MOLECULAR TRANSLATION, ROTATION, AND VIBRATION IN CHEMICAL ACTIVATION

O. OLDENBERG

Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

AND

A. A. FROST

Department of Chemistry, Northwestern University, Evanston, Illinois

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I. INTRODUCTION

In recent years a large amount of work has been done concerning the transfer of energy among translation, rotation, or vibration in molecular collisions in gases. The experiments cover fields widely different from one another, i.e., spectroscopy, dispersion of sound, and rates of chemical reactions. The main purpose of the present review of these experiments is an attempt to derive general rules and to apply them to theories of gas reactions. In some chemical theories the energy of activated molecules is specified as vibration. Rotation and translation might also contribute energy towards activation. These kinds of energy have a limited lifetime, since they incur the risk of being dissipated by collisions. Hence their lifetime is measured not in seconds, as in the familiar case of excited atoms capable of spontaneous radiation, but instead in the total number of collisions. In each individual case two questions ought to be answered: (1) Has the energy of activation a chance to survive intervening collisions until the assumed reaction takes place? (2) Is the collision process assumed for the reaction known to be more or less probable?

In this review we will neglect experimental technique as far as it is of no interest to the chemist. After a brief discussion of elementary processes that may produce molecules with a high energy of translation, rotation, or vibration, the results of the various experimental fields will be discussed: intensity distribution in band spectra as modified by pressure, dispersion of sound, rate of recombination of atoms in triple collisions, and activation of unimolecular reactions. While from these experiments direct evidence is derived on some processes and their probabilities, in the last section an attempt is made to apply these results to recent theories of gas reactions, in particular to the theory of energy chains in which a certain persistence of an activated molecule in collisions must be presupposed.

Recently a part of the same field was reviewed from the theoretical point of view by Zener (95). One cannot say that the quantum theory of collisions between atoms and molecules as yet gives a complete and accurate account of the facts. The more the theory approaches this aim, the more it seems worth while to review all related experimental evidence.

II. ORIGIN OF ABNORMAL ENERGY OF TRANSLATION, ROTATION, OR VIBRATION

Before investigating what happens with high energy of translation, rotation, or vibration in collisions, we shall discuss the processes by which they may be produced. For the present we are not much interested in the study of thermal equilibrium, since in equilibrium the distribution of energy over translation, rotation, and vibration is maintained independent of the elementary processes responsible for the exchange of energy; in particular, independent of their persistence in collisions, so that lack of such persistence does not impair the reactivity. Instead, we shall study special processes that cause a deviation from the thermal distribution, a *small* deviation in high frequency sound or monomolecular reactions, and *very large* deviations in electric discharges or in some chemical reactions.

Translation and vibration

We begin with processes in the electric discharge leading to high energy of translation or vibration. A fast electron is unable to give directly appreciable energy of translation to an atom or molecule. This is understood on the basis of the mechanical laws of impact applied to a collision between a light and a heavy body. Nevertheless, it is well known that in the excitation process of a band spectrum (electronic excitation) a large amount of vibration can be produced. This is interpreted by the Franck–Condon rule as follows (75). In a molecule like I_2 the nuclei have an equilibrium separation in the excited state widely different from that in the normal state. Suppose the molecule is excited by light or electron impact. During the excitation process proper, there is insufficient time for the heavy nuclei to change appreciably their separation, which is the equilibrium separation of the normal state. Hence an excited molecule is produced with its nuclei at the first moment far from the new equilibrium position. This molecule immediately begins to vibrate strongly. If this vibration exceeds a certain limit, the molecule dissociates and its constituent atoms or radicals might even fly apart with considerable energy as in the case of Cl_2. In this more indirect way, coupled with a dissociation process, an electron impact can produce energy of translation of the constituents far exceeding the thermal average.

But even without electronic excitation an electron with a few volt-electrons energy has a chance—in spite of its small mass—to impart vibration, for example, to a nitrogen molecule as was observed by Harries (28). Franck and Jordan (21) explain this apparent contradiction to the laws of impact as follows. From mechanics we learn that the electron cannot produce vibration by a knock on the nitrogen molecule in the direction of its axis, but mechanics is compatible with the following picture: the impinging electron penetrates the electronic structure of the molecule and by its field changes its equilibrium separation so that the molecule begins to vibrate. When the electron has passed the molecular structure, there is a chance that the molecule will continue to vibrate, the energy, of course, being provided by the electron.

In chemical changes it is obvious that the chemical energy might lead to high energies of translation, rotation, or vibration. Mulliken (55) observed, in particular, high vibration in band spectra excited by chemical processes.

Rotation

The chances for producing high rotation, however, seem to be smaller than for high vibration, so much smaller, as a matter of fact, that in spectroscopy it is assumed as a rule—although a rather fallacious rule—that the rotation as observed in band spectra indicates the temperature of the gas. By electron impact no appreciable rotation can be given to a molecule. That is observed independently of whether or not the electronic system of the molecule is being excited. It is well explained by the laws of impact. In particular, the idea just applied to vibration as excited by electron impact does not apply to rotation, since an impinging electron penetrating the electronic structure of a molecule cannot appreciably change its rotation, because its angular momentum with respect to the molecule is too small. For these reasons values of rotation far exceeding the thermal value, occasionally observed in band spectra, are called abnormal.

Elementary processes by which abnormal rotation of molecules may be produced have been discussed by Oldenberg (59, 60). They are related to the dissociation process in which the atoms fly apart with excess energy of translation. The most important process is the simultaneous excitation and dissociation of a complicated molecule, the fragments of which part from each other with considerable values of energy and possibly angular momentum, though the resulting angular momentum of the system remains small. This was first observed in the simultaneous excitation and dissociation of the $HC \equiv CH$ molecule (53). The same type of process takes place in the electric discharge through water vapor when by electron impact the H_2O molecule is dissociated into H and excited OH, the OH being produced with high rotational energy. Rieke (71) recently proved that the excitation of HgH molecules by impacts of the second kind with metastable mercury atoms is a similar process (see section III B).

But it is obvious that in general only a part of the available energy goes into the rotation of a molecule. From this consideration and, in particular, from the spectroscopic fact that abnormal rotation is an exceptional case, we infer that vibration of molecules is much more important than rotation in representing energy of activation.

III. THE LIFETIME OF HIGH ENERGY OF TRANSLATION, ROTATION, OR VIBRATION IN COLLISIONS

A. Classical mechanics and energy of translation

Since translation, rotation, and vibration of molecules are concerned with the motion of masses much heavier than electrons, it is supposed that classical mechanics describes collision processes within a certain approximation. A well-known example of the approximate validity of classical physics in describing the motion of nuclei is the Franck–Condon rule dealing with the intensity of band spectra discussed in the preceding section. Hence our discussion must start from classical physics. Conclusions derived from classical physics are as follows. Exchange of energy generally takes place in each collision process, particularly between particles of comparable mass. If one particle has an exceptionally large amount of energy, there is a tendency towards distribution over all degrees of freedom available, that is, towards thermal equilibrium. On the other hand, it rarely happens that in a collision the energies of different degrees of freedom accumulate and so create abnormal energy in one degree of freedom. It follows that translation has a chance to activate a chemical reaction only if the atom or radical, somehow produced with high energy of translation, reacts without many intervening collisions.

The progress towards thermal equilibrium, however, is slowed down in collisions between very light and very heavy atoms, for scarcely any exchange of energy takes place. A striking example for an extreme case of this type of collision is given by the enormous selective temperatures of free electrons in electric discharges through gases which as a whole do not show much more than room temperature. This phenomenon, discovered in 1925 by Langmuir (51), is partly explained as follows: the free electrons receive large amounts of energy not from thermal collisions but from the electric fields. In their frequent collisions *with atoms* they change their direction and any loss of energy is slight. In their *mutual* collisions, however, an exchange of energy takes place so easily that a separate Maxwell distribution among the electrons is established with an average energy of several volt-electrons, many hundred times surpassing the thermal energy of the gas molecules.

On the other hand, positive ions when accelerated by the electric field lose their energy readily to atoms and so raise the temperature of the gas. This may be observed by the width of spectral lines emitted from ions. They fail to indicate by Doppler broadening higher velocities for ions than for atoms.

Apart from the short life of abnormal translation, the ability of translation to activate chemical reactions is still further restricted by classical mechanics. This will be evident from an example (22). In the photochemical chlorine–hydrogen combination the light absorbed generates chlorine atoms which may well have kinetic energy as high as 0.6 volt. But in the collision of a fast chlorine atom with a hydrogen molecule only a small fraction of this energy is available for activating the reaction since the common center of gravity, largely determined by the heavy chlorine atom, is sure to continue its path. The same restriction ought to be taken into account, for example, in a chain reaction, suggested by Semenoff (35), in which one of the links consists of the dissociation of a hydrogen molecule by a fast hydrogen atom. Again the total kinetic energy is not available for the dissociation process. This restriction in the ability to activate reactions obviously does not apply to light atoms or molecules (in the extreme case electrons) when colliding with heavy ones.

In the transfer of vibrational or rotational energy of molecules in collisions similar restrictions may be explained by the laws of conservation of energy and momentum (58). The effect of rotation on chemical activation was discussed by Beutler and Rabinowitsch (4) on the basis of classical physics.

Although classical physics represents molecular processes, if at all, only by an approximation, the results discussed are of practical value, as it is certain that restrictions derived from the conservation of energy and momentum really hold. It is uncertain whether additional restrictions come in by the laws of quantization. This is to be decided by experiments which will be discussed in subsequent sections.

B. Intensity distribution in band spectra

In band spectra the vibration and rotation of molecules emitting light are directly observed. In excited molecules we are able to produce selective values of vibration and rotation and change them by collisions during the lifetime of the excited state. Here we have an outstanding opportunity to study the persistence of vibration and rotation. First we shall discuss fluorescence experiments in which the processes can be particularly well analyzed, and subsequently electric discharges.

1. Fluorescence experiments. The best known case is that of the fluorescence radiation of iodine vapor excited by monochromatic light, for example, the green mercury line. This spectrum was discovered by R. W. Wood (92). It consists of a long series, called resonance series, of very narrow doublets extending from the exciting green line through the yellow and red, representing a small selection of lines from the very complicated I_2 bands. This series was interpreted by Lenz (52) and in greater detail by Loomis (54) as follows: the green mercury line coincides with one individual sharp absorption line of the iodine band spectrum, hence it affects only molecules with definite values of rotation and vibration. It produces molecules with a certain electronic excitation and in addition 26 vibrational and 34 rotational quanta, or with energies of vibration of 0.64 volt-electron and of rotation of 0.004 volt-electron. While this rotation is within the thermal range, the vibration represents 75 per cent of the energy of dissociation of the excited electronic level. At low pressure (0.2 mm.) this excited state represents the sole initial state of the radiation process observed as fluorescence. In radiation the electronic state goes down to the normal level as there are no other levels available. This determines the situation of the spectrum in the visible. In the same radiation process the *vibration* goes over to any vibrational quantum number of the normal electronic level, as no selection rule restricts the change of vibration. These various possible changes are observed as the resonance series of nearly equidistant "lines," indicating by their mutual distances the vibrational sublevels of the normal electronic level. Again in the same process the *rotation* changes its quantum number by + or − unity according to the selection rule. These two possible changes—associated in the radiation process with any change of electronic level and vibration—can be observed only with high resolving power as a splitting up into fine doublets of all the vibrational "lines" just described. Thus we understand the main aspect of the fluorescence spectrum of I_2 at low pressure, the resonance series, each "line" consisting of a narrow doublet.

We are particularly interested in the change produced in this series by the addition of a foreign gas to the iodine vapor. In this case a much larger variety of lines (a larger selection from the complete I_2 bands) appears, as discovered by Franck and Wood (23). This is explained by collisions which during the lifetime of the excited state change its vibration or rotation. These new lines indicate by their intensities the probabilities for the transfer of vibrational or rotational energy. The intensities as functions of pressure have recently been determined by Roessler (11, 73) with photographic photometry. His chief result is that the probability for the transfer of vibrational as well as rotational energy from an excited iodine molecule to a colliding rare gas atom is of the order of magnitude one. The *vibration*, starting from a value far exceeding the thermal average, is never increased by collisions but reduced preferably by one quantum. The *rotation*, starting from a value within the thermal average, may gain as well as lose energy, readily changing by several quanta which are exceedingly small. Roessler describes in detail how this probability varies as a function of the atomic weight of the rare gas, uniformly increasing for vibration but with a certain maximum for rotation. The absolute values of probability are not so well known, since their determination depends upon a reasonable choice of the lifetime of the excited state and the cross sections. The numerical values given by Roessler indicate effective cross sections for the transfer of vibrational or rotational energy even larger than the gas kinetic cross sections.

While these quantitative results of photographic photometry indicate an easy exchange of rotation and vibration of the iodine molecules when excited by green light, an apparently contradictory result was obtained by Oldenberg (56) in the fluorescence radiation excited by ultra-violet light (2100–1849 A. U.). These experiments were recently extended by Duschinsky, Hirschlaff, and Pringsheim (10) with higher resolving power and wider ranges of temperature, pressure, and wave length. The same type of resonance series starting from the wave length of the exciting line is observed. A great difference, however, is that for long wave lengths even at the lowest pressure (no collisions during the lifetime) the resonance series gradually goes over into a much more complicated "tail." We are interested in that with increasing pressure of foreign gases the resonance series loses intensity in favor of the "tail," but, strangely, within the series no new lines come out, not even in two atmospheres of nitrogen. This failure to observe a change of vibration or rotation is probably connected with recent results of Cordes (9), who proved the occurrence of predissociation in the iodine molecule. This would materially reduce the lifetime of the excited state below the value due to spontaneous radiation. Furthermore, collisions may induce predissociation rather than changes of vibration or rotation so that they remove excited molecules rather than change their vibration or rotation. For the purpose of this review we conclude that we are justified in discarding the ultra-violet iodine bands from our consideration, because the processes we are interested in are masked by other effects of collisions.

Another opportunity of investigating the lifetime of vibration and rotation is given by abnormally high values of rotation in certain fluorescence experiments and in electric discharges. As discussed in section II, some rather special processes are alone capable of producing abnormal rotation.

The first striking case was discovered by Wood and Gaviola (25, 93) in the fluorescence radiation of HgH, observed in the mixture of very little mercury vapor and hydrogen with a few centimeters of nitrogen. Illumination with the resonance line 2537 of mercury excites HgH bands with a rotation indicating an apparent temperature of many thousand degrees, although the experiment is performed at room temperature. An interpretation was offered by Oldenberg (58) and recently experimentally confirmed by Rieke (71). His results are as follows. In the rather complicated sequence of processes, HgH molecules (excited by impact of the second kind with excited Hg) are produced with considerable excess vibration. This is a common process (described for electron impact by the Franck–Condon rule, section II). We are interested in how these vibrating molecules behave in collisions during the lifetime of the excited state, that is, how the spectrum changes with increasing pressure. These molecules when colliding with nitrogen have a good chance to transfer part of their excess vibrational energy into rotation, but a very poor chance to transfer it into translation. The reason is that before the collision the vibration consists largely of the motion of a light particle, the hydrogen atom, so that—according to classical mechanics (cf. section III A)—in the collision the translation, belonging to heavy particles (HgH and N_2), scarcely receives energy and most of it remains concentrated in the degrees of freedom of the light particle; that is, in the hydrogen atom which is vibrating and rotating with respect to the mercury. In another paper Rieke (72) discusses an apparent persistence of rotational energy of HgH in its normal state in collisions as claimed several years earlier by Beutler and Rabinowitsch (5). Extreme intensity of the light exciting fluorescence brings out some abnormal rotation in the HgH band. It is probably explained not by persistence of rotation but more indirectly by persistence of vibration from one excitation process (followed by radiation) to the next process. The vibration may change in collisions to the observed rotation. From these experiments, no quantitative results can be derived as from the fluorescence radiation of I_2, since the mean time between consecutive excitation–radiation processes is not known.

2. Electric discharges. While in fluorescence experiments the elementary processes can be traced in great detail as was done in particular by Rieke, similar phenomena in electric discharges are largely explained by analogy.

In the band spectrum of hydrogen to which a few millimeters of helium are added abnormal rotation was discovered by Richardson (70) and further investigated by Roy (74). N. D. Smith (81) traced its origin to a process similar to the one discussed for HgH. Excitation by electron impact readily leads to high vibration but normal rotation of the excited molecule (section II). If a few collisions with helium take place during the lifetime, the energy of vibration is dissipated over all degrees of freedom available; a small share goes into rotation of the same excited hydrogen molecule and becomes manifest at the radiation process. In this case (all masses about equal, different from the case HgH + N_2), according to classical mechanics, translation ought to have the same chance to benefit as rotation. Since the vibrational energy which is to be distributed might easily be 1 volt and the average thermal rotation is only about one-fortieth of this value, a small fraction of the vibration dissipated may produce an appreciable gain of the rotation kept in the same molecule. Actually the abnormal rotation observed is much less conspicuous than in the HgH experiment. This case is unusual in that both the loss of vibration and the simultaneous gain of part of the energy as rotation can well be traced in the band spectrum. For higher pressure of helium the abnormal rotation goes back towards its normal value, indicating a more complete dissipation of energy by collisions taking place during the lifetime. This experiment proves that there is no very conspicuous persistence of vibration or rotation of excited H_2 in collisions with He. But an appreciable persistence is observed at liquid air temperature. In this case, in spite of the addition of 200 mm. of helium to 0.6 mm. of hydrogen the rotation did not quite go down to the very low thermal average. The exchange between vibration, rotation, and translation seems to be slower than would be explained by the smaller number of collisions per second. An attempt to obtain quantitative results with photographic photometry seems well worth while.

At room temperature OH radicals behave similarly to hydrogen molecules (59). Their abnormal rotation, excited in the discharge through water (section II), can well be dissipated during the lifetime of the excited state by collisions with helium, indicating no conspicuous persistence of rotation. It is striking that argon seems to have about the same effect in reducing the rotation of OH (64), although because of its larger mass, according to classical physics, one would expect it to have less chance to receive energy from the light hydrogen atom rotating about the oxygen atom.[1]

A remarkable persistence of vibrational energy in the normal state of H_2 has been inferred by Beutler (3). In a discussion of intensities in an electric discharge through 0.02 mm. of hydrogen + 0.3 mm. of argon he assumes than an argon line is absorbed by H_2, although only hydrogen molecules in their normal electronic state with the vibrational quantum number $v'' = 2$ (1.00 volt-electron) are able to absorb this line. It is obvious that such vibration cannot have thermal origin but must be a residue of preceding excitation and radiation processes. Hence it must be assumed that the first few vibrational quanta of the hydrogen molecule outlast many collisions.

In the electric discharge through nitric oxide E. Kondratjewa and V. Kondratjew (48) discovered that addition of argon transfers a vibrational quantum of excited nitric oxide (energy of quantum 0.126 electron-volt) with a probability of the order of unity.

Surveying the results of band spectra presented here, we emphasize the fact that many of them apply to excited electronic levels (fluorescence of I_2 or HgH, spectra of H_2 or OH in discharges) so that there application to the normal levels, more interesting in chemical reactions, may be questioned. On the other hand, some results derived from band spectra for normal levels (fluorescence of HgH at highest intensity, discharge through H_2 + Ar) are only qualitative as the "time between consecutive excitation processes" is an unknown factor.

Persistence of vibration or rotation in collisions seems to be more pronounced the larger the individual quantum is as compared to kT. For example, the H_2 rotation seems to become more persistent in collisions the lower the temperature (see section III G).

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[1] From these results—interpreting abnormal rotation in electric discharges—one infers that some surprisingly high temperatures, recently observed (27, 31) by the rotational distribution of intensities in band spectra, might be due to collisions of highly vibrating molecules during the lifetime of the excited state and so fail to indicate the real temperature of the gas unless the experiments are carried through at a very low pressure.

C. Dispersion of sound

1. Fundamental experiments. Dispersion of sound was discovered by G. W. Pierce (63) in 1925. He devised the accurate method for the measurement of the velocity of sound that has been applied in all later work, the source of sound consisting of a piezo quartz oscillator, the frequency of which can be very accurately measured and kept constant. Dispersion of sound is observed almost exclusively far above the audible range. Absorption of sound occurs in the same frequency range as dispersion.

In the theoretical interpretation it is important to note that dispersion of sound has been observed only for molecules with excited vibration. This holds at room temperature for carbon dioxide, chlorine, nitrous oxide, ammonia (84), and, to a smaller extent for oxygen, at higher temperatures for nitrogen. (From specific heat measurements (17) it is known that at room temperature vibration is not excited in hydrogen and nitrogen. This agrees with the fact derived from band spectra that the vibrational quanta of these gases are too large to be excited at room temperature by thermal collisions.) Dispersion is observed only within a limited range of high frequencies above and below which the velocity has constant but different values. Below this range the familiar value of velocity of sound is interpreted, following Einstein's theory of specific heats, by the idea that for chlorine, for example, translation and rotation are active as for any other diatomic molecule at room temperature, but that the vibration is only partly excited, as is to be expected from the value of its quantum as compared to kT. But above the critical range, the velocity of sound approaches the same higher value which in other gases (hydrogen) indicates that the vibration has no share in the specific heat although, of course, in chlorine the thermal excitation of vibration still ought to occur.

2. Theory. Herzfeld and F. O. Rice (32) give the following explanation. The vibration is inherently slow in picking up the energy value that belongs to thermal equilibrium, so that for very rapid changes of temperature, as they occur in high frequency sound, the energy content of vibration might fail to follow and instead persist at some average value determined by the average temperature. If so, the vibration loses its ability to affect the velocity of sound.

By the mathematical treatment of this idea, using the observed values of pressure, temperature, and the frequency range of dispersion, one can derive the average number of collisions required to produce exchange of energy between vibration and the other degrees of freedom (40, 44). This is the problem of the present review.

Rotation of molecules does not seem to persist through a sufficient number of collisions to result in the dispersion of sound in the accessible frequency range (16, 69).

3. Effect of impurities. A discovery by Knudsen (46), who investigated absorption instead of dispersion of sound, gives a variety of experimental results and these are of greater importance to chemistry. He found that the critical frequency is very sensitive to certain impurities; for example, traces of water will shift it to higher frequencies (79). Such impurities as helium, for example, do not manifest dispersion of sound in themselves.

The explanation, consistent with the theory of Herzfeld and Rice, was given by Kneser (42, 43, 45). Although chlorine molecules are slow in exchanging vibrational energy in collisions among themselves, they accomplish this exchange readily in collision with water or with certain other molecules. In the more detailed theory given by Kneser, the critical frequency of dispersion leads to the number of collisions required on the average for the chlorine molecule to give its vibration to one or the other foreign atom or molecule.[2]

4. Survey of results. By the systematic investigation of dispersion of sound as it is affected by impurities Eucken (13) and his collaborators succeeded in establishing general rules for the lifetime of vibrations in collisions between various partners. Experimental results are given in table 1.[3]

An increase of temperature materially decreases the number of collisions required to dissipate one quantum. For chlorine, for example, this number decreases to one-seventh for an increase of temperature between −32° and +145°C.

5. General conclusions. From table 1 it is evident that the exchange between the vibrations of chlorine, nitrous oxide, or carbon dioxide in collisions with other molecules or atoms fails to follow a simple law, as a function of molecular weight. From the wide range of figures given in table 1 Eucken and Becker (15) derived a general law which is particularly striking when we compare the effect on chlorine of nitrogen and carbon monoxide as impurities, both molecules having the same weight and very similar physical properties (band spectra) but very different reactivity with chlorine. Nitrogen, which does not chemically react with chlorine, exchanges its vibration with chlorine once in 43,000 collisions, whereas for carbon monoxide, which under different conditions would react with

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[2] A unique result has been derived by Kneser (41) from the measurements of Knudsen. When the vibration of O_2 is dissipated by H_2O, triple collisions $O_2 + H_2O + H_2O$ seem to play an appreciable part.

[3] Attention is called to the conventional representation of results of dispersion of sound based on the "number of collisions required to dissipate one quantum." This is reciprocal to the "yield per collision" applied in table 2.

chlorine to form phosgene, the corresponding ratio is only 1/230. Here evidently the effects of the foreign gases on the dispersion of sound in chlorine correspond to their chemical reactivity.

Similar results, characteristic for certain combinations, led Franck and Eucken (20) to the idea that the mechanical picture of exciting, or dissipating, vibration by a knock on one of the chlorine atoms fails, that instead an interaction must be assumed between the electronic structure of the two colliding molecules similar to the beginning of a chemical reaction. We shall discuss the gain of vibrational energy which is a problem equivalent to its loss. We compare the excitation of vibration in a molecule by collision with another molecule with the effect of an electron impact exciting vibration as discussed in section II. The close approach of another molecule ought to change the molecular forces. It might start a vibration which would have a chance to persist when the two colliding molecules part again. Such an interaction is obviously not determined just by the masses,—as the mechanical knock probably would be. Instead it is characteristic for the individual pair of molecules.

TABLE 1

Number of collisions required to dissipate one quantum of vibration (20°C.)

ADDED GAS	PRINCIPAL GAS		
	Cl_2	N_2O	CO_2
No added gas	34000	5600	47000
N_2	43000		
A	32000		47000
He	900	1700	1700
D_2		440	
H_2	780	630	480
CO	230	3600	
CH_4	190	840	2400
HCl	120		130
NH_3		450	
H_2O		60	40
CO_2		5000	

Thus the following rule given by Eucken and Becker (15) is understood: the probability of a transfer of vibration in a collision is larger, the larger the chemical affinity between the partners, although here actually no chemical reaction takes place. Eucken (13) emphasized that in particular chemical reactions with small heats of activation ought to manifest themselves by an effect on dispersion of sound before the reaction proper occurs.

Apart from this rule, light atoms like helium seem to favor dissipation of vibrational energy. Eucken explains this property of helium by its small diameter, which allows it to penetrate more deeply into the structure of other molecules. Furthermore, Eucken and Jaacks (16) assume that collisions, the duration of which nearly coincides with the period of one vibration, are particularly effective in dissipating vibration.

One can not expect that considerations as simple as that can completely explain the interaction of atoms and molecules. For example, the great difference between the effects of hydrogen and deuterium on dispersion of sound in ethylene, observed by Richards (69), can hardly be explained so simply.

The rule of Eucken and Becker has been interpreted on the basis of potential surfaces as derived from wave mechanics by Eyring, Gershinowitz, and Sun (18), in connection with their theory of triple collisions (see sections III E and III G). In the same paper they explain the great efficiency of hydrogen by the fact that it can readily form a complex molecule with other substances, since it is in a favorable configuration about half the time at room temperature. This is due to its small moment of inertia.

Patat and Bartholomé (61) recently introduced the hypothesis that the high persistence of vibration in molecules when colliding with molecules of the same type is correlated with a high probability for the complete transfer of vibration from one molecule to another by resonance acting between equal particles. This will be further discussed in section III G.

Comparing results of dispersion of sound with spectroscopic results (section III B) from the point of view of the chemist, there is a preference for dispersion of sound. The reason is that in sound experiments no electronic excitation and no high vibrational quanta, but only the lowest vibration of the normal electronic level, play a part. This energy range, just exceeding the thermal average, is most important in chemical activation by heat. It is to be expected, therefore, that conclusions from dispersion of sound apply more directly to thermochemical processes than conclusions from most spectroscopic investigations as far as they deal with excited electronic levels.

It is striking that—apart from the wide range of probabilities—the order of magnitude of the number of collisions required for dissipation of the lowest vibrational quanta is in any case large as compared with unity. This number materially decreases with increasing temperature.

D. Time lag of specific heats of gases in explosions

In the measurement of specific heats of gases at high temperatures by the explosion method deviations are observed between experimental and theoretical values (12). Wohl and Magat (91) explain these effects on the basis of the idea—taken from the theory of dispersion of sound—that the vibrations of N_2 and O_2 approach thermal equilibrium with a certain time lag. This idea in particular explains the fact that traces of water present reduce the time lag, that is, accelerate the exchange of vibrational energy in collisions. As the explosion method is subject to various sources of error, hardly any numerical results comparable to the results of dispersion of sound can be expected.

E. Rate of recombination of atoms or radicals in triple collisions

Another group of observations, very different in its technique but related in the elementary processes involved, is concerned with the recombination of atoms or radicals. We are not interested in the wall effect, but only in collisions between gaseous atoms and molecules. It is well known that two hydrogen atoms in the ordinary binary collision have scarcely any chance to form a molecule. The reason is that they fail to get rid of their energy of combination unless there is a third body present in the collision carrying away some of the energy and so catalyzing the combination. Since the pair of colliding atoms may well be described as a molecule with vibrational energy beyond the limit of dissociation, the effect of the third body is to reduce the energy of vibration of the hydrogen molecule in a collision.

The experimental work on this process, largely reviewed in the book of Kassel (38), although not agreeing well in detail, shows consistently that a third particle in a triple collision with two hydrogen atoms has the efficiency of the order of magnitude of unity in catalyzing the combination (1, 80). This means that in this limiting case the vibrational energy fails to show appreciable persistence.

Recently the recombination of halogen atoms has been investigated. Rabinowitsch and Wood (66) observed the change of concentration of bromine and iodine molecules caused by intense illumination with a sensitive optical method. Hilferding and Steiner (33) inferred the rate constant of the recombination by observing to what extent the formation of hydrogen bromide is affected by added gases. Again we are primarily concerned with the order of magnitude of the effect. It is in the neighborhood of unity for most added gases,—quite different from all collision effects observed by dispersion of sound. Rabinowitsch (65) concludes that the effect per collision increases with the size of the molecule acting as third body and the intensity of the field surrounding the molecule. The results do not quite agree with their numerical values.

Investigating the recombination of OH radicals and H atoms with the aid of absorption spectra of OH taken in snapshots, Frost and Oldenberg (24) showed that triple collisions are required. Again they have a rate constant of the order of magnitude of unity.

The observation in these cases of recombination is restricted to the fact that triple collisions lead to real molecules, that is, to values of vibration somewhere below the critical limit. It is of minor importance that the rotation might contain energy exceeding the energy of dissociation by a certain amount (57).

Must we assume that the largest part of the vibration is carried away in the triple collision so that almost non-vibrating molecules are produced? That this is probably not the case follows from a comparison with the results discussed in the preceding sections. Excited iodine molecules with high vibration have the tendency to give away some vibration in collisions but only a small amount each time (section III B). Another argument leading to the same result is as follows: chlorine shows no persistence of vibration near the convergence limit. (This is inferred by analogy with bromine and iodine actually investigated by Rabinowitsch and Wood.) On the other hand, chlorine shows a very high persistence of its lowest vibrational quantum in dispersion of sound. We infer that the pair of atoms, when forming a molecule in a triple collision, does not lose at once the largest part of its vibrational energy, since such a loss would reduce the vibration to the range in which it is much more persistent.

While the order of magnitude of unity has been found for the simple recombination processes observed, a certain factor may be predicted which may materially reduce this probability for more complicated radicals. Only those collisions are expected to result in recombination in which the configuration of the partners is approximately the same as in the molecule to be formed. A restriction like that has been postulated for various reactions in gases, in particular by Rice and Gershinowitz (68) and by Vaughan (86).

The theoretical understanding of the effect of triple collisions in catalyzing the recombination of atoms is based on the wave-mechanical treatment given by Eyring, Gershinowitz, and Sun (18) (see section III G). They succeed in calculating the absolute rate of recombination of H + H with another H acting as a third body in good agreement with experimental results. They estimate that H is at least six times more effective than H_2 as a third body, in good agreement with the measurements of Amdur (1). Comparing the relative efficiencies of various gases as third bodies they are able to predict from their theory that the order should agree to the order of their reactivities with H_2. This rule is well supported by Bonhoeffer's (7) measurements. It is the same rule that Eucken and Becker had derived from experiments for dispersion of sound.

The obvious difference between recombination in triple collisions and the processes discussed in the preceding section is that in the dispersion of sound experiments we are dealing with quanta of vibration so large that they are comparable to kT. Here, however, we are dealing with energies to be carried away that belong to a continuous range beyond the limit, or to a quantized range near to this limit which by its large number of small quanta might behave similarly to a continuous range.

F. Activation of unimolecular decompositions

Our interest in unimolecular decompositions, which have recently been reviewed by several authors (39, 49, 62) from a general point of view, is restricted to the special question: How do they manifest the probability of gaining vibration in collisions? Obviously this question is equivalent to the other, dealt with in the preceding sections: How large is the probability that a vibrating molecule gives away energy in collisions?

In a bimolecular decomposition a collision process directly causes dissociation. In complicated molecules it can happen instead that the collision process directly produces vibrations in several degrees of freedom. These are coupled so that they are able to exchange energy among each other. So for a given total energy content of a molecule, a certain probability results for a concentration of energy in one degree of freedom sufficient to decompose the molecule. As these probabilities are intrinsic in the molecule it decomposes without further collisions after a certain lifetime. If this lifetime is small as compared with the time between two collisions (low pressure), it does not become manifest and the reaction is bimolecular. *Vice versa,* if the activation is frequent above a certain limit (high pressure) and the following decomposition infrequent (long intrinsic lifetime of activated molecules), the number of activated molecules is practically determined by thermal equilibrium and becomes independent of the number of activating collisions. So the reaction becomes unimolecular. The critical pressure range at which the reaction changes from bimolecular to unimolecular indicates how frequent collisions are required to maintain a sufficient supply of highly vibrating molecules.

For a given molecule that shows unimolecular decomposition, Hinshelwood (34) and his collaborators found that the critical pressure strongly depends upon the type of gas added. This indicates that the various molecules have very different abilities to impart vibration by collisions to the molecule to be decomposed. Here is another experimental method contributing information of the kind considered in the preceding sections.

Examples of the yield per collision with which various added gases activate F_2O (47), N_2O (87, 89), and azomethane (78) are given in table 2.[3]

Again, as in dispersion of sound, light atoms seem to have a stronger effect than heavy atoms, as is best evident from the comparison of rare gases.

Investigating organic compounds, Hinshelwood and his coworkers found that in most cases hydrogen is about as effective in causing activation as the organic molecule itself; many molecules are considerably less effective. This effect of hydrogen has been largely explained on the basis of wave-mechanics by O. K. Rice (cf. the report of Zener (95)) and by Eyring, Gershinowitz, and Sun (18).

While the relative probabilities given in table 2 are derived directly from experiments, the absolute values are much less certain. For pure nitrous oxide the probability 1/1700 results when all four vibrational degrees of freedom are supposed to be involved. With three degrees of freedom the result (88) is 1/190 and with two it is 1/12. Patat and Bartholomé (61), on the basis of a more indirect estimate, applying results of dispersion of sound, obtained the order of magnitude of unity.

TABLE 2

Relative yields per collision of gases activating unimolecular decomposition

DECOMPOSITION OF F_2O (AT 250°C.)		DECOMPOSITION OF N_2O (AT 653°C.)		DECOMPOSITION OF AZOMETHANE (AT 310°C.)	
Added gas	Yield	Added gas	Yield	Added gas	Yield
F_2O	1	N_2O	1	Azomethane	1
O_2	1.13	H_2O	1.50	H_2O	0.46
N_2	1.01	CO_2	1.32	CO_2	0.25
F_2	1.13	N_2	0.24	N_2	0.21
SiF_4	0.88	O_2	0.23	CH_4	0.20
He	0.40	He	0.66	CO	0.13
A	0.52	Ne	0.47	D_2	0.37
		A	0.20	He	0.07
		Kr	0.18		
		X	0.16		

In the preceding sections we differentiated the evidence dealing with the lowest quantum of vibration (dispersion of sound) and with high quanta near the limit (recombination of atoms, fluorescence radiation). The activation of unimolecular decompositions holds an intermediate position. While most degrees of freedom of the decomposing molecule certainly contain only a small fraction of their maximum energy content, the decomposition indicates that there is one degree of freedom that reaches its limit by the activation process.

G. General rules

1. Purpose of general rules. The experimental results reported in the preceding sections suggest general rules. The experiments, however, do not cover the ground so completely that at the present time the final shape of such rules can be given. Yet an attempt like this might be well worth while for two purposes—first, in order to find deficiencies in the experimental evidence and, secondly, in order to apply such rules to theories of gas reactions in which they have been rather neglected.

2. Translation. There is no doubt, theoretical or experimental, that translation is well described by classical physics. Rapid dissipation by elastic collisions is certain. Translation, therefore, has a chance to act as energy of activation only if the atom or radical produced with high energy has a chance to react without many intervening collisions. The ratio of masses, however, of the various partners must be considered. This is illustrated by the extreme case of free electrons keeping their high temperature separate from the temperature of the gas.

Apart from the collisions intervening between activation and reaction, at the reaction proper energy of translation can only partly be spent because of the classical laws of conservation. This was illustrated in section III A by the example of the collision $Cl + H_2$.

3. Vibration. Dissipation of vibration is observed as a rapid process in fluorescence radiation of iodine when modified by pressure, and in triple collisions leading to the combination of free atoms. In both cases we are dealing with very small quanta of vibration. In the excited iodine molecule, their energy is 0.01 volt-electron, and in the combination process we are even dealing with the limiting case,—vibrational quanta approaching the smallest values near the limit of dissociation. We infer that in cases in which the vibrational quantum is smaller than kT, the collision process is described with reasonable approximation by classical mechanics.

On the other hand a most pronounced persistence has been observed in dispersion of sound. In this case we are dealing with the lowest, that is largest, vibrational quantum which fails to be dissipated into heat in many thousand collisions with equal molecules or molecules of some other kind, specific in each case. Because this quantum is not small as compared to kT, classical physics fails to describe the collision process. The rules for dispersion of sound are given by Eucken and Becker: Light particles show a certain preference to dissipate energy. Still more striking is the other rule that partners with a chemical affinity for the vibrating molecule show a strong power to dissipate energy, although actually under the conditions of the sound experiment no reaction takes place.

The correlation between the persistence and the size of the quantum, suggested by the experimental results, does not agree with the recent argument of Patat and Bartholomé (61) and of Eucken (14). They assume that the persistence is independent of the number of vibrational quanta excited. They support this assumption by recent theoretical results of Landau and Teller (50). But since these results are derived for the harmonic vibrator, the theory fails to describe the change of persistence due to the decreasing size of the quanta with increasing quantum number. On the other hand, such a change is experimentally observed for hydrogen and chlorine. In both gases the lowest quanta are persistent (spectroscopic observation for hydrogen; dispersion of sound for chlorine); nevertheless in both gases the highest quanta are readily dissipated (recombination of atoms in triple collisions). This comparison within the same gases proves that persistence is characteristic only for the lowest, that is, largest quanta.

The temperature effect on persistence of vibration is consistent with our point of view: With increasing temperature, that is increasing kT, the persistence of vibration in collisions becomes less pronounced. This temperature effect on the persistence, however, is equally well described by Patat and Bartholomé on the basis of the idea that the closer the approach at the collision, the stronger ought to be the interaction, hence the higher the probability of an exchange of energy.

4. Rotation. In dispersion of sound no trace of persistence of rotational energy in collisions can be detected. Correspondingly in fluorescence radiation of iodine vapor an easy transfer of rotational energy is observed. Some persistence, however, has been detected by other spectroscopic methods which are presumably more sensitive than sound experiments, as the time interval during which persistence is observed is given by the lifetime of an excited electronic state instead of a period of sound. Persistence of rotation is evident in the electric discharge through hydrogen.

The comparative lack of persistence of rotation is presumably connected with the fact that rotational quanta are much smaller than low vibrational quanta. In the exceptional cases in which some minor amount of persistence is evident, the rotational quanta are larger than in most other molecules. In particular in N. D. Smith's (81, 82) investigation of the effect of temperature, the persistence of rotation of hydrogen molecules becomes more striking when at liquid air temperature the quantized rotational energy to be dissipated becomes comparable to or larger than kT. In hydrogen no less than two rotational quanta can be given away because of the well-known properties of the nuclear spin in homonuclear molecules (54, 95). These energy steps of the excited hydrogen molecule, $E_{j+2} - E_j$, in volt-electrons are given in table 3. At liquid air temperature the value of $kT = 0.0077$ volt-electron is smaller than the energy steps; at room temperature $kT = 0.025$ is of the same order.

5. General rule. The experiments discussed suggest a rule which *a priori* seems plausible: No pronounced persistence or vibration or rotation in collisions occurs if the quanta are much smaller than kT; if the opposite holds, persistence might take place, but it is a specific property of the partners in the collision. This difference in the persistence of quanta of different sizes, derived from experimental evidence, agrees well with Zener's theoretical rule (95) that internal energy will be dissipated much more rapidly if it can be given up to energy of translation as several small quanta than as one large quantum.

Comparing the specific effects among various partners by dispersion of sound, Eucken and Becker found the general rule which correlates the persistence—ranging from 47,000 down to 40 collisions—with the chemical reactivity of the partners.

6. Quantum theory of the energy transfer in collisions. Simple cases of energy transfer in collisions have been treated by quantum mechanics by applying the perturbation theory to the Schroedinger equation for the system. Zener (95) has recently reviewed this work and, also, has contributed a great share to it (see the following section on "resonance"). To what extent the results have been affected by the far-reaching simplifications, indispensable for the mathematical treatment, is difficult to estimate.

TABLE 3

Rotational energy differences of excited H_2 *(in volt-electrons)*

j	0	1	2	3	4	5
$E_{j+2} - E_j$	0.02	0.037	0.053	0.066	0.080	0.092

Great progress is due to the representation of simple collision processes by potential surfaces introduced by Eyring and Polanyi (19). The collision process $H + H_2$, which has been discussed in great detail, encounters the lowest potential wall, when all three atoms move along a straight line. For this case the potential energy as a function of r_1 and r_2 (mutual distances between adjoining atoms) is represented by a surface,—conveniently drawn as a contour map. The two possible molecular states are represented by valleys and the complete separation of all three atoms by a high plateau for large r_1 and r_2. For a special angle between the coördinates (depending on the mass ratio) the surface has the property that the mechanical motion of a masspoint, traveling over the surface, describes a curve, which by its coördinates, r_1 and r_2, represents a possible motion of the three particles. Hence the probability of formation of a molecule by a triple collision can be computed as the probability that a masspoint, approaching the valleys at random, will finally roll into one of the valleys.

These contour maps give admirable pictures of the motion. From such a map designed for H + H + H, Eyring, Gershinowitz, and Sun (18) derived their conclusions discussed in sections III C and III E. Dr. Gershinowitz kindly informed us of his extension of this theory (26), in which he applies the same method to a rare gas atom colliding either with a pair ready to form a molecule (triple collision) or with a molecule with little vibration (as observed in dispersion of sound). In both cases he compares the effect of helium as a third body with the effect of H. The potential surfaces of He + H + H are very similar to those of H + H + H as far as the bottom of the valleys are concerned, but they differ considerably at the rims. He concludes that the molecule with little vibration, represented by the bottom, is affected by helium in approximately the same way as by some other particles. The corresponding observation is that in dispersion of sound helium has about the same effect as many other particles. On the other hand near the rim of the valley (pair of colliding atoms) the specific properties of the potential wall provided by the helium atom account for the relative inefficiency of helium in triple collisions or unimolecular reactions. In general the relative efficiency of energy transfer is not only a specific property of the molecules involved, but is also dependent upon the degree of excitation of the system. There is no *a priori* reason why the relative efficiencies of gases in transferring energy should be the same for dispersion of sound and reaction rates. They might be different again in heat conductivity or in viscosity which is largely determined by the external degrees of freedom, translation, and rotation.

7. *Relation to "resonance."* Is there any rule for collisions in which vibration or rotation is given away indicating the degrees of freedom into which the energy probably changes? Since vibration and rotation are quantized we might expect "resonance," that is, nearly complete transfer in a collision of quantized energy due to the more or less accurate coincidence of energy levels. Resonance is known to be the most important factor in "collisions of the second kind" in which electronic energy is exchanged between atoms. There is a definite tendency observed that electronic energy remains concentrated as electronic energy in the transfer so that the smallest possible amount of energy goes into translation (83). On the other hand, if we apply classical physics, we expect that, for example, vibration far exceeding the thermal average should show a tendency to spread over all degrees of freedom available at the collision,—degrees of freedom of the partner and the vibrating molecule itself.

In our search for some direct evidence of resonance in the transfer of rotation or vibration we failed. One might search for such a case in investigations of band spectra as modified by added diatomic gases. No evidence of it could be found in the literature. More experimental work seems desirable.

There are a few cases which indicate that energy of vibration given away is distributed over several degrees of freedom. In the electric discharge through hydrogen with helium the disappearance of high vibration can be observed together with a simultaneous increase of rotation, the rotation, however, gaining only a part of the energy of vibration lost; obviously the balance goes into translation. Similar is the process observed in the fluorescence radiation of HgH. In these cases the tendency of dissipation over the degrees of freedom available seems to prevail.

It is to be expected—on the basis of "resonance" as well as on the basis of classical mechanics—that a degree of freedom which before the collision has a large amount of excess energy does not gain any more by collisions. This is observed in the fluorescence radiation from I_2. Actually, collisions during the lifetime of the excited state take away vibration but never contribute additional vibration.

The failure to find direct evidence of resonance in the transfer of rotation or vibration—inadequate as the experimental evidence is—is well understood in cases in which from mechanics the production of a considerable amount of translation is to be expected. This is most evident in the transfer of rotation into rotation since such a transfer can hardly take place without the centers of gravity of the molecules picking up kinetic energy (58). (An exception would be the limiting case, represented, for example, by HgH, in which the kinetic energy of rotation because of the mass ratio is centered in the hydrogen atoms. According to the laws of impact, transfer of rotation energy may happen with a negligible amount of translation being produced.) A similar mechanical objection holds against resonance, that is *complete* transfer, in the exchange between rotation and vibration. It would violate the law of conservation of angular momentum.

The case is not clear, however, in the transfer of vibration into vibration. It is true that the simple picture of this transfer, consisting in a mechanical knock of vibrating particles, would necessarily lead to some energy being imparted to the centers of gravity so that the translation would spoil the resonance.

However, resonance would not be excluded by the principles of mechanics if, instead, we describe the transfer of vibration into vibration by the picture of Eucken and Franck (section III C): during the collision process, one molecule by its close approach modifies the field of force acting within the other molecule and so starts vibration.

While no case of resonance other than electronic was known in the transfer of energy of heavy particles in collisions, a high probability, even of the order of magnitude of unity, caused by resonance has recently been assumed by Patat and Bartholomé (61) on the basis of the following, rather complicated argument. They compare dispersion of sound, activation of unimolecular reactions, and recombination by triple collisions. Within each group they compare the effects in pure gases with those in mixed gases, that is, the efficiency of equal and foreign molecules in dissipating excess energy. They conclude from the experimental evidence that equal molecules prove very effective in unimolecular reactions and triple collisions, but very ineffective in dispersion of sound. In order to describe these facts they assume as a general principle that equal molecules are very effective in the transfer of vibration into vibration by resonance. By this idea they explain the dissipation of energy by collisions in unimolecular reactions and triple collisions. In dispersion of sound, however, the situation is peculiar in that only the one lowest vibrational quantum comes into play. The authors assume a very frequent transfer by resonance. But this peculiar case of resonance does not become manifest, since the transfer of the lowest quantum from one molecule to another has no effect on the observations. So they correlate the ineffectiveness of molecules of the same gas with a transfer, not at all excluded, but instead taking place with a probability of the order of magnitude of unity. This would lead, for example, in carbon dioxide (see table 1, section III C) to a transfer of vibration in collisions taking place with the order of magnitude 47,000 times before dissipation.

Objections are as follows: (1) Resonance can hardly increase the effectiveness of triple collisions like $Br + Br + Br_2$. The reason is that the pair $Br + Br$ is ready to give away its highest vibrational quanta while Br_2 is ready to receive its lowest vibrational quanta. The size of these quanta differ so that, on the basis of resonance, Br_2 is not expected to have a greater effectiveness than other molecules. (2) In dispersion of sound equal molecules are not greatly distinguished from some foreign molecules. This is evident from table 1 (section III C). (3) Both for unimolecular reactions and triple collisions[4] the experiments (see table 2, section III F) do not indicate a pronounced preference for the effect of equal molecules. In both of these cases one might rather infer from the experiments a preferred effect of diatomic and polyatomic gases as compared with monatomic gases. Patat and Bartholomé explain such a preferred effect of molecules by their ability to take up energy in more degrees of freedom than the monatomic gases.

It can hardly be said that in dispersion of sound the hypothesis of a frequent transfer of vibration from one molecule to another explains the unexpected fact that this energy withstands dissipation. Since the vibration is not destroyed but only transferred, it remains available for dissipating collisions. (The argument is different for excited, highly vibrating iodine molecules (section III B) which in collisions have a great chance to lose electronic energy. This destroys all future possibility to observe what happens to their vibration.) It seems evident that in collisions between polyatomic molecules like carbon dioxide a transfer of vibration by resonance can take place only for a rather special configuration of the two colliding molecules. Hence many collisions must happen without such transfer of vibration. Their failure to dissipate the vibrational energy remains unexplained.

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[4] The table of probabilities of triple collisions given by Patat and Bartholomé is not reproduced since, according to Rabinowitsch, some results are questionable.

The experimental proof for a very high probability of the transfer of vibration into vibration seems to us not conclusive. It may be assumed that such a probability, as far as it exists, is largest among equal molecules because of resonance. The objection holds only against the high absolute value of this probability as inferred from experiments.

The theoretical treatment given by Zener (95) leads to such an effect of resonance on the probability of transfer. But the numerical value of this probability is very small when compared to unity; for example, in collisions between two nitrogen molecules, one of them vibrating, the theoretical probability of transfer is only of the order of magnitude 10^{-5}. Zener's theory, however, does not deal with exactly the same processes as the hypothesis of Patat and Bartholomé. Zener only estimates the probability of a transfer of vibration into vibration, in particular for equal molecules. He is not concerned with competing transfers of vibration into other degrees of freedom, whereas Patat and Bartholomé—deriving their hypothesis from experimental results of the lifetime of vibration—deal with all possible types of transfer.

It seems to be a rule that resonance which dominates the transfer of electronic energy has no great effect on the exchange of the quantized energies—vibration and rotation—between heavy particles. Instead dissipation of energy among all degrees of freedom available seems to prevail. The transfer of vibration into vibration represents a possible exception to this rule which it is hoped will be cleared up by more experimental work.

IV. APPLICATION TO GAS REACTIONS: ENERGY CHAIN REACTIONS

The general rules derived in the preceding sections have application to all types of gas reactions. In particular, two types of gas reactions have already been discussed because of the information which they give us concerning the transfer of energy in collisions. We shall now discuss the application to energy chain reactions.

A. General characteristics of energy chain reactions

Chain reactions may be classified theoretically into two types: first, atom or radical chain reactions, such as in the hydrogen–chlorine reaction

$$H + Cl_2 \rightarrow HCl + Cl$$

$$Cl + H_2 \rightarrow HCl + H$$

where the atoms H and Cl are the "chain carriers," or second, energy chain reactions in which one or more chain carriers are considered to be ordinary molecules with excess internal energy. For example, a suggested mechanism of the hydrogen–oxygen reaction is

$$O + H_2 \rightarrow H_2O^*$$

$$H_2O^* + O_2 \rightarrow H_2O + O + O$$

the asterisk indicating an "activated molecule,"—a molecule with excess energy. Here the excess energy of the first step of the reaction is assumed to be transferred specifically to the oxygen molecule. Atom or radical chain reactions will not be discussed here, because these reactions are merely a set of successive ordinary chemical processes. Energy chain reactions, however, are of a more physical nature since they depend upon the persistence of internal energy.

The concept of energy chain reactions was first introduced by Bodenstein (6) to explain the photochemical combination of hydrogen and chlorine,—a reaction which is now explained by the atom chain used above as an example. Later Christiansen and Kramers (8) applied the idea of energy chains to explain the unusually high speed of certain unimolecular reactions. This application was also replaced by a preferable theory. No doubt these early unsuccessful attempts to use the idea of energy chains contributed to the present tendency of always giving preference to an atom or radical chain mechanism over an energy chain mechanism.

In order for an energy chain to be possible the activated molecule which acts as a chain carrier must have a lifetime at least as great as the time between collisions with a reactant molecule, i.e., it must have a good chance of not being deactivated before it completes its link in the chain. Clearly then we have here an excellent opportunity to make use of the conclusions of section III to determine the reasonableness of certain postulated energy chains. Only activated molecules with particular types of electronic or vibrational energy can conceivably persist through many collisions without deactivation. In particular, metastable electronic states have a sufficient lifetime to take part in an energy chain. Furthermore, they transfer their energy specifically to molecules with which there is resonance (36, 37, 90). These two characteristics cause molecules in metastable electronic states to behave as though they were different chemical species from the same molecules in their normal states. In section III it is concluded that persistence of vibration might occur if the energy difference between vibrational energy levels is comparable to or greater than the mean thermal energy kT. In this case there is some specificity in the transfer of the energy to other molecules, but certainly there is no such well-defined resonance effect as exists in the transfer of electronic energy.

The conclusion that may be drawn from this discussion is that energy chain reactions can most probably occur if the chain carriers are in metastable electronic states. Chain reactions involving activated molecules in high vibrational states are not so probable. With this in mind we now consider two postulated examples of energy chains.

B. Decomposition of ozone

After many years of experimental study of the thermal and photochemical decomposition of ozone there is at present some agreement as to the mechanism of the reaction. (For a brief review consult Semenoff's book (77), p. 400.) The steps in the reaction are believed to be as follows:

$$O_3 + h\nu \rightarrow O_2 + O \qquad \text{(photochemical)} \tag{1a}$$
$$O_3 + O_3 \rightarrow O_3 + O_2 + O \qquad \text{(thermal)} \tag{1b}$$
$$O + O_3 \rightarrow O_2^* + O_2^* \tag{2}$$
$$O_2^* + O_3 \rightarrow O_2 + O_2 + O \tag{3}$$
$$O + O_2 + M \rightarrow O_3 + M \tag{4}$$
$$O_2^* + O_3 \rightarrow O_2 + O_3 \tag{5a}$$
$$O_2^* + M \rightarrow O_2 + M \qquad \text{(M represents any molecule)} \tag{5b}$$

It is apparent that steps 2 and 3 constitute an energy chain. The chain length of course depends on the ability of steps 4 and 5 to break the chains. According to Heidt and Forbes (30), the photochemical quantum yield—molecules of ozone decomposed per quantum of light absorbed—which is a lower limit to the chain length varies from less than one to more than six. If step 3 were unimportant the quantum yield could be no greater than two. The fact that it can be greater than two requires assuming a chain reaction. Since no atom or radical chain mechanism can be devised, it is necessarily an energy chain.

Reaction 5a is about three times more probable than reaction 3, or the chances are about three to one in favor of a deactivation of the chain carrier before it can react. The efficiency of foreign molecules in causing deactivation (reaction 5b) has been investigated by Beretta and Schumacher (2). They find that oxygen, carbon dioxide, and nitrogen are slightly less effective than ozone and that the inert gases are less effective by at least an order of magnitude. The absolute rates of these processes cannot be determined from the experimental data, so that it is not known whether there is persistence of the activated molecule through many collisions with ozone or other molecules. However, persistence is not necessary to explain the reaction.

These data do not enable one to decide whether the O_2^* is in a high vibrational state or in a metastable electronic state. Energy considerations are of interest in this connection. Reaction 2 is exothermic by 83 kg-cal., so that each oxygen molecule resulting may have at least 41 kg-cal. of activation. The dissociation of ozone into O_2 and O requires only 24 kg-cal., so that there is plenty of energy available for reaction 3. It is known spectroscopically that O_2 has a metastable $^1\Sigma$ electronic state with an energy of 37 kg-cal. Heidt (29) suggests that the chain carrier is this metastable state,—an assumption which is probably preferable to assuming that it is a high vibrational state.

In spite of the uncertainties the decomposition of ozone probably provides the best example of an energy chain reaction.

C. Low pressure explosion of hydrogen and oxygen

As another example of a possible energy chain we now consider the interesting low pressure explosion of hydrogen and oxygen. This is one of a group of low pressure explosive oxidation reactions and so is of general interest. The reaction has been reviewed by Hinshelwood and Williamson (41) and by Semenoff (77). Most work has had to do with the attempt to determine the mechanism of the reaction not by studying the rate of the reaction in the usual way but by studying the explosion limits. At a given temperature between approximately 450° and 550°C. there are two limiting values of the total pressure of a given hydrogen–oxygen mixture between which explosion can occur. The explosion limits of course depend on the temperature and composition of the gas mixture.

The general characteristics of the reaction are adequately explained by the theory of *branching* chain reactions. The exact mechanism of the branching chain, however, is unknown. No atom or radical chain has stood the test of experiment, so an energy chain is in order. Semenoff (77) has tentatively suggested the following:

$$O + H_2 \rightarrow H_2O^* \qquad \text{(bimolecular collision)} \tag{1}$$

$$H_2O^* + O_2 \rightarrow H_2O + O + O \tag{2}$$

As no suitable *electronic* level of H_2O is known it is assumed that H_2O is in high *vibrational* level. Its total energy supplied by the formation process (1) is 115,760 kg-cal. In the transfer process (2) 117,300 kg-cal. are required. Hence reaction 2 involves the assumption that H_2O^* does not suffer any loss by intervening collisions. Furthermore, since the vibrational energy of H_2O^* is probably distributed over several degrees of freedom, reaction 2 involves a concentrated transfer of all this energy into one degree of freedom of a colliding molecule. According to the discussion given in section III, these assumptions are highly improbable. The difficulty becomes still greater by the following consideration. The experimental data for the upper explosion limit indicate that the chain branching process—that is, reaction 2—has an activation energy of 24 to 26 kg-cal.; the colliding molecules must have this amount of thermal energy in addition to any special energy which the chain carriers may supply. But an activated molecule such as H_2O^* could certainly not persist through 10^6 to 10^7 collisions which this activation energy requires.

In order to improve the mechanism Semenoff (76) has recently suggested the following additional processes in which deactivation is allowed but counteracted by a possible return of a partially deactivated molecule to the activated state:

$$H_2O^* + M \rightarrow H_2O^{*/2} + M \qquad (3)$$

$$H_2O^{*/2} + H_2O^{*/2} \rightarrow H_2O + H_2O^* \qquad (4)$$

$H_2O^{*/2}$ indicates a molecule that has lost approximately one half of its original energy of formation. Undoubtedly process 3 is quite probable. But reaction 4 followed by reaction 2 means that energy which has already been dissipated over several degrees of freedom becomes concentrated again—in spite of intervening collisions—first in the various vibrations of one water molecule, next still more concentrated in the one vibration of oxygen. This is against all experimental evidence (section III G) indicating a tendency towards gradual dissipation of excess energy over all degrees of freedom available. Although it is probably necessary to use an energy chain, this particular mechanism does not agree with the various results discussed above.

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