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# Some Concepts in Reaction Dynamics[†]

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In 1929 London[1] published a very approximate solution of the Schroedinger equation for a system of chemical interest: $H_3$. To the extent that chemistry can be regarded as existing separately from physics, this was a landmark in the history of chemistry, comparable in importance to the landmark in the history of physics marked by the appearance of the Heitler–London[2] equation for $H_2$. The expression for $H_3$, was, of necessity, even less accurate than that for $H_2$, but chemists, like the habitual poor, were accustomed to this sort of misfortune. Together with the physicists they enjoyed the sensation of living in a renaissance. The physicists still could not calculate a great deal that was of interest to them, and the chemists could calculate less, but both could now dream.

It would be too easy to say that their dreams were dreams of unlimited computer time. Their dreams were a lot more productive than that. Two years after London published his equation, H. Eyring and M. Polanyi[3] obtained the first numerical energy surface for $H_3$. They infused the London equation with a measure of empiricism to produce an energy surface which, whether or not it was correct in its details, provided a basis for further speculations of an important sort.[4]

The existence of a tangible energy surface in 1931 stimulated speculation along two different lines. The following year Pelzer and Wigner[5] used this London–Eyring–Polanyi (LEP) energy surface for a thermodynamic treatment of the reaction rate in $H + H_2$. This important development reached its full flowering a few years later.[6]

In these remarks I shall be concerned with another line of development. A second more-or-less distinct category of speculation that began with (and, indeed, in) the 1931 paper[3] has to do with the dynamics of individual reactive encounters under the influence of specified interaction potentials.

Questions concerning the effect of specific features of the potential-energy surface on the reaction dynamics across the surface were being raised—as already indicated—early in the history of this field. For thermoneutral reactions there was discussion (by Eyring, Hirschfelder, and coworkers[7]) of the effect on reaction probability of a shallow potential hollow in the region of close approach. For exothermic reactions there was, a few years later, discussion of the effect of shifting the downhill part of the surface from the entry valley (where it is located on the type of surface that we now refer to as "attractive") to the exit valley (on "repulsive" surfaces). M. G. Evans and M. Polanyi[8] were the first to make this distinction and to argue that, in the former case (the "attractive" surface), the product should be highly vibrationally excited; they therefore identified the attractive surface with the alkali-metal plus halogen reactions. This identification, based on purely qualitative reasoning, has, with modifications and adumbrations, stood the test of time quite well.

## Exothermic Reaction

The notion that in a reaction $A + BC \rightarrow AB + C$ energy released as A approaches BC becomes motion in AB (product vibration), whereas energy released as AB separates from C becomes motion along the BC coordinate (product translation), is an appealing one. It is illustrated schematically in Figures 1a and 1b.

*Professor Polanyi obtained his higher education at Manchester University, in England. His interest in energy transfer and chemiluminescence received impetus during his postdoctoral work at the National Research Council Laboratories in Ottawa and in further work at Princeton. In 1955 he joined the staff at the University of Toronto. Working with a graduate student, J. K. Cashion, Polanyi observed the ir emission from the reaction $H + Cl_2 \rightarrow HCl^{+} + Cl$, and at that time (1958) wrote about the potential of the method in elucidating details of reaction dynamics, an abiding interest. Professor Polanyi has also worked actively for the past 12 years on problems of arms control.*

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[†] A shorter version of this paper is to be found in the "Proceedings of the Conference on Potential Energy Surfaces in Chemistry," IBM Publication RA 18, IBM Research Laboratory, San Jose, Cal., 1971. The present paper is intended to provide background material for a film of the same title. The film (in 30-minute or 40-minute versions) can be obtained on loan from the writer.

(1) F. London, "Probleme der modernen Physik (Sommerfeld Festschrift)," S. Hirzel, Leipzig, 1928, p 104; *Z. Elektrochem.*, **35**, 552 (1929).

(2) W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

(3) H. Eyring and M. Polanyi, *Z. Phys. Chem., Abt. B*, **12**, 279 (1931).

(4) For recent *ab initio* calculations of the potential-energy surface for $H_3$ see C. Edmiston and M. Krauss, *J. Chem. Phys.*, **42**, 1119 (1965); **49**, 192 (1968); H. Conroy and B. L. Bruner, *ibid.*, **47**, 921 (1967); I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, *ibid.*, **48**, 2700 (1968). These computations are only just now approaching the level of accuracy required for the calculation of quantities (such as reaction rate and detailed dynamics) of interest to chemists.

(5) H. Pelzer and E. Wigner, *Z. Phys. Chem., Abt. B*, **15**, 445 (1932).

(6) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); *J. Amer. Chem. Soc.*, **57**, 985 (1935); W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 492 (1935); M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

(7) J. O. Hirschfelder, H. Eyring, and B. Topley, *J. Chem. Phys.*, **4**, 170 (1936); also J. O. Hirschfelder, Ph.D. Thesis, Princeton University, 1935.

(8) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **35**, 178 (1939).

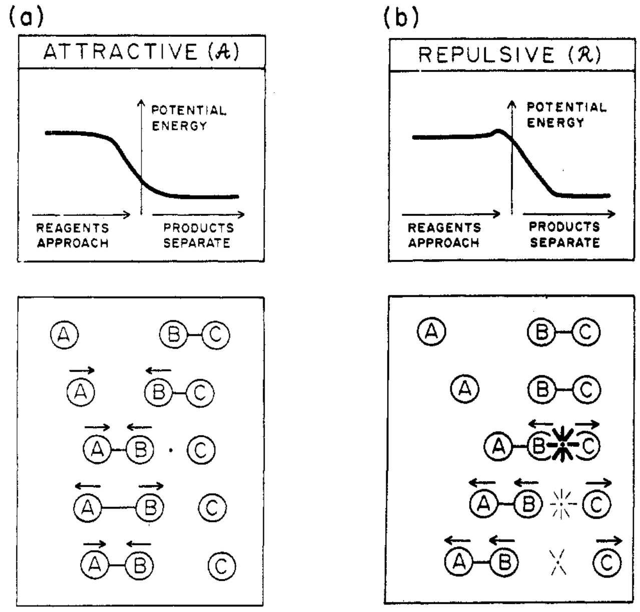

Figure 1. (a) The potential-energy change along the reaction path (termed the "potential-energy profile") for an exothermic reaction with predominantly attractive energy release. Beneath the energy profile there is shown a simple animation of the motion of three atoms involved in a collinear reactive encounter, $A + BC \rightarrow AB + C$, on the largely attractive energy surface. The modest repulsion between B and C is indicated by a dot. (b) The potential-energy profile for predominantly repulsive energy release. The strong repulsion between B and C evidences itself only after A and B have reached (approximately) normal bonding distance; this gives the most marked contrast between the attractive surface ($\mathcal{A}$) and the repulsive surface ($\mathcal{R}$). The extreme behavior shown here for the repulsive surface is only observed if atom A is light; see Figure 2b.

The validity of this simple but powerful concept is seen, on closer examination, to rest on the assumptions (a) that the reaction prefers to take place through more-or-less collinear configurations A–B–C, (b) that motion along the AB coordinate occurs separately from motion along the BC coordinate (not the case in "mixed energy release"; see below), and (c) that the reaction takes place in a single "direct" encounter, in which the reagents approach only once and the products separate once. The first of these assumptions is likely to be a good approximation in many cases. Its failure will have the consequence that repulsive energy release leads to rotational as well as translational excitation (see the bent configuration in Figure 2). The existence and significance of the further assumptions b and c have become evident through more recent work (see below). If these further requirements are not fulfilled, as they frequently are not, then the effect is to rob the system of its "adiabaticity," *i.e.*, energy released along the coordinate $r_{AB}$ (separating A from B) need no longer remain in the product as motion in AB, and the same applies, *mutatis mutandis*, for energy released along $r_{BC}$. All this became evident when computers made it possible to replace qualitative speculation by quantitative calculation.

The first application of high-speed computers to the solution of the classical equations of motion for reactive encounters was made by Wall, Hiller, and Mazur in 1958.[9] In 1961[10] they went on to demonstrate the use of the Monte Carlo method for selecting initial-state parameters in trajectory studies. Shortly afterward several laboratories became active in this field. Work of Blais and Bunker,[11] as well as that of Karplus and coworkers,[12] was prompted by the first results which were just being obtained in crossed molecular-beam studies of the exothermic reaction between potassium and alkali halides. Parallel work at the University of Toronto followed more closely along the lines suggested by M. G. Evans and M. Polanyi; an attempt was made to investigate a "spectrum" of exothermic energy surfaces ranging from the most repulsive to the most attractive.[13]

In broad agreement with the conjecture of Evans and Polanyi, our computations indicated that attractive energy surfaces tended to channel the reaction energy into vibration, whereas repulsive energy surfaces channeled the energy into product translation. The energy surfaces used in our work were an extension of the London–Eyring–Polanyi–Sato (LEPS) potential-energy surface.[13c,e] Blais and Bunker came to the same conclusion using a very different type of energy surface.[11]

It was mentioned above that the simple categorization into attractive and repulsive interaction, resulting in product vibration and translation respectively, was found to be inadequate under certain circumstances. The studies made in this laboratory indicated that repulsive energy surfaces resulted in the efficient conversion of energy release into product vibration in the common case that the attacking atom had a mass $m_A \gtrsim m_C$. The dynamics in this case corresponded to

[9] F. T. Wall, L. A. Hiller, Jr. and J. Mazur, *J. Chem. Phys.*, **29**, 255 (1958).

[10] F. T. Wall, L. A. Hiller, Jr., and J. Mazur, *ibid.*, **35**, 1284 (1961).

[11] (a) N. C. Blais and D. L. Bunker, *ibid.*, **37**, 2713 (1962); **39**, 315 (1963); (b) D. L. Bunker and N. C. Blais, *ibid.*, **41**, 2377 (1964).

[12] M. Karplus and L. M. Raff, *ibid.*, **41**, 1267 (1964).

[13] (a) J. C. Polanyi, "Transfert d'Energie Dans Les Gaz," R. Stoops, Ed., Interscience, New York, N. Y., 1962, pp 177, 526; (b) J. C. Polanyi and S. D. Rosner, *J. Chem. Phys.*, **38**, 1028 (1963); (c) J. C. Polanyi, *J. Quant. Spectrosc. Radiat. Transfer*, **3**, 471 (1963); (d) J. C. Polanyi, *Appl. Opt., Suppl.*, **2**, 109 (1965); (e) P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, *J. Chem. Phys.*, **44**, 1168 (1966). In the simplest case the attractive energy release, $\mathcal{A}_\perp$, is the energy released as atom A approaches BC (with BC "clamped" at its normal equilibrium separation $r_{BC}^0$) collinearly up to the normal AB bonding distance, $r_{AB}^0$. (The repulsive energy release, $\mathcal{R}_\perp$, is the balance of the energy release.) Where there is an energy barrier the attractive energy release is reckoned from the crest of the barrier, since the total energy available to the products includes the energy released in the trip down the far side of the barrier. If, as most commonly happens, atom A approaching a "clamped" BC encounters repulsion before reaching the equilibrium separation $r_{AB}^0$, then $\mathcal{A}_\perp$ is taken to be the energy released up to that point (the point at which the onset of "core repulsion" puts an end to purely attractive energy release). This division of the energy release into $\mathcal{A}_\perp$ and $\mathcal{R}_\perp$ provides a crude index of the nature of the energy surface. Since the extent of mixed energy release, $\mathcal{M}$, depends not only on the nature of the surface but also on the masses reacting across that surface, where we wish to bring $\mathcal{M}$ into the picture we use a method of categorization based on a single collinear reactive trajectory. The trajectory is divided (see e) into an incoming, a corner-turning, and an outgoing portion, designated $\mathcal{A}_T$, $\mathcal{M}_T$, and $\mathcal{R}_T$ (note the suffix T for trajectory, not $\perp$). This is a more revealing method of categorization. It should be borne in mind that $\mathcal{A}_T$, $\mathcal{M}_T$, and $\mathcal{R}_T$ depend *both* on the nature of the energy surface *and* on the mass combination reacting across that surface.

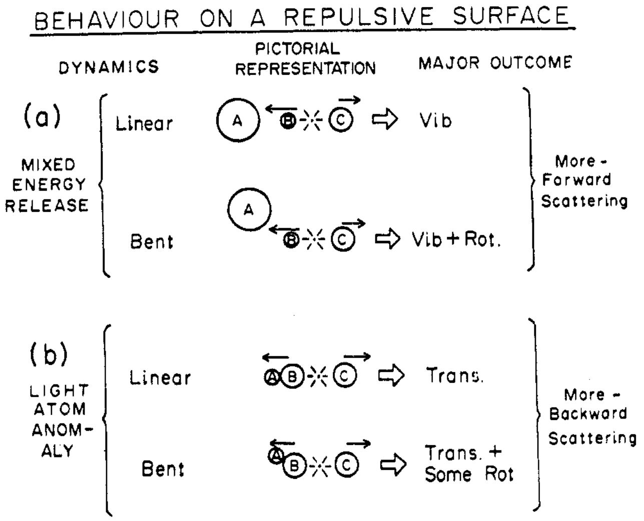

Figure 2. Two types of reaction dynamics on a repulsive energy surface. Type a, mixed energy release, is observed in the common case that the attacking atom is heavy. Type b, the light-atom anomaly, is observed if the attacking atom is very light.

what was termed "mixed energy release"[13d,e] on a repulsive surface. This type of behavior is shown pictorially in Figure 2a. The repulsive energy between B and C is released while A is still approaching B; consequently B (and not AB as a whole) recoils from C.

In the linear case this motion of B becomes, to a significant extent, vibration in AB. In the bent case the motion of B becomes vibration and rotation in AB. This behavior is in marked contrast to that observed on the same (repulsive) energy surface in the special case that $m_A \ll m_C$.[14] In this case (also shown in Figure 1b) atom A moves with a sufficiently high relative velocity that it has reached the normal bonding separation from B before the bulk of the B–C repulsion is released. Consequently AB recoils as a whole away from C, *i.e.*, AB and C separate with substantial relative translational energy. If the repulsion is released in a bent configuration, AB picks up some rotation, but not as much as in the case of mixed energy release, since the torque on AB is less than that on the extended A—B (see Figure 2).

These generalizations cannot, of course, be arrived at with any degree of confidence on the basis of pictures of the type shown in Figures 1 and 2. Such pictures are useful *post hoc,* in order to rationalize results obtained from the solution of the equations of motion for statistical groups of trajectories. An even more revealing method of illustration involves the display of three-dimensional trajectories that have been selected from a statistically meaningful sample in order to typify important types of behavior.

A movie provides a good medium for displaying three-dimensional trajectories. In the film that illustrates many of the points made in this paper, the atoms are represented by colored (soft) spheres that penetrate a certain distance into one another in the course of energetic collisions and that increase or diminish in size according to whether they are approaching or retreating from the observer. The collisions are pictured as they would appear to an observer fixed relative to the center-of-mass of the system of particles. This is advantageous since we are only interested in the relative motion of the atoms with respect to one another, and not in their joint motion with respect to some reaction vessel. The reactive event, in the center-of-mass frame of reference, can be viewed from various perspectives. The perspective chosen by the filmmakers, P. E. Charters and C. A. Parr, was usually such as to bring the reaction approximately into coincidence with the plane of the screen; an angle can be chosen that puts the particles initially and finally in the plane of the screen. This perspective was used since it made it easiest for the viewer to see internal motion in newly formed bonds, and also to gauge visually the scattering angle. (These pedagogic advantages, sad to say, had to be purchased at the price of visual impact, since the viewer is no longer in danger of being hit in the eye by a scattered atom.)

The scattering angle referred to in the previous paragraph is a further index of the reaction dynamics. The scattering is termed "forward" if the molecular product is ejected along the continuation of the direction of approach of the attacking atom, in a reaction $A + BC \rightarrow AB + C$. It turns out that the "attractive" and "repulsive" criteria correlate quite strongly with scattering angle; attractive interaction favors forward scattering, repulsive interaction favors backward scattering. (Reference 15 gives the angular scattering for surfaces ranging from attractive to repulsive.) As with product energy distribution, the angular distribution on a repulsive surface is affected by the mass combination; the light-atom case (Figure 2b) gives rise to more backward scattering than does mixed energy release.

The complications outlined in the preceding paragraphs relate to behavior in reactive systems governed by repulsive potential-energy surfaces. There is another type of complication that is most commonly (though not exclusively) met in cases where the interaction is attractive.

The special feature on the attractive surface is a tendency for "indirect" (also called "complex") encounters to take place. A trajectory may be said to be indirect (or complex) if the separation between the products once it has started to increase subsequently decreases.[16] This frequently has the consequence that the force between the products, having begun to diminish in absolute magnitude, exhibits a secondary peak—this is termed a "secondary encounter."[15] Secondary encounters can be either "clouting" (if the secondary peak in the force is positive in magnitude) or "clutching" (if the secondary peak in the force is negative). The effect of secondary encounters is to reduce vibrational excitation on *highly* attractive surfaces.[13e] Secondary encounters are rare on repulsive surfaces since the products tend to be thrown apart before secondary interaction can take place. The exceptions are the reactions with a high degree of mixed energy release, since they tend to channel the repulsion quite efficiently into internal excitation of the products—

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(14) The most markedly mixed energy release is observed for the mass combination $m_A \gg m_C$ with $m_B$ large; the most marked light-atom anomaly is observed for $m_A \ll m_C$ with $m_B$ large. See B. A. Hodgson and J. C. Polanyi, *J. Chem. Phys.*, **55**, 4745 (1971).

(15) P. J. Kuntz, M. H. Mok, and J. C. Polanyi, *ibid.*, **50**, 4623 (1969).

(16) J. C. Polanyi, *Discuss. Faraday Soc.*, **44**, 293 (1967).

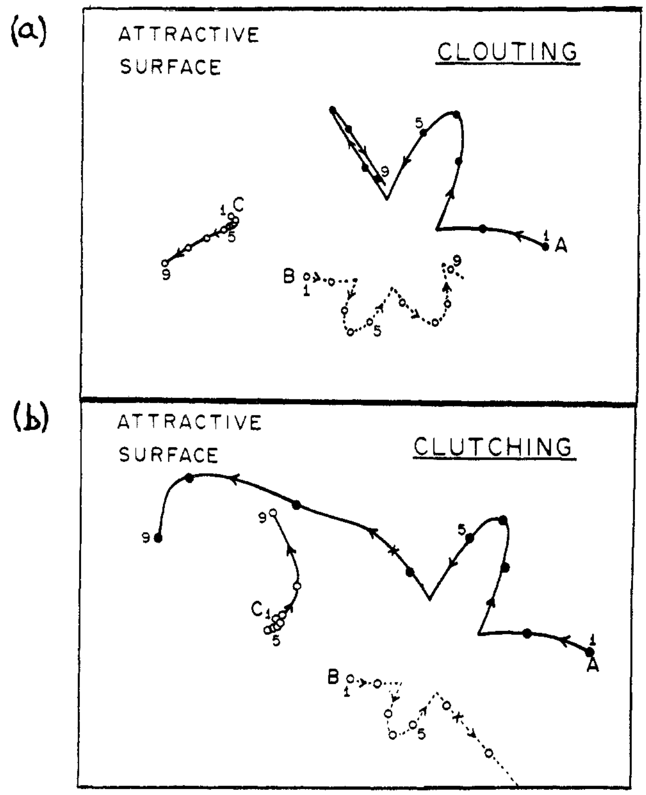

Figure 3. Successive positions of three atoms engaged in a coplanar reactive encounter, A + BC → AB + C, as seen by an observer fixed relative to the center of mass. In both types, a and b, A is attracted to B, and strong vibration plus rotation is evident in AB. Atom C moves away slowly (since there is little product translation), and a secondary encounter occurs. In type a atom A *clouts* C, and the direction of rotation of AB is reversed. C is scattered forward, and the molecular product AB is scattered backward. In type b the interaction is such as to allow A to react with either B or C. In this case, A, instead of clouting C, *clutches* it. The molecular product AC is scattered sharply forwards.[15]

hence the products separate slowly (Cl + HI → HCl + I is an example[13d,17]).

Because of secondary encounters the effect of making an energy surface highly attractive is not, as one might have guessed it would be, to produce sharply forward scattering. (Sharply forward scattering is observed, for example, in the alkali metal plus halogen reactions, $M + X_2$.[18,19]) Clouting secondary encounters (Figure 3a) tend to scatter the products broadly. In order to get very sharp forward scattering it appears necessary to have *attractive* secondary encounters (Figure 3b), so that A swings around BC, instead of bouncing backwards off BC.[15,20] Reference 21 uses simple product attraction, comparable to surface −II below, to achieve sharp forward scattering; ref 15 and 22, 23, employ a more specialized form of product attraction arising from the possibility of charge "migration" in

$$M + X_2 \xrightarrow{1} M^+ + X^-X \xrightarrow{2} XX^- + M^+ \xrightarrow{3} X + X^-M^+$$

where 2 is migration.

For even a qualitative insight into the dynamics of exothermic reactions it is clearly necessary to consider more than simply the extent of attractive and repulsive energy release. Nonetheless a knowledge of the percentage attractive and repulsive energy release ($\% \mathcal{A}_\perp = 100 - \% \mathcal{R}_\perp$; see ref 13e) provides a valuable starting point for understanding of the reaction dynamics. Except in rare cases for which the forces are especially simple (the electron-jump reaction $M + X_2$ may be a case in point) it is not yet possible to calculate $\% \mathcal{A}_\perp$ directly from a knowledge of the nature of the reagents. Progress is being made with *ab initio* computations (see ref 4, and the example of $H_3^+$ in the following section). It is also illuminating to explore trends in $\% \mathcal{A}_\perp$ in related families of reaction. This has been done theoretically using two different approximations (the LEPS and the BEBO approximations) and has revealed a strong correlation between decreasing barrier height and increasing $\% \mathcal{A}_\perp$. The intervening steps in the argument involve a recognition of the fact that, in both these different approximations, low barriers have their crests located early along the reaction coordinate.[24,25] (Though it was not recognized by the authors—due to a communication gap between organic and physical chemists—this study provides a theoretical rationale for Hammond's postulate.[26]) An early barrier, it then turns out, implies an early downhill slope on the energy surface, *i.e.*, increased $\% \mathcal{A}$.

In order not to overburden (some would say further overburden) the movie, the important matter of the correlation between barrier height and $\% \mathcal{A}_\perp$ was not mentioned. Instead the section on exothermic reactions attempted to illustrate the contrast between attractive and repulsive energy profiles, mixed energy release and the light-atom anomaly on repulsive surfaces, and the role of secondary encounters on attractive and (for mixed energy release) repulsive surfaces.

## Thermoneutral Reaction

The discussion of the previous paragraphs related to substantially exothermic reactions (say 30–50 kcal mole$^{-1}$). Typically such reactions have activation barriers, in the exothermic direction, of only a few kcal mole$^{-1}$. The barrier is, therefore, not a major feature on the surface (though its height may be a valuable index to $\% \mathcal{A}_\perp$). In order to isolate the effect of moderate energy barriers, or hollows, it is instructive to study the dynamics of (hypothetical) thermoneutral reactions; for these the major significant feature is an energy barrier (or energy hollow) in the region of close interaction. Several such studies have been made. For thermoneutral reactions A + BC → AB + C it has been found that if the crest of a 7 kcal mole$^{-1}$ bar-

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(17) K. G. Anlauf, J. C. Polanyi, W. H. Wong, and K. B. Woodall, *J. Chem. Phys.*, **49,** 5189 (1968).

(18) J. H. Birely and D. R. Herschbach, *ibid.*, **44,** 1690 (1966).

(19) T. T. Warnock, R. B. Bernstein, and A. E. Grosser, *ibid.*, **46,** 1685 (1967).

(20) K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, *Discuss. Faraday Soc.*, **44,** 183 (1967).

(21) N. Blais, *J. Chem. Phys.*, **49,** 9 (1968).

(22) M. Godfrey and M. Karplus, *ibid.*, **49,** 3602 (1968).

(23) J. C. Polanyi, *Trans. Roy. Soc. Canada*, **5,** 105 (1967); P. J. Kuntz, E. M. Nemeth, and J. C. Polanyi, *J. Chem. Phys.*, **50,** 4607 (1969).

(24) J. C. Polanyi, *ibid.*, **31,** 1338 (1959).

(25) M. H. Mok and J. C. Polanyi, *ibid.*, **51,** 1451 (1969).

(26) G. S. Hammond, *J. Amer. Chem. Soc.*, **77,** 334 (1955).

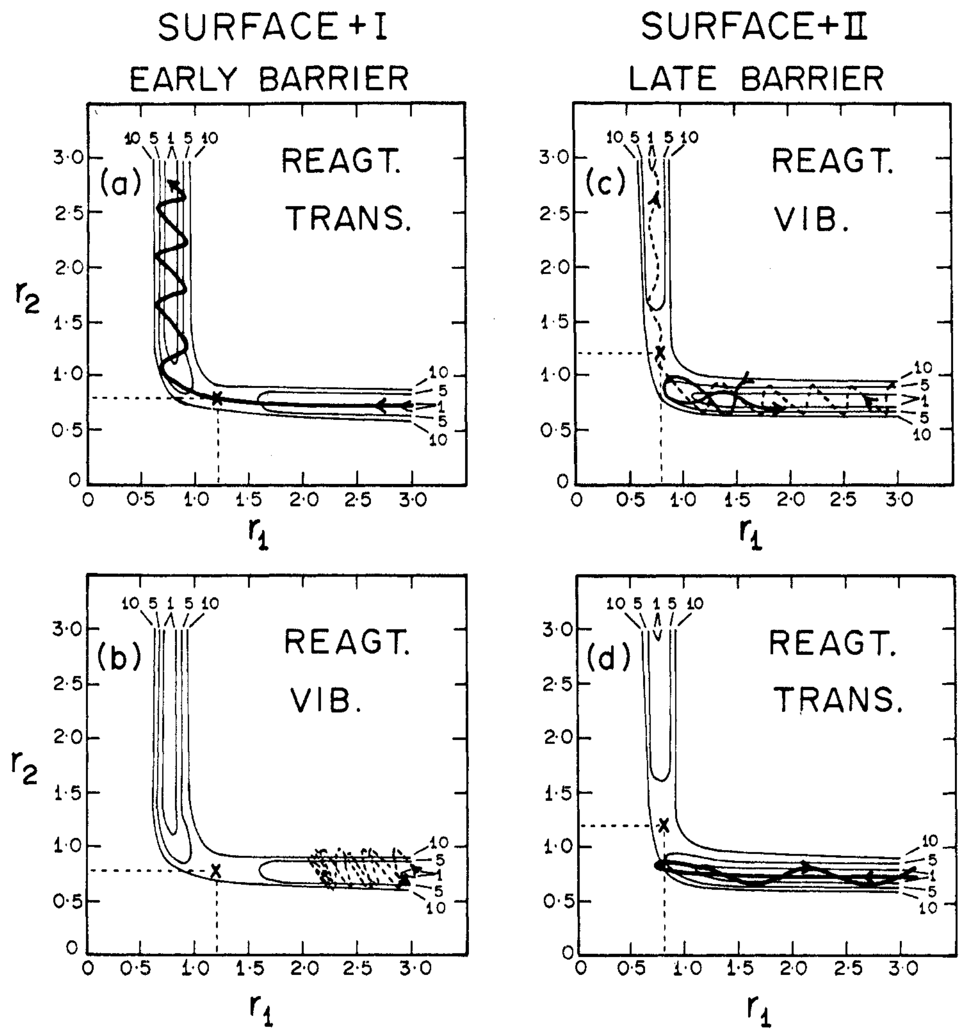

Figure 4. a and b refer to surface +I, c and d to surface +II. The barrier heights on both surfaces are 7 kcal $\text{mole}^{-1}$. On surface +I in a the reagent translational energy was $T = 9.0$ kcal $\text{mole}^{-1}$ and the reagent vibrational energy was zero; in b $T = 1.5$ kcal $\text{mole}^{-1}$ (to bring the reagents together) and the reagent vibration was $V = 14.5$ kcal $\text{mole}^{-1}$. On surface + II in c the reagent energy for the reactive trajectory was $T = 1.5$ and $V = 7.5$ kcal $\text{mole}^{-1}$ (the unreactive trajectory had the same energy but the opposite vibrational phase); in d $T = 16.0$, $V = 0.0$ kcal $\text{mole}^{-1}$.[27]

rier is displaced slightly (0.3 Å) into the entry valley of the potential-energy surface (surface +I), then translational energy in the reagents is vastly more effective than vibrational energy in promoting reaction.[27,28] If, however, the crest of the barrier is displaced by the same amount into the exit valley (surface +II), then vibration in the bond under attack is vastly more effective than is reagent translational energy in producing reaction. It should be stressed that in each case much of the barrier is located in *both* the entry and the exit valley; it is the crest that is slightly shifted.

The origin of this effect is clearly evident from the trajectories of Figure 4. The trajectories, which refer only to strictly collinear reaction (whereas the generalizations apply to reaction in 3D), are shown superimposed on the collinear potential-energy surfaces. The coordinates are $r_1 \equiv r_{AB}$, and $r_2 \equiv r_{BC}$. The contours are potential energies in kilocalories $\text{mole}^{-1}$ relative to the reagent energy (A + BC) which is taken as zero. Since the reaction is thermoneutral, the products AB + C are also at zero energy. In Figures 4a and 4b the surfaces are identical, both being of type +I. The trajectories, which were actually obtained by numerical solution of the equations of motion, could have been obtained by sliding a frictionless mass across the surface.[3,7] For the case that the reagent energy is present as translation, $r_1$ decreases rapidly, *i.e.*, the sliding mass moves with substantial momentum from right to left along the entry valley and is carried smoothly over the barrier whose crest is located in that valley. Reagent vibration, by contrast, gives rise to motion transverse to the entry valley; it is therefore ineffective in carrying the sliding mass over the barrier in that valley. This is illustrated in Figure 4b. The sliding mass is reflected by the barrier, even though the reagent energy is over double that required for barrier crossing. Figures 4c and 4d illustrate the very different behavior on a surface having the same barrier, but with its crest displaced into the exit valley. Reagent vibrational excitation, provided that it has the

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(27) J. C. Polanyi and W. H. Wong, *J. Chem. Phys.*, **51**, 1439 (1969).

(28) The effect of reagent rotation and of varying reagent mass combination has been investigated, and been shown to leave these qualitative generalizations intact.[14]

correct phase, starts by being transverse motion in the entry valley and ends by being motion along the exit valley; hence it carries the sliding mass over the barrier situated in that valley (see Figure 4c). Reagent translation on surface +II (Figure 4d) gives rise to motion across the exit valley, and consequently is ineffective in carrying the sliding mass over a barrier with its crest located in that valley.

Stated still more simply, a barrier along the approach coordinate is most efficiently surmounted by motion along the approach coordinate (reagent translation), whereas a barrier along the coordinate of separation is most efficiently surmounted by motion along that coordinate (reagent vibration). The concept, stated in this broad fashion, may be applicable to systems of many atoms as well as to the three-atom exchange reaction considered above.

A similar study has already been made of a hypothetical bimolecular exchange reaction, $AB + CD \rightarrow AC + BD$, on a thermoneutral energy surface.[29] The barrier height in this case was 35 kcal mole$^{-1}$. The magnitudes of the displacements of the barrier crest on surfaces +I and +II were again 0.3 Å into the entry valley and exit valley, respectively. Once again reagent translation was vastly more effective than reagent vibration in producing reaction on +I, and the converse was the case on +II. The result held true even if the masses of the reacting species were very different.

In recent years reactions have been studied in crossed molecular beams that give evidence of proceeding across potential-energy surfaces with hollows in them.[30] It appeared of interest, therefore, to extend the study of idealized thermoneutral reactions to include those with surfaces of types −I (hollow in the entry valley) and −II (hollow in the exit valley).[31] Neither surface had a barrier (combinations of barriers and hollows have also been studied[31]). Only the minimum of the hollow (7 kcal mole$^{-1}$ deep) shifted in going from −I to −II. Since there was no barrier to be crossed the surfaces were less selective than +I and +II; nonetheless at low collision energy selectivity was apparent. The favored degree of freedom for reaction on −I was reagent vibration, and on −II reagent translation: the *converse* of the behavior on +I and +II. The dynamics on −II were unusual; because of the tendency for the products to cling together, orbiting collisions occurred which had the consequence that low impact parameters could give rise to forward scattering whereas high impact parameters could give backward scattering—once again, the converse of commonly observed behavior.

In certain reactions $A + BC \rightarrow AB + C$, the intermediate ABC has substantial binding energy, *i.e.*, the potential-energy surface has a *deep* potential hollow at some intermediate configuration. An important example of this type of potential, from a theoretical standpoint, is the reaction $D^+ + H_2 \rightarrow DH + H^+$. This is, so far, the only reaction for which trajectory calculations have been performed on a potential-energy surface obtained by *ab initio* calculation, *i.e.*, by the variational solution of the Schroedinger equation.[32] A trajectory obtained in this way gives evidence of numerous secondary encounters, since the particles have difficulty escaping from the deep potential well. The interaction persists over a time which exceeds a rotational period. It is useful in such a case to speak of indirect reaction. The angular distribution of the products (but not their energy distribution) was found to be almost random;[32] the products have "forgotten" the direction from which the $D^+$ approached.[30,33]

## Endothermic Reaction

The effect of barrier location is so marked that it is important to consider its implications for endothermic reactions, $AB + C \rightarrow A + BC$. These are, of course, the converse of the exothermic reactions considered above. Examination of the exothermic reactions shows that, whether they are attractive or repulsive, the crest of the barrier is located in the entry valley of the exothermic surface, and hence is in the exit valley of the endothermic reaction.[24,25] Consequently the particles attempting to surmount the barrier in the endothermic direction see a surface of type +II. This is illustrated in Figure 5. For successful reaction the endothermicity (say 30–55 kcal mole$^{-1}$) must be present largely as vibration in the bond under attack.[24,25,34] Experimental results bear this out.[35–37] The most detailed experimental data at the present time come from application of microscopic reversibility to the "detailed rate constants" for exothermic reactions, obtained by the infrared chemiluminescence method.[36,38] An example is given in Figure 6.[37]

The data of Figure 6 were obtained by recording the infrared chemiluminescence from the reaction $F + H_2 \rightarrow HF + H$ under conditions of "arrested relaxation."

Behavior on surfaces −I and −II (shallow potential hollows) is illustrated in the longer, 40-min, version of the movie. Only the effect of a deep potential hollow on an *ab initio* surface (see below) is shown in the shorter 30-min version.

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[29] M. H. Mok and J. C. Polanyi, *J. Chem. Phys.*, **53**, 4588 (1970).

[30] The best-established examples are the alkali atom + alkali halide reactions: W. B. Miller, S. A. Safron, and D. R. Herschbach, *Discuss. Faraday Soc.*, **44**, 108 (1967); D. O. Ham, J. L. Kinsey, and F. S. Klein, *ibid.*, **44**, 174 (1967). The potential-energy surface has been examined by A. C. Roach and M. S. Child, *Mol. Phys.*, **14**, 1 (1968).

[31] Y. Nomura and J. C. Polanyi, *J. Chem. Phys.*, in preparation.

[32] I. G. Csizmadia, J. C. Polanyi, A. C. Roach, and W. H. Wong, *Can. J. Chem.*, **47**, 4097 (1969). The energy surface is reported in I. G. Csizmadia, R. E. Kari, J. C. Polanyi, A. C. Roach, and M. A. Robb, *J. Chem. Phys.*, **52**, 6205 (1970). Earlier *ab initio* calculations of portions of the $H_3^+$ energy surface were performed by R. E. Christoffersen, *ibid.*, **41**, 960 (1964); W. Kutzelnigg, R. Ahlrichs, I. Labib-Iskander, and W. A. Bingel, *Chem. Phys. Lett.*, **1**, 447 (1967); M. E. Schwartz and L. J. Schaad, *J. Chem. Phys.*, **47**, 5325 (1967).

[33] A more realistic study of the reaction $D^+ + H_2$ should include the possibility of "hopping" from the surface leading to $DH + H^+$, to the surface leading to $DH^+ + H$. This novel type of trajectory calculation has been performed by J. C. Tully and R. K. Preston, *ibid.*, **55**, 562 (1971), using diatomics-in-molecules energy surfaces.

[34] J. B. Anderson, *J. Chem. Phys.*, **52**, 3849 (1970); R. L. Jaffe and J. B. Anderson, *ibid.*, **54**, 2224 (1971).

[35] J. H. Parker and G. C. Pimentel, *ibid.*, **51**, 91 (1969).

[36] K. G. Anlauf, D. H. Maylotte, J. C. Polanyi, and R. B. Bernstein, *ibid.*, **51**, 5716 (1969).

[37] J. C. Polanyi and D. C. Tardy, *ibid.*, **51**, 5717 (1969).

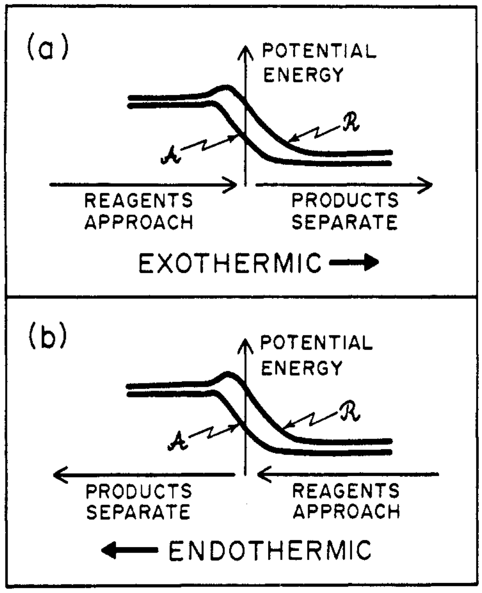

Figure 5. Potential-energy profiles along the reaction coordinate: (a) for predominantly attractive and predominantly repulsive energy surfaces with reaction proceeding in the exothermic direction, and (b) for the same pair of surfaces with reaction proceeding in the endothermic direction (both endothermic barriers are seen to have their crests along the coordinate of separation). The approach coordinate can be regarded as meeting the coordinate of separation when the extension of the new bond relative to its equilibrium bond length is equal to the extension of the old bond relative to its equilibrium bond length (see ref 25).

This yielded the detailed rate constant into the accessible states of product vibration, rotation, and translation, symbolized $k_{\text{exo}}(V',R',T')$. Application of microscopic reversibility to a rate constant at this level of detail yields $k_{\text{endo}}(V',R',T')$, where $V'$, $R'$, $T'$ are now the vibrational, rotational, and translational energies of the *reagents* for the endothermic reaction HF $(v',J')$ + H → F + $H_2$ ($v'$ and $J'$ are the quantum numbers corresponding to the energies $V'$ and $R'$). The contours in Figure 6 are lines of equal detailed rate constant, $k_{\text{endo}}(V',R',T')$, plotted against $V'$, $R'$, and $T'$. The values of $V'$ and $R'$ are given along the ordinate and abscissa, respectively. ($V'$ is given relative to the energy of vibrational level $v' = 0$.) Since the total energy available for distribution is fixed by the nature of the experiment (equal to the energy made available by the exothermic reaction, 34.7 kcal mole$^{-1}$ in the present case), a grid of diagonal lines gives the translational energies, $T'$, increasing from right to left. Any point in the figure has a $V'$, $R'$, and $T'$ specified by the coordinate grid, and a rate constant $k_{\text{endo}}(V', R',T')$ given (on a relative scale) by the height of the contour which passes through that point.

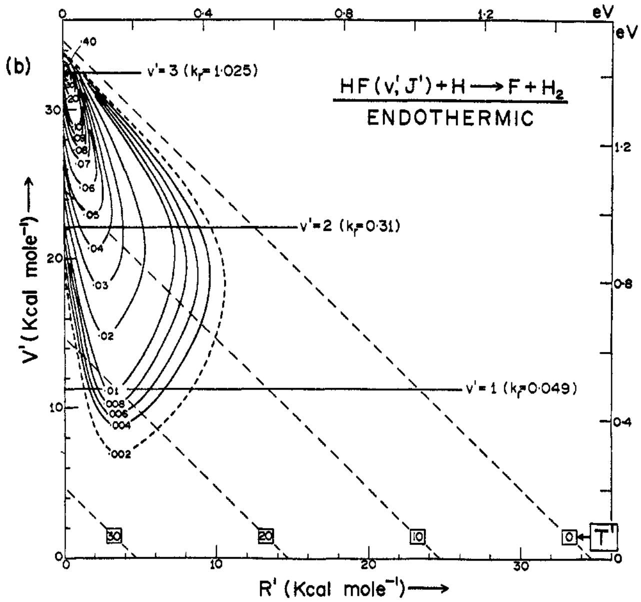

Figure 6. The contours record the detailed rate constants, $k_{\text{endo}}(V',R',T')$, for the endothermic reaction specified, on a relative scale. Detailed rate constants summed over $R'$ are recorded for each vibrational level, $v'$, of the reagents.[37]

Inspection of the figure shows that the detailed rate constants for endothermic reaction are low for low vibrational levels of the molecule under attack. Vibrational level $v' = 0$ lies at zero energy on the $V'$ scale. From the contours it is apparent that the highest rate constant for $v' = 0$ comes at a reagent translational energy of $T' \approx 30$ kcal mole$^{-1}$ and a reagent rotational energy of $R' \approx 5$ kcal mole$^{-1}$. The magnitude of $k_{\text{endo}}(V' = 0, R' = 5, T' = 30)$ is, judging by the downward slope of the $k_{\text{endo}}$ "hill" from $v' = 3$ to 1, $\ll 0.001$. If we take 28 kcal of this translational energy, and also the major part of the rotational energy, and put it into vibration, we obtain the detailed rate constant in $v' = 3$ which has a value $k_{\text{endo}} = 0.40$. By redistributing the reagent energy for endothermic reaction so as to favor reagent vibration, we have increased $k_{\text{endo}}$ by $\gtrsim 10^3$.[39]

As would be anticipated there is a (partial) exception to the rule that vibration favors endothermic reaction; we term this exceptional case "the reverse light-atom anomaly." It consists in the fact that when a light atom is ejected in the course of the endothermic formation of a heavy molecule, then too much vibration in the reagents markedly reduces the probability of endothermic reaction.[36]

Both the rule and this exception are illustrated in the movie.

## Reaction at High Collision Energy

At high reagent collision energies the angle of scattering of the molecular product shifts toward the forward direction. If the surface has a deep potential well (such as the −108 kcal mole$^{-1}$ potential well for the reaction $D^+ + H_2 \rightarrow DH + H^+$ [32]) then, as already noted, at low collision energies long-lived complexes tend to be formed. At high collision energies the lifetime of these complexes will drop sharply (as was ob-

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(38) K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, *Discuss. Faraday Soc.*, **44**, 183 (1967); K. G. Anlauf, P. E. Charters, D. S. Horne, R. G. Macdonald, D. H. Maylotte, J. C. Polanyi, W. J. Skrlac, D. C. Tardy, and K. B. Woodall, *J. Chem. Phys.*, **53**, 4091 (1970).

(39) A recent molecular-beam study provides striking evidence of the effect of reagent vibrational excitation in promoting the (slightly endothermic) reaction K + HCl → KCl + H: T. J. Odiorne, P. R. Brooks, and J. V. V. Kasper, *ibid.*, **55**, 1980 (1971).

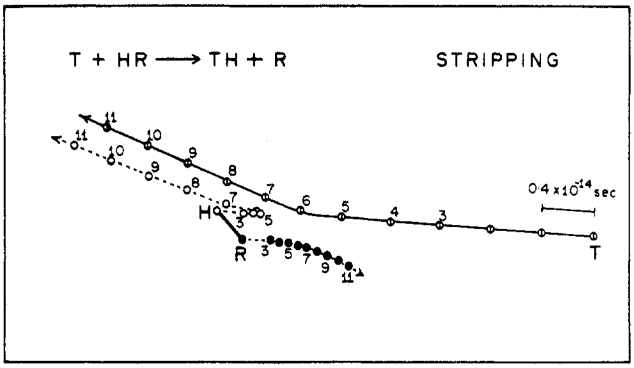

Figure 7. Record of a high-energy collision between three particles of masses $m_T = 3$, $m_H = 1$, and $m_R = 15$ amu (collision energy, $T$, = 12 eV). Though the tritium atom T may be said to "strip" H off R, giving rise to sharply forward scattering, this is not "spectator stripping"; considerable energy was transferred to R to produce the deflection in its trajectory that is evident in the figure. See ref 39.

served in the trajectory calculation across the *ab initio* $D^+ + H_2$ surface[32]), and reaction can become direct. At the same time the product angular distribution changes from isotropic to more-forward scattered.

The shift toward more-forward scattering arises from a change in the dynamics to something approaching "stripping" dynamics.[40] In "stripping" atom A only has time to interact with B; particle C is a "spectator." A reactive collision of this type is shown in Figure 7. Under these circumstances (or, more usually, conditions approaching them) the momentum of A carries B forward to produce the forward scattering characteristic of high collision energy. It is possible to define a "stripping threshold energy" and to use it as a measure of the force between atoms B and C when A is at close range, *i.e.*, as a measure of the slope along the exit valley of the potential-energy surface.[15,16]

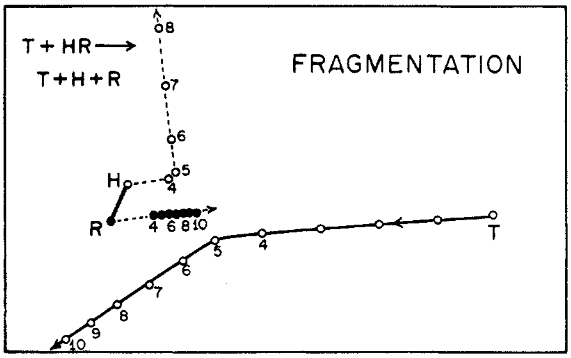

Figure 8. A high-energy ($T$ = 6 eV) collision between the same three particles as in Figure 7, with the same interaction potential but different initial orientation; this time the outcome is fragmentation (dissociation) into three atoms, scattered in widely different directions.[41]

At these high collision energies a further new reaction path opens up: $A + BC \rightarrow A + B + C$.[41] The dynamics of this process (termed fragmentation, or dissociation) have been studied on surfaces with barriers[42,43] and surfaces with deep potential wells[32]—in the latter case the onset of fragmentation is very sharp. A fragmentation collision is illustrated in Figure 8.

*The computer-animated film which illustrates the majority of the phenomena outlined above (including the reactions at high collision energy) was made possible by the ingenuity and enthusiasm of a number of people: Christopher Parr who nursed it from beginning to end, Peter Charters who made a major contribution to the programming, and a number of others who provided their trajectories and generous assistance: P. J. Kuntz, M. H. Mok, E. M. Nemeth, A. C. Roach, J. L. Schreiber, D. C. Tardy, Y. Nomura, and W. H. Wong.*

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(40) A. Henglein and G. A. Muccini, Z. *Naturforsch. A*, **17,** 452 (1962); *A*, **18,** 753 (1963), A. Henglein, K. Lacmann, and B. Knoll, *J. Chem. Phys.*, **43,** 1048 (1965).

(41) R. Wolfgang, *Progr. Reaction Kinetics*, **3,** 97 (1965).

(42) P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, and W. H. Wong, *ibid.*, **52,** 4654 (1970).

(43) M. Karplus, R. Porter, and R. Sharma, *J. Chem. Phys.*, **45,** 3871 (1966).