

Potential-Energy Surfaces and Transition-State Theory

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One of the major objectives in reaction kinetics is to calculate the rate constant for an elementary reaction from first principles. This is a formidable task which has not yet been fully achieved in even the simplest case without making several simplifying assumptions.

The earliest approach used simple collision theory and was helpful in clarifying some of the main features involved in calculating a reaction rate. However, the simple form of the theory was difficult to make quantitative. The current favored approach to rate constants from truly first principles seems to be through reaction dynamics (1, 2). This method examines the progress of individual collisions by solving the equations of motion with an assumed form of interaction potential. Although the methods of collision dynamics are elegant, the results are difficult to use in understanding reactions involving the large molecules which are of more general interest to chemists.

Almost half a century ago, transition state theory was proposed (3) as a method of dealing with complex reactants, although the details of the theory are usually considered for a simple triatomic system (A—B—C) initially. In principle, this theory uses the potential energy surface for a triatomic system to decide the reaction coordinate, i.e., the path from reactants to products which requires passage over the lowest energy barrier. Figure 1 clearly shows reactant and product valleys separated by a low col, or saddle point. The configuration corresponding to the saddle point is known as the transition state. The energy of the transition state relative to the reactants determines the classical activation energy of the reaction (disregarding zero-point vibrational energies). The reaction is then written:



where ABC^\ddagger represents the transition state or activated complex.

Although the activated complex is only a stage in a reactive collision, not an intermediate, transition state theory treats the activated complex as a more-or-less normal molecule in equilibrium with the reactants. The reaction rate is then the rate at which the complex changes into products and the rate constant for the bimolecular reaction becomes

$$k = (RT/Lh) \cdot K^\ddagger \quad (1)$$

where K^\ddagger is the equilibrium constant for formation of the complex and $(RT/Lh) = 6.21 \times 10^{12} \text{ s}^{-1}$ at 298K (see standard texts (4, 5) for derivations of this equation). For simple reactants, the methods of statistical mechanics may be used provided the molecular properties of the transition state and the reactants are sufficiently well defined. If the transition state can be accurately located on the potential energy surface, the interatomic distances may be read off at once. The shape of the surface around the transition state also determines the vibrational properties of the complex. Thus, an appropriate potential energy surface may be used for the complete calcu-

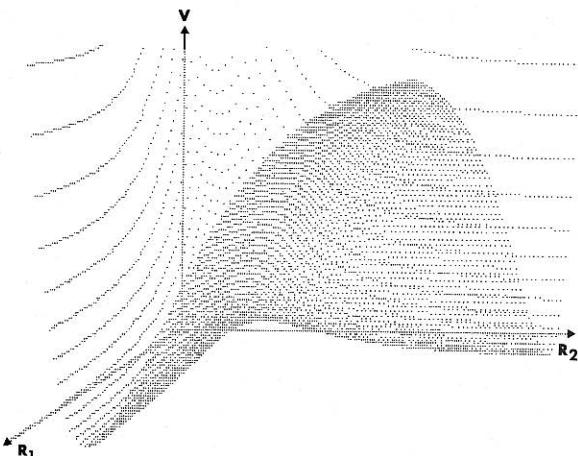


Figure 1. Potential energy surface for linear H—H—H.

lation of a rate constant by means of transition-state theory.

When an atom as small as hydrogen is transferred, quantum mechanical tunnelling may significantly modify the rate constant. See Bell (6) for an extensive discussion of the chemical significance of the tunnel effect. In this study, we ignore tunnelling completely.

The set of programs to be described allows students to carry out the following studies of any selected triatomic system.

- 1) Construct a plausible potential energy surface (program LEPS).
- 2) Use the surface to find the dimensions and energy of the activated complex.
- 3) Determine the classical activation energy for the system.
- 4) Take sections through the surface at the transition state to find the force constants, vibration frequencies and zero-point energy of the complex (program TS PROPERTIES).
- 5) Use the zero-point energies to correct the classical activation energy.
- 6) Calculate the A-factor for the reaction from the molecular properties using statistical thermodynamics (program A-FACTOR).
- 7) Compare the calculated quantities with experimental values.

We begin the detailed discussion with methods of calculating potential energy surfaces.

Potential Energy Surfaces

To calculate the potential energy, V , of a triatomic system we must, in principle, use the methods of quantum mechanics. In general, V will depend on three variables, i.e., three interatomic distances or two distances and an angle, as shown in Figure 2(a). It is, however, common practice to restrict the three atoms to a straight line, as in Figure 2(b), so that only

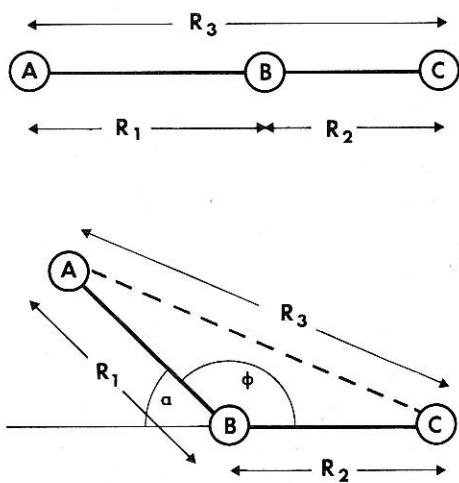


Figure 2. Linear (a) and bent (b) configurations for a triatomic system.

Table 1. Morse Parameters for Some Diatomic Molecules (δ)

Molecule	D_e (kJ/mol)	R_e (Å)	$10^{-8}\beta^a$ (cm $^{-1}$)	ω_e (cm $^{-1}$)	
H ₂	458.39	0.741	1.944	4401.2	52.65
F ₂	160.1	1.412	2.974	916.6	10.96
Cl ₂	242.57	1.988	2.001	559.7	6.70
Br ₂	192.08	2.281	1.964	325.3	3.89
I ₂	150.1	2.666	1.857	214.5	2.57
O ₂	503.02	1.208	2.654	1580.2	18.90
HF	591.01	0.917	2.218	4138.3	49.50
HCl	445.66	1.275	1.868	2990.9	35.78
HBr	378.43	1.414	1.809	2649.0	31.69
HI	308.47	1.609	1.751	2309.0	27.62

$$^a \beta = \left(\frac{2\pi^2 c \mu}{D_e} \right)^{1/2} \cdot \omega_e = 1.2177 \times 10^7 \left(\frac{\mu}{D_e} \right)^{1/2} \cdot \omega_e$$

(β is in cm $^{-1}$ when ω_e and D_e are in cm $^{-1}$ and μ is in atomic units: 1 cm $^{-1}$ = 0.011963 kJ mol $^{-1}$)

two independent variables are required and a three-dimensional plot of the surface may then be made (Fig. 1). The linear approach is expected to lead to the lowest activation energy (4, 5). We shall examine surfaces for "bent" systems later and find that this expectation seems to be justified.

The calculation of the potential energy for even a diatomic system by *ab initio* methods in quantum mechanics is much too complex a task for a microcomputer. It is essential to resort to approximate methods which give a reasonably meaningful result. The simplest of the approximations is the Heitler-London treatment which gives the following expressions for attractive and repulsive curves for a diatomic molecule:

$$V_{att} = \frac{Q + J}{1 + S^2}; V_{rep} = \frac{Q - J}{1 - S^2} \quad (2)$$

where Q is the coulombic energy arising from electrostatic attraction between electrons and nuclei, J is the exchange energy and has no classical analogy, and S is the overlap integral. Q , J , and S all depend strongly on the internuclear separation. Figure 3 shows the form of the attractive and repulsive curves for H₂ and HCl.

London expressed the potential energy of a triatomic system in terms of the three diatomic molecules considered to form the system, leading to the following equation:

$$V_L = Q_{AB} + Q_{BC} + Q_{AC} \pm \{ \frac{1}{2}[(J_{AB} - J_{BC})^2 + (J_{BC} - J_{AC})^2 + (J_{AC} - J_{AB})^2] \}^{1/2} \quad (3)$$

A derivation of this equation has been given which makes clear stringent limitations which should be applied to its use (7),

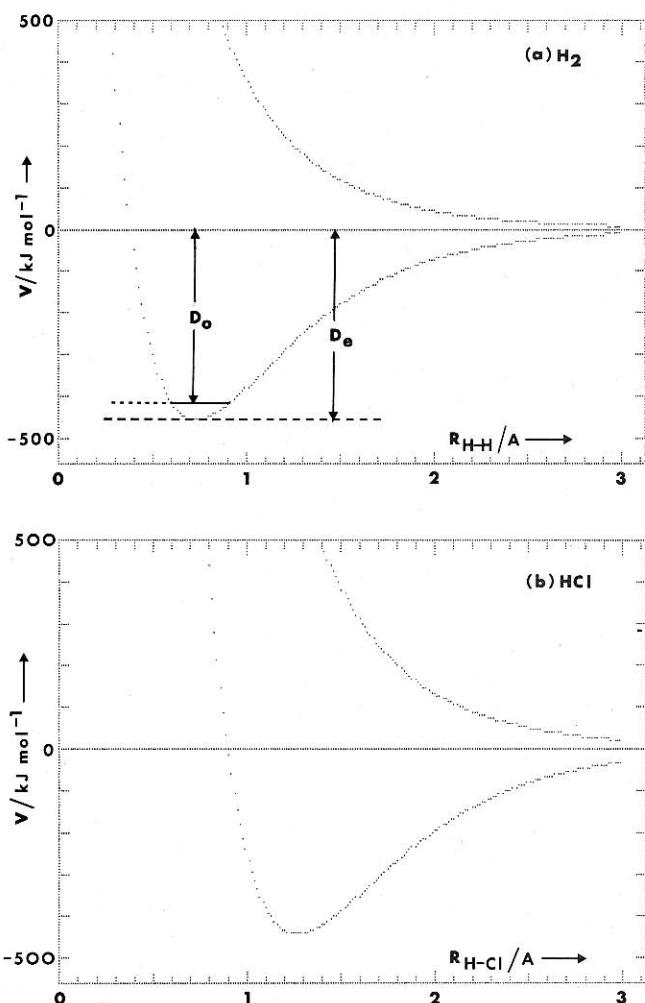


Figure 3. Morse and anti-Morse curves for (a) H₂ and (b) HCl. Morse parameters are listed in Table 1.

e.g., homopolar molecules with electrons in *s*-orbitals and neglect of overlap integrals. Nevertheless, for want of a more suitable alternative, the London equation is regularly used in apparently invalid circumstances. In order to use eqn. (3) to calculate the potential energy of the system at any values of R (AB) and R (BC), one must be able to calculate separate Q and J values for each pair of molecules at each internuclear distance.

The London-Eyring-Polanyi-Sato Method (LEPS)

If one wishes to use an entirely theoretical approach, then the Q and J values should be calculated from the appropriate Heitler-London integrals. This is impractical on a microcomputer and, in any case, gives only approximate potential energies. A substantial improvement is obtained by using the actual potential energy curves for the diatomic molecules or close approximations. An approach of this kind which makes some use of experimental data in dealing with a theoretical problem is called a semi-empirical method. The Morse equation shown below is a good approximation to the potential energy curve for a diatomic molecule.

$$V_M = D_e [e^{-2\beta(R-R_e)} - 2e^{-\beta(R-R_e)}] \quad (4)$$

In this equation, D_e is the classical dissociation energy (i.e., to the minimum of the curve), R_e is the equilibrium bond length and β is a constant for the molecule. Table 1 contains Morse parameters for some diatomic molecules of interest. Even in this semi-empirical approach, the problem still remains of dividing the total potential energy of a diatomic

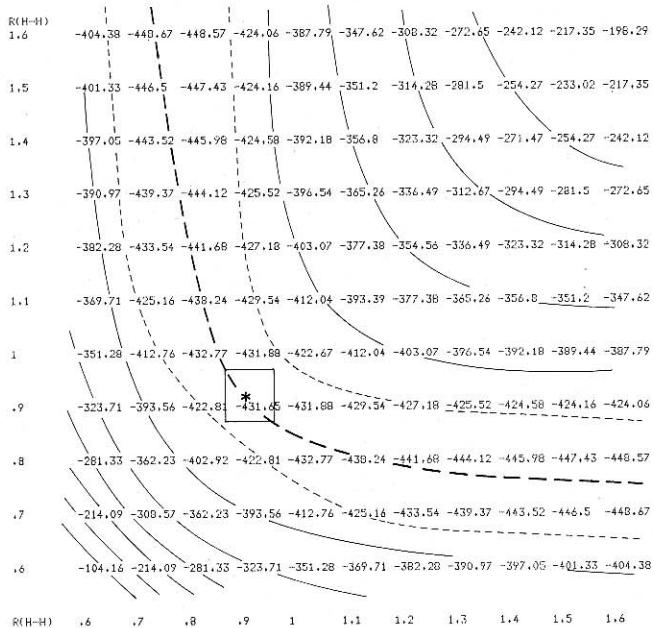


Figure 4. LEPS Surface for H—H—H ($K = 0.17$).

system at every separation distance into separate Q and J components. The earliest and simplest method, used by Eyring and Polanyi, treats the coulombic energy as a constant fraction of the total (usually between 10% and 20%) at all interatomic distances. The method was useful in early studies but has many limitations and has now been superseded.

A method devised by Sato (9) has frequently been used. Since the Morse equation describes only the attractive potential energy curve (empirically), Sato introduced an empirical "anti-Morse" equation to approximate the repulsive curve using the same parameters as the Morse equation. Sato's anti-Morse equation is

$$V_{AM} = \frac{1}{2}D_e\{e^{-2\beta(R-R_e)} + 2e^{-\beta(R-R_e)}\} \quad (5)$$

Equation (5) was obtained from (4) by changing the sign in the bracket and dividing by two to obtain a better fit with a calculated repulsive curve for hydrogen. Figure 3 shows Morse and anti-Morse curves for H_2 and HCl produced by a program MORSE GRAPH.

In eqn. (2), Sato replaced S^2 by K which is treated as an adjustable constant. The use of eqns. (2), (4), and (5) then leads to the separate expressions for Q and J in eqns. (6) and (7):

$$Q = \frac{1}{4}D_e\{(3+K)e^{-2\beta(R-R_e)} - (2+6K)e^{-\beta(R-R_e)}\} \quad (6)$$

$$J = \frac{1}{4}D_e\{(1+3K)e^{-2\beta(R-R_e)} - (6+2K)e^{-\beta(R-R_e)}\} \quad (7)$$

The separate values of Q and J may then be used to calculate the potential energy for the triatomic system at any values of R_1 and R_2 by substituting in Sato's slightly modified form of the London equation

$$V_{Sato} = V_L/(1+K) \quad (8)$$

Equations (3), (6), (7), and (8) contain the essentials of the LEPS method and form the basis of the computer programs used in this study.

LEPS Surface for HHH

The LEPS program for a linear triatomic system requires the user to enter the Morse parameters for the three diatomic species, to choose a value for the Sato constant (K), and to specify the ranges and step intervals for $R(AB)$ and $R(BC)$. The printout begins with a heading and repetition of the input

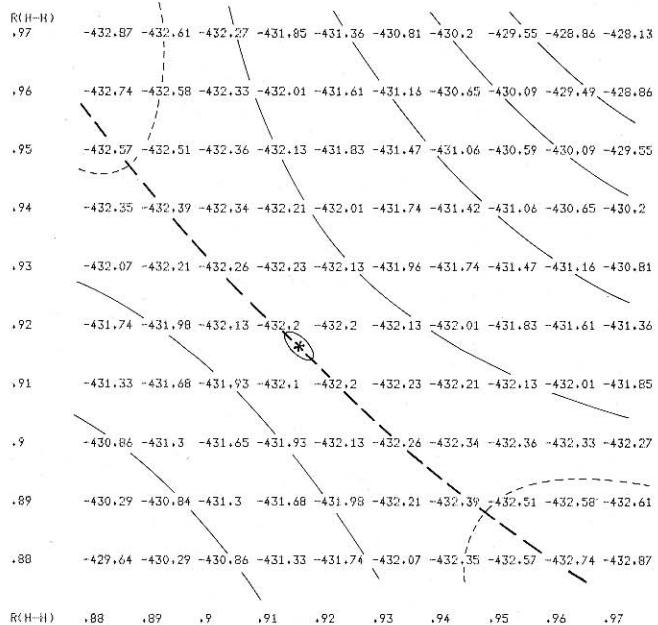


Figure 5. LEPS Surface for H—H—H: detail around transition state.

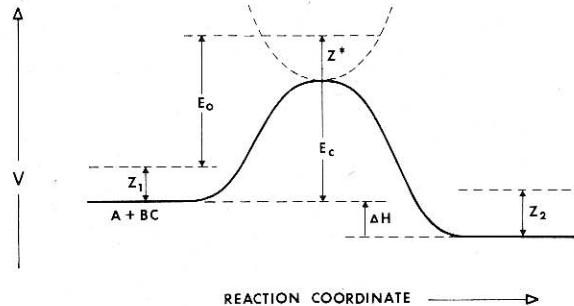


Figure 6. Section through a reaction coordinate. Z_1 , Z_2 , and Z^\ddagger , are zero-point energies for BC, AB, and ABC^\ddagger , respectively. For the reaction



the classical activation energies, E_c , should be corrected by

$$E_0 = E_c + Z^\ddagger - Z_1$$

data. For each selected combination of $R(AB)$ and $R(BC)$, the program calculates V and prints the results in the form of a square grid with the R values alongside, as in Figure 4 for the HHH system; the horizontal and vertical spacings of the grid points need not be identical. With our printer (a Paper Tiger 445) set on the smallest print size, a maximum of fifteen values may be printed across the width of the paper. The calculation and printout take about three minutes on the Apple II for a 15×15 grid. To improve clarity of reproduction, a larger print size with fewer points has been used in the preparation of Figures 4 and 5.

The student sketches appropriate contours on the grid with accuracy sufficient only to locate the position of the transition state. The region around the transition state in Figure 4 has been recalculated on a larger scale in Figure 5 which clearly shows that the transition state may be easily located to within about 0.002 \AA . Once the transition state has been located properly, the classical activation energy may be calculated and a sketch of a section through the reaction coordinate may be made, as in Figure 6, which also shows the way the classical activation energy, E_c , should be corrected for zero-point energies in the reactants and complex.

The shape of the LEPS surface around the transition state

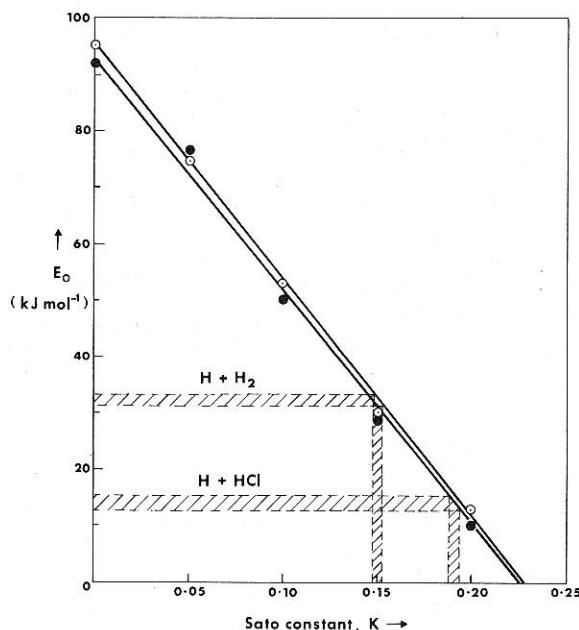


Figure 7. Corrected Activation Energy (E_0) from LEPS Surfaces as a function of Sato Constant, K .

○—linear H—H—H
●—linear H—H—Cl

Shaded areas show plausible limits to experimental activation energies (10).

depends strongly on the value of K . As Figure 7 shows, small values of K give large barriers while values of K greater than about 0.25 lead to increasingly deep potential wells suggesting stable H_3 and H_2Cl species. Such features appeared on the original LEP surfaces and are not found on the best theoretical surfaces.

The usual way of selecting K is to choose the value which gives the best agreement with the experimental activation energy for a particular reaction. For example, for $H + H_2$ the best value would be $K = 0.15$ (Fig. 7), but for $H + HCl$, the preferred value of K is 0.19. We adopted the compromise value of 0.17 and obtained the transition state properties listed in Table 2 for an interesting series of reactions. A detailed comparison with experimental values will be made later.

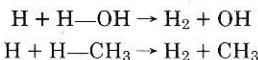
It is a simple matter to extend the LEPS program to calculate potential energies for "bent" systems, i.e., for a fixed angle of approach α ($\alpha = 0$ in Fig. 2(b)). For a linear system, R_3 is the sum of R_1 and R_2 while the cosine rule, eqn. (9), applies in the nonlinear case.

$$R_3^2 = R_1^2 + R_2^2 - 2R_1R_2 \cos \phi \quad (9)$$

Table 3 shows that the barrier height is lowest in the linear system (for a fixed value of K) as expected.

LEPS Surfaces for Systems with More Than Three Atoms

The LEPS method may be applied to such reactions as the following



by regarding the group to which the abstracted H atom is attached as a single "atom" A (A = OH or CH_3 in the above examples). If the bond dissociation energy, vibration frequency, and equilibrium bond length of H—A are known, or may be estimated, then the Morse parameters may be calculated and the LEPS method applied normally. We have used this approach for these reactions, for a series of halogen-substituted methanes and for a few other systems. It seems desirable not to present extensive results here but to allow interested users

Table 2. Transition-State Properties from Some LEPS Surfaces ($K = 0.17$)

$A—B—C$	R_{AB}^\ddagger (Å)	R_{BC}^\ddagger (Å)	E^\ddagger (kJ mol ⁻¹)
H—H—H	0.917	0.917	-432.2
H—H—F	0.752	1.677	-455.8
H—H—Cl	0.970	1.418	-423.0
H—H—Br	1.340	1.445	-372.8
H—H—I			No barrier found

Table 3. Comparison of Linear and Angled Approaches ($K = 0.17$ in all cases)

Reaction	α	E_c /kJ mol ⁻¹
$H + H_2$	0	23
$H + H_2$	45°	40
$H + H_2$	90°	105
$H + HCl$	0	21
$H + HCl$	45°	39
$H + HCl$	90°	130

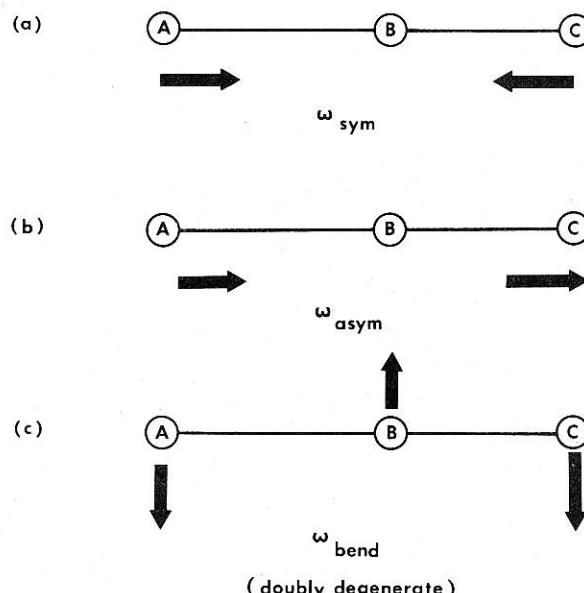


Figure 8. Normal Modes of Vibration for a Linear Triatomic Molecule.

to discover for themselves the successes and failures of the LEPS method. One point worth making is that it is generally necessary to select a new value of K when changing the reaction type.

Vibrations of the Activated Complex

A linear triatomic molecule has four normal modes of vibration, two stretching vibrations and a doubly degenerate bending vibration (Fig. 8). For an activated complex, the asymmetric stretching vibration clearly corresponds to motion through the reaction coordinate. The vibration frequencies of the complex are used in two ways:

- 1) to correct the classical activation energy for zero-point energies;
- 2) to obtain the vibrational partition functions needed in the A-factor calculation.

Johnston has described in detail (11) the procedures for calculating vibrational properties of an activated complex from the potential energy surface. We present here a summary of his treatment.

The potential energy function may be expanded in a Taylor series about the transition state to give

$$V - V^\ddagger = \frac{1}{2} \left(\frac{\partial^2 V}{\partial R_1^2} \right) r_1^2 + \frac{1}{2} \left(\frac{\partial^2 V}{\partial R_2^2} \right) r_2^2 + \left(\frac{\partial^2 V}{\partial R_1 \partial R_2} \right) r_1 r_2 \quad (10)$$

where $r_1 = R_1 - R_1^\ddagger$ and $r_2 = R_2 - R_2^\ddagger$, ($R_1^\ddagger, R_2^\ddagger$, and V^\ddagger are bond lengths and energy of the complex. Stretching force constants are defined by eqn. (11).

$$F_{11} = \left(\frac{\partial^2 V}{\partial R_1^2} \right) : F_{22} = \left(\frac{\partial^2 V}{\partial R_2^2} \right) : F_{12} = \left(\frac{\partial^2 V}{\partial R_1 \partial R_2} \right) \quad (11)$$

$$F_\phi = \left(\frac{\partial^2 V}{\partial \phi^2} \right)_{R_1, R_2} \quad (12)$$

Equation (12) defines a bending force constant in a similar way. The potential energy around the saddle point then becomes

$$V - V^\ddagger = \frac{1}{2} \{ F_{11} r_1^2 + F_{22} r_2^2 + 2F_{12} r_1 r_2 + F_\phi \phi^2 + F_\phi (\phi')^2 \} \quad (13)$$

(where ϕ and ϕ' represent angular displacements in two mutually perpendicular directions).

The vibration frequencies, ω , are related to the force constants through eqns. (14)–(19).

$$\omega_i = \lambda_i^{1/2}/2\pi \quad (14)$$

$$\lambda_{\text{sym}} = \frac{1}{2} [B + (B^2 - 4C^2)^{1/2}] \quad (15)$$

$$\lambda_{\text{asym}} = \frac{1}{2} [B - (B^2 - 4C^2)^{1/2}] \quad (16)$$

$$B = F_{11}/M_1 + F_{22}/M_2 + (F_{11} + F_{22} - 2F_{12})/M_3 \quad (17)$$

$$C = (F_{11}F_{22} - F_{12}^2)(M_1 + M_2 + M_3)/M_1 M_2 M_3 \quad (18)$$

$$\lambda_{\text{bend}} = F_\phi \left\{ \frac{1}{R_1^{\ddagger 2} M_1} + \frac{1}{R_2^{\ddagger 2} M_3} + \left(\frac{1}{R_1^\ddagger} + \frac{1}{R_2^\ddagger} \right)^2 \frac{1}{M_2} \right\} \quad (19)$$

Calculation of the Force Constants

The first step is to locate the transition state as precisely as possible on the LEPS surface. A program called TS PROPERTIES then extracts the force constants by carrying out all the following tasks.

Stretching Force Constants. Force constants F_{11} and F_{22} are easily evaluated by taking sections through the surface at the transition state parallel to the R_1 and R_2 axes (i.e., sections CD and EF in Figure 9). If the results show that the surface

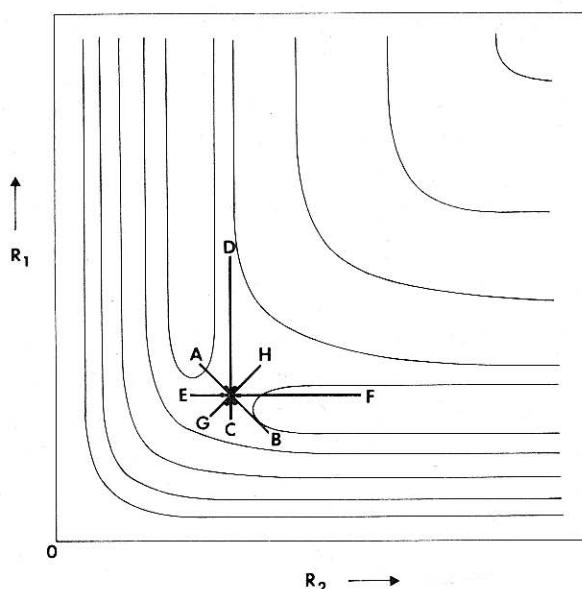


Figure 9. Schematic Potential Energy Surface.

is close to parabolic, then the force constants may be calculated from eqns. (20a) and (20b).

$$F_{11} = 2(V_1 - V^\ddagger)/r_1^2 \quad (20a)$$

$$F_{22} = 2(V_2 - V^\ddagger)/r_2^2 \quad (20b)$$

The program calculates V using the LEPS expression over a range of 0.05 Å at step intervals of 0.01 Å and averages the quantities calculated from eqns. (20a) and (20b).

The force constant F_{12} requires a less direct approach. The curvature of sections along some other line of slope c is used; the force constant, F_c , along this line is then given by eqn. (21).

$$F_c = (F_{11} + c^2 F_{22} + 2c F_{12})/(1 + c^2) \quad (21)$$

The program always takes a section through a line of unit slope (the "diagonal" section GH in Figure 9), so that F_{12} is obtained from eqn. (22) by rearranging eqn. (21).

$$F_{12} = \frac{1}{2}(2F_c - F_{11} - F_{22}) \quad (22)$$

Table 4 shows results for the HHH system. The force constants are very sensitive to the exact shape of the surface; if the transition state is correctly located, the deviations from parabolic shape are generally small in all sections.

The Bending Force Constant. Essentially the same procedure is followed, except that the bond lengths in the transition state are held constant and the structure is bent out of the linear shape. The TS PROPERTIES program bends the complex over a 10° range with 2° step intervals (see Table 5).

Once the force constants have been determined, the calculation of the vibration frequencies is straightforward and is automatically carried out in the TS PROPERTIES program using the atomic masses initially entered. Since the potential energy surface is independent of the atomic masses, the same

Table 4. Sections through LEPS Surface for H—H—H (K = 0.17)

R_{AB} (Å)	R_{BC} (Å)	$V - V^\ddagger$ (kJ mol ⁻¹)	$(V - V^\ddagger)/r^2$
Section Parallel to A—B Axis			
0.917	0.917	0	
0.927	0.917	0.018	178
0.937	0.917	0.095	237
0.947	0.917	0.225	250
0.957	0.917	0.401	250
0.967	0.917	0.617	247
			Mean = 233
			$F_{11} = F_{22} = 466$
Diagonal Section			
0.917	0.917	0	
0.927	0.927	0.135	675
0.937	0.937	0.584	730
0.947	0.947	1.329	739
0.957	0.957	2.353	735
0.967	0.967	3.637	727
			Mean = 721
			$F_c = 1442$

Table 5. Transition-State Bending in H—H—H System

ϕ (deg/rad)	R_{AC} (Å)	$V - V^\ddagger$ (kJ mol ⁻¹)	$(V - V^\ddagger)/\phi^2$
0/0	1.834	0	—
2/0.0349	1.8337	0.0236	19.38
4/0.0698	1.8329	0.0946	19.40
6/0.1047	1.8315	0.2131	19.43
8/0.1396	1.8295	0.3795	19.47
10/0.1745	1.827	0.5944	19.51
			Mean = 19.45
			$F_\phi = 38.9$

Table 6. Force Constants, Vibration Frequencies and Zero-point Energies for Some Activated Complexes (LEPS Surfaces with $K = 0.17$)

$A-B-C^\ddagger$	F_{11} (kJ mol $^{-1}$ A $^{-2}$)	F_{22} (kJ mol $^{-1}$ A $^{-2}$)	F_{12} (kJ mol $^{-1}$ A $^{-2}$)	F_ϕ (kJ mol rad)	ω_{sym} (cm $^{-1}$)	ω_{asym} (cm $^{-1}$)	ω_{bend} (cm $^{-1}$)	Z^\ddagger (kJ mol $^{-1}$)
H—H—H	465	465	977	38.9	2016	2082i	884	22.7
H—D—H					2016	1700i	722	20.7
H—H—D					1731	1980i	847	20.5
H—D—D					1727	1569i	675	18.4
D—H—D					1426	1900i	807	18.2
D—D—D					1426	1472i	625	16.0
H—H—F	3123	-3	156	8.0	4091	131i	353	28.7
H—H—Cl	316	709	906	47.4	1301	1721i	740	16.6
H—H—Br	-92	1691	281	20.9	1817	759i	394	15.6

force constants may be used to calculate the vibration frequencies for any isotopic variation. The program gives the user the option of doing this. Some results for the systems of Table 2 are collected in Table 6.

We have verified the correct operation of the programs used in this study by hand calculation in selected instances and by comparing our results with those published by others. In the latter context, we note here that we obtain very close agreement with the properties of the HHH complex calculated by Johnston using the LEPS procedure (reference (11), page 189, calculated with $K = 0.18$).

A-Factors from Transition-State Theory

If tunnelling is ignored, we may write eqn. (1) as follows using statistical mechanics:

$$k = \sigma(RT/Lh) \cdot \frac{Q^\ddagger}{Q_A Q_{BC}} \cdot e^{-E_0/RT} \quad (23)$$

where Q^\ddagger , Q_A , and Q_{BC} are partition functions expressed relative to the same energy zero and σ is a factor determined by the number of reaction channels available (e.g., $\sigma = 2$ for $H + H_2 \rightarrow H_2 + H$ and $\sigma = 1$ for $H + HCl \rightarrow H_2 + Cl$). We adopt the simple approach of equating the A-factor to the pre-exponential term in eqn. (23) leading to

Table 7. Partition Functions

Species	$10^{-30} \cdot q_t^a$	q_r	q_v	$10^{-30} \cdot Q^a$
H	0.97			0.97
F	80.0			80.0
Cl	200.1			200.1
Br	679			679
H_2	2.73	3.38	1.000	9.23
HF	86.4	9.83	1.000	850
HCl	208.7	19.45	1.000	4059
HBr	691.5	24.3	1.000	16800
HHH ‡	5.02	20.67	1.00, 1.014	73.4
HHF ‡	93.0	97.19	1.00, 1.222	6671
HHCl ‡	217.5	89.97	1.002, 1.029	11549
HHBr ‡	704.5	118.25	1.00, 1.199	49639

^a Values of q_t and Q refer to a volume of one cubic meter per molecule.

$$A = \sigma(RT/Lh) \frac{Q^\ddagger}{Q_A Q_{BC}} \quad (24)$$

If the vibrational, rotational, and translational energies are independent, the total partition function may be factorized into separate translational, rotational, and vibrational terms so that we may write $Q = q_t \cdot q_r \cdot q_v$. The usual expressions for the separate terms (5) are used by the program A-FACTOR.

Some care is needed in managing the units when the A-factor is calculated from transition state theory (see Robinson (12) for a general treatment of the problem). In particular, the translational energy levels and partition functions depend on the volume available to the molecule (5, 13). When the volume is set equal to unity and S.I. units are employed in eqn. (24), the calculated values of q_t and Q refer to a volume of one cubic meter per molecule. Table 7 contains some partition functions evaluated in this way by the program A-FACTOR. Since the preferred units for the A-factor are $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, equivalent to a volume of one cubic centimeter per mole, a conversion factor of $L \times 10^6$ is applied in calculating the A-factor (at 298 K) from the partition functions in Table 7. Calculated Arrhenius parameters are collected in Table 8 for comparison with experimental values.

Comparison with Experimental Results

Table 8 clearly demonstrates that a complete application of transition state theory using LEPS surfaces can lead to remarkably close agreement between calculated and experimental Arrhenius parameters. The treatment used here seems to overestimate A-factors somewhat since the agreement is closer than expected when one recalls that tunnelling effects have been neglected (the magnitude of the tunnel correction should not exceed a factor of about four—see reference (6), page 67).

As described earlier, activation energies for $H + H_2$ and $H + HCl$ were used to fix a suitable value of K , the Sato constant. The results show that the same value of K gives a good account of all the activation energies for the series in Table 8. However, as also noted earlier, the same value of K is not applicable to reactions of a different type, such as the transfer of hydrogen atoms from polyatomic molecules or the transfer of atoms

Table 8. Arrhenius Parameters

Reaction	Computed Values			Experimental Values ^a		
	$E_c/\text{kJ mol}^{-1}$	$E_0/\text{kJ mol}^{-1}$	$10^{-13} A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$E/\text{kJ mol}^{-1}$	$10^{-13} A/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$
$H + H_2 \rightarrow H_2 + H$	26.2	22.6	8.9	31–34	5–10	0
$H + HF \rightarrow H_2 + F$	135.2	139.1	6.2	146	0.2–1	134.1
$F + H_2 \rightarrow HF + H$	2.6	5.0	13.7	6–10	5–12	-134.1
$H + HCl \rightarrow H_2 + Cl$	22.7	21.4	2.0	13.3	0.5	-5.3
$Cl + H_2 \rightarrow HCl + H$	35.4	25.7	8.4	19–22	2–8	5.3
$H + HBr \rightarrow H_2 + Br$	5.6	5.4	2.8	9	6.3	-69.5
$Br + H_2 \rightarrow HBr + H$	85.6	74.9	14.3	75–83	8–25	69.5
$H + HI \rightarrow H_2 + I$				3–5	6	-137.4
$I + H_2 \rightarrow HI + H$	No barrier found			140–142	-20	137.4

^a Experimental values taken from reference (10).

other than hydrogen. The experimental values for the H—H—Cl system have been the subject of some controversy over the past few years (14–16).

Energy Release in Exothermic Reactions

The details of the potential energy surface determine the way in which the energy is released in an exothermic reaction; i.e., whether mainly as translational energy of the products, as vibrational (and rotational energy) in the diatomic product, or as a mixture of both. Experimental information on the degree of excitation in the products has become increasingly available during the last two decades through studies of crossed molecular beams, infrared chemiluminescence, etc. This information has encouraged much theoretical work with potential energy surfaces.

Trajectory calculations using a variety of potential energy surfaces have been carried out to determine the form of the surface which best fits the experimental results (17); a major testing ground for such procedures is the F + H₂ reaction (18). Although the simple LEPS surface obtained in this study is inadequate for a detailed treatment, the surface has a broadly correct form. In particular, the transition state is located early in the approach valley (see Table 2), with a long H—F bond and scarcely any increase in the H—H bond. This type of surface is usually described as being of the "attractive" or "early downhill" variety. The energy is released after passing through the transition state as the new bond forms and the old bond is severed, which favors the formation of vibrationally excited HF.

We intend shortly to prepare a program for an Apple II to perform trajectory calculations with a LEPS surface (1). Although such treatments would be inappropriate for an introductory study of transition state theory, they would add greatly to the interest for suitably advanced students.

Extensions of the LEPS Method

In spite of the many assumptions in the LEPS procedure, potential energy functions of the LEPS type are still used in assessing experimental rate constants (16) or in trajectory calculations because of the relatively simple form of the LEPS function. Several variations have been used to obtain surfaces in better agreement with experiment (see reference (7), Chapter 2). In those treatments which remain close to the basic LEPS method, the main possibilities are (a) to use improved anti-Morse functions, or (b) to adopt an alternative approach to K. A simple extension in the latter case uses three different constants K_1 , K_2 , and K_3 chosen separately for each of the three diatomic molecules involved. This provides a

convenient way to modify the shape of the surface for use in trajectory calculations (17, 18).

The programs described in this paper may be easily modified in a variety of ways, although we feel that it would be inappropriate, in this study, to introduce extra adjustable parameters into the LEPS equation. We have examined several variations in the basic LEPS method, some of which will be reported elsewhere.

Conclusions

We believe that the LEPS program described in this paper provides a valuable means of introducing students to potential energy surfaces and to the foundations of transition state theory. Among the advantages of using the full procedure to calculate A-factors lies in the range of physical chemistry involved. This includes molecular quantum mechanics, molecular vibrations, and statistical thermodynamics. All these areas may provoke discussions with more advanced students as may also such topics as kinetic isotope effects, tunnelling, and energy release in exothermic reactions.

Listings of the programs with copies of student scripts are available from SJM for a postage and handling charge of \$10. The set of programs described is available on a DOS 3.3 disc at an additional cost of \$30.

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