

It is not likely that the effect is due to the impurities rejected by the growing crystal. These might accumulate at a constriction, so lowering the temperature of crystallization, but the amount would vary with the rate of cooling which does not happen in the special case described.

In conclusion, I should particularly like to thank Dr. J. K. Roberts for many discussions and criticisms of this work, and for undertaking the proof-reading of this paper; and also Professor Kapitza for his interest and encouragement throughout.

Dissociation of Excited Diatomic Molecules by External Perturbations.

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1. *Introduction.*—An excited attractive state of a diatomic molecule, in the absence of an external field, is not affected by the crossing of a repulsive state with different symmetry.* An appropriate external field will, however, induce perturbations between the two states.

It is generally recognized that the probability of transition from an attractive

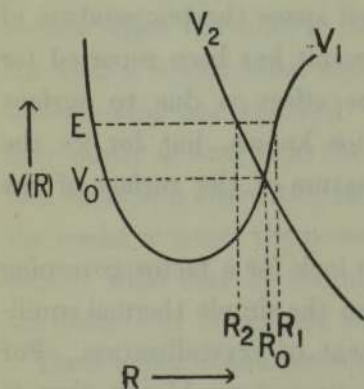


FIG. 1.—Potential energy curves of attractive and repulsive states. $E > V_0$.

to a repulsive state, during one oscillation, will be very small, except when the molecule is in an energy level, E , which is very close to the value of the potential energy at the point of crossing, V_0 . However, even a very small transition probability, per oscillation, may give a high probability that the molecule will dissociate before returning, by radiation, to the normal state. Hence the calculation of these small probabilities is of interest.

In section 2 these calculations are made for $E > V_0$, and in section 3 for $E < V_0$. The calculations are applied to electric and magnetic fields in section 4, and to collisions in section 5.

2. A simplification will be made by considering the internuclear separation R as the only nuclear variable. This neglect of the angular co-ordinates is

* R. Kronig, 'Z. Physik,' vol. 50, p. 357 (1928).

justified since the transition occurs only in the immediate vicinity of the point of crossing, R_0 , and because the rotation of the molecule, while R is in this vicinity, must be quite small. The effect of rotation will be taken into account sufficiently by considering the potential energy curves of the attractive and repulsive states, $V_1(R)$ and $V_2(R)$, as functions of the rotational quantum numbers.

With this simplification, the standard perturbation theory gives the transition probability proportional to the square of the integral

$$J = \int U_1(R) (1|H_1|2) U_2(R) dR. \quad (1)$$

Here $(1|H_1|2)$ is the matrix element of the perturbation H_1 , introduced by the external field, with respect to the attractive and repulsive electronic states; $U_1(R)$, $U_2(R)$ are the vibrational wave functions, with energy E , which belong to the attractive and repulsive states, respectively. When $E > V_0$, the oscillatory portions of U_1 and U_2 overlap. The integrand of (1) is then an oscillating function, and a small error in the wave functions will thus introduce a large error in J .

Landau* has shown how this difficulty may be avoided. His method consists essentially in using the Wentzel-Brillouin-Kramers approximate wave functions for U_1 and U_2 . The oscillatory factor in the integrand of (1) is then given by

$$\cos \left\{ \int_R^{R_1} p_1 dR - \frac{1}{4}\pi \right\} \cos \left\{ \int_{R_2}^R p_2 dR - \frac{1}{4}\pi \right\}.$$

Here R_1 , R_2 are the points of intersection of $V_1(R)$, $V_2(R)$ with E ; and

$$p_k(R) = \frac{2\pi}{h} \sqrt{2m\{E - V_k(R)\}}. \quad (2)$$

Rewriting this factor in the form

$$\frac{1}{2} \cos \left\{ \int_R^{R_1} p_1 dR - \int_{R_2}^R p_2 dR \right\} + \frac{1}{2} \cos \left\{ \int_R^{R_1} p_2 dR + \int_{R_2}^R p_2 dR - \frac{1}{2}\pi \right\},$$

we see that by discarding the second term the rapid oscillations in the region of R_0 may be eliminated. The argument of the first cosine has a minimum at R_0 . Expanding this argument about its minimum, neglecting powers of $(R - R_0)$ higher than the second, neglecting the variation of the other factors $(1|H_1|2)$, $p_1^{\frac{1}{2}}$, $p_2^{\frac{1}{2}}$, and extending the integral to $\pm \infty$, we obtain an approxi-

* 'Phys. Z. Sowjetunion,' vol. 1, p. 88 (1932).

mate value to the integral. This approximation is better the higher E is above V_0 .

Applied to our one dimensional problem, Landau's method gives

$$P_{12} = \frac{4\pi^2 \epsilon_{12}^2}{\hbar v |s_2 - s_2|} \quad (3)$$

as the probability that the change from attractive to repulsive state occurs when R passes once through R_0 . Here ϵ_{12} is the value of $(1|H_1|2)$ at $R = R_0$;

$$\left. \begin{aligned} v &= \sqrt{2(E - V_0)/m} \\ s_k &= \frac{dV_k(R_0)}{dR} \end{aligned} \right\} \quad (4)$$

Since this result has been obtained by a perturbation method, (3) is valid only when $P_{12} \ll 1$. In the other extreme case, when P_{12} is nearly unity, the probability $P = 1 - P_{12}$ may be calculated by a similar perturbation method, with $U_1(R)$, $U_2(R)$ being the wave functions associated with the adiabatic electronic states. Landau* has carried out this calculation, finding

$$P = \exp \left\{ - \frac{4\pi^2 \epsilon_{12}^2}{\hbar v |s_1 - s_2|} \right\}. \quad (5)$$

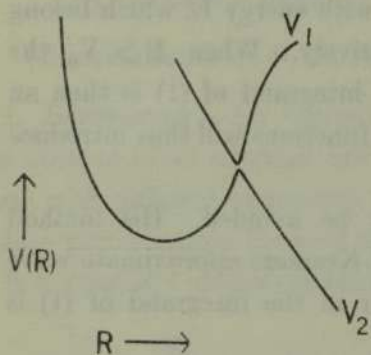


FIG. 2. — Adiabatic potential energy curves with external perturbation present.

The author has treated the same problem from another standpoint.† By introducing the same approximations, constant $(1|H_1|2)$ and velocity in the vicinity of R_0 , not at the end of the calculation, but at the beginning, I was able to reduce the problem to one for which the transition probabilities could be found exactly. I obtained

$$P_{12} = 1 - \exp \left\{ - \frac{4\pi^2 \epsilon_{12}^2}{\hbar v |s_1 - s_2|} \right\}, \quad (3')$$

while P proved to be identical with (5). The expression (3') is valid, subject to the approximations, for all values of P_{12} . It agrees with (3) in the range of validity of the latter.

* 'Phys. Z. Sowjetunion,' vol. 2, p. 46 (1932).

† C. Zener, 'Proc. Roy. Soc.,' A, vol. 137, p. 696 (1932). The apparent discrepancy, mentioned in this reference, between the P derived by Landau and that derived by the author arose through confusing the ordinary \hbar with the Dirac \hbar , which was used by Landau.

The transition probability per oscillation, γ , is equal to twice P_{12} , provided $P_{12} \ll 1$. For then the two methods of dissociation indicated in fig. 3 are independent, and therefore their probabilities are cumulative.

Thus, for small γ ,

$$\gamma = \frac{8\pi^2 \varepsilon_{12}^2}{\hbar \nu |s_1 - s_2|}. \quad (6)$$

3. When the vibrational energy of the molecule is less than V_0 , the usual perturbation methods may be applied, since the integrand of (1) is not oscillatory, as when $E > V_0$, in the region between R_1 and R_2 .

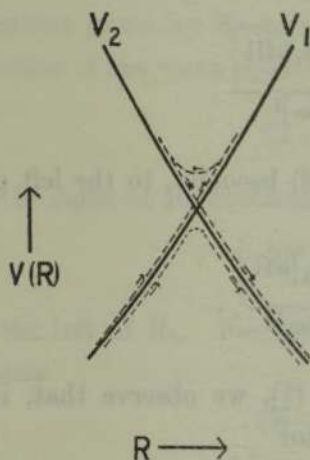


FIG. 3.—Two methods of dissociation. The broken lines indicate the two paths $V(R)$ may follow in dissociation.

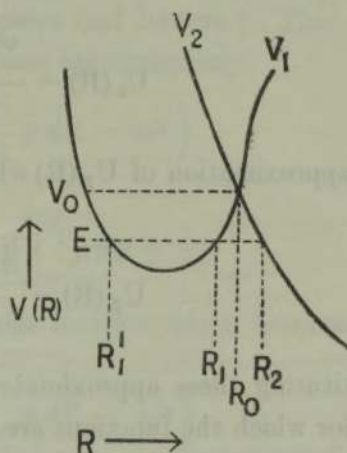


FIG. 4.—Potential energy curves of attractive and repulsive states. $E < V_0$.

The perturbation theory gives the probability of dissociation during one oscillation to be

$$\gamma' = \frac{1}{\nu} \left| \frac{4\pi}{\hbar} \int U_1(R) (1 | H_1 | 2) U_2(R) dR \right|^2. \quad (7)$$

Here ν is the frequency of oscillation; $U_1(R)$ is the normalized wave function of the attractive state, with eigenvalue E ; and $U_2(R)$, the wave function of the repulsive state, with energy E , is so normalized that

$$\lim_{R \rightarrow \infty} U_2(R) = \frac{\cos \left\{ \frac{2\pi}{\hbar} \sqrt{2m [E - V_2(\infty)]} + \delta \right\}}{\{2 [E - V_2(\infty)]/m\}^{\frac{1}{2}}}. \quad (8)$$

Except when E is nearly equal to V_0 , the product $U_1(R) U_2(R)$ is much smaller at R_1 and R_2 than at its maximum value between R_1 and R_2 . We

may thus, except when $E \sim V_0$, calculate γ' directly by means of the Wentzel-Brillouin-Kramers approximate wave functions. In the region between R'_1 and R_1 , exclusive of the immediate vicinity of R'_1 and R_1 , the appropriate approximate function for $U_1(R)$ is

$$U_1(R) = \frac{2v^{\frac{1}{2}} \cos \left\{ \int_R^{R_1} p_1 dR - \frac{1}{4}\pi \right\}}{[2(E - V_1)/m]^{\frac{1}{2}}},$$

with p_1 given by (2). Associated with this function is a flux of magnitude v in each direction. Hence it is properly normalized. To the right of R_1 ,

$$U_1(R) \rightarrow \frac{v^{\frac{1}{2}} \exp \left\{ - \int_{R_1}^R |p_1| dR \right\}}{[2(V_1 - E)/m]^{\frac{1}{2}}}.$$

The approximation of $U_2(R)$ which satisfies (8) becomes, to the left of R_2 ,

$$U_2(R) \rightarrow \frac{\frac{1}{2} \exp \left\{ - \int_R^{R_2} |p_2| dR \right\}}{[2(V_2 - E)/m]^{\frac{1}{2}}}.$$

Substituting these approximate functions in (7), we observe that, in the region for which the functions are valid, the factor

$$Q(R) = \exp \left\{ - \int_{R_1}^R |p_2| dR - \int_R^{R_2} |p_2| dR \right\}$$

varies rapidly in comparison with the other factors. Slight error will thus be introduced by giving these other factors their values at the maximum of $Q(R)$, namely, at R_0 . Since $Q(R)$ has the general shape of a Gauss error curve, we shall expand the exponent of $Q(R)$ about R_0 , and neglect powers of $(R - R_0)$ higher than the second.

The region of integration is then extended to $\pm \infty$. This procedure gives

$$\int_{R_1}^{R_2} Q(R) dR \sim \int_{-\infty}^{\infty} Q(R) dR \sim T^{\frac{1}{2}} \sqrt{\frac{hv}{|s_1 - s_2|}}$$

where

$$T^{\frac{1}{2}} = Q(R_0),$$

and v, s_k are defined by (4).

Substitution of this result in (7) gives finally

$$\gamma' = \frac{4\pi^2 \epsilon_{12}^2}{hv |s_1 - s_2|} T.$$

On comparing this probability with (3), we see that γ' is the product of two probabilities, an electronic transition probability and an atomic transmission probability. For the coefficient of T would be the probability, per crossing, of the electronic transition if E lay above V_0 by the amount it lies below; while T would be the probability of dissociation per oscillation if the molecule had the potential energy

$$V(R) = \begin{cases} V_1(R), & R < R_0 \\ V_2(R), & R > R_0 \end{cases}$$

This well-known interpretation* of T may be most readily derived from the relations given by Kramers and by Kramers and Ittman.† That particular solution of the wave equation which becomes approximately

$$(E - V)^{-\frac{1}{2}} \cos \left(\int_{R_2}^R p \, dR - \pi/4 \right)$$

to the right of R_2 becomes

$$-\frac{1}{2}T^{\frac{1}{2}}(E - V)^{-\frac{1}{2}} \sin \left(\int_R^{R_1} p \, dR - \pi/4 \right)$$

to the left of R_1 . Further, that particular solution which becomes approximately

$$(E - V)^{-\frac{1}{2}} \sin \left(\int_{R_2}^R p \, dR - \pi/4 \right)$$

to the right of R_2 becomes

$$-2T^{-\frac{1}{2}}(E - V)^{-\frac{1}{2}} \cos \left(\int_{R_1}^R p \, dR - \pi/4 \right)$$

to the left of R_1 . Hence corresponding to the approximate solution

$$(E - V)^{-\frac{1}{2}} \exp i \left(\int_{R_2}^R p \, dR - \pi/4 \right)$$

to the right R_2 , we have a solution to the left of R_1 whose dextro-flux is T^{-1} times as great.‡

* G. Gamow, "Constitution of Atomic Nuclei and Radioactivity," Oxford University Press (1932), equation (26), p. 42. Here the factor 4 has arisen through an incorrect joining of the solutions at R_1 and R_2 .

† 'Z. Physik,' vol. 39, p. 828 (1926); vol. 58, p. 222 (1929). These relations have been written in detail by Rice, *ibid.*, vol. 35, p. 1542 (1930).

‡ [Note added in proof, February, 13, 1933.—The calculation of transition probabilities by the above approximate methods is not valid if $|E - V_0|$ is too small. A calculation with exact wave functions shows the results of sections 2 and 3 to be valid provided $2\pi m v |R_1 - R_2|/\hbar > 1$. This condition is satisfied by the applications in the following sections.]

4. The above theoretical considerations will now be applied to various external perturbations. It is of particular interest to know the width, ΔE , of the band of energy levels which are dissociated by a given perturbation.

With an external perturbation which is constant in time, dissociation is probable if the probability of dissociation per oscillation, as given by (6), multiplied by the number of oscillations in the left time of the excited state is comparable to unity.

Let τ and ν be the normal lifetime and the frequency of the excited molecule. We may then define ΔE by the equation

$$\tau\nu\gamma(\Delta E) = 1,$$

where $\gamma(\Delta E)$ is given by (6), with

$$v = \sqrt{2\Delta E/m},$$

m being the reduced mass of the molecule. Solving for ΔE gives

$$\Delta E = \frac{32\pi^4\tau^2\nu^2m\epsilon_{12}^4}{h^2(s_1 - s_2)^2}.$$

In order to see how large ϵ_{12} must be for ΔE to have the order of magnitude of 1 electron volt, put

$$(2\pi\nu)^2 m = \frac{d^2V_1(R_m)}{dR^2}.$$

where R_m is that value of R which makes $V_1(R)$ a minimum. We then see that $(2\pi\nu)^2 m / (s_1 - s_2)^2$ has the magnitude of (electron volt) $^{-1}$. If $\tau = 10^{-8}$ seconds, we find that ϵ_{12} must be about 3.4×10^{-16} ergs for ΔE to be 1 electron volt.

An electric field will induce optically allowed transitions between two crossing states. If E is the magnitude of the electric field in volts cm.^{-1} , $\epsilon_{12} \sim eAE/300$ ergs. Thus E must be about 20,000 if $\Delta E \sim 1$ electron volt.

The component of a magnetic field parallel to the molecular axis will induce transitions between crossing $O^+_u(O^+_g)$ and $O^-_u(O^-_g)$ states. However, unless the lifetime of the excited state is much longer than 10^{-8} seconds, or unless $|s_1 - s_2| \ll$ electron volt/A, the strength of the magnetic field necessary to give appreciable effects will be larger than can be obtained experimentally with convenience. A magnetic field has been found to have a dissociative effect upon the excited O^+_u state of I_2^* which is probably crossed by a repulsive

* Turner, 'Z. Physik,' vol. 65, p. 464 (1930).

O_u^- state.* It is thus likely that this crossing lies to the left of the minimum of the excited state, as such a crossing allows $|s_1 - s_2|$ to be much smaller.

5. Transitions induced by collisions are forbidden by no general selection rule. All collisions may induce even ∇ odd transitions. Changes in multiplicity may occur by an exchange of electrons having opposite spins, provided the perturbing molecule is in a doublet state. Positive \rightarrow negative transitions may occur if the perturbing molecule undergoes a similar transition.

Since we cannot in general assume the collision to last for more than one vibration, we are here interested in the maximum value of $E - V_0$, say ΔE , for which the transition probability per oscillation is large. Defining ΔE by

$$\gamma(\Delta E) = 1,$$

with γ given by (6), we obtain

$$\Delta E = \frac{32\pi^4 m \epsilon_{12}^4}{h^2 (s_1 - s_2)^2}.$$

Giving $|s_1 - s_2|$ the reasonable value of 1 electron volt/A, we finally get

$$\Delta E \sim 1.8 \frac{m}{m_H} \left(\frac{10\epsilon_{12}}{\text{electron volt}} \right)^4 \text{ electron volts.}$$

In a direct collision, ϵ_{12} will be comparable to the relative kinetic energy of the two colliding molecules. Since this is about 0.1 electron volts in a discharge tube, every excited molecule with $E > V_0$ is likely to be dissociated upon its first direct collision, provided it is crossed by an appropriate repulsive state.

Optically allowed transitions between crossing states will be induced by molecules having permanent dipoles. Taking the permanent dipole moment to be $eA/5$ (as in HCl), in order that $\Delta E > 0.1$ electron volt the radius of the collision must not be greater than 5×10^{-8} cm.

6. *Summary.*—The theory of inducing transitions by external perturbations between crossing attractive and repulsive states of different symmetry has been discussed. The theoretical results are of particular interest when the vibrational energy of the molecule is less than the potential energy at the

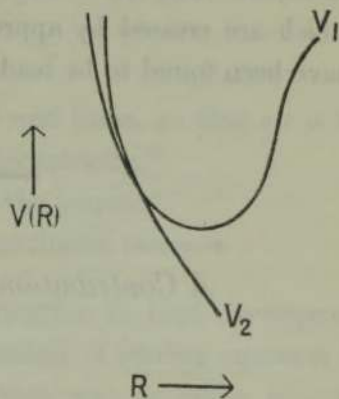


FIG. 5. — Potential energy curves of attractive and repulsive states. Point of crossing is to left of minimum.

* Mulliken, 'Rev. Mod. Phys.', vol. 4, p. 17 (1932).

point of crossing. The transition probability is then equal to the product of an electronic transition probability and the probability that the nuclei pass through a potential barrier.

Applications have been discussed. It has been found that electric fields of 20,000 volts cm.⁻¹ have a marked dissociative effect upon excited states which are crossed by appropriate repulsive states. All types of transitions have been found to be readily induced by collisions.

A Contribution to the Theory of Film Lubrication.

By A. M. ROBB.

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The fundamental equation of the Reynolds' theory of film lubrication is

$$\frac{dp}{dx} = \lambda \frac{d^2w}{dy^2}, \quad (1)$$

where

p is the pressure.

λ is the coefficient of viscosity.

w is the velocity of the lubricant at any point between the surfaces.

x is measured in the direction of motion.

y is measured perpendicular to the direction of motion.

This equation can be transformed into

$$\frac{dp}{dx} = 6\lambda u \frac{(h - h^1)}{h^3}, \quad (2)$$

where

u is the velocity of the moving surface.

h is the distance between the surfaces at any point other than that corresponding to

h^1 , which is the distance between the surfaces at the section where the pressure is maximum or minimum. The case of minimum pressure is, however, rejected from the immediate consideration.

For the particular case of the journal bearing, in which the distance between fixed and moving surfaces depends on the mean "play," or clearance, between