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THE QUANTUM MECHANICS OF CHEMICAL REACTION*

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Abstract

It is shown that the quantum mechanics is capable of describing processes which have all the aspects of certain chemical reactions. It turns out that a system may change from one configuration to another when a quantum level of the one configuration has the same energy as a quantum level of the other. Among such reactions mention is made and some discussion given of the large classes of molecular rearrangements, and decompositions, including radioactive disintegration. The dependence on pressure and temperature is slightly discussed and it is indicated that the present theory quite explains the necessity of the old "activation hypothesis" of Arrhenius. The old notions should, however, be modified to take into account that it is not sufficient to have at least the "activation energy" but the molecule must be in a particular state to react. Moreover when there are several "activated" states the rate of reaction from different ones may be very different indeed. Insight is gained into the nature of certain types of catalytic action including special wall catalyses. Some features of photochemical reactions are made clear by the theory.

THE quantum mechanics have been shown[2] capable of dealing with very general types of transition problems which were outside the scope of the old quantum theory. The methods developed have been used[3] in a great variety of important applications with such marked success that it may be hoped that any physical phenomenon will be susceptible to the same treatment.

With this optimistic point of view the problem of chemical change is approached. It is closely related to the problems already discussed and its importance justifies any serious effort even though much is left to be desired.

The treatment of the present article is not the only one possible but it has the advantage that it can be discussed in familiar chemical and mechanical terms. The chief result of this first paper is that it gives a plausible picture of a certain kind of chemical change. The reason for an "activation hypothesis" appears clearly but it seems that modifications are necessary in the form which this hypothesis has taken up to the present. It will be shown that reaction takes place not when the energy content of a molecule exceeds a certain critical value out rather when a molecule is in a particular

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[2] Especially in the hands of P. A. M. Dirac, Proc. Roy. Soc. **114**, 243 (1927); E. Schroedinger, Ann. d. Physik **83**, 956 (1927) and M. Born, Zeits. f. Physik **38**, 803 (1926).

[3] E.g., C. Fues, Zeits. f. Physik **43**, 726 (1927); G. Wentzel, Zeits. f. Physik **43**, 524 (1927); F. Hund, Zeits. f. Physik **40**, 742 (1927); Heitler and London, Zeits. f. Physik **44**, 455 (1927); Gamow, Zeits. f. Physik **51**, 204 (1928); Gurney and Condon, Phys. Rev. **33**, 127 (1929).

state whose energy is equal to that of some other physically distinguishable state. The chance that the change will take place depends of course on the interaction between parts of the system and this interaction is dependent not only on the forces involved but most essentially on the distances involved. For example, in the reaction $H+Cl_2 \rightarrow HCl+Cl$, the chlorine molecule might well have too much energy to favor the reaction. The energy required will at no stage be enough to separate the two chlorine atoms. When the molecule is in the right state the chance that a hydrogen atom remove one chlorine to form hydrochloric acid will go down exponentially with the distance between the chlorine molecule and the hydrogen atom.

At present it seems that these same features characterize practically all types of chemical reaction, and what is especially interesting, they may also govern the heretofore mysterious field of catalysis.

I. INTRODUCTION

Since the "activation hypothesis" of Arrhenius no important advance has been made in the understanding of the nature of chemical reaction. Arrhenius designed the hypothesis to interpret the most striking fact of chemical reactions, namely, their enormous temperature coefficient. The assumption is that only molecules having more energy than the average (activated molecules) actually undergo reaction. So nicely did this assumption lead to the observed change of reaction rate with temperature, and so difficult has it proved to provide an alternative explanation, that chemists almost without exception believe the "activation hypothesis" to be sound. Apart from the one success for which the hypothesis was invented, it has led only to difficulties. The existence of activated molecules has in general not been demonstrated experimentally.[4] Until within the last few years workers in chemical kinetics had been unable to imagine how molecules of the very high energy required by the "activation hypothesis" in the case of homogeneous unimolecular gas reactions could be supplied fast enough to account for the observed reaction rates. This question is by no means completely solved even now. Perhaps most disheartening was the failure of classical models in the matter of furnishing a convincing picture showing why a molecule was inert until it had a large excess of energy.

Nowadays this failure is easily understood. Classical mechanics could not even approximate the phenomena of chemistry because it did not include the principles which govern the forces between atoms. The "quantum resonance" has no direct counterpart in the older mechanics. Moreover, as will appear later, changes in configuration of a molecular system depend essentially on the very features of the problem which were quite immaterial in the classical theory, namely, the regions where the potential energy is greater than the total energy, and therefore inaccessible to a Newtonian system, which must have positive kinetic energy.

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[4] See, however, M. Cantor, Wied. Ann. **62,** 482 (1897), also O. Wulf, Proc. National Acad. **12,** 129 (1926).

In the considerations which follow, the question might arise as to whether it is proper to assume, as we do, that atoms brought close enough together to interact chemically can be approximately described by the functions which describe them when they are alone. This assumption is justified by the success with which the "zero*th*" approximation has dealt with the homopolar bond. The work of Heitler and London has shown that in the main the phenomena of chemical combination are reproduced without consideration of higher order effects. The phenomena of chemical reaction should have less stringent requirements for presumably reaction takes place only when the binding between parts of the molecules is normally loose or is greatly loosened (compared with the normal state) by a large excess of internal energy. This state of affairs is very fortunate for the development of the quantum theory of chemistry, for the higher approximations are extremely complicated.

I. QUALITATIVE DISCUSSION OF THE WAVE EQUATION

Whereas formerly the difficulty was to find any mechanism for a chemical reaction, the difficulty now is to decide which of many possible mechanisms is the actual one for a particular reaction. It is the chief purpose of this paper to describe a process which, with only slight modifications, will be applicable to many special types of reaction. The case in which the energy of activation, determined from the temperature coefficient, is greater than the energy of dissociation of the bond where reaction occurs is perhaps the most difficult but it will not be treated because it is not certain that such cases exist among chemical reactions. A possible treatment of this case has already been sketched[5] but it might be remarked here that the mention of certain reactions in the reference does not imply that these reactions are necessarily members of the class considered.

It will be desirable first to discuss the wave equation for a case of one degree of freedom from a point of view which is well known.[6] We may write it in the form

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0. \tag{1}$$

If $V(x)$ were constant this equation would have the simple solution

$$\psi=Ae^{\pm(2\pi i/h)[2m(E-V)]^{1/2}x}. \tag{2}$$

When V is not constant we may hope to approximate the solution by a similar form in which the amplitude and wave-length of oscillation or the decay constant (depending on the sign of $(E\text{-}V)$) are variable. The forms

$$\psi=\frac{e^{\pm(2\pi i/h)\int[2m(E-V)]^{1/2}dx}}{[2m(E-V)]^{1/4}} \tag{3}$$

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[5] R. M. Langer, Phys. Rev. **33**, 290 (1929).

[6] H. A. Kramers, Zeits. f. Physik **39**, 828 (1926); G. Wentzel, Zeits. f. Physik **38**, 518 (1926).

have been shown capable of yielding a good approximation. For $(E\text{-}V)>0$ the solutions can be combined to give a real function

$$\psi=\frac{\cos\left\{(2\pi/h)\int[2m(E-V)]^{1/2}dx\right\}}{[2m(E-V)]^{1/4}} \tag{4}$$

and for $(E\text{-}V)<0$ the boundary conditions are satisfied by the solution

$$\psi=\frac{e^{+(2\pi i/h)\int[2m(E-V)]^{1/2}dx}}{[2m(E-V)]^{1/4}}\cdot \tag{5}$$

Kramers has shown how the constant of integration can be chosen so that the solutions for the different regions will go continuously into one another through the singular points where $E-V=0$ in which (4) and (5) fail. The condition that this can be accomplished is approximately the old quantum condition on the energy, namely,

$$\oint pdx=2\int_{x_1}^{x_2}[2m(E-V)]^{1/2}dx=nh \tag{6}$$

where x_1 and x_2 are two successive points at which $E-V=0$. Between these two points there are n zeros of ψ_n.

It should be noticed that the amplitude of ψ is especially large (although it turns out to be finite) at x_1 and x_2. Moreover the exponential decay outside of the region x_1 to x_2 is so rapid that it will usually be permissible to use linear approximations for V and actually carry out the integration indicated in (5). For values of x even moderately remote from x_1 or x_2, ψ will be practically zero.

III. A SYSTEM CAPABLE OF CHEMICAL REACTION

The problem we wish to consider is the case in which there are more than two points at which $E-V=0$. For the sake of definiteness let us speak of a special but typical example—an atom A of free valence two is acted on by two heavy atoms, B and C, each with one free valence. Let the motion be restricted to one dimension.

According to present notions of chemical forces in the configuration

$$\dot{B} \qquad \dot{A} \qquad \dot{C}$$

the potential energy between B and A might be of the type shown in Fig. 1 by the dotted curve BA, that between C and A by the dotted curve AC (the potential energy at infinite separation is taken as zero). Then if we assume that all separations are large enough so that no other mutual potentials arise, and that the two mentioned are not appreciably changed, the potential energy of the system will be represented by the full curve BAC.

Under the circumstances a classical system could not undergo the reactions $BA+C\rightleftarrows B+AC$ unless the initial compound had almost the dissociation energy over its normal state. However, we know many reactions which fit our case but which could not possibly depend on the molecules having such a large energy. We shall see that in quantum mechanics the reaction might proceed even for certain lower values of E.

First we shall inquire as to the allowed values of the energy of the composite system. For values of E less than the maximum of the curve BAC (and only such values are interesting here) condition (6) will be satisfied for almost the same energies that were characteristic for the curves BA and AC. The composite system has therefore all the levels of the two simple systems which could be formed from it by removal of either B or C. For a particular value of E, characteristic of one of these systems, the solution of the wave equation for one of the regions where (4) holds (namely, the one where (6) also holds) will be practically the same as though the corresponding simple system were alone. Condition (6) assures that this solution will go to the proper exponential form (5) just outside this region. The question now arises how shall this solution be prolonged into the other region where $(E - V)$ is positive. In general the condition (6) will not hold for this region and it will therefore be impossible to get a continuous function different from zero in this region which will satisfy the boundary requirements beyond it. We conclude that if (6) is not satisfied in each region separately the solutions for the composite system are approximately the solutions for the two component systems. In the special case in which the two component systems have an energy level in common, (6) is satisfied for each of the two regions and a continuous solution can be made up of a linear combination of those solutions for the separate systems which correspond to the common level. It is this coincidence which forms the basis for the present theory of chemical reaction.

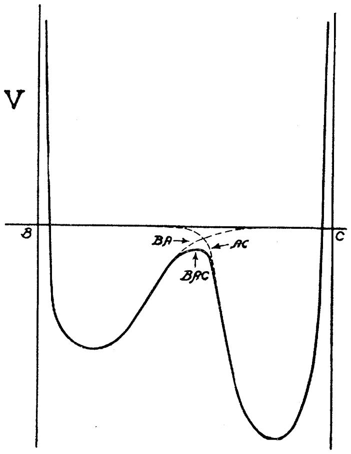

Fig. 1. Potential distribution for rearrangement reaction.

The argument just outlined indicates that it will be possible to treat the problem by the methods used in perturbation theory although there is no small quantity which can be considered as a perturbation potential. The point is that the problem can be formulated so that the matrix elements of the perturbation functions are small quantities.

We shall do this by the method of variation of constants[7] starting with the wave equation in the form

$$\Delta\Psi-\frac{8\pi^2m}{h^2}V\Psi-\frac{4\pi mi}{h}\dot{\Psi}=0. \tag{7}$$

The potential energy $V=V^{(1)}+V^{(2)}$ where $V^{(1)}$ is the potential between B and A, and $V^{(2)}$ that between A and C. The general solution of (7) is

$$\Psi=\Sigma_k C_k\psi_k e^{2\pi iE_kt/h} \tag{8}$$

where the functions ψ_k satisfy the equation

$$\Delta\psi_k+\frac{8\pi^2m}{h^2}(E_k-V)\psi_k=0 \tag{9}$$

for the appropriate energy E_k. For simplicity we shall always take the functions satisfying (9) to be real and to include a normalizing constant such that

$$\int|\psi_k|^2dx=1. \tag{10}$$

The equations

$$\Delta\psi^{(1)}-\frac{8\pi^2m}{h^2}V^{(1)}\psi^{(1)}-\frac{4\pi mi}{h}\dot{\psi}^{(1)}=0 \tag{11}$$

$$\Delta\psi^{(2)}-\frac{8\pi^2m}{h^2}V^{(2)}\psi^{(2)}-\frac{4\pi mi}{h}\dot{\psi}^{(2)}=0 \tag{12}$$

describe the component systems A with B, C at infinity and A with C, B at infinity, respectively. If the solutions of (11) are known functions

and those of (12)

$$\left.\begin{array}{l}\psi_i{}^{(1)}e^{(2\pi i/h)E_it}\\ \psi_j{}^{(2)}e^{(2\pi i/h)E_it}\end{array}\right\} \tag{13}$$

we are led to expect that a zero'th approximation to (8) will be given by

$$\Psi_0=\sum_i C_i\psi_i{}^{(1)}e^{(2\pi i/h)E_it}+\sum_j\gamma_j\psi_j{}^{(2)}e^{(2\pi i/h)E_jt}. \tag{14}$$

To justify this we try for a better approximation by regarding the quantities C_i and γ_j as functions of the time instead of constants. Their derivatives will prove to be small and therefore (14) is a proper approximation. Substituting (14) in (7), considering C_i and γ_j functions of t and using (11) and (12) we can get for example

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[7] P. A. M. Dirac, Proc. Roy. Soc. **112,** 674 (1926); E. Schroedinger, Ann. d. Physik **83,** 956 (1927). The method of breaking up the potential energy has also been used by F. Bloch, Zeits. f. Physik **52,** 555 (1928).

$$-(4\pi mi/h)\left(\sum_i \dot{C}_i\psi_i^{(1)}e^{(2\pi i/h)E_it}+\sum_j \dot{\gamma}_j\psi_j^{(2)}e^{(2\pi i/h)E_jt}\right)$$
$$-(8\pi^2 m/h^2)\left[V^{(2)}\sum_i C_i\psi_i^{(1)}e^{(2\pi i/h)E_it}+V^{(1)}\sum_j \gamma_j\psi_j^{(2)}e^{(2\pi i/h)E_jt}\right]=0$$

from which by multiplying by $\psi_{i'}^{(1)}$ and integrating

$$\dot{C}_{i'}=(2\pi i/h)\left[\sum_i C_iV_{ii'}^{(2)}e^{(2\pi i/h)(E_i-E_{i'})t}+\sum_j \gamma_jV_{ji'}^{(2)}e^{(2\pi i/h)(E_j-E_{i'})t}\right] \tag{15}$$

where

$$V_{ii'}^{(2)}=\int V^{(2)}\psi_i^{(1)}\psi_{i'}^{(1)}dx, \quad V_{ji'}^{(1)}=\int V^{(1)}\psi_j^{(2)}\psi_{i'}^{(1)}dx \tag{16}$$

similarly

$$\dot{\gamma}_{j'}=(2\pi i/h)\left[\sum_i C_iV_{ij'}^{(2)}e^{(2\pi i/h)(E_i-E_{j'})t}+\sum_j \gamma_jV_{jj'}^{(1)}e^{(2\pi i/h)(E_j-E_{j'})t}\right] \tag{17}$$

where

$$V_{ij'}^{(2)}=\int V^{(2)}\psi_i^{(1)}\psi_{j'}^{(2)}dx, \quad V_{jj'}^{(1)}=\int V^{(1)}\psi_j^{(2)}\psi_{j'}^{(2)}dx. \tag{18}$$

When it is considered that the functions $\psi_i^{(1)}$ diminish extremely rapidly in receding from the region where E_i-V is positive and corespondingly for $\psi_i^{(2)}$ it is seen that the quantities of (16) and (18) are very small, as they should be, to establish our procedure. In the integrations, besides using

$$\int \psi_i^{(1)}\psi_{i'}^{(1)}=0 \quad i\neq i' \tag{19}$$

$$\int \psi_j^{(2)}\psi_{j'}^{(2)}=0 \quad j\neq j' \tag{20}$$

we have used the fact that

$$\int \psi_i^{(1)}\psi_j^{(2)}dx\doteq 0 \tag{21}$$

and have therefore neglected $\dot{\gamma}_\gamma\int\psi_j^2\psi_{i'}^1dx$ and $\dot{C}_i\int\psi_i^1\psi_{j'}^2dx$ as being of second order. If the problem is to be completely and properly solved then the functions $\psi^{(1)}$ and $\psi^{(2)}$ would have to be really orthogonal and (21) would be exactly zero. It is believed. however, that the results then obtained would be qualitatively the same as those here given. Of course in cases where (21) does not hold, i.e., where the functions are not even approximately orthogonal, our method does not apply. This failure will occur only when $(E-V)$ near the maximum of V is fairly small which is a very special case of little importance in most problems.

If the E_i's and E_j's are all distinct we can integrate (15) and (17) by discarding all terms excepting the important one which has zero exponent and obtain a first approximation instead of (14)

$$\Psi_1(t)=\sum_i C_i^0\psi_i^{(1)}e^{(2\pi i/h)(E_i+V_{ii}^{(2)})t}+\sum_j \gamma_j^0\psi_j^{(2)}e^{(2\pi i/h)(E_j+V_{jj}^{(1)})t} \tag{22}$$

If the system is initially in a particular state so that the constant coefficients in (22) are all zero except one, then that one state will persist with only a slight energy displacement (i.e., phase change) due to the presence of a third body. That is to say no appreciable reaction occurs and therefore the case of all different energy levels is of no special interest for us.

Something new arises when one of the E_i's coincides with an E_j. Then there are two terms in (15) and (17) with zero exponents and which therefore may undergo a considerable variation in amplitude. For these two states we shall label the energies (E_i and E_j) E_1 and E_2 respectively, and the wave functions ($\psi_i^{(1)}$ and $\psi_j^{(2)}$) u and v[8] respectively. Then with $E_1=E_2$, (15) and (17) reduce to

$$\dot{C}=(2\pi i/h)[CV_{uu}^{(2)}+\gamma V_{vu}^{(1)}] \quad \dot{\gamma}=(2\pi i/h)[CV_{uv}^{(2)}+\gamma V_{vv}^{(1)}] \tag{23}$$

with

$$\begin{aligned} V_{uu}^{(2)}&=\int V^{(2)}u^2dx & V_{vu}^{(1)}&=\int V^{(1)}vudx \\ V_{uv}^{(2)}&=\int V^{(2)}uvdx & V_{vv}^{(1)}&=\int V^{(1)}v^2dx \end{aligned} \tag{24}$$

Equations (23) are solved by the substitution

$$C=C^0\exp\,[(2\pi i/h)\alpha t] \qquad \gamma=\gamma^0\exp\,[(2\pi i/h)\alpha t]$$

The values of α are determined from

$$\begin{vmatrix} V_{uu}^{(2)}-\alpha & V_{vu}^{(1)} \\ V_{uv}^{(2)} & V_{vv}^{(1)}-\alpha \end{vmatrix}=0 \tag{25}$$

The roots are

$$\begin{aligned} \alpha_+&=\tfrac{1}{2}(V_{uu}^{(2)}+V_{vv}^{(1)})+[(V_{uu}^{(2)}+V_{vv}^{(1)})^2/4+V_{vu}^{(1)}V_{uv}^{(2)}-V_{uu}^{(2)}V_{vv}^{(1)}]^{1/2} \\ &=\tfrac{1}{2}(V_{uu}^{(2)}+V_{vv}^{(1)})+[(V_{uu}^{(2)}-V_{vv}^{(1)})^2/4+V_{vu}^{(1)}V_{uv}^{(2)}]^{1/2} \end{aligned} \tag{26}$$

[8] There is an ambiguity of the sign of u with respect to the sign of v. Consequently $V_{vu}^{(1)}$ and $V_{uv}^{(2)}$ may be either positive or negative although their product is always positive. Correspondingly there are two linearly independent solutions for the composite system. For two similar component systems one is symmetrical, the other antisymmetrical, in the attracting centers B and C. The symmetrical and antisymmetrical solutions which appear in problems involving several degrees of freedom involve oscillations which play a part in certain chemical changes and will be considered elsewhere. F. Hund, (Zeits. f. Physik **40**, 742 (1927); also **43**, 805 (1927)) in discussing the wave equation, more particularly from the spectroscopic point of view, has emphasized the existence of solutions symmetric and antisymmetric in the coordinate, and has shown how in some cases these might describe a change in activity of a symmetrical optically active substance.

and

$$\alpha_- = \tfrac{1}{2}(V_{uu}{}^{(2)} + V_{vv}{}^{(1)}) - [(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})^2/4 + V_{vu}{}^{(1)}V_{uv}{}^{(2)}]^{1/2}. \tag{27}$$

These are always real because $V_{vu}{}^{(1)}$ and $V_{uv}{}^{(2)}$ have the same sign. For these values of α (23) can be solved in the form

$$\begin{aligned} C &= C^{0+}e^{(2\pi i/h)\alpha_+ t} + C^{0-}e^{(2\pi i/h)\alpha_- t} \\ \gamma &= \gamma^{0+}e^{(2\pi i/h)\alpha_+ t} + \gamma^{0-}e^{(2\pi i/h)\alpha_- t} \end{aligned} \tag{28}$$

where the constants C^{0+}, γ^{0+} and C^{0-}, γ^{0-} satisfy the relations

$$\begin{aligned} C^{0+} &= V_{vu}{}^{(1)}\gamma^{0+}/(\alpha_+ - V_{uu}{}^{(2)}) = (\alpha_+ - V_{vv}{}^{(1)})\gamma^{0+}/V_{uv}{}^{(2)} \\ &= \{(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})/2 + [(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})^2/4 + V_{vu}{}^{(1)}V_{uv}{}^{(2)}]^{1/2}\}\gamma^{0+}/V_{uv}{}^{(2)} \\ &\text{and} \\ C^{0-} &= V_{vu}{}^{(1)}\gamma^{0-}/(\alpha_- - V_{uu}{}^{(2)}) = (\alpha_- - V_{vv}{}^{(1)})\gamma^{0-}/V_{uv}{}^{(2)} \\ &= \{(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})/2 - [(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})^2/4 + V_{vu}{}^{(1)}V_{uv}{}^{(2)}]^{1/2}\}\gamma^{0-}/V_{uv}{}^{(2)}. \end{aligned} \tag{29}$$

If the system is initially in any state other than u or v then it stays there as in the case of Eq. (22). Let us say, however, that the system is, for example, initially in state u. Then the first approximation to the wave function is

$$\Psi_1 = Cue^{(2\pi i/h)E_1 t} + \gamma v e^{(2\pi i/h)E_2 t} \tag{30}$$

where C and γ are determined by the Eqs. (29) together with the initial conditions

$$\begin{aligned} |C^0|^2 &= |C^{0+} + C^{0-}|^2 = 1 \\ |\gamma^0|^2 &= |\gamma^{0+} + \gamma^{0-}|^2 = 0. \end{aligned} \tag{31}$$

Writing $C^{0+} = |C^{0+}|e^{i\delta+}$, $C^{0-} = |C^{0-}|e^{i\delta-}$ the Eqs. (29) and (31) give $\delta^+ - \delta^- = (2n+1)\pi$

$$\begin{aligned} |\gamma^{0+}| = |\gamma^{0-}| &= |V_{uv}{}^{(2)}|/(\alpha_+ + \alpha_-) \\ &= |V_{uv}{}^{(2)}|/2[(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})^2/4 + V_{vu}{}^{(1)}V_{uv}{}^{(2)}]^{1/2} \end{aligned} \tag{32}$$

Using Eqs. (26) to (32) and with the abbreviation

$$h\nu_q = [(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})^2/4 + V_{vu}{}^{(1)}V_{uv}{}^{(2)}]^{1/2} \tag{33}$$

Eq. (30) reduces to

$$\begin{aligned} \Psi_1 = (1/2h\nu_q)\{&[(V_{uu}{}^{(2)} - V_{vv}{}^{(1)}) \sin 2\pi\nu_q t + 2h\nu_q \cos 2\pi\nu_q t]u \\ &+ [2V_{uv}{}^{(2)} \sin 2\pi\nu_q t]v\}e^{(2\pi i/h)(E_1 + (V_{uu}{}^{(2)} - V_{vv}{}^{(1)})/2)t + i\delta^+} \end{aligned} \tag{34}$$

This can also be written

$$\begin{aligned} \Psi_1 = (1/h\nu_q)\{&[(h\nu_q)^2 + (V_{uu}{}^{(2)} - V_{vv}{}^{(1)})^2/4]^{1/2} u \sin 2\pi(\nu_q t + \phi) \\ &+ V_{uv}{}^{(2)} \cdot v \cdot \sin 2\pi\nu_q t\}e^{(2\pi i/h)(E + (V_{uu}{}^{(2)} - V_{vv}{}^{(1)})/2)t + i\delta^+} \end{aligned} \tag{35}$$

where $\tan 2\pi\phi = 2h\nu_q/(V_{uu}{}^{(2)} - V_{vv}{}^{(1)})$

The coefficients of u and v in (35) inside the bracket are harmonic functions of the same period and amplitude. There is a phase displacement so that at one moment the coefficient of u is zero and at a time ϕ/ν_q later, that of v is zero. The frequency of this oscillation ν_q as defined in Eqs. (33) and (24) depends on the shape of the potential energy curve. Usually the equation $h\nu_q \doteq V_{vu}^{(1)} \doteq V_{uv}^{(2)}$ will hold approximately. Consideration of this shows that the rate of transfer from u to v depends on the height of the maximum of V above E and especially on the range of x over which V-E has large positive values. These quantities enter exponentially in ν_q which is therefore sensitive to slight changes in them.

IV. Application of Results to Chemistry

The valence properties attributed to the system previously used as an example had of course no practical significance. The calculation of the last section will apply to any case where the potential energy curve is of the type shown in Fig. 1. And even Fig. 1 is to be considered in a generalized way. The potential energy need not go up indefinitely high on two sides; it might become asymptotically horizontal on one side or on both. There need not even be two minima, although if there is only one a slight modification must be introduced in the calculation; this will be done elsewhere. The particular features which are really characteristic are that the equation $E_n - V = 0$ shall have more than two finite roots, and that E_n shall approximately satisfy Eq. (6) in at least two different regions.

A few remarks may be made about the assumption that the energy E_n should exactly match in the two regions. The problem can be solved even when this is only approximately fulfilled. No essential change results. When there is a continuous distribution of solutions in one region, one must integrate over all which nearly match the energy E_n and this also involves no change in principle. A question arises as to how often even an approximate match can be expected in molecular systems. First it should be pointed out that one of the characteristic features of infra-red spectroscopy is the ease with which it is possible to arrange all lines in a single or a very few series. The interpretation of this is that the different fundamentals have multiple relations between them which means that the energy match we require will be nearly satisfied quite often. Moreover, superposed on the vibration is the rotation spectrum so that each level is effectively broadened, especially when we consider that these rotations have long periods and are therefore easily subject to perturbation so that they may become practically continuous over considerable ranges. Of course when there is a large continuous range of energies or when the two component systems are exactly alike, there will be many different values of energy which match exactly.

We can describe the matter in more nearly chemical language. A system may be capable of existence in two geometrically different configurations. In each of these configurations it may have only certain motions characterized by the total energy. If one of the allowed energies of one configuration coincides with one of the other then according to Eq. (35) the system will periodically change from one configuration to the other. If the configurations are physically distinguishable then this change can well be called a chemical reaction. It is important to notice that one configuration changes to the other not from the normal state but only when it is in the excited state of the first configuration. This is the theoretical foundation for the "activation hypothesis."

The rate at which the reaction proceeds depends on external conditions such as pressure, temperature, etc., as well as on the forces of the system itself, for these external conditions determine how many systems will be in a favorable state for reaction at any moment. Let us say that a system changes in a reaction from configuration I to configuration II, let us call the states of equal energy u for configuration I and v for II. Then among a large number N of states in configuration I a fraction f_u will be in the important state u. This fraction will depend on the temperature according to the Boltzmann law. The full Boltzmann quota will however not be reached unless the pressure is high enough so that the number of collisions raising molecules of configuration I to state u is large compared with the number which leave state u according to Eq. (35). The rate will therefore depend on the temperature in the way required by the "activation hypothesis" and will also diminish with the pressure in the manner already discussed in the study of unimolecular gas reactions.[9] There is still a further interesting possibility. According to the ordinary interpretations of the wave equation the fractional number of systems in state v will be given by the square of the coefficient of v in the solution (35) of the equation. In our case this is

$$\left| V_{uv}^{(2)} \right|^2 \sin^2 2\pi\nu_q t/(h\nu_q)^2. \tag{36}$$

If collisions played no part, the systems would pass back and forth between u and v, but actually they will tend to remove the systems from state v to other states of configuration II while on the whole they will scarcely affect the number of systems in state u which is nearly in equilibrium with other states of configuration I. Under ordinary conditions when this action of collisions is taken into account the expression (36) will be changed into one with linear initial dependence on the time so that the reaction will follow unimolecular exponential law. But if the pressure is low enough, that is, so that the time between collisions is long compared with the period $1/\nu_q$ in (36) the periodic feature will be important and the rate of reaction will be enormously diminished. Such an effect has been observed[10] and been interpreted in another way which may of course be the correct way.

V. MOLECULAR REARRANGEMENTS

The process which has here been treated may not be clearly in evidence in some reactions because of preliminary or consequent steps in the reac-

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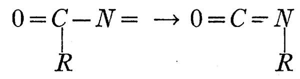
[9] O. K. Rice and H. C. Ramsperger, Jour. Am. Chem. Soc. **49**, 1927, and **50**, 1928. See also L. S. Kassel, Jour. Phys. Chem. **32**, 1928.

If there is more than one pair of states u and v, then the most general dependence on pressure considered by these authors can be reproduced without taking on their special assumptions.

[10] Chariton and Z. Walta, Zeits. f. Physik **39**, 547 (1926); N. Semenoff, Zeits. f. Physik **46**, 109 (1927); **48**, 571 (1928); also G. Sprenger, Zeits. f. Physik. Chemie **136**, 49 (1928).

tions. Nevertheless there are cases where the existence of such a process has been fairly well established as a part of a chemical change. For example in the so-called Hofmann rearrangement one of the steps is the change



$$0=\underset{\underset{R}{|}}{C}-N= \;\rightarrow\; 0=C=\underset{\underset{R}{|}}{N}$$

A common rearrangement is from the "cis" to the "trans" configuration of a complicated molecule. This is represented diagrammatically in Fig. 2.

It is easy to picture in these rearrangements a potential energy curve of the type of Fig 1. The various types of photochemical behavior in these reactions are easily understood on the present theory. Consider for example the case where the reaction of Fig. 2 can be made to go almost completely in one direction or another by illuminating with different wave-lengths. In the configuration I it might take $h\nu_u$ to raise the system to state u while in configuration II, it might require a different energy $h\nu_v$ to raise the system to state v. Illumination by frequency around ν_u will clearly tend to make the reaction go in one direction while frequencies around ν_v will push it in the other. If the values $h\nu_u$ and $h\nu_v$ are large compared with kT the reaction may be made to go almost to completion in either direction. Other types of photochemical reactions can be treated in a similar manner.

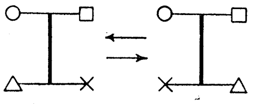


Fig. 2. Diagrammatic representation of the "cis" to "trans" reaction.

VI. CATALYSIS

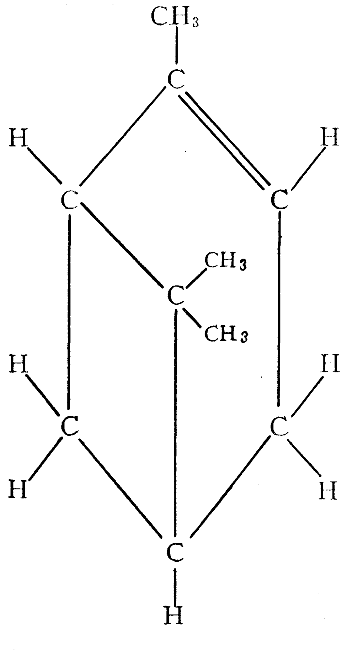
The fundamental requirement that two configurations of a system must have a common energy level will of course not always be sufficiently met to permit appreciable reaction. A suggestion comes immediately from the quantum mechanical theory which may explain a very important type of catalysis. The curious thing about catalysts is that often without any very energetic interaction with a molecular system they have a great influence on the rate at which the system undergoes a change involving considerable energy. One might imagine that the catalyst have a fairly weak attraction—that of an induced dipole for example—on the molecule. The proximity of the catalyst will change the shape of the potential of Fig. 2 and even a small change may suffice to bring about an equality of energy in two configurations. The reaction then proceeds without affecting the catalyst. This perturbing influence may be a specific one where a particular substance affects another so as to match energy levels just accidentally. That substance may then catalyze only one type of reaction. Another substance may naturally have a strong field of force so that it will perturb almost anything. Moreover this perturbation may be variable, depending on the orientation or concentration of molecules and so there will always be a match in energy level for some molecules. Such a substance will be a catalyst for many reactions. A solid body has a good chance of being of this type. The natural irregularity of the surface may provide the variability which is required for different reactions. We have evidence that a catalytic surface often is especially active in special "spots" and this is nicely in accord with our picture. On these spots, possibly with rapidly varying curvature, some molecules are sure to be perturbed just the right amount.

To be sure this theory does not preclude the existence of many totally different kinds of catalysis.

VII. THE RACEMIZATION OF PINENE

Since its investigation in vapour and liquid phase[11] the unimolecules transformation of pinene from a dextro to a laevo variety or vice versa has been of great interest to workers in chemical reaction theory. This reaction involving no change of heat content is carried out only through molecules having an average internal energy of about 40,000 cal. per gram mol.

This is a particularly simple case under our theory. The pinene molecule has the structure



The reaction presumably involves a rearrangement of the central group from a position above the plane of the ring to a symmetrical configuration below it. Whether the motion is through the ring or around the corner carbon, the potential energy can be represented in a way of the type of Fig. 1 with

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[11] D. Smith, Jour. Am. Chem. Soc. **49**, 47 (1927).

the special feature that it is symmetrical to a line through the maximum of the potential. In this case all the energy levels in one configuration will be matched by levels in the other and so the reaction could proceed from any level. The rate at which the change takes place is extremely sensitive to the value of E since in the important part of (35) or (36) namely ν_q, there is a negative exponential factor involving $(V\text{-}E)$. The symmetry of the potential makes

$$V_{vv}^{(1)} = V_{uu}^{(2)} \quad \text{and} \quad V_{vu}^{(1)} = V_{uv}^{(2)}$$

so that ν_q reduces to

$$h\nu_q = V_{uv}^{(2)} = V_{vu}^{(1)} = \int_{-\infty}^{\infty} V^{(2)} uv\,dx. \tag{37}$$

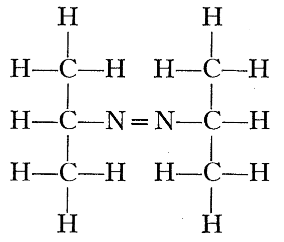
The only values of x at which there is an appreciable contribution to the integral are those between which $E\text{-}V$ is negative. In this region u and v will be given by expressions of the form of Eq. (5). It can be shown from these that (37) will contain as an essential factor exp $[(2\pi i/h)\int[2m(E\text{-}V)]^{1/2}dx]$ where the integral is taken over the range where $E-V<0$ and where V is the resultant potential energy function. The square of this expression determines the rate of conversion between u and v and we see why the change is faster for molecules of higher energy. On the other hand there are fewer molecules of higher energy so that the average energy of the reacting molecules is limited.

There is some possibility of computing numerical values for this reaction from the variation with pressure. We shall however in this paper avoid numerical comparison with data.

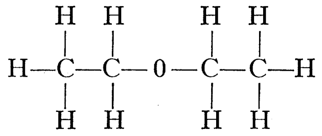
Other reactions of this type are known in liquid phase although not all appear to be as simple. In particular it is by no means necessary to have a symmetrical potential energy function. In fact the potential function is usually not symmetrical. This however is no complication in principle.

VIII. Decomposition

The straightforward breaking up of a molecular system is a very important class of reaction. Many of the homogeneous unimolecular gas reactions are of this type. A common feature of most of these reactions is that they involve the ejection of a part from a central position in a more or less symmetrical system. Notice for example the structures



azoisopropane



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & -0- & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

diethyl ether

It might be imagined that for small oscillations about the horizontal axis of symmetry the central part is attracted. If the amplitude becomes large the opposite parts of the molecule might attract each other directly and then repel the displaced central part. The potential energy curve would be of the type shown in Fig. 3. For every allowed positive value of the energy in the region with the minimum there is a continuous range of nearly equal values allowed in the outside region. A similar diagram holds for radioactive problems which therefore also come under the class here considered.[12]

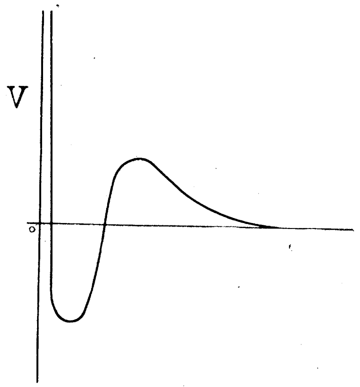


Fig. 3. Potential distribution for a decomposition.

The existence of a continuous range of energies requires a slight deviation from the development of Eq. (35). We shall go through with this without striving for completeness mathematically so that it must not be expected that our results will cover all cases satisfactorily.[13] The failure of the present treatment comes about just as in the case when there are two minima, namely, when E-V does not become a large negative quantity over a sufficient range near the maximum of V.

Under the conditions assumed, the solution to the wave equation must be written

$$\Psi(x) = \sum_i C_i \psi_i^{(1)}(x) e^{(2\pi i/h)E_i t} + \int \gamma(E) \psi^{(2)}(E, x) e^{(2\pi i/h)Et} dE \tag{38}$$

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[12] Radioactive disintegration has recently been treated by Gamow, Zeits. f. Physik **51**, 204 (1928), and by Gurney and Condon, Phys. Rev. **33**, 127 (1929).

[13] A similar treatment has already been given by J. R. Oppenheimer, Phys. Rev. **31**, 66 (1928).

where we normalize the orthogonal functions $\psi^{(2)}(E, x)$ so that

$$(\Delta E)^{-1}\int\int_{\Delta E}\psi^{(2)}(E,x)\psi^{(2)}(E,'x)dEdx=1 \tag{39}$$

provided $|E'-E|\ll\Delta E$ where ΔE is any arbitrary interval of energy, while the same integral is zero when $|E'-E|>\Delta E$. The condition

$$\int\psi_i^{(1)}(x)\psi^{(2)}(E,x)dx\doteq 0 \tag{40}$$

is still required.

We can now repeat the process used with Eq. (7) and find

$$\dot{C}_{i'}=(2\pi i/h)\left[\sum_i C_i V_{ii'}^{(2)}e^{(2\pi i/h)(E_i-E_{i'})t}+\int\gamma(E)V_{Ei'}^{(1)}e^{(2\pi i/h)(E-E_{i'})t}dE\right]$$

$$\dot{\gamma}(E')=(2\pi i/h)\left[\sum_i C_i V_{iE'}^{(2)}e^{(2\pi i/h)(E_i-E')t}+\int\gamma(E)V_{EE'}^{(1)}e^{(2\pi i/h)(E-E')t}dE\right] \tag{42}$$

where

$$\begin{aligned}
V_{ii'}^{(2)}&=\int V^{(2)}\psi_i^{(1)}\psi_{i'}^{(1)}dx\\
V_{Ei'}^{(1)}&=\int V^{(1)}\psi^{(2)}(E,x)\psi_{i'}^{(1)}(x)dx\\
V_{iE'}^{(2)}&=\int V^{(2)}\psi_i^{(1)}(x)\psi^{(2)}(E',x)dx\\
V_{EE'}^{(1)}&=\lim_{\Delta E'=0}(\Delta E')^{-1}\int dx\int_{\Delta E'}V^{(1)}\psi^{(2)}(E,x)\psi^{(2)}(E',x)dE.
\end{aligned} \tag{43}$$

As before we wish to have the system initially in state u so that we take

$$C_{i'}=|C^0|e^{i\delta},\qquad \psi_{i'}^{(1)}=u,\qquad |C^0|=1,\quad C_i^0=0\quad\text{for}\quad i\neq i'$$
$$\gamma^0(E)=0,\qquad \psi^{(2)}(E',x)=v$$

Since the quantities (43) are small we can solve (41) and (42) with enough approximation for short intervals of time by putting for C and $\gamma(E)$ their initial values. The integrals then are

$$C=(2\pi i/h)\cdot C^0V_{uu}^{(2)}t+C^0 \tag{44}$$

$$\gamma(E')=C^0V_{uv}^{(2)}/(E_u-E')\cdot\left[e^{(2\pi i/h)(E_u-E')t}-1\right]. \tag{45}$$

The initial change in the fractional number of systems in states v is given by integrating the square of (45) over all energies E'. If N_u is the number of systems in state u

$$
\begin{aligned}
-\Delta N_u/N_u &= \int \left| V_{uv}^{(2)} \right|^2/(E_u-E')^2\cdot(2-2\cos\left\{(2\pi/h)(E_u-E')\Delta t\right\}dE' \\
&= 4\int \left| V_{uv}^{(2)} \right|^2/(E_u-E')^2\cdot\sin^2\left\{(\pi/h)(E_u-E')\Delta t\right\}dE'.
\end{aligned}
\tag{46}
$$

If we note that only values of E' near E_u contribute to the integral, and that $V_{uv}^{(2)}$ is a slowly varying function of E' we may write

$$
\begin{aligned}
\Delta N_u/N_u &= -4\left| V_{uv}^{(2)} \right|^2 \int_{-\infty}^{\infty} \frac{\sin^2\left\{\pi/h(E_u-E')\Delta t\right\}\cdot dE'}{(E_u-E')^2} \\
&= -4\pi/h\cdot \left| V_{uv}^{(2)} \right|^2 \Delta t \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}dx \\
&= -(4\pi^2/h)\cdot \left| V_{uv}^{(2)} \right|^2 \Delta t.
\end{aligned}
\tag{47}
$$

In integral form

$$
N_u = N_u^0 e^{-(4\pi^2/h)|V_{uv}^{(2)}|^2 t} \tag{48}
$$

showing the exponential decay characteristic of decomposition processes.

IX. CONCLUSION

The sketchy treatment of this paper is of course not sufficient to establish the theory proposed. It will be necessary to show numerical agreement with experiment. This will be attempted in a more concrete treatment to be published in the Bureau of Standards Journal of Research. Some special experiments which might test the point of view will be mentioned in future papers.

It should be emphasized that the analysis which has been presented applies not only to one-dimensional cases such as those mentioned in this article but, without appreciable change, can be made to describe similar problems from the point of view of electron coupling, or the very important reactions in which two parts of the system interchange positions. The fundamental requirement is simply that a molecular system be capable of existing in physically distinguishable states of equal energy. From this general point of view practically any type of chemical change can be treated in the manner of the present paper. The special problem in each case is to find the perturbing potential which acts on the reactants, making it possible for them to go over into the reaction products. This question will be further discussed elsewhere.