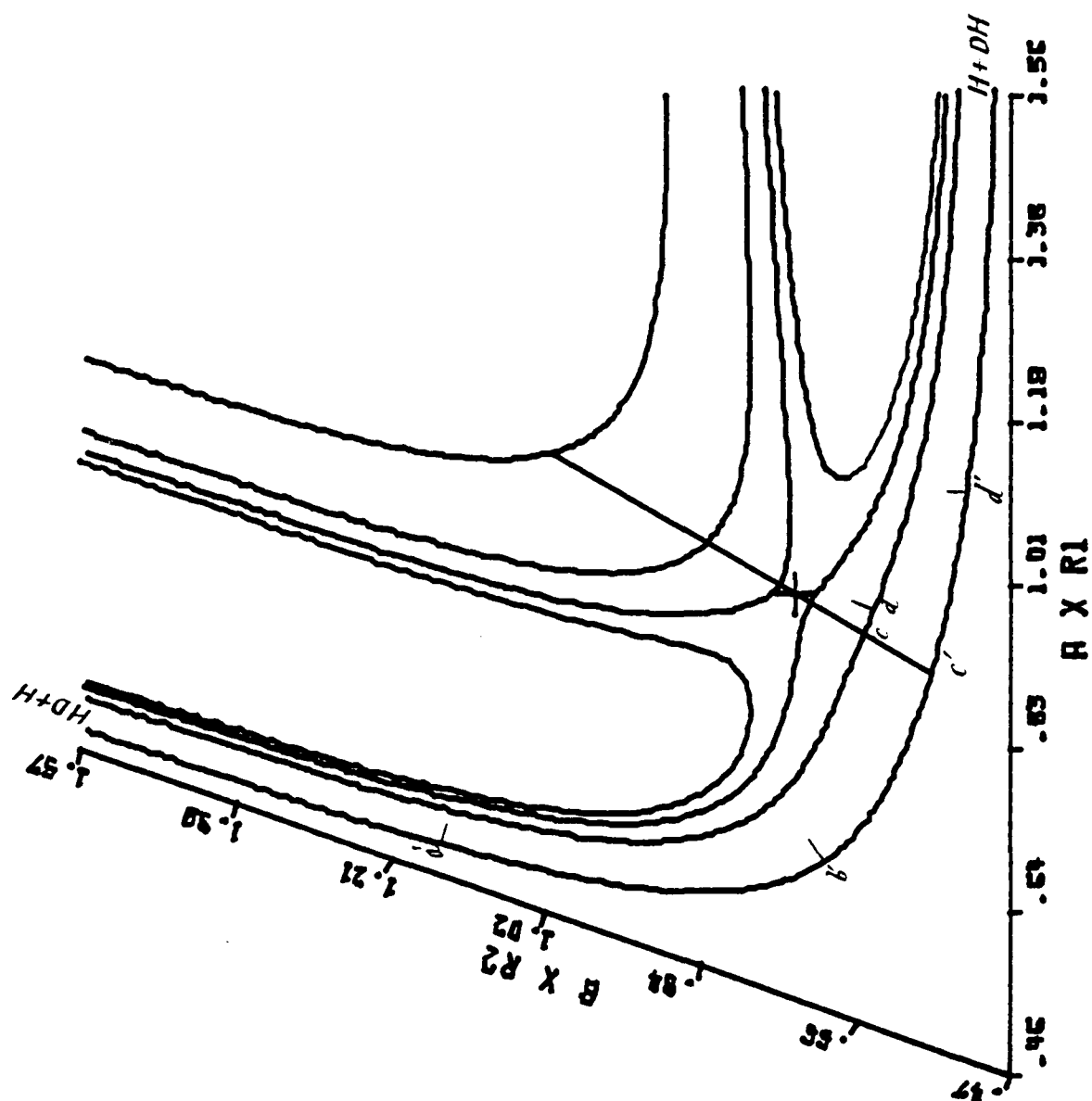


FIGURE 21

SKEWED PW PES FOR THE REACTION $\text{H} + \Delta\text{-H} \rightleftharpoons \text{H-}\Delta + \text{H}$
 ENERGY OF CONTOURS = .9, .5, .4, .35ev

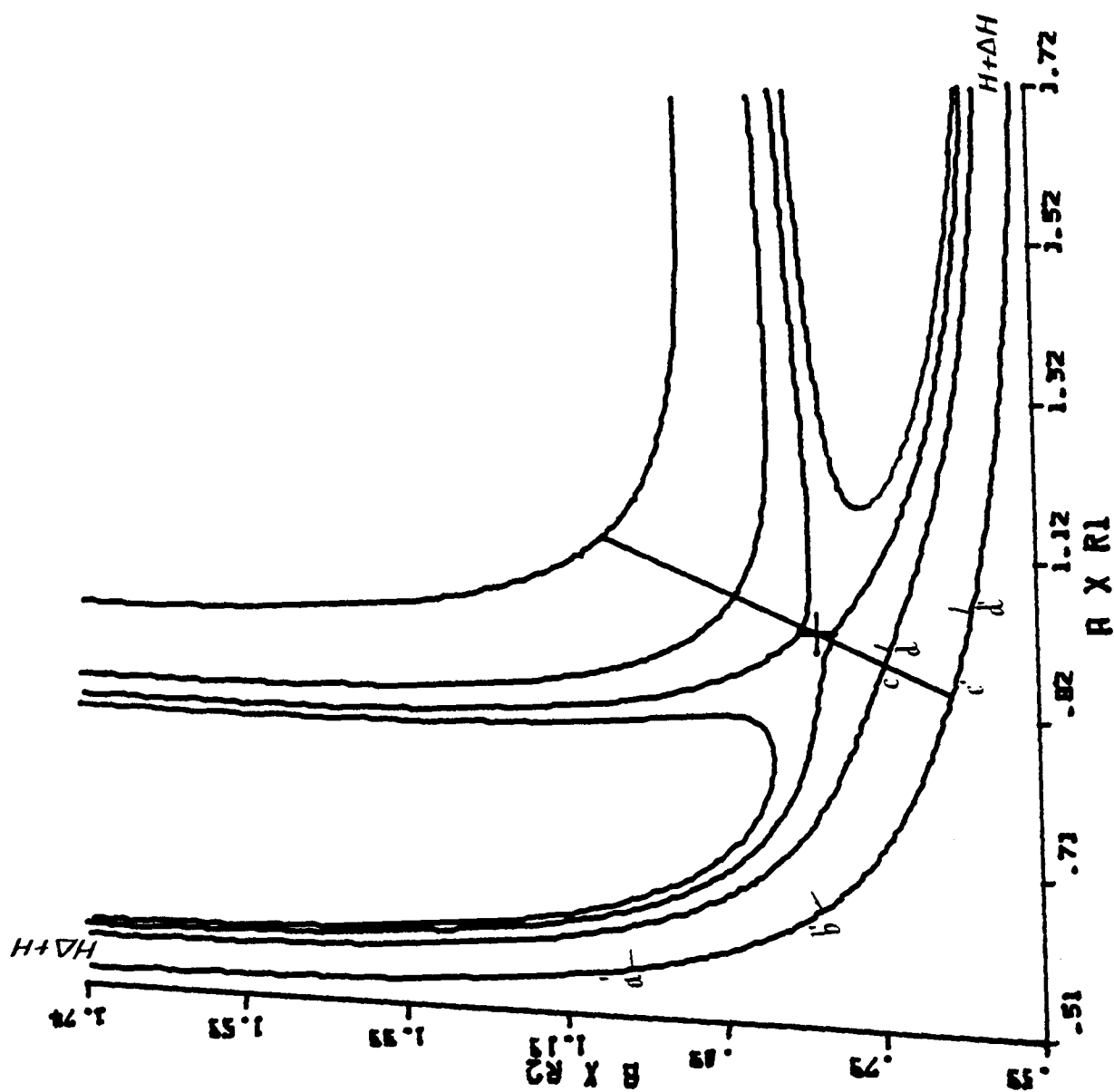


FIGURE 22

SKEWED PW PES FOR THE REACTION $D + H-D \rightleftharpoons D-H + D$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

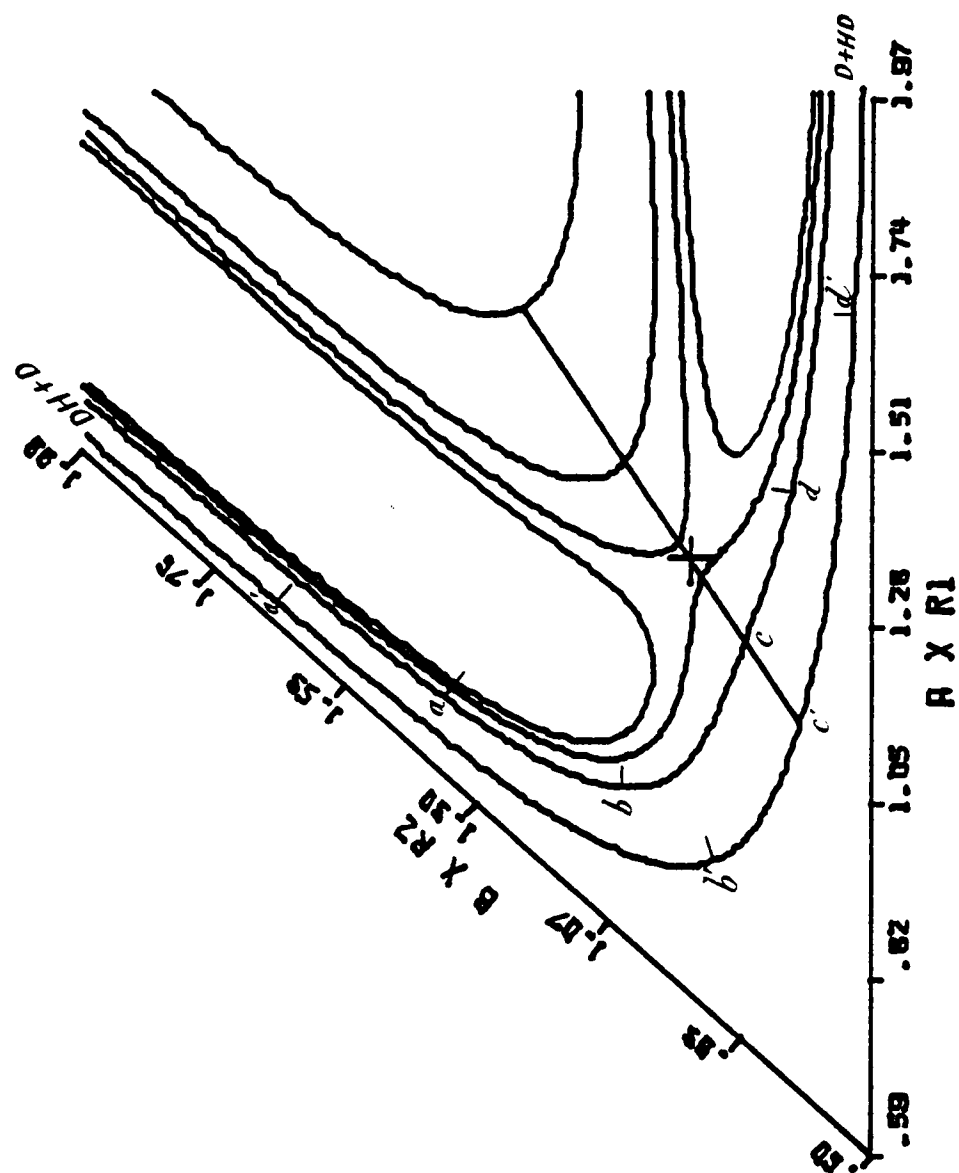


FIGURE 23

SKEWED PW PES FOR THE REACTION $\Delta + \text{H}-\Delta \rightleftharpoons \Delta-\text{H} + \Delta$
 ENERGY OF CONTOURS = .9, .5, .4, .35ev

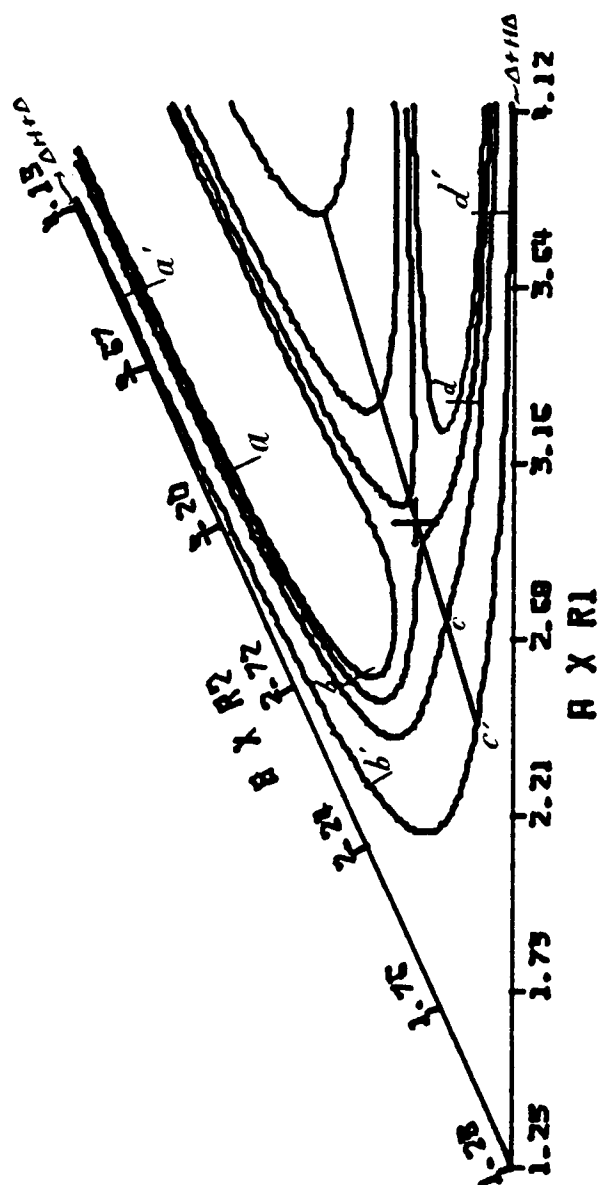


FIGURE 24

SKEWED LEPS PES FOR THE REACTION $\text{H} + \text{D-H} \rightleftharpoons \text{H-D} + \text{H}$

$E - E_c = .424, .174, .074, -.002 \text{ev}$

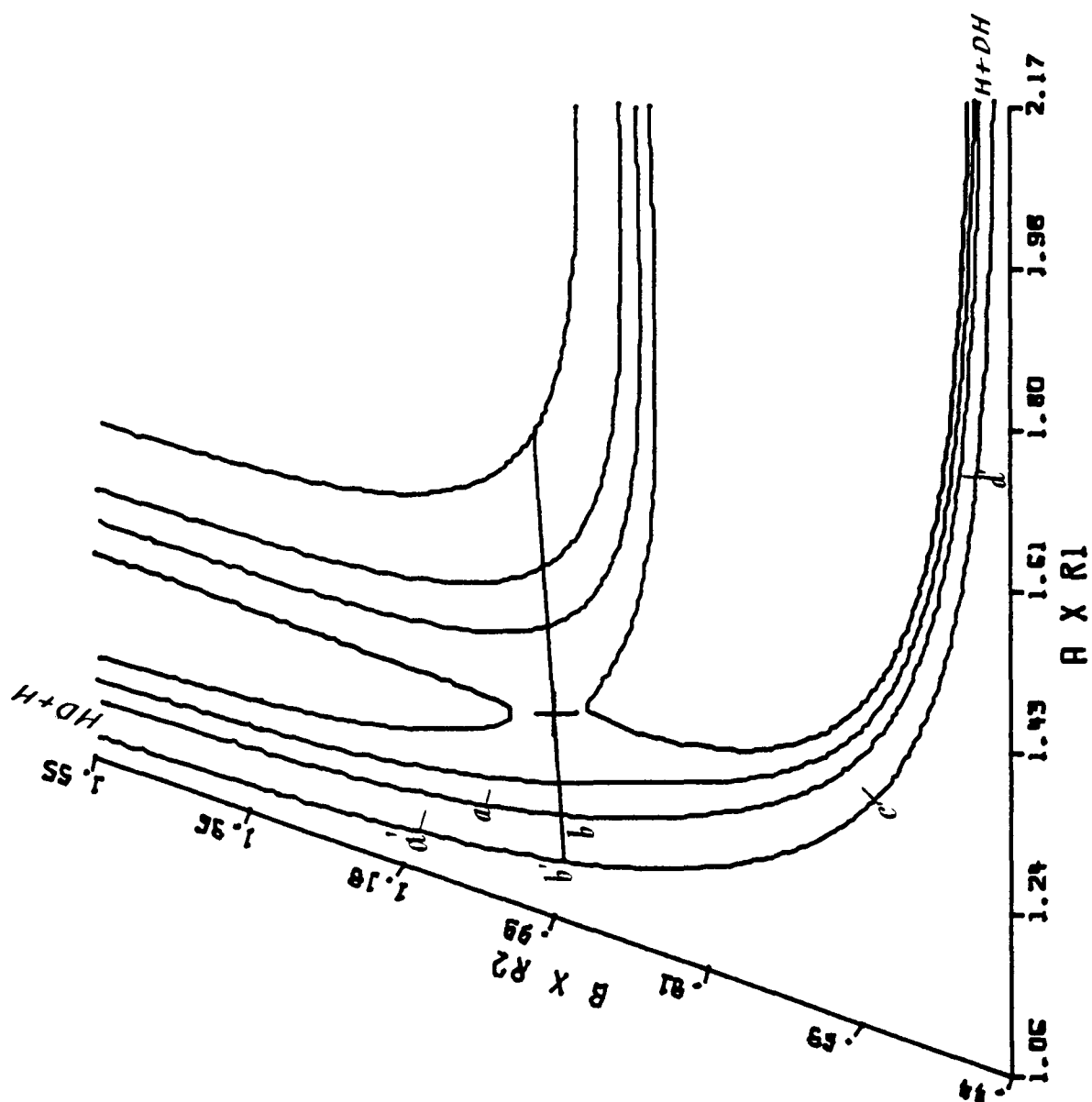


FIGURE 25

SKEWED LEPS PES FOR THE REACTION $H + \Delta-H \rightleftharpoons H-\Delta + H$

$E - E_c = .424, .174, .074, -.002\text{ev}$

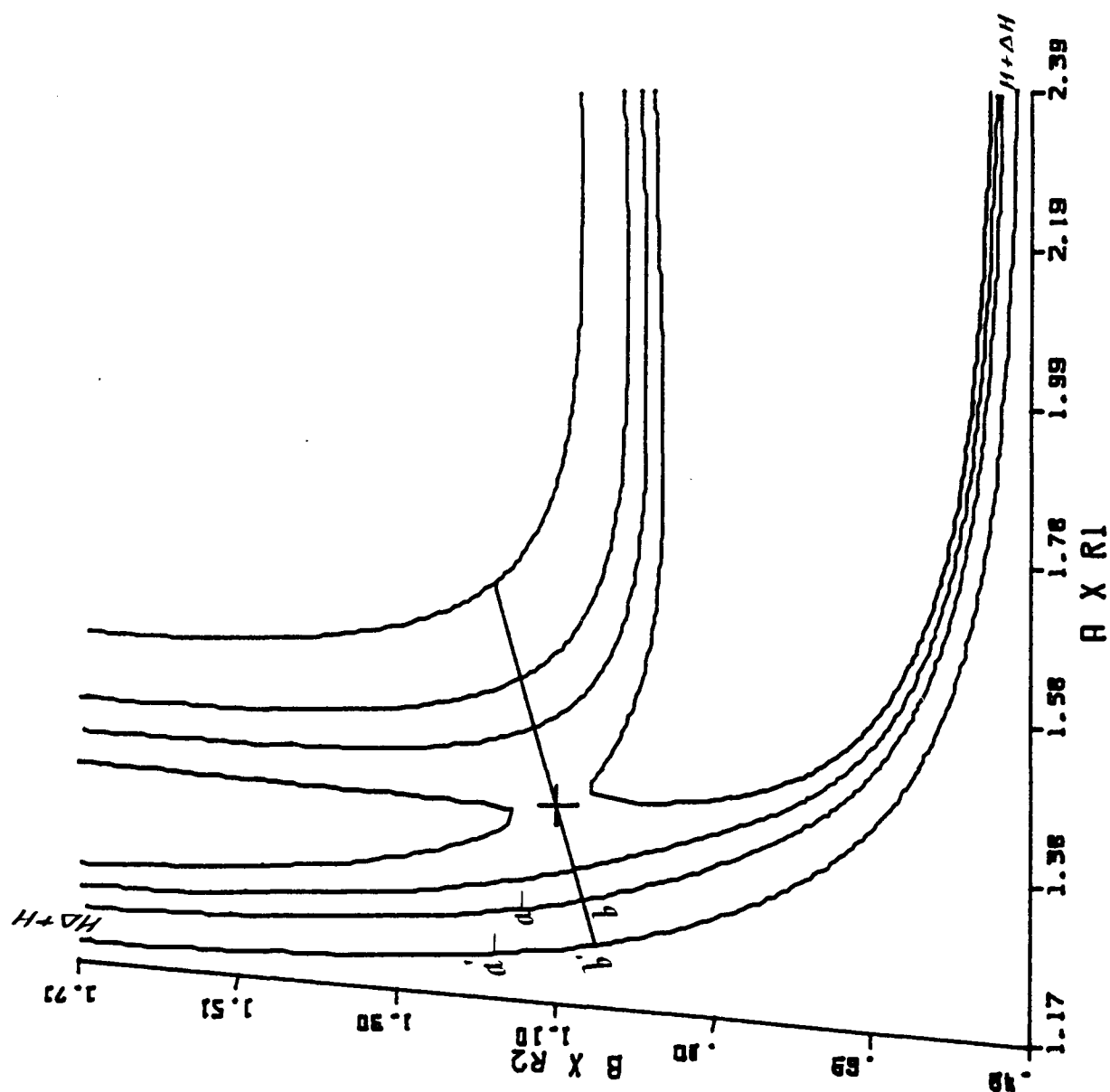


FIGURE 26

SKEWED LEPS PES FOR THE REACTION $D + H-D \rightleftharpoons D-H + D$

$E - E_c = .424, .174, .074, -.002 \text{ ev}$

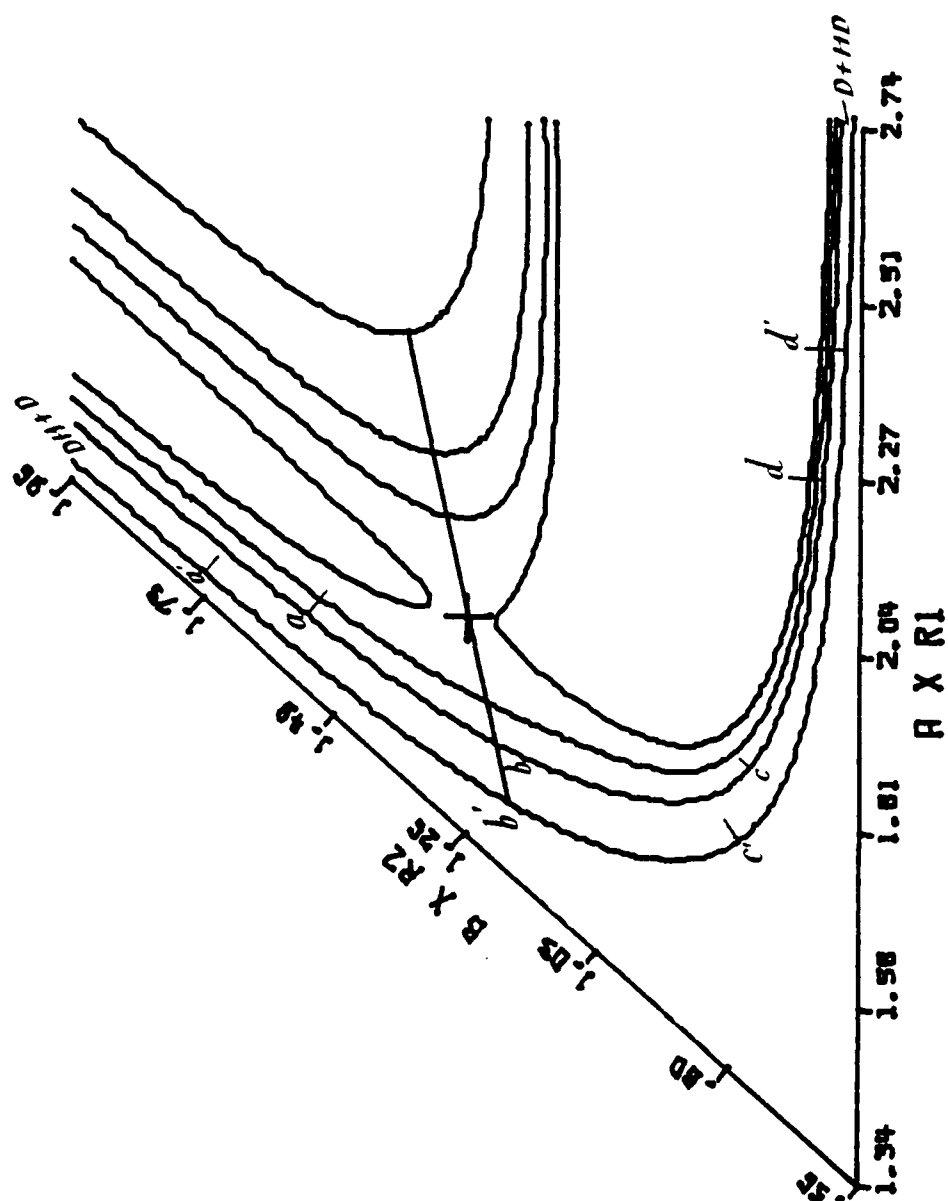


FIGURE 27

SKEWED LEPS PES FOR THE REACTION $\Delta + H \rightleftharpoons \Delta + H$

$E - E_c = .424, .174, .074, -.002 \text{ ev}$

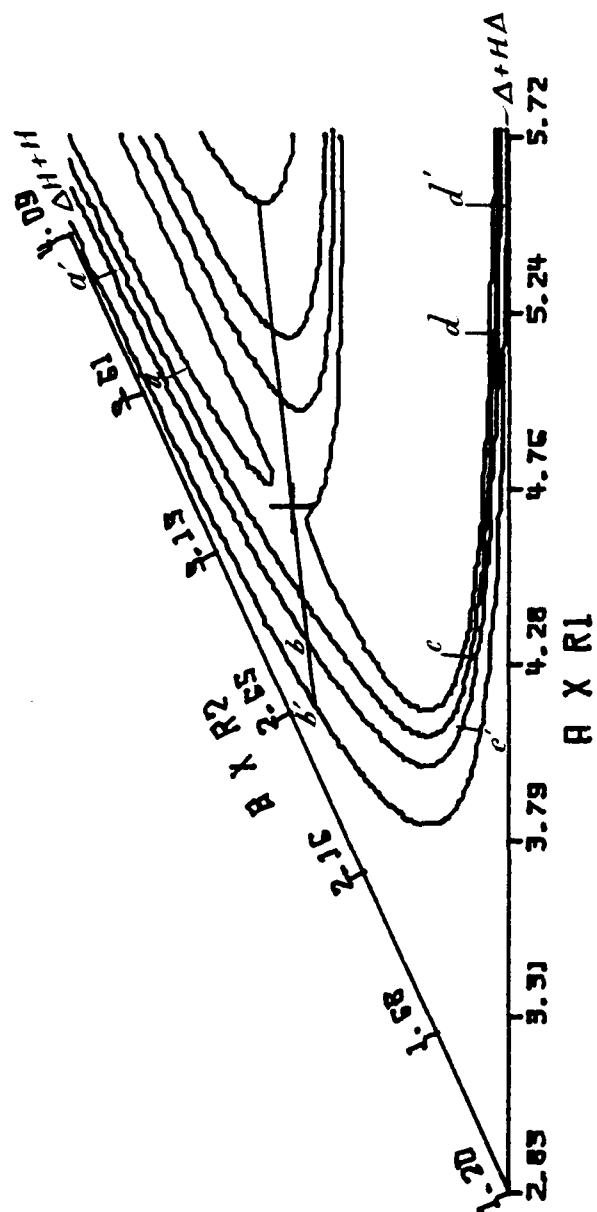


FIGURE 28

SKEWED PK PES FOR THE REACTION $D + D-H \rightleftharpoons D-D + H$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

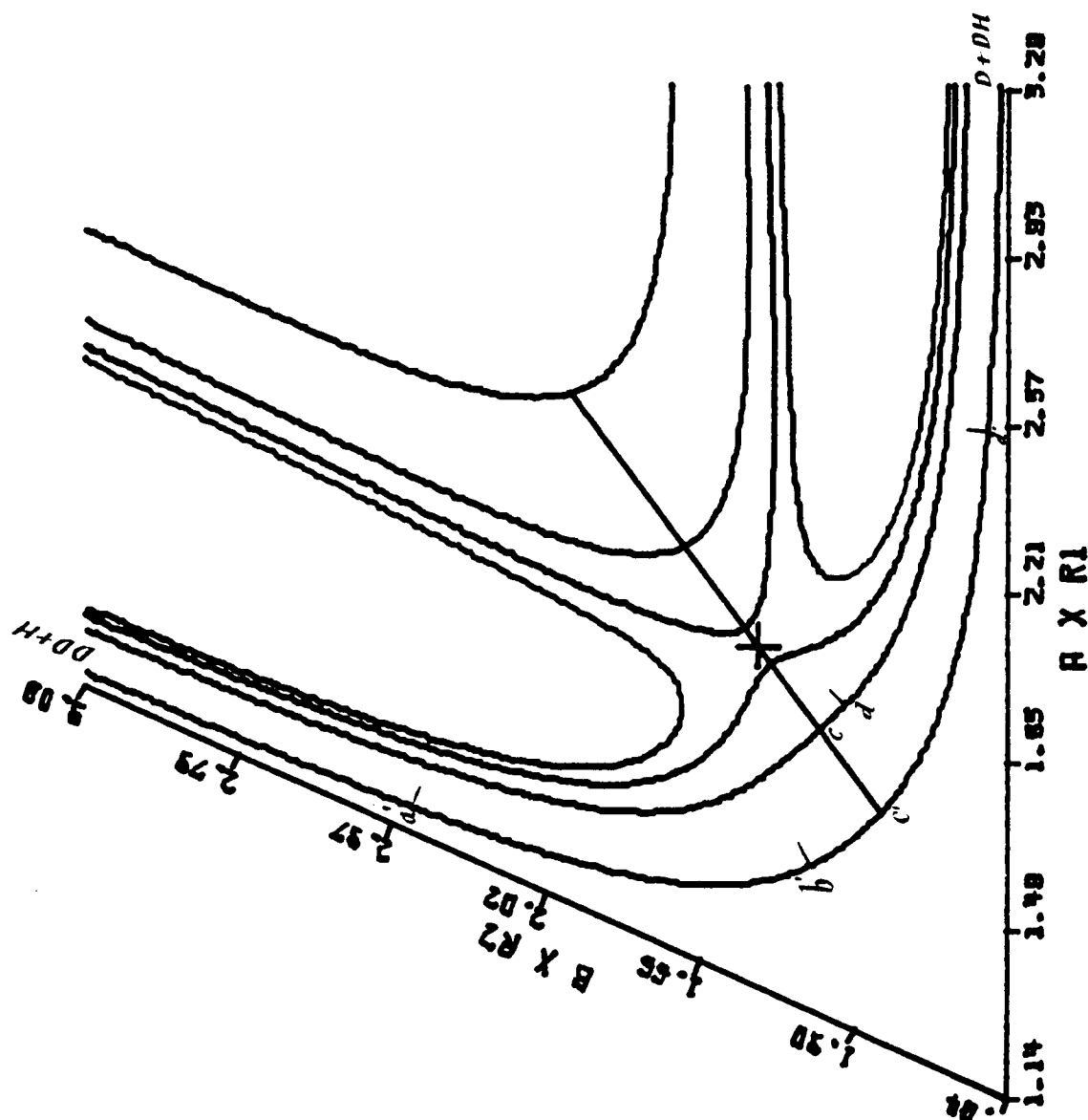


FIGURE 29

SKEWED PK PES FOR THE REACTION $\Delta + \Delta-H \rightleftharpoons \Delta-\Delta + H$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

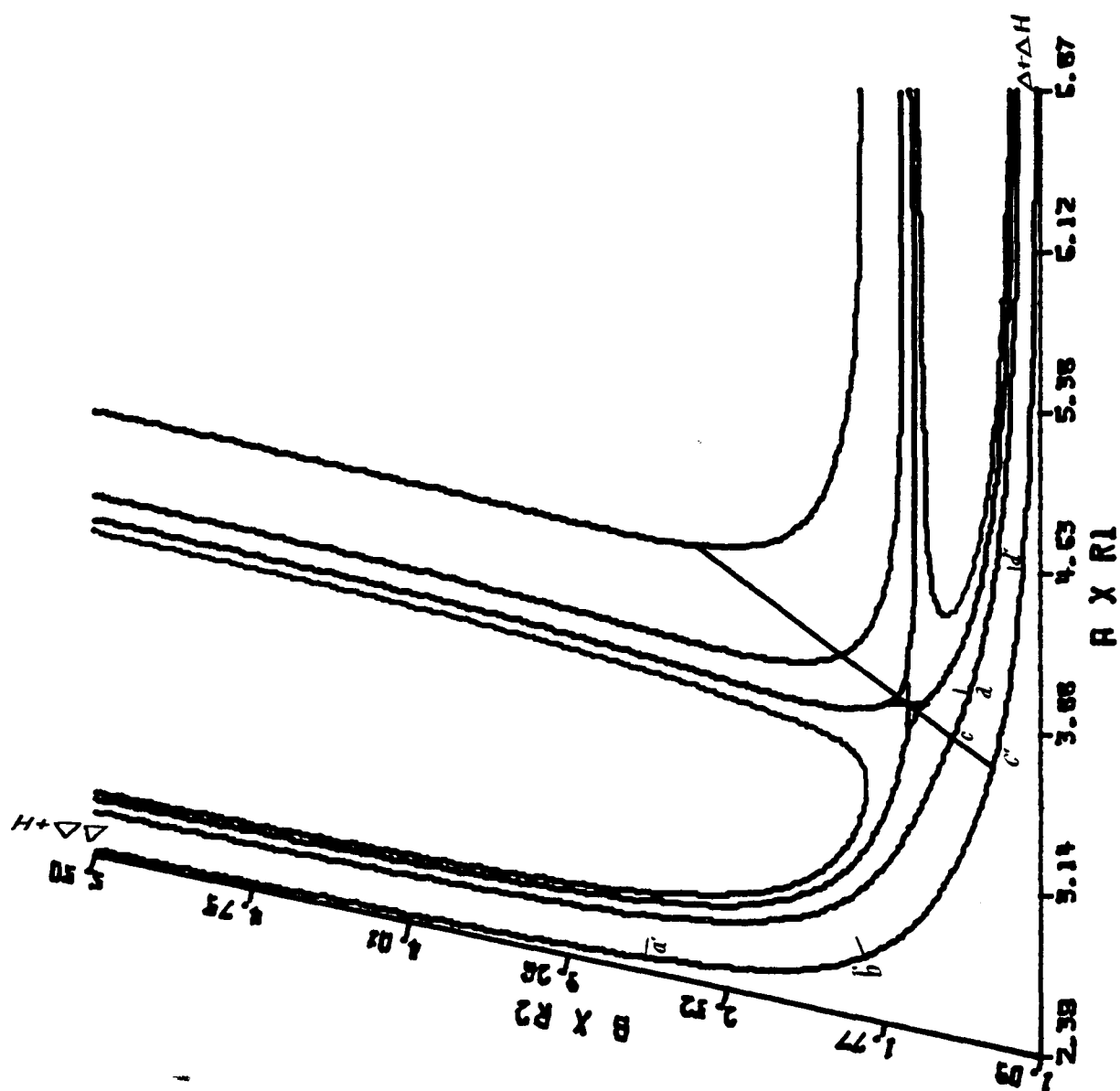


FIGURE 30

SKEWED PW PES FOR THE REACTION $D + D-H \rightleftharpoons D-D + H$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

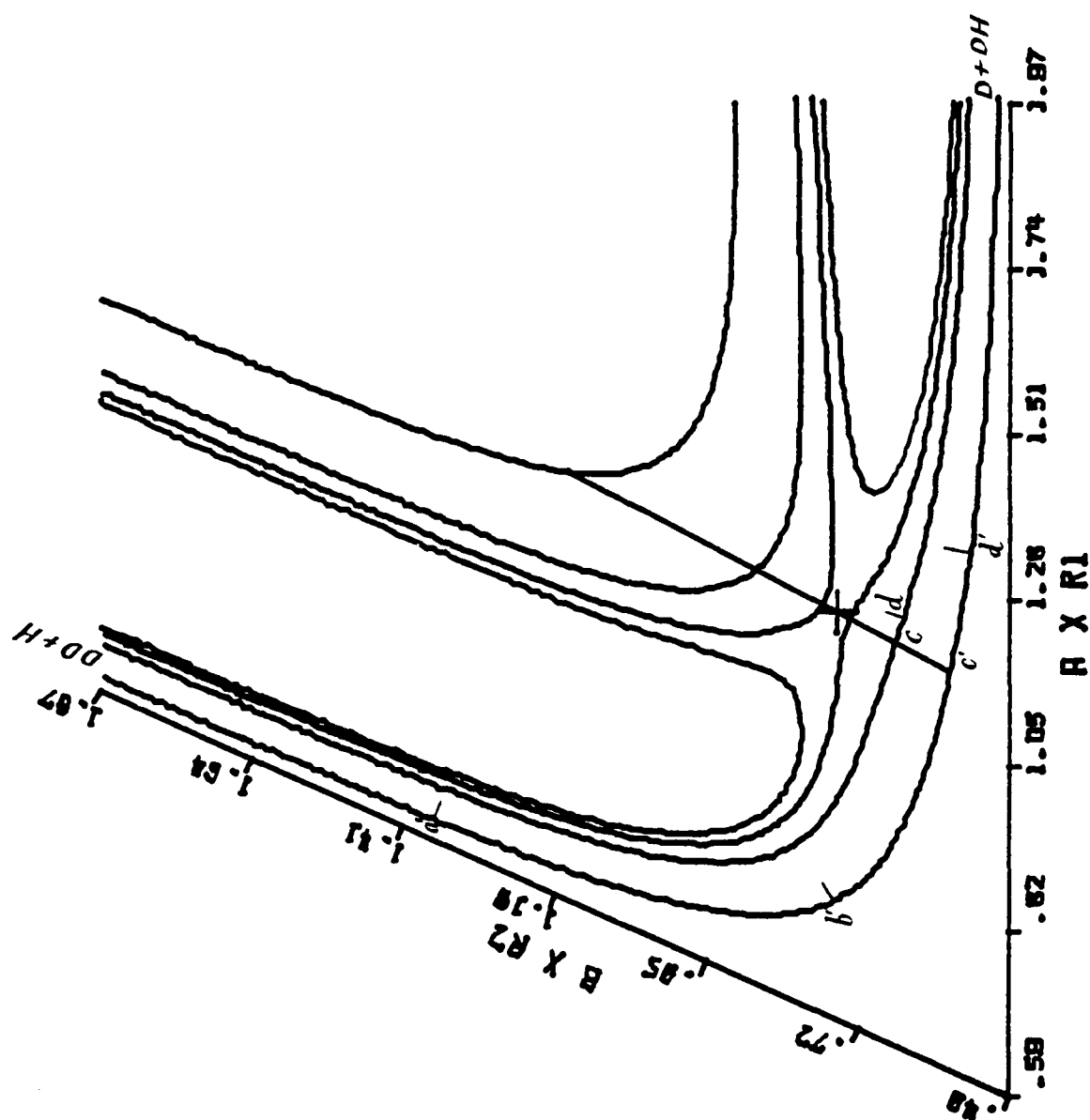


FIGURE 31

SKEWED PW PES FOR THE REACTION $\Delta + \Delta-H \rightleftharpoons \Delta-\Delta + H$

ENERGY OF CONTOURS = .9,.5,.4,.35ev

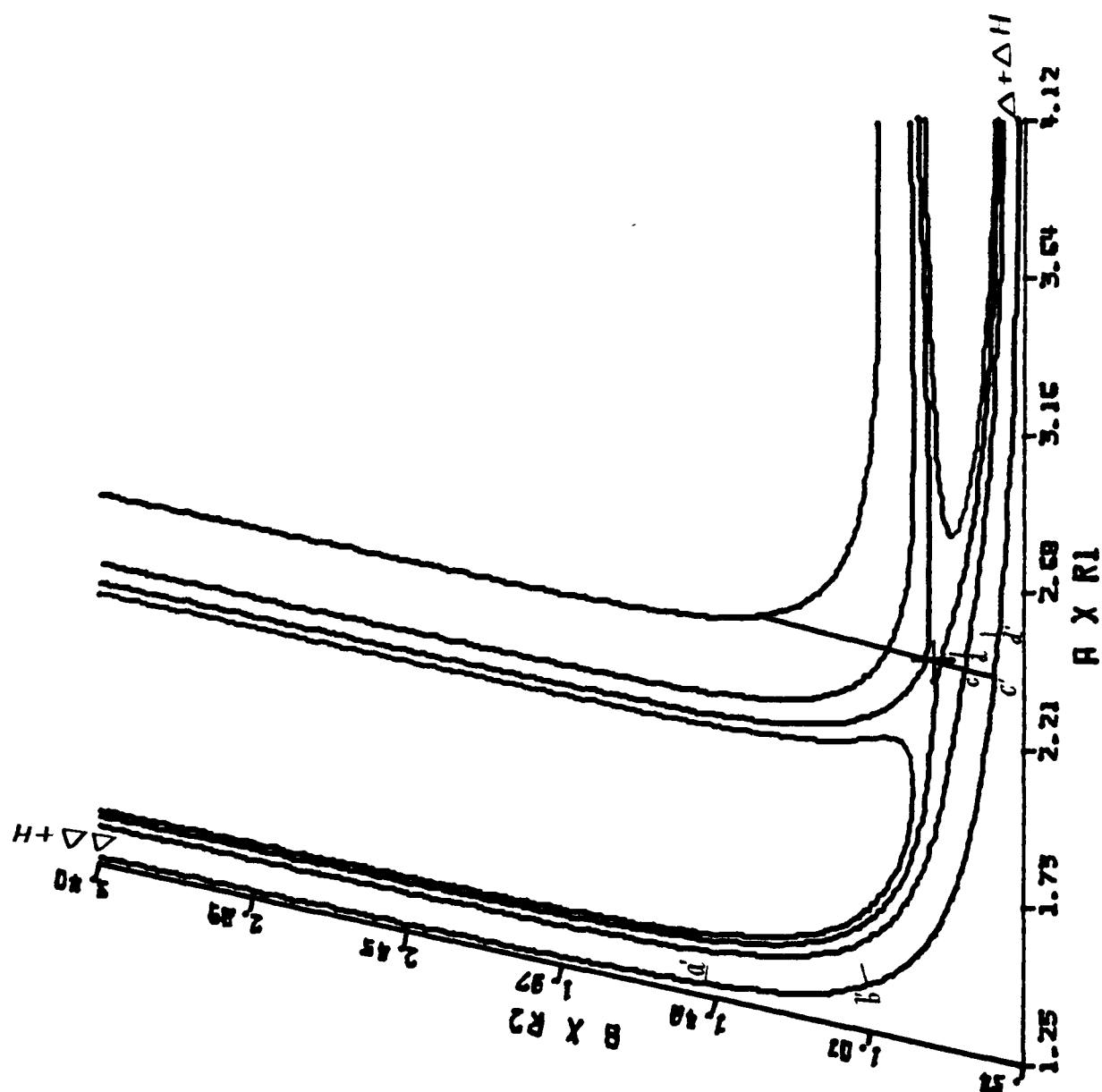


FIGURE 32

SKewed PW PES FOR THE REACTION $\text{H} + \text{D-D} \rightleftharpoons \text{H-D} + \text{D}$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

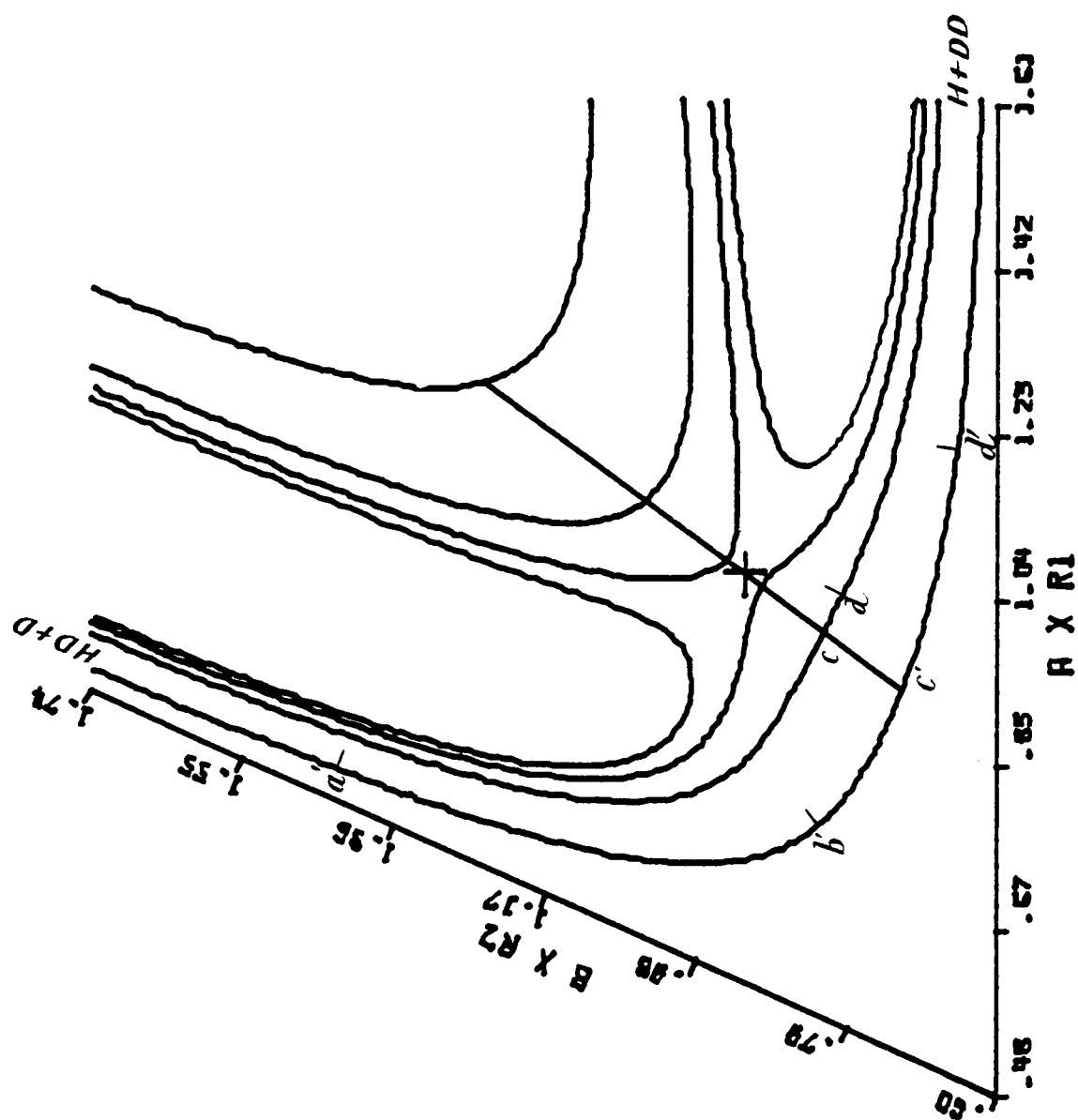


FIGURE 33

SKEWED PW PES FOR THE REACTION $H + \Delta - \Delta \rightleftharpoons H - \Delta + \Delta$

ENERGY OF CONTOURS = .9, .5, .4, .35ev

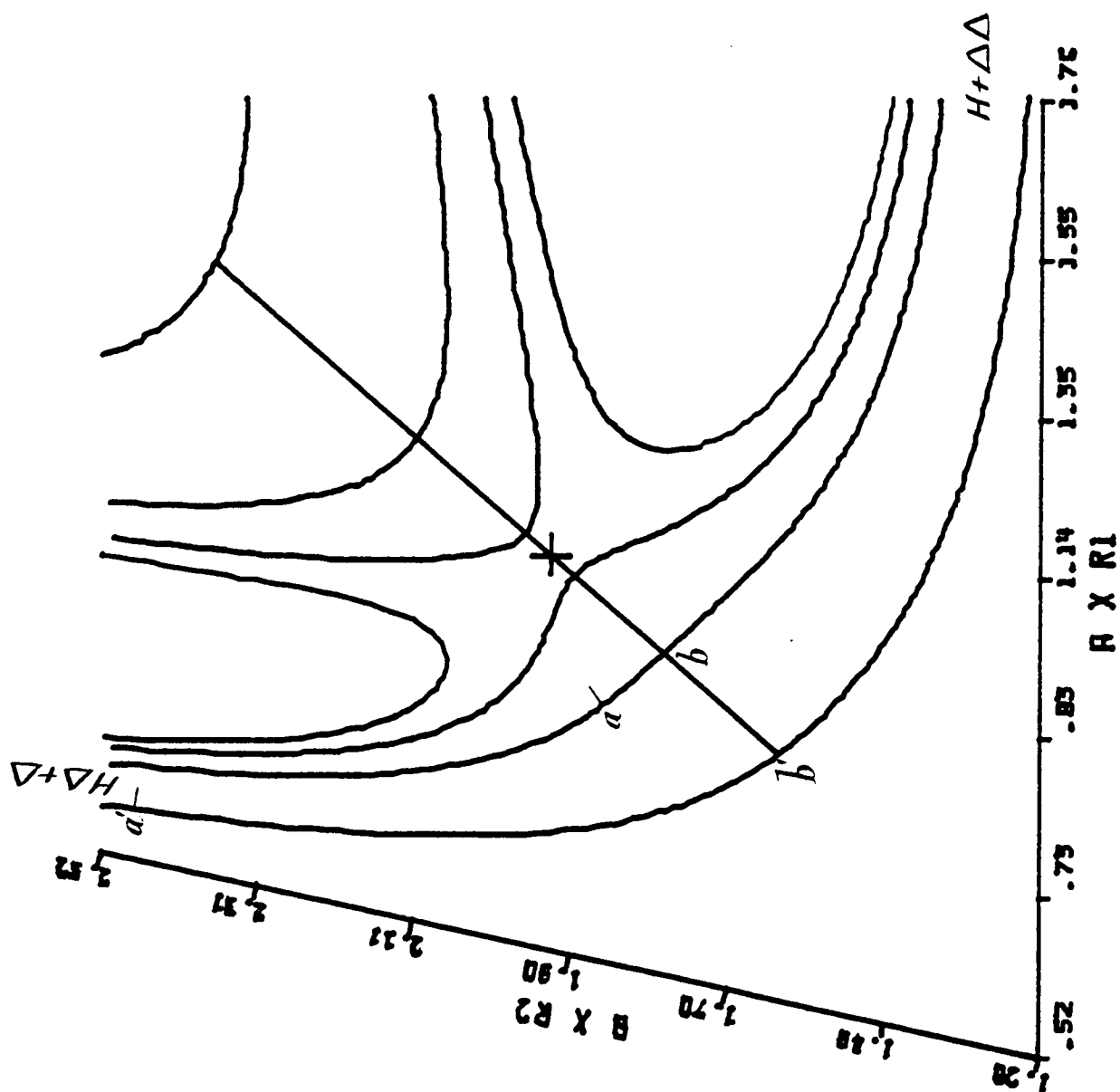


FIGURE 34

SKEWED LEPS PES FOR THE REACTION $D + D-H \rightleftharpoons D-D + H$

$E - E_c = .424, .174, .074, -.002 \text{ ev}$

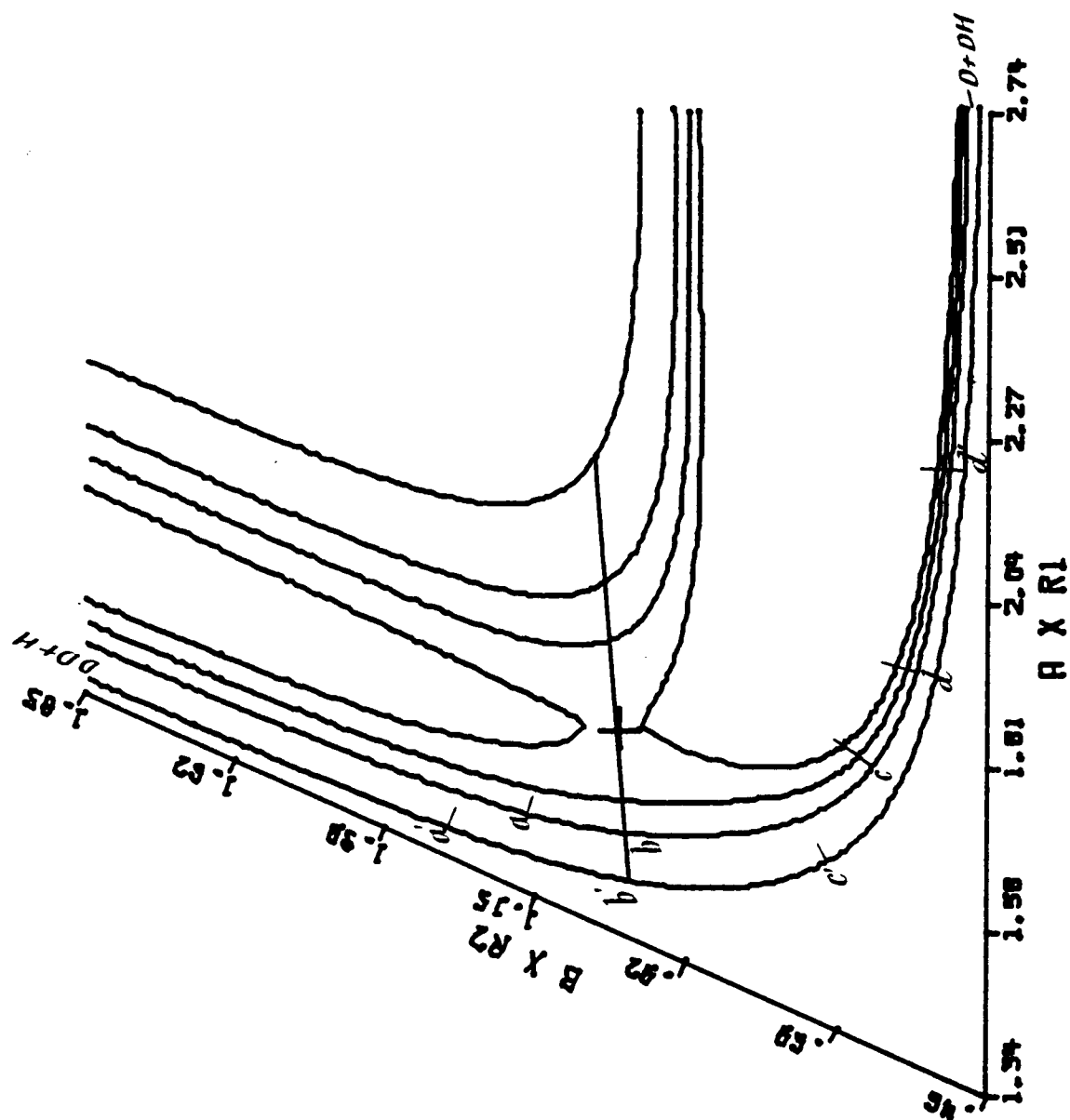


FIGURE 35
 SKEWED LEPS PES FOR THE REACTION $\Delta + \Delta-H \rightleftharpoons \Delta-\Delta + H$
 $E - E_c = .424, .174, .074, -.002\text{ev}$

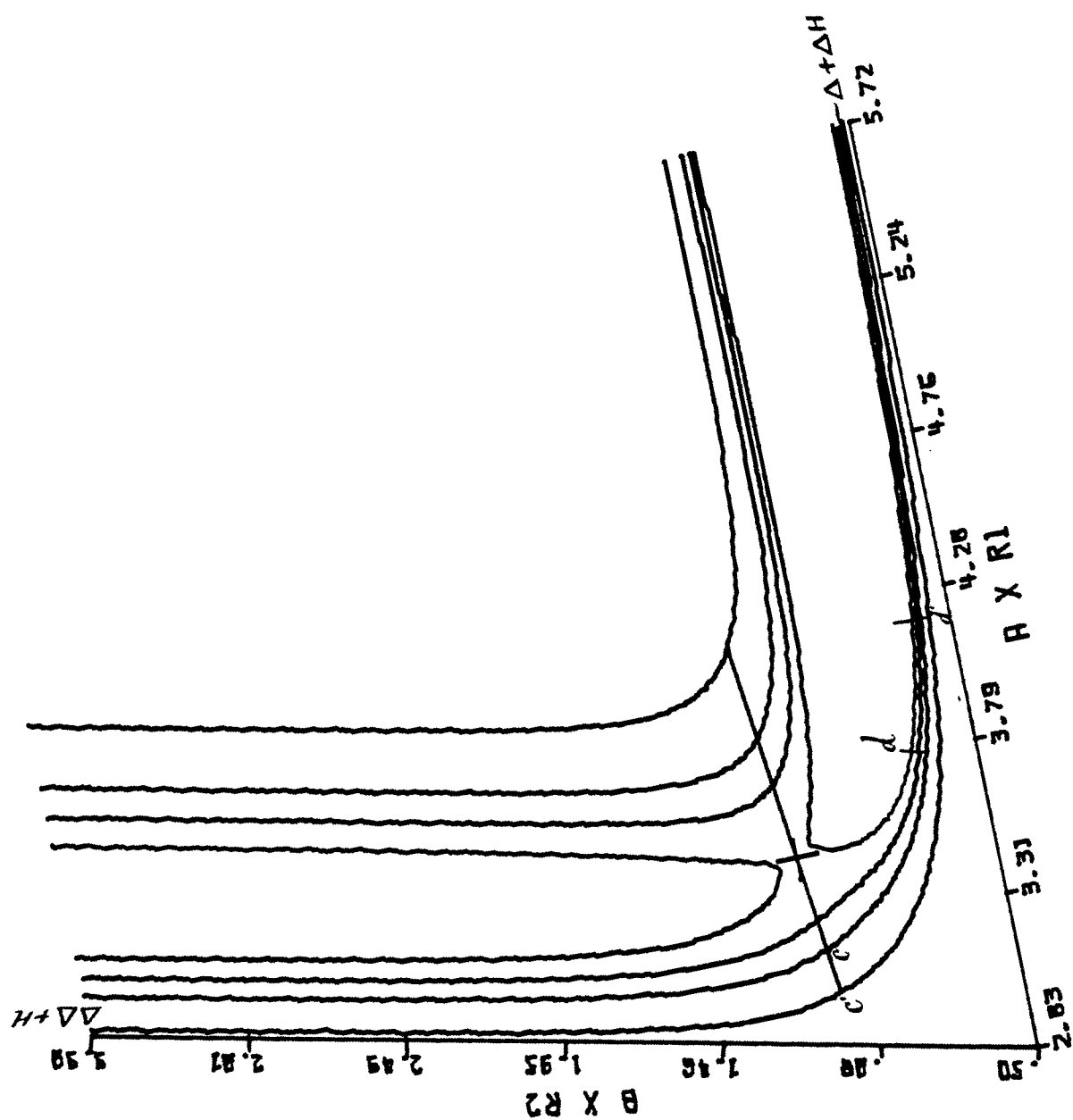


FIGURE 36

SKEWED LEPS PES FOR THE REACTION $\text{H} + \text{D-D} \rightleftharpoons \text{H-D} + \text{D}$

$E - E_c = .424, .174, .074, -.002\text{ev}$

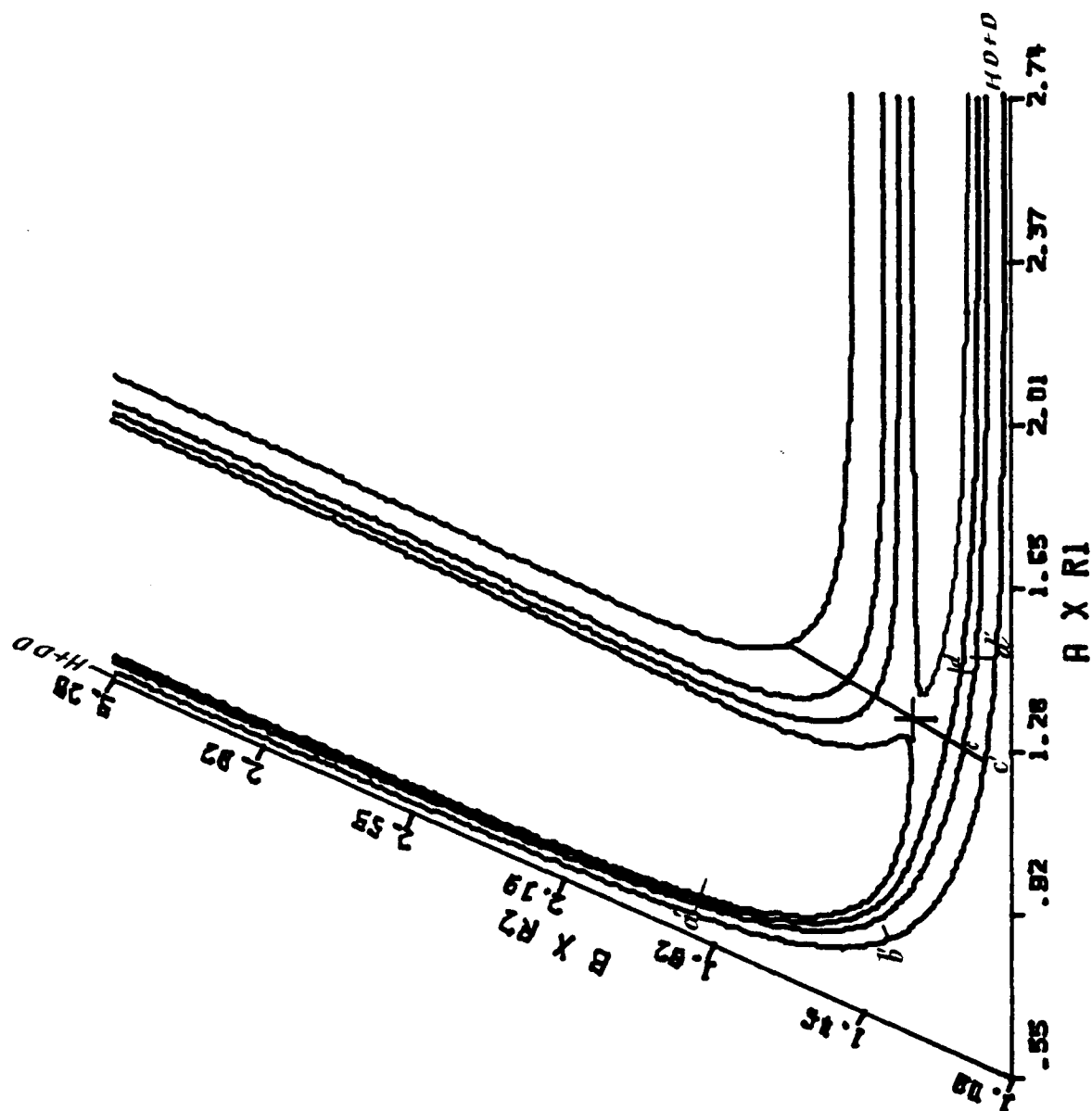
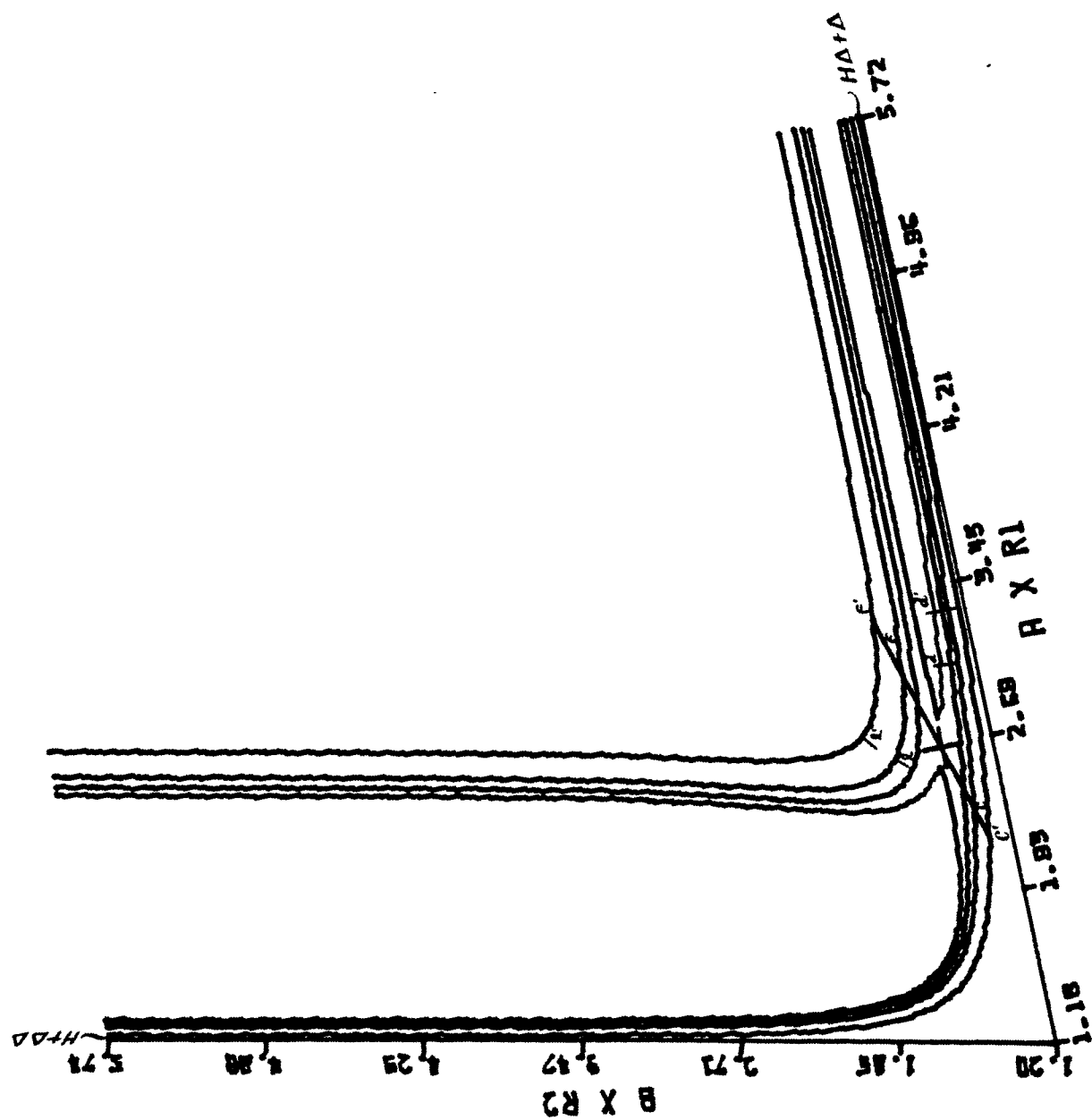


FIGURE 37
 SKEWED LEPS PES FOR THE REACTION $H + \Delta - \Delta \rightleftharpoons H - \Delta + \Delta$
 $E - E_c = .424, .174, .074, -.002 \text{ ev}$



FIGURES 38 - 43

FIGURE 38

Direct trajectory ($E = .9\text{ev}$) for the reaction $\text{H} + \text{H-H} \rightleftharpoons \text{H-H} + \text{H}$ on the Polanyi-Wong surface. This trajectory has one transition state.

FIGURE 39

Reflected reactive trajectory ($E = .9\text{ev}$) for the reaction $\Delta + \text{H-}\Delta \rightleftharpoons \Delta\text{-H} + \Delta$ on the Porter-Karplus surface. This trajectory has eleven transition states.

FIGURE 40

Reflected reactive trajectory ($E = 1.328\text{ev}$) for the reaction $\text{H} + \Delta\text{-}\Delta \rightleftharpoons \text{H-}\Delta + \Delta$ on the LEPS surface. This trajectory has three transition states and is reflected by arcs ef and cd shown in figure 37. Note that arc ab which is responsible for most reflected trajectories is not involved here.

FIGURE 41

Randomly chosen nonreactive trajectory ($E = .5\text{ev}$) for the reaction $\text{H} + \text{H-}\Delta \rightleftharpoons \text{H-H} + \Delta$ on the Porter-Karplus surface. This trajectory does not reach the DS and therefore has no transition states.

FIGURE 42

Randomly chosen nonreactive reflected trajectory ($E = .5\text{ev}$) for the reaction $\text{H} + \text{H-}\Delta \rightleftharpoons \text{H-H} + \Delta$ on the Porter-Karplus surface. This trajectory has two transition states. Note the greater number of peaks between 2.75 and 4.52 on the $A \times R_i$ axis in figure 41 compared to figure 42. This indicates more vibrational energy for the trajectory shown in

figure 41.

FIGURE 43

Nonreactive trajectory ($E = 1.328\text{ev}$) for the reaction $\text{H} + \text{H}-\Delta \rightleftharpoons \text{H}-\text{H} + \Delta$ on the LEPS surface. Although this trajectory does not reach the DS, it is unlike the trajectory shown in figure 41 in that the vibrational energy is a smaller fraction of the total energy.

FIGURE 38

TRAJECTORY PLOT FOR THE REACTION $\text{H} + \text{H}-\text{H} \rightleftharpoons \text{H}-\text{H} + \text{H}$ ON THE
 PW PES. ENERGY OF TRAJECTORY = .9ev. ENERGY OF CONTOURS =
 .9, .5, .4, .35ev.

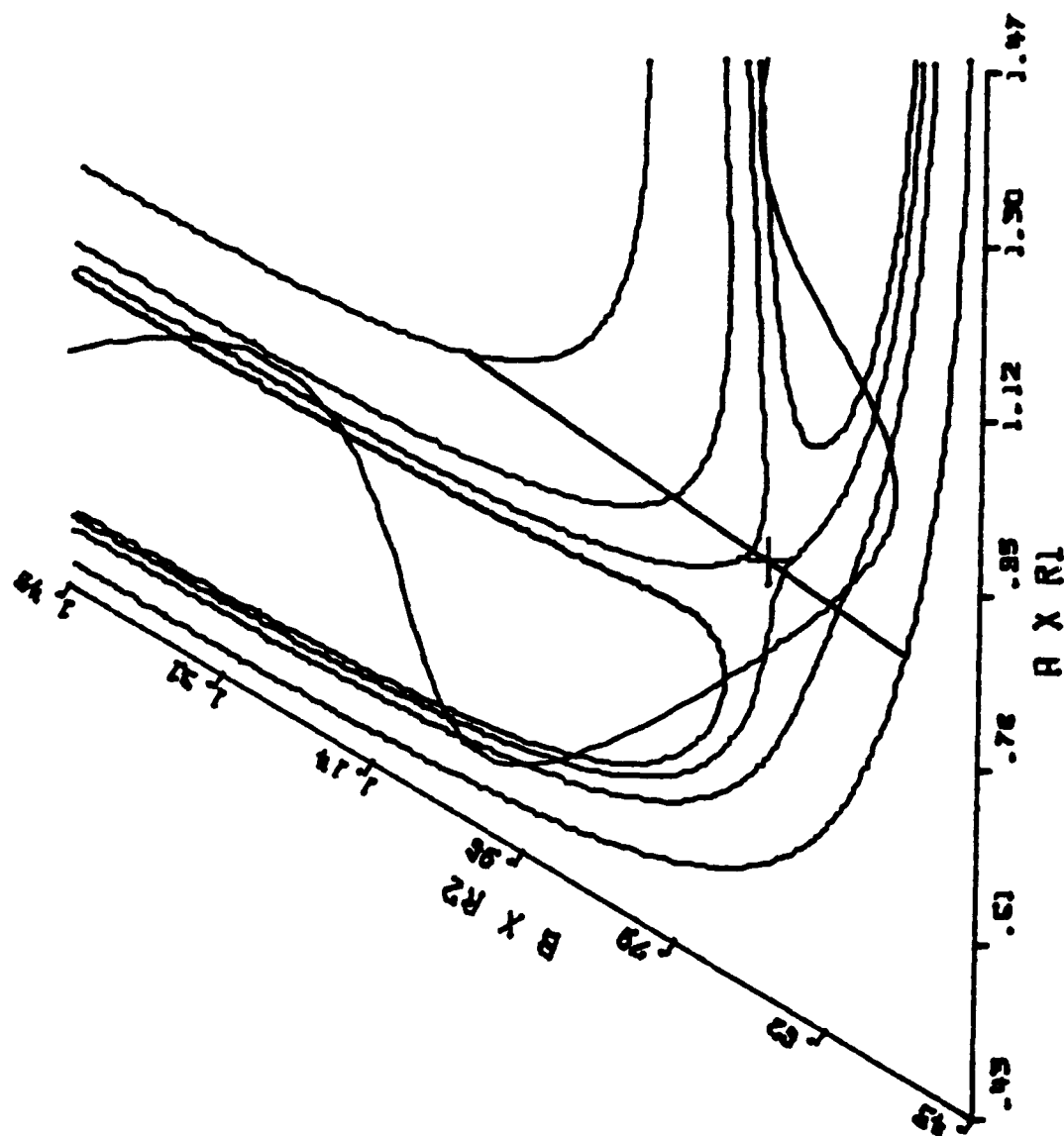


FIGURE 39

TRAJECTORY PLOT FOR THE REACTION $\Delta + \text{H}-\Delta \rightleftharpoons \Delta-\text{H} + \Delta$ ON THE
 PK PES. ENERGY OF TRAJECTORY = .9ev. ENERGY OF CONTOURS =
 .9, .5, .4, .35ev.

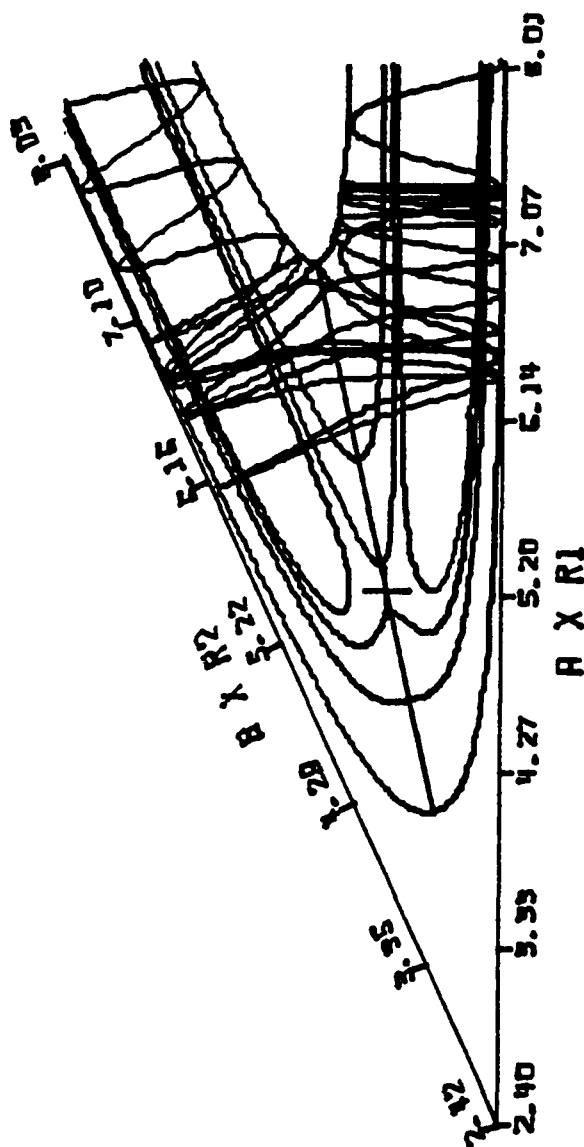


FIGURE 40

TRAJECTORY PLOT FOR THE REACTION $H + \Delta - \Delta \rightleftharpoons H - \Delta + \Delta$ ON THE
LEPS PES. ENERGY OF TRAJECTORY = 1.328ev. $E - E_c =$
.424, .174, .074, -.002ev.

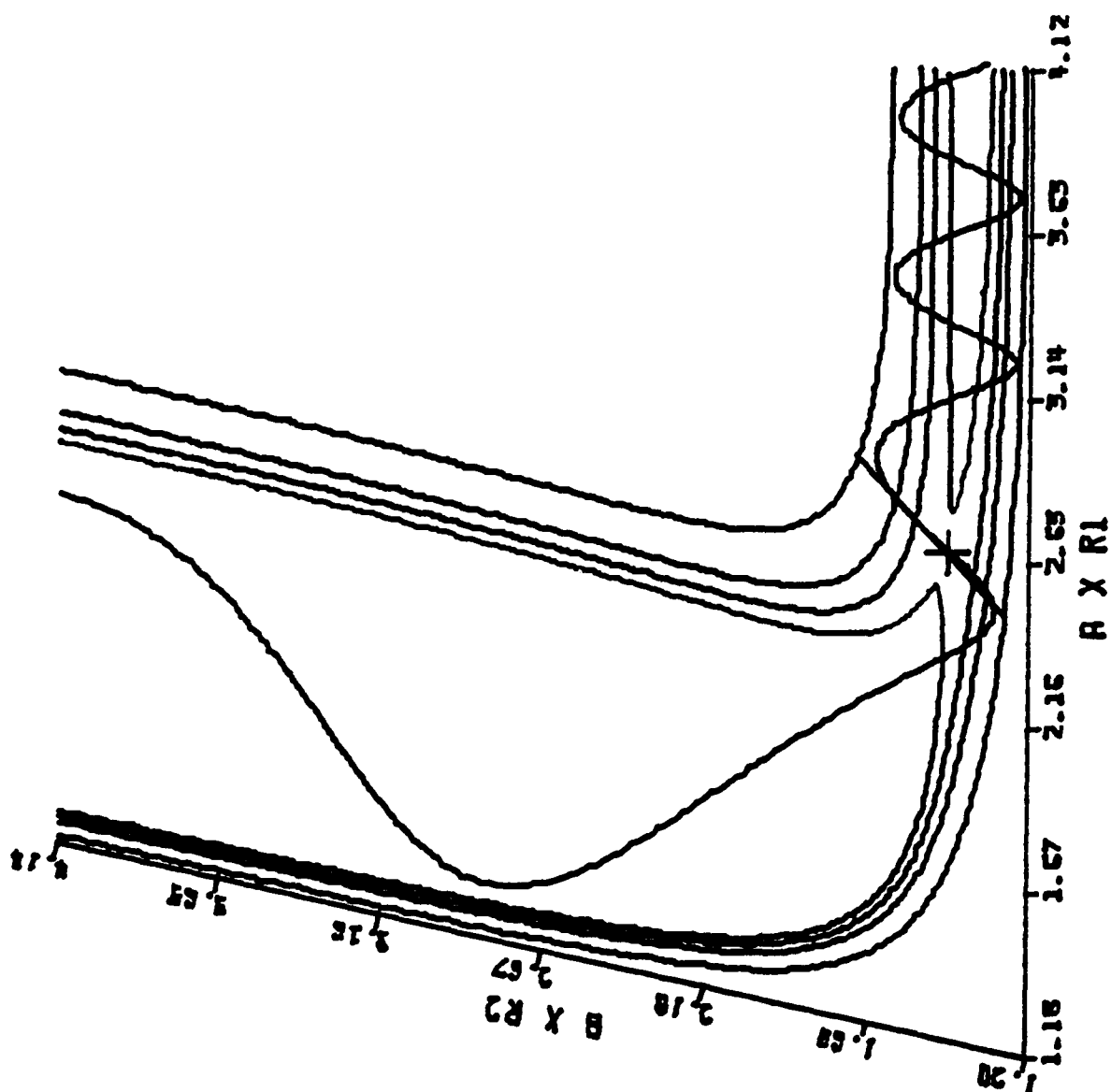


FIGURE 41

TRAJECTORY PLOT FOR THE REACTION $\text{H} + \text{H}-\Delta \rightleftharpoons \text{H}-\text{H} + \Delta$ ON THE
 PK PES. ENERGY OF TRAJECTORY = .5ev. ENERGY OF CONTOURS =
 .9, .5, .4, .35ev.

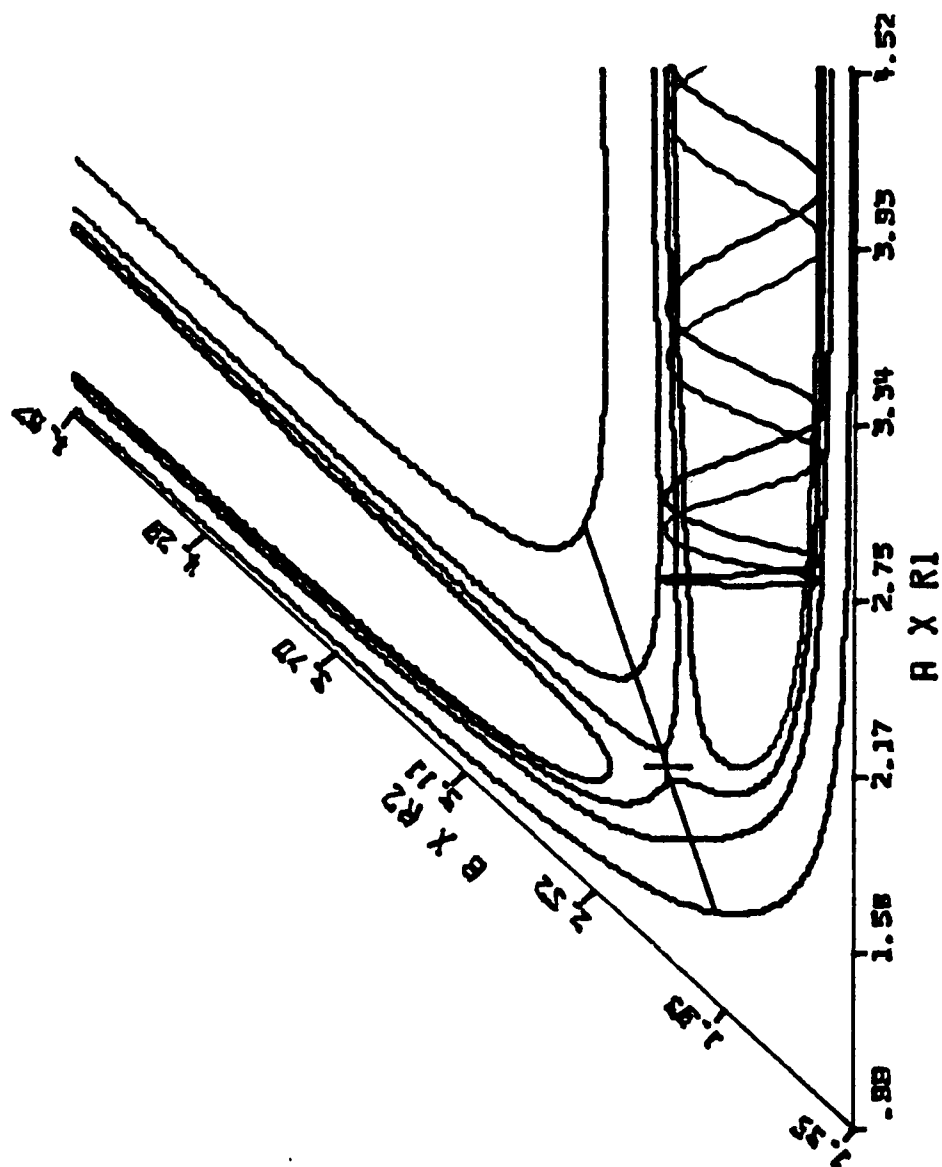


FIGURE 42

TRAJECTORY PLOT FOR THE REACTION $\text{H} + \text{H}-\Delta \rightleftharpoons \text{H}-\text{H} + \Delta$ ON THE PK PES. ENERGY OF TRAJECTORY = .5ev. ENERGY OF CONTOURS = .9, .5, .4, .35ev.

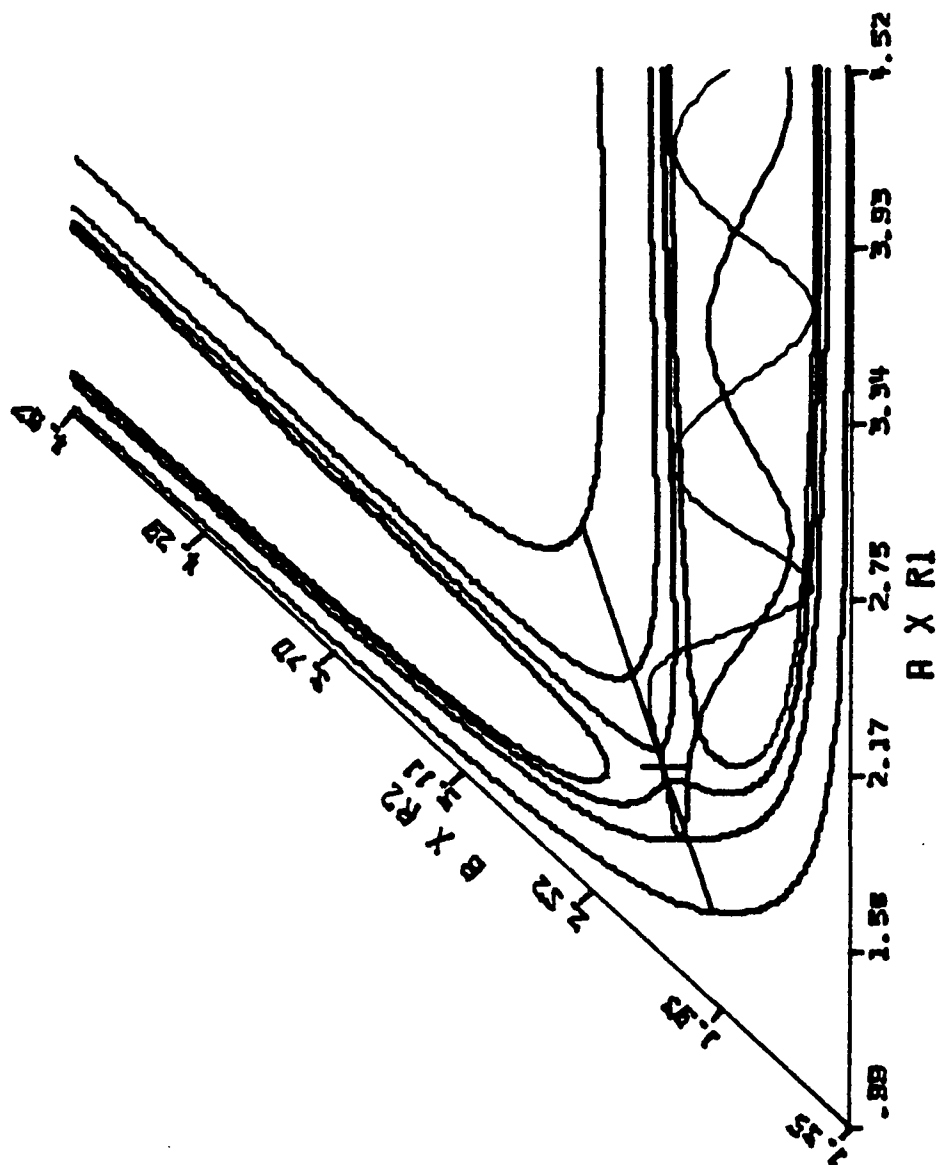
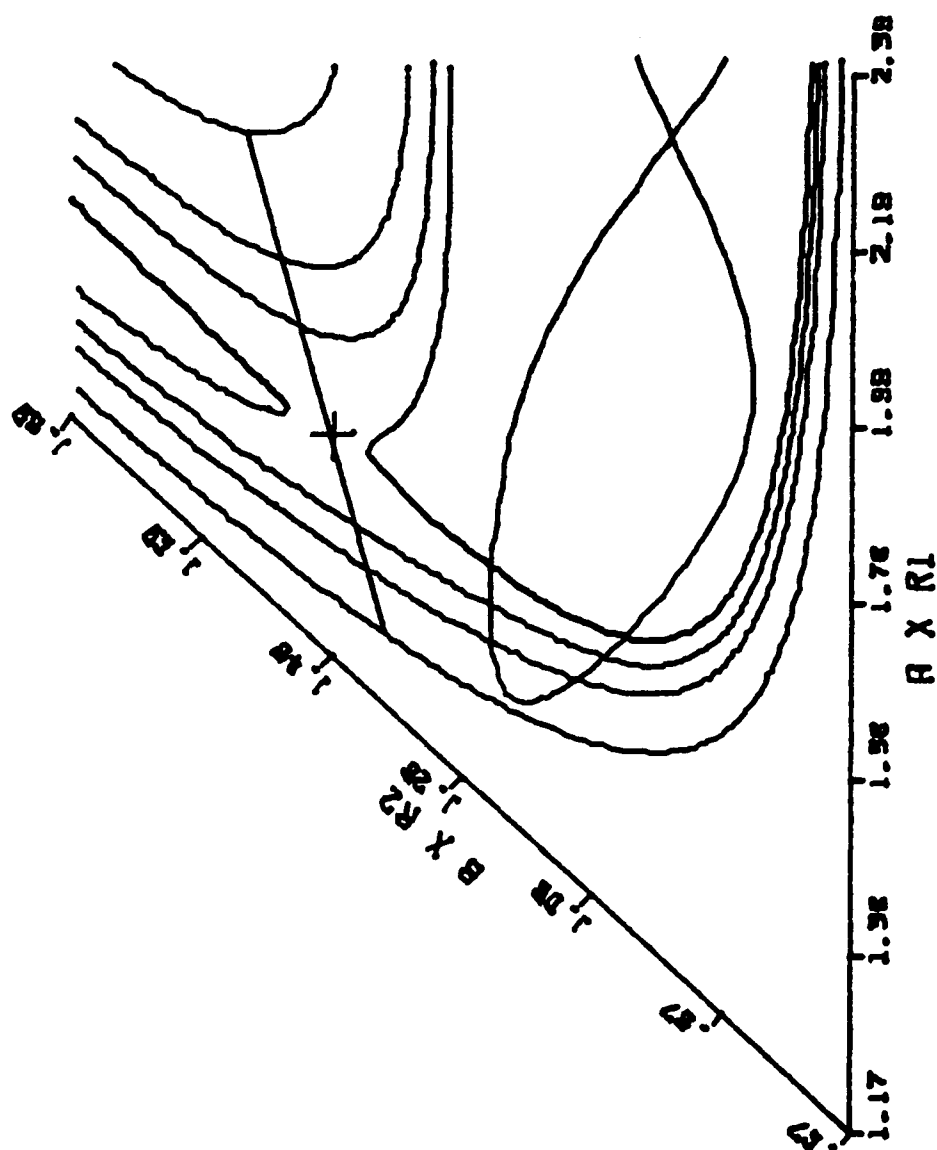


FIGURE 43

TRAJECTORY PLOT FOR THE REACTION $H + H-\Delta \rightleftharpoons H-H + \Delta$ ON THE
LEPS PES. ENERGY OF TRAJECTORY = 1.328ev. $E - E_c =$
.424, .174, .074, -.002ev.



IV. Summary of Results

In chapter three, we have attempted to analyze the trends in the trajectory mean reaction probability, and test the validity of ART. Whenever possible, we have related the features of the skewed PES to our discussions. In this chapter we will attempt to generalize what we have learned in chapter three.

We have discussed the trajectory mean reaction probability in terms of the number of trajectories which reach the DS and the number of nonreactive reflected trajectories. The former is partially determined by the length and effectiveness of the arcs on the reactant side of the DS which are capable of directing trajectories toward the DS. Arcs which are less effective are further away from the DS. The effectiveness of an arc at directing trajectories toward the DS will also be reduced if the direction of the forces perpendicular to the arc do not point toward products in a very direct manner. As a typical example of this consider the reaction $\Delta + \Delta-H$ on the PK surface. From the skewed PES illustrated by figure 29, we see that arcs cd and $c'd'$ are adjacent to the DS while arc $a'b'$ is not. Note also that the direction of the forces perpendicular to arcs cd and $c'd'$ are pointed toward the $\Delta-\Delta + H$ side more directly than the direction of the forces perpendicular to arc $a'b'$ are pointed toward the $\Delta + \Delta-H$ side. It is reasonable therefore that more trajectories reach the DS for the reaction $\Delta + \Delta-H$ than for the reaction $\Delta-\Delta + H$. It is interesting to point

out the relationship between the skew angle and the number of trajectories which reach the DS. We note that for most of the series of reactions, the number of trajectories which reach the DS are about the same or increases as the skew angle decreases. There are some exceptions to this, e.g. the number of trajectories which reach the DS for the reaction $X + X-H$ on the LEPS surface decreases as the skew angle decreases. From figures 11, 34 and 35 however we can see that as the skew angle decreases, the lengths of arcs bc and $b'c'$ increases, thus making it possible for trajectories with a relatively large amount of translational energy to be reflected by arc bc or $b'c'$ before they reach the DS.

The same arcs which effect the number of trajectories which reach the DS for the forward reaction also effect the number of nonreactive reflected trajectories for the reverse reaction. Consider for example the reactions $X + H-H$ ($X = D$ and Δ) on the PK surface. The skewed surfaces illustrated by figures 4 and 5 show that arcs cd and $c'd'$ are closer to the DS than arcs ab and $a'b'$ are. Also the direction of the forces perpendicular to the former arcs are pointed toward the DS more directly than are the forces perpendicular to the latter arcs. Thus, as we have noticed before $T_1' > T_1^R$ at .5 and .9ev. As we mentioned in our discussion of the reaction $H-\Delta + \Delta$ on the LEPS surface, we must also be aware of forces perpendicular to contours above the saddle point which can direct a trajectory to the DS. While none of the trajectories reflected by arcs ef and $e'f'$ are nonreactive, the fact that these arcs caused some trajec-

ories to cross the DS more than once makes it possible that a similar type of arc could result in nonreactive reflected trajectories on other surfaces.

We now summarize the trends in the trajectory and phase space mean reaction probability in table 33. The symbols used to express the trends in the mean reaction probability for an increasing mass of atom(s) X are: $\uparrow$ (increasing), $\downarrow$ (decreasing), $\cup$ (decreasing from X = H to X = D and increasing from X = D to X = Δ), $—$ (remains approximately the same for the series), $—\uparrow$ (remains approximately the same for X = H and X = D and increases from X = D to X = Δ), $—\downarrow$ (same as $—\uparrow$ except decreases from X = D to X = Δ), $\uparrow—$ (increases from X = H to X = D then remains about the same for X = D and X = Δ), $\downarrow—$ (same as $\uparrow—$ except decreases from X = H to X = D). The values of the mean reaction probability were assumed to remain approximately the same if the differences in their values for two reactions (e.g. X = H and X = D) were less than the error in the mean reaction probability at the 95% confidence level. The trends for the phase space mean reaction probability appears in parenthesis. From our discussions in chapter three, we are aware that the trends in $\bar{P}_r^t(E)$ and $\bar{P}_r(E)_{ps}^{acc}$ will not always be the same because of the presence of reactive and nonreactive reflected trajectories. Consider for example the series of reactions X + H-H on the PW surface at .9ev. From table 33 we see that the trend in $\bar{P}_r^t(.9)$ is opposite the trend in $\bar{P}_r(.9)_{ps}^{acc}$. From table 5 we note that the increase in $\bar{P}_r(E)_{ps}^{acc}$ for the series is rel-

atively small compared to the decrease in ξ (.9); thus there is a decreasing trend for $\bar{P}_r^t(.9)$. With few exceptions the trends in $\bar{P}_R(E)_{\rho_S}^{A\alpha}$ and $\bar{P}_R(E)_{\rho_M}^{A\alpha}$ are the same, thus table 33 would not be appreciably altered if the best straight DS corresponding to the minimum phase space mean reaction probability were used. It will be interesting to see the results of Koeppel and Sverdlik, who as we mentioned before are calculating periodic trajectories which correspond to the best DS; not necessarily straight or passing through the saddle point. Since these periodic trajectories correspond to the ART or SD DS on the PK skewed surfaces when a symmetrical arrangement of masses (e.g. H + X-H or X + H-X) are used, we do not expect much of a difference between $\bar{P}_R(E)_{\rho_M}^{A\alpha}$ and the value of the phase space mean reaction probability calculated using a periodic trajectory for approximately symmetrical surfaces (periodic trajectories are shown in figure 44)⁴⁴.

We have noted in our discussions of the energy distributions for nonreactive trajectories the factors which effect $F_{vib}^{B\alpha}(E)$. A relatively large number of nonreactive trajectories which do not reach the DS for example will tend to increase the value of $F_{vib}^{B\alpha}(E)$. A relatively large number of nonreactive reflected trajectories tend to decrease the value of $F_{vib}^{B\alpha}(E)$. We have also seen that as $\bar{P}_r^t(E)$ decreases the value of $F_{vib}^{B\alpha}(E)$ becomes approximately .5. When discussing the energy distributions for reactive molecules, it is informative to compare the values of $F_{vib}^{AB}(E)$ for the forward and reverse reactions. Polanyi and Wong have done this for the H + H-H reac-

TABLE 33

Trends in Trajectory and Phase Space Mean Reaction Probability**

Reaction Series	PK Surface		PW Surface		LEPS Surface	
	.5*	.9	.5	.9	1.078	1.328
X + H-H	$\uparrow - (\uparrow)$	$- \downarrow (\uparrow)$	$- (\uparrow)$	$\downarrow (\uparrow)$	$\uparrow - (\uparrow)$	$- \downarrow (\uparrow)$
X + X-H	$- (-\uparrow)$	$\uparrow - (-\uparrow)$	$\downarrow - (\downarrow)$	$- \uparrow (-)$	$\uparrow (\uparrow)$	$- \uparrow (\uparrow)$
H + X-H	$\downarrow - (\downarrow)$	$- \uparrow (\downarrow)$	$- \downarrow (\downarrow)$	$\uparrow - (\downarrow)$	$- \downarrow (\downarrow)$	$- (\downarrow)$
X + H-X	$- \downarrow (\uparrow)$	$\cup (\uparrow)$	$- \downarrow (\uparrow)$	$\cup (\uparrow)$	$- \downarrow (\uparrow)$	$\downarrow - (\uparrow)$
H + H-X	$- (-\uparrow)$	$\downarrow (-\uparrow)$	$- (\uparrow)$	$\downarrow (-\uparrow)$	$\downarrow - (-)$	$\downarrow (\downarrow -)$
H + X-X	$\downarrow (\downarrow)$	$- \downarrow (\downarrow)$	$- \downarrow (\downarrow)$	$- \downarrow (\downarrow)$	$\downarrow (\downarrow)$	$\downarrow (\downarrow)$

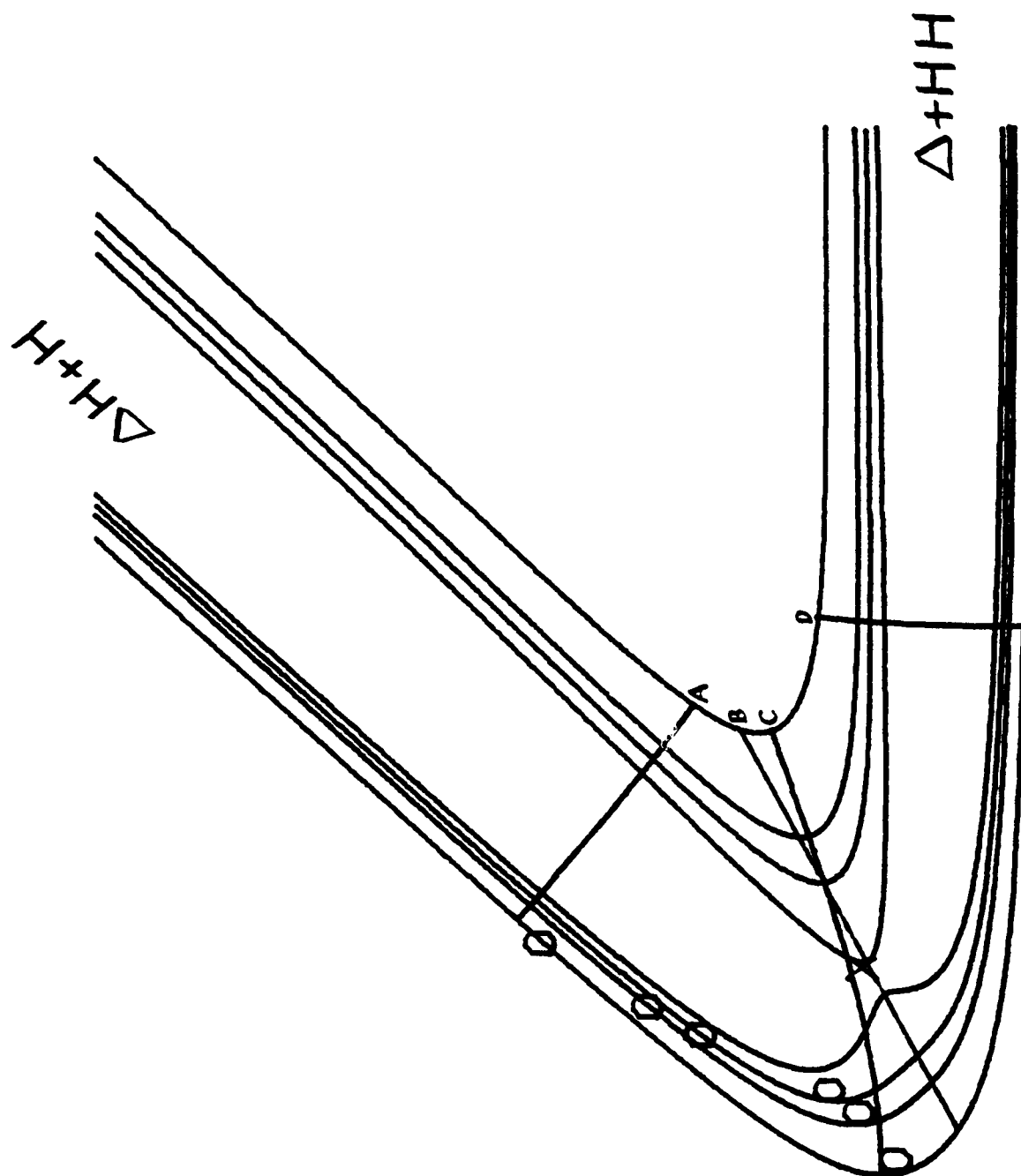
*Energy is in ev. **Trends for phase space mean reaction probabilities appear in parenthesis.

FIGURE 44

PLOT OF THREE PERIODIC TRAJECTORIES* FOR THE REACTION
 $\Delta + \text{H}-\text{H} \rightleftharpoons \Delta-\text{H} + \text{H}$ ON THE PK PES. ENERGY OF PERIODIC
TRAJECTORIES = .8961ev. ENERGY OF CONTOURS = .8961,
.6, .5, .4ev.

*Curves A, C, D are periodic trajectories. Line segment
B is ART DS. Forces perpendicular to contours on product
side ($\Delta-\text{H} + \text{H}$) of ART DS that point to reactant side
($\Delta + \text{H}-\text{H}$) lie between circled regions.

FIGURE 44



tion. They have found that when the barrier is in the entrance valley the value of $F_{vib}^{AB}(E)$ is greater than when the barrier is in the exit valley. Our results show that this is true for all mass combinations examined at both energies on the PW surface. For the most part, we note that $F_{vib}^{AB}(E)$ is also less for the reverse reaction on the LEPS surface. There are exceptions to this however; most notably for the reactions $H + H-\Delta$ and $\Delta + H-\Delta$ at both energies. Because of symmetry, $F_{vib}^{AB}(E)$ is the same for the forward and reverse reactions when a symmetrical combination of masses are used on the PK surface. For the unsymmetrical mass combinations on the PK surface, $F_{vib}^{AB}(E)$ is approximately the same for the forward and reverse reactions. We also note that without exception, the values of $F_{vib}^{AB}(E)$ for the forward reactions on the PK surface are less than the corresponding values of $F_{vib}^{AB}(E)$ on the PW surface. This trend is reversed for most reverse reactions. Thus most reactive trajectories require more translational energy on the PW surface than on the PK surface. There is also a greater conversion of translational energy to vibrational energy on the PW surface than there is on the PK or LEPS surface (except for the reaction $H + \Delta-H$ on the LEPS surface).

The data we presented in chapter three helps us determine the accuracy of the ART assumptions. We have seen that when the DS has no holes, the results for $P_A(E)_{P_3}^{acc}$ and $P_A(E)_{P_3}^{sva}$ are approximately the same for all surfaces and mass combinations at the energies we examined. Thus, one of the basic

assumptions of ART which states that the potential energy can be approximated by a harmonic oscillator is a good one.

The second assumption that one usually associates with ART is the directness assumption; i.e. do reactive trajectories go directly from reactants to products crossing the DS only once, and do all nonreactive trajectories fail to reach the DS. It is difficult to give a simple answer to this question as many factors are involved. It is evident however, that besides the type of surface used, the validity of the directness assumption depends heavily on the arrangement of the masses. This is because the arrangement of masses determines the skew angle and the distortion of the PES defined by the skewed coordinates. The location of the DS is another factor which the directness assumption is dependent on. However, just as $P_R(E)_m^{AC}$ and $P_R(E)_{ART}^{AC}$ are approximately the same if the ART DS has no holes, so are the number of direct and reflected trajectories. Utilizing the ideas of Pechukas¹³ we can predict the energy where the directness assumption is no longer valid. These predictions are pessimistic however; e.g. the directness assumption is predicted to break down between .5 and .6ev for the reaction $H + H-H$ on the Porter-Karplus surface. ART actually has been found to be valid up to an energy of .6026ev.⁴²

APPENDIX I

Analysis of Errors

The sample standard deviation^q is defined by the equation

$$S = \left[\frac{1}{N-1} \sum_{i=1}^N (X_i - \bar{X})^2 \right]^{1/2} \quad (1)$$

where N is the number of trials and $\bar{X}$ is the mean value which is defined by the equation

$$\bar{X} = \frac{1}{N} \sum_{i=1}^N X_i \quad (2)$$

Since N is much greater than unity for all our numerical work, we use N rather than $N-1$ in the denominator in all the equations which follow. Equation 1 can also be written

$$S = \left[\frac{1}{N} \sum_{i=1}^N (X_i^2 - \bar{X}^2) \right]^{1/2} \quad (3)$$

The quantity $\xi_x(E)$ has been defined previously as

$$\frac{\mathcal{J}}{N} \sum_{i=1}^N H(E - E_i) \text{ where } \mathcal{J} = 1.3026 (p^{\max} - p^{\min}) (q^{\max} - q^{\min}).$$

The sample standard deviation for $\xi_x(E)$ may be expressed as

$$S_{\xi_x(E)} = \left\{ \frac{1}{N} \sum_{i=1}^N \left[(\mathcal{J} H(E - E_i))^2 - \left(\mathcal{J}/N \sum_{i=1}^N H(E - E_i) \right)^2 \right] \right\}^{1/2} \quad (4)$$

where $\mathcal{J} H(E - E_i) = X_i$ and $\xi_x(E) = \bar{X}$.

We may use the identity $[H(E - E_i)]^2 = H(E - E_i)$

and re-express equation (4) as

$$S_{\xi_x(E)} = \frac{\mathcal{J}}{N} \left[\sum_{i=1}^N H(E - E_i) (N - 1) \right]^{1/2}. \quad (5)$$

The error of the mean for the quantity $\xi_x(E)$ is given by the expression

$$E_{\xi_I(E)} = 1.96 S_{\xi_I(E)} / N^{1/2} \quad (6)$$

where 1.96 is the value of the student T which corresponds to the 95% confidence level. Using a similar procedure to evaluate the sample standard deviation for $\xi_{\pm}(E)$, we obtain the result

$$S_{\xi_{\pm}(E)} = \sqrt{\frac{1}{N} \left[\sum_{i=1}^N H(E - E_c - E_T) (N-1) \right]} \quad (7)$$

The error of the mean for the quantity $\xi_{\pm}(E)$ is given by the expression

$$E_{\xi_{\pm}(E)} = 1.96 S_{\xi_{\pm}(E)} / N^{1/2} \quad (8)$$

The phase space mean reaction probability $(\bar{P}_r(E))$ which is calculated as the ratio of $\xi_{\pm}(E) / \xi_{\mp}(E)$ has a sample standard deviation which can be evaluated using the equation

$$S_{\bar{P}_r(E)} = \bar{P}_r(E) \left[\left(\frac{S_{\xi_{\mp}(E)}}{\xi_{\mp}(E)} \right)^2 + \left(\frac{S_{\xi_{\pm}(E)}}{\xi_{\pm}(E)} \right)^2 \right]^{1/2} \quad (9)$$

The error in $\bar{P}_r(E)$ is given by the expression

$$E_{\bar{P}_r(E)} = 1.96 S_{\bar{P}_r(E)} / N^{1/2} \quad (10)$$

The number of transition states traveling toward products and originating from reactants can be calculated from the expression

$$N_R^{\pm} = \frac{N_T (T_1^R + T_2^R + 2(T_3^R + T_4^R) + 3(T_5^R + T_6^R) + \dots)}{N_T} \quad (11)$$

where N_T is equal to the number of trajectories calculated.

The number of reactive trajectories is given by the expression

$$N_r = \frac{N_T (T_1^R + T_2^R + T_3^R + \dots)}{N_T} \quad (12)$$

The number of transition states traveling toward products and originating from products is given by the equation

$$N_P^{\overline{P}} = \frac{\left[\omega(E) \cdot N_T (T_2^P + T_3^P) + 2(T_4^P + T_5^P) + 3(T_6^P + T_7^P) + \dots \right]}{N_T} \quad (13)$$

where $\omega(E)$ is the weighting factor defined in chapter 3.

The sample standard deviations for the quantities defined by equations 11 - 13 are

$$S_{N_R^*} = \left[N_T \left\{ (T_1^R + T_2^R) + 4(T_3^R + T_4^R) + 9(T_5^R + T_6^R) + \dots \right\} - N_R^{*2} \right]^{\frac{1}{2}} \quad (14)$$

$$S_{N_r} = \left[N_r \cdot (N_T - N_r) \right]^{\frac{1}{2}} \quad (15)$$

$$S_{N_P^{\overline{P}}} = \left[N_T (\omega(E))^2 \left\{ (T_2^P + T_3^P) + 4(T_4^P + T_5^P) + 9(T_6^P + T_7^P) + \dots \right\} - N_P^{*\overline{P}2} \right]^{\frac{1}{2}} \quad (16)$$

We can use equations 14 and 15 to calculate the sample standard deviation and error in the transmission coefficient ($\chi(E)$). They are given by the expressions

$$S_{\chi(E)} = \chi(E) \left[\left(\frac{S_{N_r}}{N_r} \right)^2 + \left(\frac{S_{N_R^*}}{N_R^*} \right)^2 \right]^{\frac{1}{2}} \quad (17)$$

$$\text{and } E_{\chi(E)} = 1.96 S_{\chi(E)} / N \quad (18)$$

respectively. The product coefficient ($\eta(E)$) is calculated by the ratio $N_R^{\overline{P}}/N_{*}$, where $N_{*} = N_R^{\overline{P}} + N_P^{\overline{P}}$. The sample standard deviation and error in $\eta(E)$ are given by the expressions

$$S_{\eta(E)} = \eta(E) \left[\left(\frac{S_{N_R^{\overline{P}}}}{N_R^{\overline{P}}} \right)^2 + \left(\frac{S_{N_P^{\overline{P}}}}{N_{*}} \right)^2 \right]^{\frac{1}{2}} \quad (19)$$

$$\text{and } E_{\eta(E)} = 1.96 S_{\eta(E)} / N \quad (20)$$

respectively where

$$S_{N_{*}} = \left[(S_{N_R^{\overline{P}}})^2 + (S_{N_P^{\overline{P}}})^2 \right]^{\frac{1}{2}} \quad (21)$$

The conversion coefficient ($\xi(E)$) defined by the ratio N_r/N_{*} has a sample standard deviation and error which are given by the equations

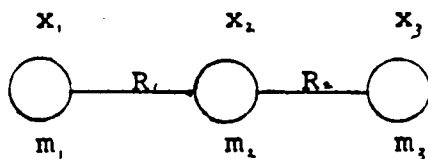
$$S_{\xi(E)} = \xi(E) \left[\left(\frac{S_{N_r}}{N_r} \right)^2 + \left(\frac{S_{N_{*}}}{N_{*}} \right)^2 \right]^{\frac{1}{2}} \quad (22)$$

$$\text{and } E_{\xi(E)} = 1.96 S_{\xi(E)} / N. \quad (23)$$

APPENDIX II

Derivation of the Normal Coordinates³⁰

In this appendix we will derive expressions for the normal coordinates of the stable and unstable stretching vibration for the collinear three atom system. For a more detailed discussion see references 31 and 32.



In the above diagram, the x_i ($i = 1, 2, 3$) are the cartesian coordinates for the nuclear masses m_i ($i = 1, 2, 3$) and the R_i ($i = 1, 2$) are the internuclear separations given by the equations

$$\begin{aligned} R_1 &= x_2 - x_1, \\ R_2 &= x_3 - x_2. \end{aligned} \tag{1}$$

The displacement coordinates ΔR_i ($i = 1, 2$) are given by the expressions

$$\begin{aligned} \Delta R_1 &= R_1 - R_1^0, \\ \Delta R_2 &= R_2 - R_2^0. \end{aligned} \tag{2}$$

We require that the velocity of the center of mass is zero, this allows us to write

$$m_1 \dot{x}_1 + m_2 \dot{x}_2 + m_3 \dot{x}_3 = 0. \tag{3}$$

The total vibrational energy is the sum of the kinetic and potential energy. The potential energy corresponding to the small vibrations approximation (SVA) is given by the equation

$$V_{sva} = \frac{1}{2} F_1 \Delta R_1^2 + \frac{1}{2} F_2 \Delta R_2^2 + F_{12} \Delta R_1 \Delta R_2 \tag{4}$$

where the force constants are defined by the expressions

$$\begin{aligned}
F_1 &= \left(\frac{\partial^2 V}{\partial R_1^2} \right)_{R_1^e, R_2^e}, \\
F_2 &= \left(\frac{\partial^2 V}{\partial R_2^2} \right)_{R_1^e, R_2^e}, \\
F_{12} &= \left(\frac{\partial^2 V}{\partial R_1 \partial R_2} \right)_{R_1^e, R_2^e},
\end{aligned} \tag{5}$$

and V is the accurate energy given by the potential energy surface. The total kinetic energy for the three atom system is given by the expression

$$T = \frac{1}{2} \sum_{i=1}^3 m_i \dot{x}_i^2. \tag{6}$$

Equation (6) will provide the vibrational kinetic energy if the values of $\dot{x}_i$ ($i = 1, 2, 3$) satisfy equation (3). Using equations (2) and (3) we obtain the following equations for $\dot{x}_i$ ($i = 1, 2, 3$)

$$\begin{aligned}
\dot{x}_1 &= -(m_2 + m_3) \Delta \dot{R}_1 / M - (m_3 / M) \Delta \dot{R}_2, \\
\dot{x}_2 &= (m_1 / M) \Delta \dot{R}_1 - (m_3 / M) \Delta \dot{R}_2, \\
\dot{x}_3 &= (m_1 / M) \Delta \dot{R}_1 + [(m_1 + m_2) / M] \Delta \dot{R}_2,
\end{aligned} \tag{7}$$

where $M = m_1 + m_2 + m_3$.

The vibrational kinetic energy T_v can now be expressed as

$$T_v = \frac{1}{2} (a_{11} \Delta \dot{R}_1 + a_{22} \Delta \dot{R}_2 + 2a_{12} \Delta \dot{R}_1 \Delta \dot{R}_2) \tag{8}$$

where

$$\begin{aligned}
a_{11} &= m_1 (m_2 + m_3) / M, \\
a_{22} &= m_3 (m_1 + m_2) / M, \\
a_{12} &= m_1 m_3 / M.
\end{aligned} \tag{9}$$

Newton's equations for the vibrational displacement coordinates ΔR_i ($i = 1, 2$) may be expressed as

$$\left(\frac{d}{dt} \right) \frac{\partial T_v}{\partial \Delta \dot{R}_i} + \frac{\partial V}{\partial \Delta R_i} = 0 \quad (i = 1, 2) \tag{10}$$

Using equations (4) and (8), we obtain the expression

$$\begin{aligned}
& c_1 (a_{11} \Delta \ddot{R}_1 + a_{12} \Delta \ddot{R}_2 + F_1 \Delta R_1 + F_{12} \Delta R_2) \\
& + c_2 (a_{21} \Delta \ddot{R}_1 + a_{22} \Delta \ddot{R}_2 + F_2 \Delta R_1 + F_{12} \Delta R_2) = 0
\end{aligned} \quad (11)$$

where c_1 and c_2 are arbitrary constants. Equation (11) may be re-expressed as

$$\begin{aligned}
& (c_1 a_{11} + c_2 a_{21}) \Delta \ddot{R}_1 + (c_1 a_{12} + c_2 a_{22}) \Delta \ddot{R}_2 \\
& + (c_1 F_1 + c_2 F_{12}) \Delta R_1 + (c_1 F_{12} + c_2 F_2) \Delta R_2 = 0.
\end{aligned} \quad (12)$$

The normal coordinates q_i ($i = 1, 2$) have the form given by the expression

$$q = h_1 \Delta R_1 + h_2 \Delta R_2 \quad (13)$$

$$\text{where } h_1 = c_1 a_{11} + c_2 a_{21} = (1/\lambda) (c_1 F_1 + c_2 F_{12}), \quad (14)$$

$$h_2 = c_1 a_{12} + c_2 a_{22} = (1/\lambda) (c_1 F_{12} + c_2 F_2), \quad (15)$$

and λ is the vibrational eigenvalue which corresponds to q .

Using equations (14) and (15), we can write

$$\begin{aligned}
& (\lambda a_{11} - F_1) c_1 + (\lambda a_{12} - F_{12}) c_2 = 0, \\
& (\lambda a_{12} - F_{12}) c_1 + (\lambda a_{22} - F_2) c_2 = 0.
\end{aligned} \quad (16)$$

The determinant of the coefficients of equation (16) may be expressed as

$$\begin{vmatrix} \lambda a_{11} - F_1 & a_{12} - F_{12} \\ \lambda a_{12} - F_{12} & a_{22} - F_2 \end{vmatrix} = 0 \quad (17)$$

The expansion of this determinant provides the result

$$\lambda^2 A + \lambda B + C \quad (18)$$

where

$$\begin{aligned}
A &= a_{11} a_{22} - a_{12}^2, \\
B &= 2 a_{12} F_{12} - F_1 a_{12} - F_2 a_{11}, \\
C &= F_1 F_2 - F_{12}^2.
\end{aligned} \quad (19)$$

We may solve this quadratic equation for the vibrational eigenvalues λ_s and λ_v . For a transition state $F_{12}^2 - F_1 F_2 > 0$, and one of the eigenvalues (λ_s) is positive. This eigen-

value corresponds to the stable stretching vibration. The eigenvalue λ_v is negative and corresponds to the unstable stretching vibration. Using equation (16), we can write

$$\frac{c_1}{c_2} = - \frac{(\lambda a_{12} - F_{12})}{(\lambda a_{12} - F_{12})} . \quad (20)$$

Since c_1 and c_2 are arbitrary constants, we may let $c_1 = 1$; then c_2 is given by the expression $-(\lambda a_{12} - F_{12})/(\lambda a_{12} - F_{12})$. A unique value for c_1 may be determined by using the expression below for the vibrational kinetic energy

$$T_v = \frac{1}{2} \dot{q}_v^2 + \frac{1}{2} \dot{q}_s^2 . \quad (21)$$

Equation (21) may be obtained if we multiply each normal coordinate by an appropriate constant. These constants are defined by the equations

$$\begin{aligned} q_v &= k_v (h_v^v \Delta R + h_v^s \Delta R) , \\ q_s &= k_s (h_s^v \Delta R + h_s^s \Delta R) . \end{aligned} \quad (22)$$

Using equations (21) and (22), we obtain the expression

$$\begin{aligned} T_v &= \frac{1}{2} \left[k_v^2 (h_v^{v^2} \Delta \dot{R}_1^2 + 2h_v^v h_v^s \Delta \dot{R}_1 \Delta \dot{R}_2 + h_v^{s^2} \Delta \dot{R}_2^2) \right. \\ &\quad \left. + k_s^2 (h_s^{v^2} \Delta \dot{R}_1^2 + 2h_s^v h_s^s \Delta \dot{R}_1 \Delta \dot{R}_2 + h_s^{s^2} \Delta \dot{R}_2^2) \right] . \end{aligned} \quad (23)$$

When we compare this expression with equation (8), we find that

$$k_v^2 h_v^{v^2} + k_s^2 h_s^{v^2} = a_{11} , \quad (24)$$

$$k_v^2 h_v^{s^2} + k_s^2 h_s^{s^2} = a_{22} , \quad (25)$$

$$\text{and } k_v^2 h_v^v h_v^s + k_s^2 h_s^v h_s^s = a_{12} . \quad (26)$$

These equations may be solved for the values of the constants k_v and k_s ; these constants are given by the expressions

$$k_v = \left[\frac{(a_{11} + a_{22})h_s^v h_s^s - a_{12}(h_s^{v^2} + h_s^{s^2})}{h_s^v h_s^s (h_v^{v^2} + h_v^{s^2}) - h_v^v h_v^s (h_s^{v^2} + h_s^{s^2})} \right]^{\frac{1}{2}} , \quad (27)$$

$$k_s = \left[\frac{(a_{11} + a_{22})h_1^v h_2^v - a_{12}(h_1^{v^2} + h_2^{v^2})}{h_1^v h_2^v (h_1^{v^2} + h_2^{v^2}) - h_1^s h_2^s (h_1^{v^2} + h_2^{v^2})} \right] k_s^2. \quad (28)$$

The normal coordinate coefficients used in the text are given by the expressions

$$C_1^v = h_1^v k_v, \quad (29)$$

$$C_2^v = h_2^v k_v, \quad (30)$$

$$C_1^s = h_1^s k_s, \quad (31)$$

$$C_2^s = h_2^s k_s. \quad (32)$$

APPENDIX 3

Computer Graphics

It has often been said that one picture is worth a thousand words. With this in mind, we found it informative to make plots of potential energy surfaces (PES) and trajectories. The PES was displayed using Eyring's skewed coordinates³³. These coordinates are mass weighted ones which diagonalize the kinetic energy of the chemical reaction system. The relationship between the Eyring coordinates α and β and the internal coordinates R_1 and R_2 is given by the equations

$$\alpha = a \cdot R_1 + b R_2 \cdot \cos(\theta) \quad (1)$$

$$\beta = b \cdot R_2 \cdot \sin(\theta) \quad (2)$$

The cartesian coordinates and the atomic masses of the three collinear particles are denoted by x_i ($i = 1, 2, 3$) and m_i ($i = 1, 2, 3$) respectively. The internal coordinates R_1 and R_2 are $x_2 - x_1$ and $x_3 - x_2$ respectively. The parameters for the skewed surface are defined by the expressions

$$\begin{aligned} \theta &= \cos^{-1} \left(m_1 m_3 / ((m_1 + m_2) \cdot (m_2 + m_3)) \right)^{1/2} \\ a &= (m_1 (m_2 + m_3) / M)^{1/2} \\ b &= (m_3 (m_1 + m_2) / M)^{1/2} \end{aligned} \quad (3)$$

where $M = m_1 + m_2 + m_3$.

Now that the skewed coordinates have been defined, we are ready to discuss the procedure used to plot the potential energy contours. The starting location in our procedure is the point of minimum potential energy in the reactant or product valley. If the reactant valley is chosen, this position corresponds to the equilibrium internuclear distance of the diatomic reactant molecule (R_1^r) when R_2 is chosen

FIGURE 45

Relationship Between the Skewed and Internal Coordinates

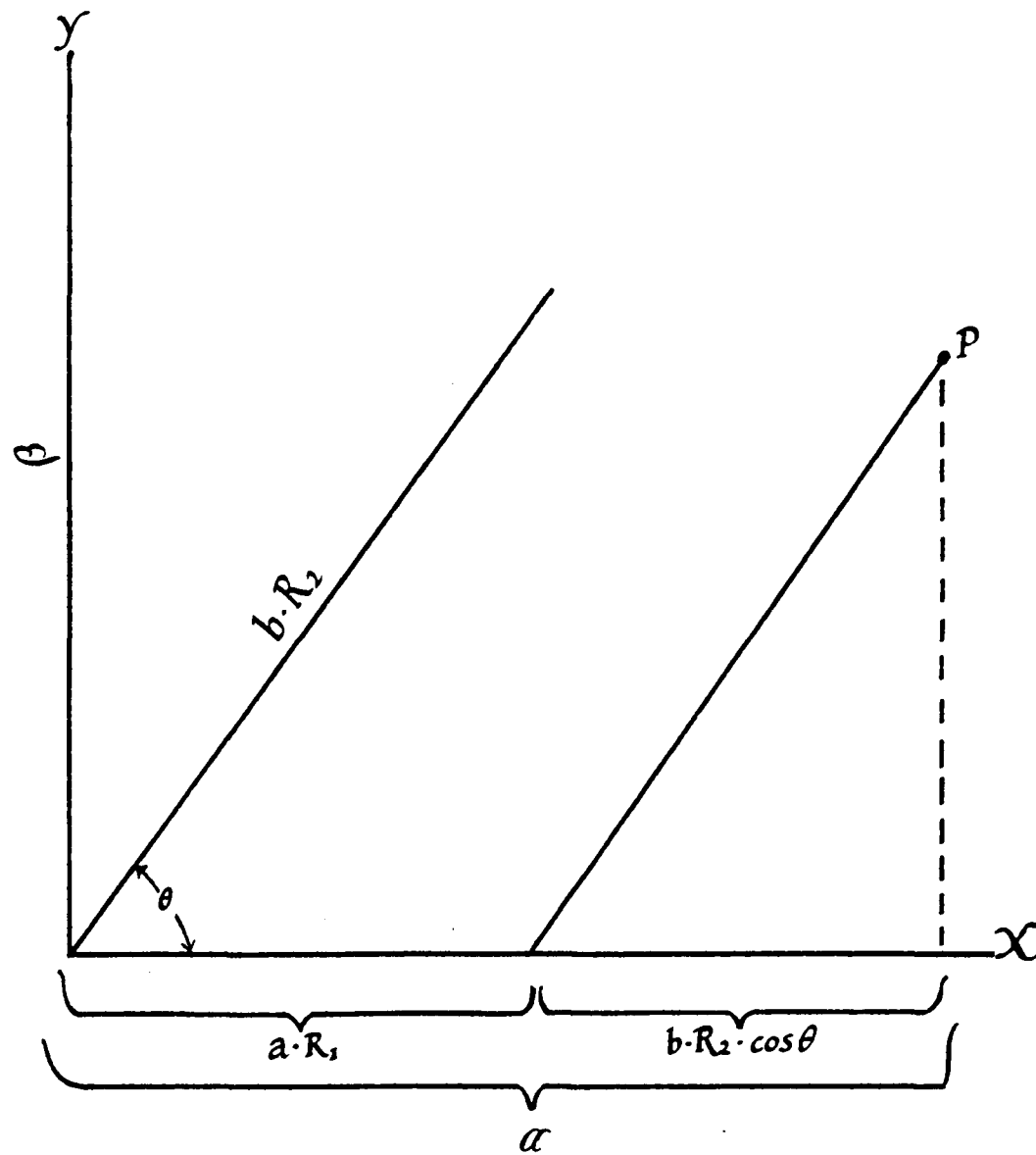
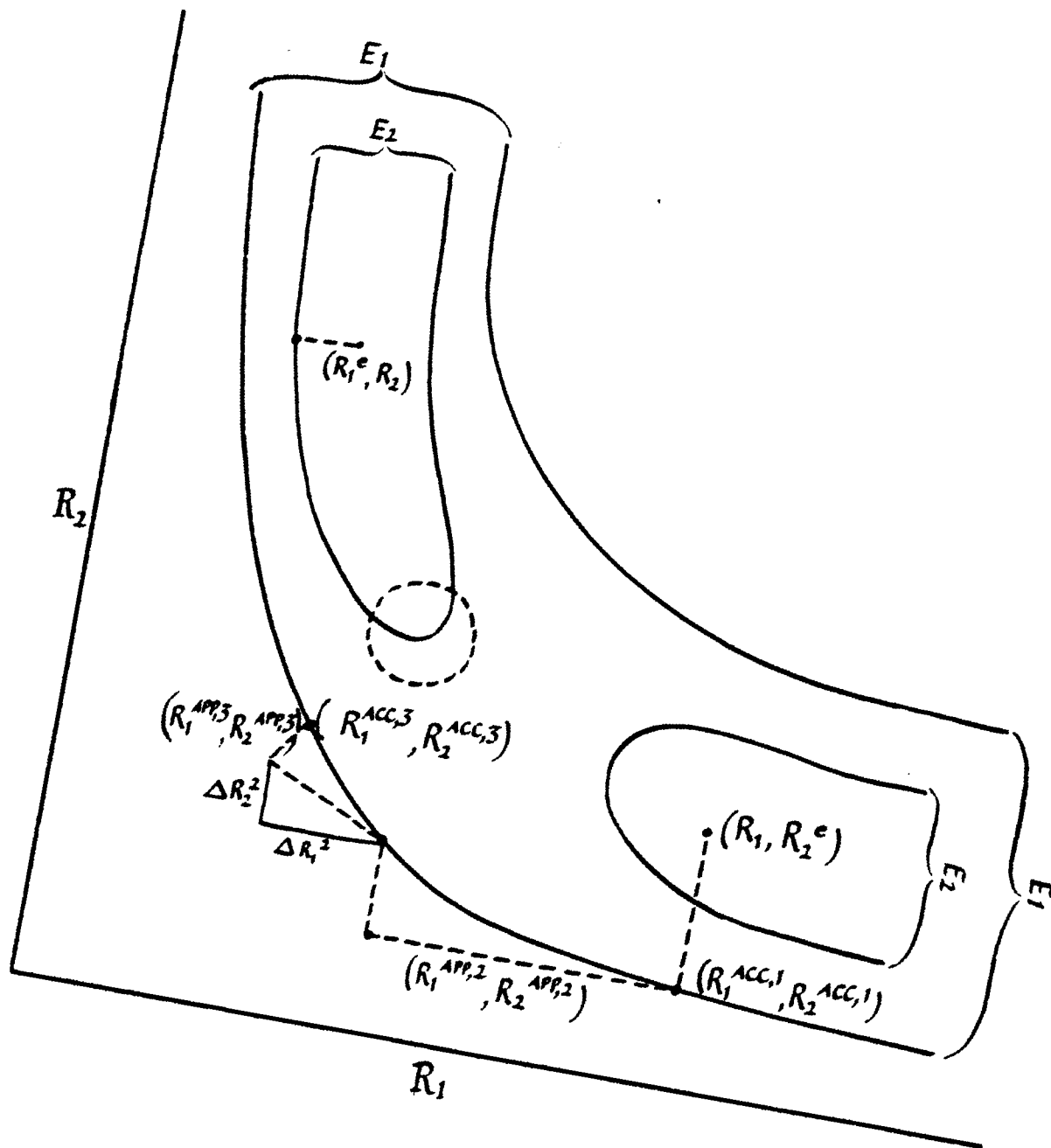


FIGURE 46



large enough so there is negligible interaction between the reactants (see figure 46). We hold R_1 constant and vary R_2 stepwise until the desired energy is almost reached. At this position, the step size in R_2 is reduced and the process repeated until the position on the PES corresponds to an energy which is within 10^{-4} energy units of the desired energy. Equations (1) and (2) are then used to convert the internal coordinates corresponding to this energy to the skewed coordinates. We could then specify another value of R_1 and repeat this procedure. In this way, the process could be used to find points which define the equipotential contour at this energy. This method however, would be quite inefficient in that it would require a great deal of computer time. Instead, we take 0 as a first approximation to the slope of the contour at the first accurate point. The approximate increments corresponding to the next point on the contour are then $\Delta R_1' = -1 \cdot m$ and $\Delta R_2' = m \cdot 0 = 0$ where the quantity m determines the distance between points on the contour. The approximate values of R_1 and R_2 corresponding to the second point on the contour ($R_1^{app,2}$, $R_2^{app,2}$ respectively) are given by the expressions

$$R_1^{app,2} = R_1^{acc,1} + \Delta R_1' \quad (4)$$

$$R_2^{app,2} = R_2^{acc,1} + \Delta R_2' \quad (5)$$

The second point can be found more accurately by evaluating the energy at points along a line which is perpendicular to the initial tangent at the point defined by equations (4) and (5). This operation may be specified in terms of the equations

$$R_1^{acc,2} = R_1^{app,2} - f \Delta R_2^1 \quad (6)$$

$$R_2^{acc,2} = R_2^{app,2} - f \Delta R_1^1 \quad (7)$$

where f is determined by the same trial and error method which was used to determine the first accurate point $(R_1^{acc,1}, R_2^{acc,1})$. An increase in f corresponds to movement along the perpendicular to the initial approximate tangent to the contour. The value of f is varied using the above procedure until the energy at the second point is within 10^{-4} energy units of the desired energy. To convert the second accurate point to the skewed coordinates, equation (1) and (2) are used. The increments which determine the approximate location for the next point $(R_1^{app,3}, R_2^{app,3})$ are given by the equations

$$\Delta R_1^2 = m(R_1^{acc,2} - R_1^{acc,1})/D \quad (8)$$

$$\Delta R_2^2 = m(R_2^{acc,2} - R_2^{acc,1})/D \quad (9)$$

where $D = |R_1^{acc,2} - R_1^{acc,1}| + |R_2^{acc,2} - R_2^{acc,1}|$.

The purpose of the factor D is to insure that the distance between an accurate point and the next approximate one is less than or equal to the quantity m . The general relationship between values of the coordinate at a point on the contour $(R_1^{acc,n}, R_2^{acc,n})$ and the values of the next approximate location $(R_1^{app,n+1}, R_2^{app,n+1})$ is given by the equations

$$R_1^{app,n+1} = R_1^{acc,n} + \Delta R_1^n \quad (10)$$

$$R_2^{app,n+1} = R_2^{acc,n} + \Delta R_2^n \quad (11)$$

The accurate values of the coordinate of the point $n + 1$ are related to the approximate values by the expressions

$$R_1^{acc,n+1} = R_1^{app,n+1} - f \Delta R_2^n \quad (12)$$

$$R_2^{acc,n+1} = R_2^{app,n+1} - f \Delta R_1^n \quad (13)$$

The process determined here is given a pictorial representation in figure 46. After each accurate point on the contour is determined, the values of $R_1^{acc,n}$ and $R_2^{acc,n}$ are checked. If $R_2^{acc,n}$ is equal to or greater than a predetermined end point, the contour is complete and the search begins from the point (R_1, R_2^a) in the opposite direction for the other contour which has the same energy as the contour we have just determined (energy E , in figure 46). If $R_1^{acc,n} \geq R_1$, then a contour corresponding to energy E_2 in figure 46 has been found and the search begins from the point labeled (R_1^a, R_2) in figure 46 for the second contour corresponding to energy E_2 . Contours of the type corresponding to energy E_2 turn much more sharply on the LEPS or PW surface than on the PK surface (circled part of contour corresponding to energy E_2 in figure 46). Consequently it is possible that the above process will "lose" the contour in the circled region. If this happens, the last accurate point on the contour is returned to, and smaller values of m are used until the circled region is passed.

It is also of interest to find the region of each contour corresponding to arcs ab and cd discussed in chapter 3; i.e. that portion of the contour which has forces that are perpendicular to it and can return a trajectory to the DS. The slope of a point $(\alpha_n^{acc}, \beta_n^{acc})$ on a contour in the skewed coordinate system can be approximated by the equation

$$\text{slope} = (\beta_{n+1}^{acc} - \beta_n^{acc}) / (\alpha_{n+1}^{acc} - \alpha_n^{acc}) \quad (14)$$

The direction of the force perpendicular to the contour at this point (S_p) is given by the ratio

$$S_p = - (\alpha_{n+1}^{acc} - \alpha_n^{acc}) / (\beta_{n+1}^{acc} - \beta_n^{acc}) \quad (15)$$

The value of β along the perpendicular to the contour at point $(\alpha_n^{acc}, \beta_n^{acc})$ which intercepts the DS at the point (α, β) is given by the equation

$$\beta = \beta_n^{acc} + S_p (\alpha - \alpha_n^{acc}) \quad (16)$$

The same value of β along the DS can be expressed by the equation

$$\beta = \beta_{ps}^{min} + S_{ps} (\alpha - \alpha_{ps}^{min}) \quad (17)$$

where α_{ps}^{min} and β_{ps}^{min} are the minimum values of α and β on the line segment which defines the DS and S_{ps} is the slope of the DS in the skewed coordinate system. Equations (16) and (17) are equated, and the value of α is given by the expression

$$\alpha = \frac{(\beta_n^{acc} - \beta_{ps}^{min}) + (S_{ps}\alpha_{ps}^{min} - S_p\alpha_n^{acc})}{(S_{ps} - S_p)} \quad (18)$$

Equation (16) or (17) can now be used to solve for β . The quantities α and β are then converted to the internal coordinates and the energy is evaluated. If the energy is less than or equal to the energy of the contour, the point $(\alpha_n^{acc}, \beta_n^{acc})$ has forces which may direct the trajectory back across the DS, and the conversion coefficient ($\xi(E)$) may not be unity.

APPENDIX IV

Description of Potential Energy Surfaces

The three potential energy surfaces used in chapter 3 for our trajectory and phase space calculations are the modified London-Eyring-Polanyi-Sato (LEPS)³⁴, Polanyi-Wong (PW)¹², and Porter-Karplus (PK)³⁹ surfaces. The LEPS and PW surfaces are based on the London equation where the energy of the diatomic molecule at infinite separation between the diatomic molecule and atom is given by the Heitler-London equation³⁶ for the ground state, and is approximated using the Morse potential¹⁷. One can criticize the LEPS and PW surfaces for their lack of quantum mechanical rigor, and point out the weakness of the Morse potential in reproducing spectroscopic data^{37,38}. Our work however provides a test of the validity of ART and not of the potential energy surfaces.

The PK surface is based on a more rigorous quantum mechanical treatment than the LEPS or PW surfaces. It employs a non-ionic valence bond treatment of a three orbital three electron system given by Slater.⁴⁰ Unlike the LEPS and PW surfaces, the PK surface does not treat the overlap integrals as parameters and does not assume the multiple exchange integrals are zero. The parameters we must specify when using the PK surface are given in table 34.

Table 34

$$D_1 = 4.7466\text{ev} \quad D_2 = 1.9668\text{ev} \quad R_2 = 1.40083\text{a.u.}$$

$$\alpha = 1.04435\text{a.u.} \quad \beta = 1.000122\text{a.u.} \quad \delta = 28.2\text{ev}$$

$$\xi = -17.5\text{ev} \quad \kappa = 0.60 \quad \lambda = .65$$

The quantities D_1 and D_3 are the dissociation energies for the singlet state and triplet first excited state respectively for the H-H molecule. The quantities α and β are the Morse parameters corresponding to D_1 and D_3 respectively. The equilibrium internuclear separation for H-H is given by R_1 . The quantities χ and λ are constants used for the calculation of a screening constant. The quantities δ and ϵ are constants of the potential energy surface. Of the three surfaces we use for our calculations, only the PK surface is symmetrical.

The parameters used for our calculations on the PW surface are given in table 35.

Table 35

<u>Diatomic Molecule</u>	<u>D_1 [k.cal. mole⁻¹]</u>	<u>α (Å⁻¹)</u>	<u>R_1 (Å)</u>	<u>S</u>
A - B	109.43	1.942	.7417	.05
B - C	109.43	1.942	.7417	.2187626
A - C	79.435	1.942	.7417	.05

where the diatomic molecules are related by the equation

$A + B-C \rightleftharpoons A-B + C$, D_1 , α and R_1 have the same meanings they had on the PK surface and S is the overlap parameter. The parameters in each row of table 35 correspond to the diatomic molecule listed on the left. The PW and PK surfaces are both thermoneutral, and the activation energy on both surfaces is 9.13 k.cal.mole⁻¹.

Table 36 lists the parameters for the LEPS surface. Rows one and two in table 36 are reversed when studying the reverse reaction (the same is true for the parameters in

Table 36

<u>Diatomic Molecule</u>	<u>D_e [k.cal./ mole⁻¹]</u>	<u>α (Å⁻¹)</u>	<u>R_e (Å)</u>	<u>S</u>
A - B	90.33	1.8109	1.4138	.076
B - C	109.43	1.942	.7417	.225
A - C	90.33	1.8109	1.4138	.076

table 35). In contrast to the PW and PK surfaces, the LEPS surface is not thermoneutral (endothermic for the forward reaction). The saddle point on the LEPS and PW surfaces is in the entrance valley for the forward reaction, and the classical activation energy on the LEPS surface is 20.85 k.cal. mole⁻¹.

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- 42) Private communication with Dr. D. Sverdlik.