

## The Transfer of Energy in Molecular Systems

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## COMPARISON OF THE ENTROPY VALUES FROM CALORIMETRIC AND SPECTROSCOPIC DATA

The entropy of carbon dioxide gas was calculated from the available band spectrum data on this substance. Adel and Dennison<sup>17</sup> have given a classified summary of the observations. They have also derived equations for calculating the possible vibrational levels of the molecule. The moment of inertia in the normal state was taken to be  $70.1 \times 10^{-40}$  g cm<sup>2</sup>.

The entropy calculation has been given in detail in Table XI. The symmetry number  $\sigma$  is 2. The vibrational entropy was calculated by means of the state sum,  $Q_{\text{vib.}} = \sum_p p_v e^{-\epsilon_v/kT}$ , where  $p_v$  and  $\epsilon_v$  are the *a priori* weight and energy of the

$v$ th state. The values of all natural constants used here are those given in the I.C.T.<sup>6</sup>

The entropy at 298.1°K has also been calculated by Badger and Woo<sup>18</sup> and by Gordon and Barnes.<sup>19</sup> These authors obtain the values 51.07 and 51.09 cal./deg. mole, respectively.

The calorimetric and spectroscopic values of the entropy have been compared in Table XII. The experimental value given at 298.1°K was obtained by using the spectroscopic data to calculate the entropy change of the gas between 194.67 and 298.1°K.

It is evident from Table XII that the entropy obtained from the third law of thermodynamics and the experimental data is in excellent agreement with that calculated from statistics and band spectrum data.

<sup>17</sup> Adel and Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).

<sup>18</sup> Badger and Woo, J. Am. Chem. Soc. **54**, 3523 (1932).

<sup>19</sup> Gordon and Barnes, J. Chem. Phys. **1**, 308 (1933).

The Transfer of Energy in Molecular Systems<sup>1</sup>

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A method of investigating problems of energy transfer, by means of potential energy surfaces, outlined in an earlier paper, has been extended to include a more general type of surface. The probability of energy transfer among atoms has been related with the rate of change of curvature of the equipotential lines. It has been shown that the relative reactivity of atoms depends on the degree of excitation of the system. An explanation has been suggested for the discrepancy existing between the data on the relative efficiencies of the inert gases as obtained from sound dispersion experiments and from reaction rate measurements.

## I

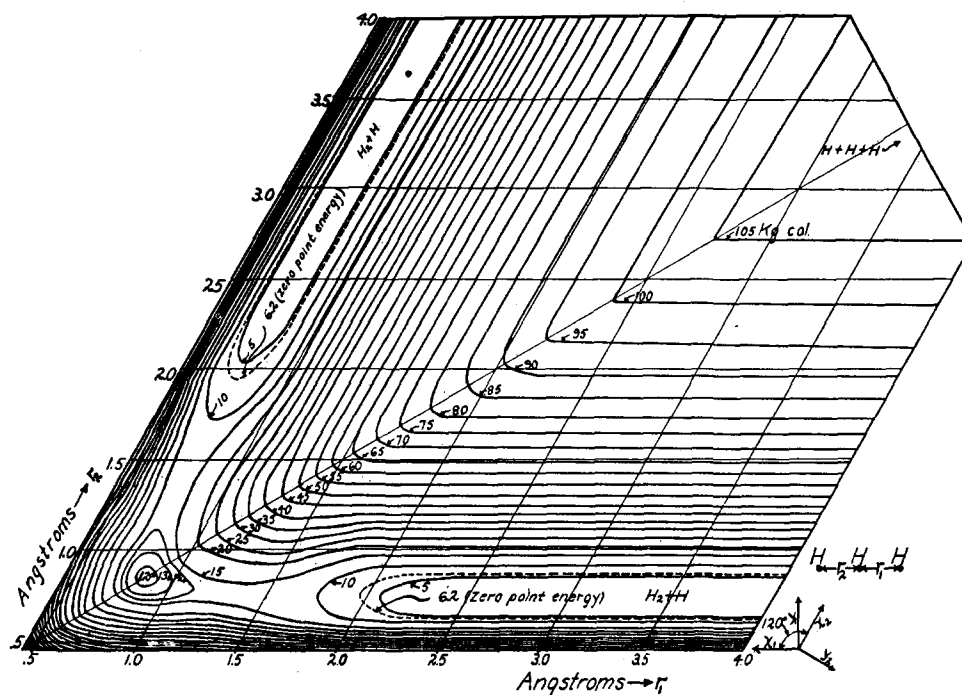
**I**N a recent communication, hereafter called (I),<sup>2</sup> a technique was developed that seems to be applicable to the study of the transfer of energy. A complete calculation of the rate of combination of hydrogen atoms to form molecules was carried out by means of a potential energy surface. Since the problem is essentially one of energy transfer, the rate determining factor being the probability that some of the relative translational energy of two atoms will be removed

by a third body before the atoms separate, it was possible to make some qualitative deductions concerning the more general problem of energy transfer. These were given only briefly in (I), since it was only indirectly concerned with this problem. This paper elaborates on them and gives some further extensions of the method.

It has long been obvious that classical mechanics alone can help us but little in the problem of calculating theoretically the mechanism and probability of the transfer of energy among the degrees of freedom of a system. The transfer of energy is essentially a quantum phenomenon, and the characteristics of molecules considered as hard spheres, or even as ensembles of classical oscillators, give little information about the

<sup>1</sup> Presented at the group symposium on Quantum Mechanics and Chemical Kinetics at the Pittsburgh meeting of the A. C. S.

<sup>2</sup> Eyring, Gershinowitz and Sun, J. Chem. Phys. **3**, 786 (1935).

FIG. 1. Energy contour map of linear  $H_3$  molecule.

behavior of actual molecules. It is possible, however, to use many of the laws of classical mechanics to good advantage in these problems, provided that we also take care of the quantized nature of the phenomena. A considerable amount of work has been done in the application of quantum mechanics to energy transfer, making use of the perturbation theory applied to the Schrödinger equation for the system.<sup>3</sup> This work has not been too successful, however. The difficulty is one that always arises when one attempts to apply rigorous quantum mechanics to chemical problems, i.e., the practical impossibility of solving the mathematical equations that one gets. Before any results are obtained it is necessary so to simplify the problem that it is doubtful that the conclusions apply to any actual experiments. But while the actual numerical results are of doubtful validity, the qualitative conclusions seem to be quite trustworthy, and have been of great value in the interpretation of experimental data. Because of the mathematical difficulties, it seems doubtful that many more valuable results can be obtained by these methods at the present time.

<sup>3</sup> (a) Zener, *Phys. Rev.* **37**, 556 (1931); (b) O. K. Rice, *J. Am. Chem. Soc.* **54**, 4558 (1932); (c) Rosen, *J. Chem. Phys.* **1**, 319 (1933).

In (I) it was shown that transfer of energy, and hence reaction, took place when the mass point that represented the system traveled across a ridge that separated the potential energy surface into two regions, in each of which a different set of coordinates was the normal set. The calculation of the probability of energy transfer then became a straightforward problem of statistical mechanics. This method of employing potential energy surfaces to represent the quantum character of the potential fields and then using classical mechanics to determine the motion of the nuclei in these fields affords a convenient semi-empirical approach to the problem of energy transfer.

In (I) it was shown that the greatest probability of reaction occurs when the three atoms involved lie on the same straight line; that the transverse vibrational degrees of freedom may be separated from the motions along the line to good approximation; and that the rotation of the system can be considered as adding another term to the expression for the potential energy of the system. In view of these results, in the following we shall concern ourselves only with the two degrees of freedom representing the relative motions of the three atoms along a straight line.

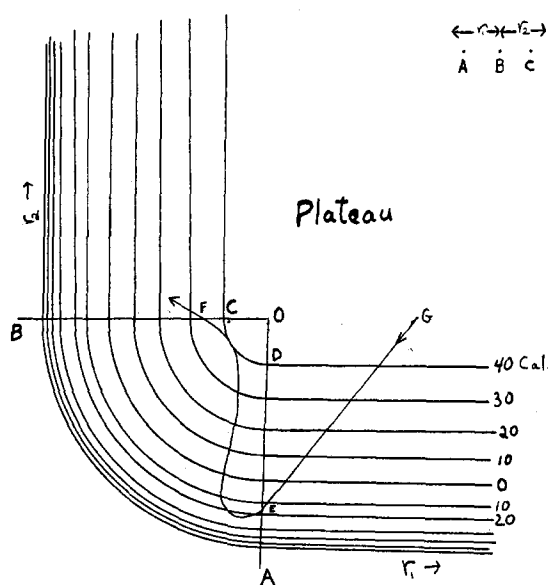


FIG. 2. Portion of potential energy surface for three collinear atoms.\*

The results may be expected to hold for all cases except those for which the total and relative angular momenta are very large. Since most of the atoms concerned in the processes to be discussed have kinetic theory velocities, this exception is not of importance.

## II

In the cases treated in (I), the ruled regions of the surface were separated by a straight line along a ridge (see Fig. 1). Since this represents a very special case, let us consider the situation in cases in which there is a curved region separating the parts of the surface which are ruled in terms of rectangular coordinates, assuming that the curve is the arc of a circle (Fig. 2). In such a region, in which the potential field is centrally symmetrical, the angular momentum  $M = \mu r^2 \dot{\theta}$  must be conserved, where  $\mu$  is the reduced mass,  $r$  the distance from the center of curvature  $O$ , and  $\dot{\theta}$  is the angular velocity. Since the total energy must also be conserved, while the mass point remains in the curved region, energy will be transferred between the  $r$  and the  $\theta$  directions. The amount of energy transferred will depend upon the phase relationships at the points at which the mass point that represents the system

enters and leaves the curved region. These relationships will have to be determined individually for each specific case that is treated. We shall examine briefly a qualitative solution, in order to find out something about the determining factors.

Fig. 2 represents a portion of a potential energy surface for a hypothetical system of three atoms.  $r_1$  is the distance between  $B$  and  $C$ , and  $r_2$  the distance between atoms  $A$  and  $B$ . If  $r_1$  and  $r_2$  were used as the coordinates, they would not be perpendicular to each other, but at an angle determined by the masses of the atoms.  $K$  is a function of the masses which compensates for this fact by introducing a different scale for distances along the ordinate and abscissa.<sup>4</sup> As in Fig. 1, each of the two valleys represents the existence of a diatomic molecule and an atom, while the plateau to the north-east represents three separate atoms. The formation of a diatomic molecule corresponds to the passage of the mass point representing the triatomic system from the plateau into the valley without returning to the plateau. Any particle which leaves the plateau and does not enter the curved region must necessarily return to the plateau, since it is not possible for energy to be transferred between the directions normal to and along the valley. In the circular part of the valley, the angular momentum,  $M = \mu r^2 \dot{\theta}$ , is conserved, as well as the total energy, so that the energy perpendicular to the direction of the radius vector,  $M^2/2\mu r^2$ , decreases as the square of the distance from the center of curvature,  $O$ . If the particle enters the circular region at a point  $E$ , and emerges at a point  $F$ , and if it has not made exactly an even number of oscillations, energy will have been transferred between the directions normal to and along the valley. To increase the probability of staying in the valley, the transfer must of course be from the direction normal to the bottom of the valley to the direction along the bottom, i.e., if  $r_e$  is the radius at the point at which the mass point enters the curved region, and  $r_f$  the radius at the point at which it leaves (see Fig. 2) then  $M^2/2\mu r_f^2 > M^2/2\mu r_e^2$ , whence  $r_e > r_f$ . If at some point on the plateau  $G$  we represent the en-

\* In Fig. 2 the coordinate  $r_2$  should be replaced by  $Kr_2$ . In Fig. 3,  $r_2$  should be replaced by  $Lr_2$ .

<sup>4</sup> (a) Eyring and Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931); (b) reference 1, p. 790.

ergy parallel to the bottom of the valley as  $E_p = M^2/2\mu r_e^2$ , and normal to it by  $E_n$ , then for this trajectory to lead to a stable molecule we must have  $M^2/2\mu r_f^2 - M^2/2\mu r_e^2 > E_n$ . Thus the four conditions that favor the formation of a diatomic molecule are that  $M$  and  $r_e$  be large and that  $E_n$  and  $r_f$  be small. In general,  $E_n$  will be of the order of  $\frac{1}{2}kT$ . For  $E_n > 0$ , there is no possibility of satisfying the above conditions if the trajectory enters the curved part of the valley by crossing the rim anywhere along the arc  $CD$ , since then  $r_f$  can never be less than  $r_e$ . Only trajectories that cross both  $AD$  and  $BC$  can give stable molecules. The smaller the radius of curvature, the greater the probability that  $r_e$  will be very much different from  $r_f$ , hence the greater the probability of energy transfer. Such a sharp curvature indicates a great reactivity, i.e., that the potential field is greatly disturbed by the presence of a third body in the compass of a very short distance.

It must not be imagined, however, that for energy to be transferred it is necessary for the mass point representing the system to pass completely through a curved region. It may be reflected back from a potential barrier and still transfer energy. If, for example, a high potential barrier were set up in the curved region of Fig. 2, so that the mass points would be reflected back into the valley whence they came, energy would still be transferred if they reentered the straight portion of the valley at a different point than they had left from. The type of potential energy surface that we have been considering in Figs. 1 and 2 is one that applies to the case in which all the particles involved can form valence bonds with each other. If the catalyzing particle repels the others at all distances (except for van der Waals forces), there will be only one deep valley in the potential energy surface with a hill closing off the end of this valley. If the potential field is such that this hill causes a curving of the equipotential lines of the surface, then energy will be transferred if the mass point goes partly up the hill at the end of the valley and then falls back in such a way that it reenters the valley at a different point.

Fig. 3 shows roughly the general nature of the potential energy surface for the interaction of an inert gas and a diatomic molecule. X represents

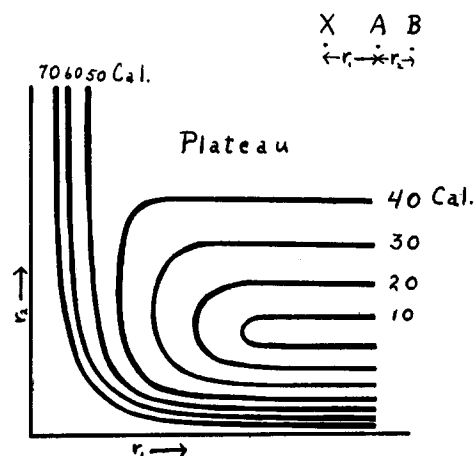


FIG. 3. Approximate potential energy surface for an inert gas atom (X) and a diatomic molecule (AB).

the inert gas and A and B the atoms of the diatomic molecule. (As shown, the molecule AB has a dissociation energy of about 40 Cal.)  $r_1$  is the distance between X and A and  $r_2$  the distance between A and B, the constant  $L$  being, as previously, a function of the masses. A collision between X and AB will be described by the motion of a mass point moving in the valley from right to left, towards the potential hill that represents the repulsive field of X. It can be seen that in the region at the bottom of the valley, i.e., for a diatomic molecule in an unexcited state, the nature of the surface can hardly be distinguished from that of Fig. 1. For high vibrational energies, however, the situation is entirely different from that in Fig. 1, and correspondingly, one would expect a much different probability for the transfer of energy. For the formation of a diatomic molecule, the mass point must move from the plateau into the region in which the equipotential lines are curved, so that there may be a transfer of energy between the two degrees of freedom.

### III

It has long been fairly clear that in many cases the probability of energy transfer is related to the reactivity of the gases involved. Purely qualitative considerations have shown that strong intermolecular fields which perturb the energy should increase the probability of energy transfer. From this it has been concluded that those foreign gases will be most efficient in transferring energy which can react with the gas in

TABLE I. *Relative efficiencies of gases in transferring energy to Cl<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>, from data on the dispersion of sound.<sup>6</sup>*

	Cl <sub>2</sub>	N <sub>2</sub> O	CO <sub>2</sub>
Cl <sub>2</sub>	1.0	—	—
N <sub>2</sub> O	—	1.0	—
CO <sub>2</sub>	—	1.1	1.0
N <sub>2</sub>	0.88	—	—
A	1.1	—	1.0
He	33.3	3.3	33.3
D <sub>2</sub>	—	12.5	—
H <sub>2</sub>	50.0	9.1	125.0
CO	167	1.6	—
CH <sub>4</sub>	200	6.7	25
HCl	200	—	500
NH <sub>3</sub>	—	12.5	—
H <sub>2</sub> O	—	100	2000

<sup>6</sup> Eucken, Oesterr. Chem. Ztg. (1935) 1.

question. This was the conclusion which was stated in (I). While this is true, it is very liable to misinterpretation. It is necessary to be careful in the definition of reactivity. We have shown above that, in the sense with which energy transfer is concerned, reactivity should be defined quantitatively in terms of the rate of change of curvature of the equipotential lines of the system. That is, reaction means the perturbation of the system so that a different set of normal coordinates must be used. The more a third body bends the equipotential lines of the system, the more reactive it is. This leads to the result that the relative reactivity depends on the region of the potential energy surface that is being considered. This can be seen by reference to Fig. 1, in which

TABLE II. *Relative efficiencies of gases in transferring energy in unimolecular reactions.*

	F <sub>2</sub> O <sup>6</sup>	N <sub>2</sub> O <sup>7</sup>	AZO-METHANE <sup>8</sup>
F <sub>2</sub> O	1.00	—	—
N <sub>2</sub> O	—	1.00	—
azomethane	—	—	1.00
O <sub>2</sub>	1:13	.23	—
N <sub>2</sub>	1.01	.24	.21
F <sub>2</sub>	1.13	—	—
SiF <sub>4</sub>	.88	—	—
He	.40	.66	.07
A	.52	.20	—
Ne	—	.47	—
Kr	—	.18	—
X	—	.16	—
H <sub>2</sub> O	—	1.50	.46
CO <sub>2</sub>	—	1.32	.25
CO	—	—	.13
CH <sub>4</sub>	—	—	.20
D <sub>2</sub>	—	—	.37

<sup>6</sup> Koblitz and Schuhmacher, Zeits. f. physik. Chemie **B25**, 283 (1936).<sup>7</sup> Volmer and Frohlich, Zeits. f. physik. Chemie **B19**, 85 (1932); Volmer and Bogdan, *ibid.* **B21**, 257 (1933); Volmer and Briske, *ibid.* **B25**, 81 (1934).<sup>8</sup> Sickman and Rice, J. Chem. Phys. **4**, 608 (1936).

it is very clear that reactivity of an H atom with respect to an H<sub>2</sub> molecule depends on whether the molecule is in the normal state or is highly excited, i.e., the bending of the equipotential lines and hence the probability of energy transfer, is different in the region  $r_1=2.0A$ ,  $r_2=0.74A$  than it is in the region  $r_1=2.0A$ ,  $r_2=2.0A$ . This affords an immediate explanation of the discrepancy that exists between the data on energy transfer obtained from experiments on the dispersion of sound and those obtained from reaction rates.

The most extensive investigations of transfer of energy among gases have been made in connection with the measurements of the rates of unimolecular and atomic reactions and of the dispersion of sound. Table I shows the results of some dispersion of sound experiments, giving the relative efficiencies of various foreign gases in transferring energy to Cl<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>. There are no very noticeable regularities, but it can be seen that helium seems to be at least as effective as other molecules. Table II shows the relative efficiencies of various gases in the activation of fluorine oxide, nitrous oxide and azomethane. The inert gases are here noticeably less efficient than the others. Table III shows the relative efficiencies of various gases as third bodies in the recombination of Br<sub>2</sub> and I<sub>2</sub>. Here also, it is apparent that the inert gases are less efficient than the others. Thus there is a discrepancy between the results of sound dispersion experiments and those of reaction kinetic experiments.

That there should be such a discrepancy is readily understood when one examines the nature of the potential energy surfaces. We are concerned with quite different regions of the surface in these two cases. In the case of the dispersion of sound, the experiments take place at low temperatures, when most of the molecules are in low energy states and are therefore represented by mass points moving along far down in the valley. In the reaction rate experiments the molecules

TABLE III. *Efficiency of gases in catalysing the recombination of halogen atoms.<sup>9</sup>*

	H <sub>2</sub>	He	CH <sub>4</sub>	N <sub>2</sub>	O <sub>2</sub>	A	CO <sub>2</sub>
Br	2.2	.76	3.6	2.5	3.2	1.3	5.4
I	4.0	1.8	12	6.6	10.5	3.8	18

<sup>9</sup> Rabinowitsch and Wood, Trans. Faraday Soc. **32**, 907 (1936); *ibid.* **31**, 689 (1935); J. Chem. Phys. **4**, 497 (1936).

are highly excited and are represented by mass points moving across and high up on each side of the valley. The two situations are thus not analogous. In the case of dispersion of sound the energy transfer must take place in a comparatively small region of phase space at the bottom of the valley. In the case of reaction, the energy transfer may take place throughout a much larger region of phase space, in which the properties of the surface may be quite different from those of the limited region at the bottom of the valley. Translating into the older terminology of the kinetic theory, this means that in the two cases there will be different "collision diameters," referring to the spatial separation of the centers of gravity of the molecules when energy transfer takes place, different "steric factors," referring to the geometric orientation of the particles, and different transition probabilities.

With the aid of the two potential energy surfaces given in Fig. 1 and Fig. 3, it is possible to arrive at a more quantitative explanation of the fact that the inert gases are relatively more efficient in transferring energy to molecules in low energy states. An examination of these two surfaces shows that in the lower parts of the valley there will be a repulsive field even if the molecules involved are those which may react with each other. The inert gases, therefore, will have the same sort of effect as any other atoms. When large internuclear distances are involved, however, as in the case of dissociation, the attractive forces come into play, and change the nature of the surface, so that we should expect that atoms which may interact with valence forces should be more effective than those in which only van der Waals forces are present.

Since the surfaces referred to above are for triatomic systems, these arguments hold rigorously only for three atom processes. When polyatomic molecules are involved the situation is complicated by the presence of other degrees of freedom which may help in the transfer of energy. In general it may be expected that an increase in the number of degrees of freedom will increase the transition probabilities. Even though the number of degrees of freedom is increased, the

situation will still be analogous to that of the three atom reaction. In the case in which reaction is taking place, there will be at least one degree of freedom in which large amplitude anharmonic vibrations will be taking place, while in the sound dispersion experiments all the degrees of freedom will be in low energy states. The essential characteristics of the problem therefore remain, and the conclusions reached with the aid of triatomic surfaces should be applicable. The interaction between the colliding particles depends on their state of excitation and the probability of energy transfer will be very different for different types of collision.

The above considerations apply to the transfer of vibrational and translational energy. It is easily seen that similar results would be obtained for transfer of other types of energy, such as rotational and electronic. The relative efficiencies of various molecules in transferring energy to a given molecule will depend on the type of process that is being considered and may well be different for different processes. There is no *a priori* reason why the relative efficiencies of gases in transferring energy in problems of heat conduction, sound dispersion, reaction rates, viscosity etc. should be the same. From the general principles that have been developed it is clear that the meaning of the term "collision" depends on the nature of the process that is being considered. The effective collision diameter will be different for the transfer of translational, vibrational or rotational energy. It will also depend on the nature of the molecules involved. For this reason one must be very careful in comparing data that are not strictly analogous. The term "collision" as it has been used in the classical kinetic theory is much too vague to be of any use when one considers that the particles involved have many internal degrees of freedom. Each of the problems of energy transfer will have its own peculiar set of conditions that will determine the relative probabilities of the configurations in which energy transfer may take place.

I wish to acknowledge my indebtedness to Professor Henry Eyring, with whom this work was begun.