Nonadiabatic Reactions. Chemiluminescence

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activation energy >6 kcal. and (6) >4.8 kcal., indicating that reaction between H (or D) and DCl (or HCl) tends to produce HD and Cl rather than HCl (or DCl) and D (or H).

Of the large number of possible mechanisms for the exchange reaction between HCl and D_2, all of which are of nearly the same order of importance, the results reported here appear to favor chains of reactions (3) and (4) as having the greatest influence on the kinetics of the photochemical exchange under the experimental conditions employed. Similarly, for $DCl+H_2$ mixtures, chains of (3r) and (4r) are indicated. Before these conclusions can be taken as final there are factors which may require further study. These include the effect of wall reactions, the effect of variations in the rates of the chain terminating reactions, the possible difference in the efficiency of HCl and D_2 as third bodies in the atomic recombinations, and the possibility that the activation energies may be in error by an amount sufficient to alter the conclusions drawn from their relative magnitudes. Also, the entire treatment

has assumed sufficient diffusion to insure that the local and over-all rates are the same.

At the photostationary state the forward and reverse reactions given above, together with the reactions of the H, D, and Cl atoms with HD molecules, reach a state of balance in which the differences in rates should result in the attainment of thermal equilibrium proportions. Actually the photostationary states are displaced in the direction of higher hydrogen content in the D_2+HD+H_2 mixture than that corresponding to thermal equilibrium (Table II). Although it is uncertain just what significance should be attached to this difference, it probably arises from a stronger absorption by HCl than by DCl in the region 2000–2150A, which is to be expected from the lower zero point energy of DCl. A difference of about 10 percent in the absorption of the zinc lines by HCl and DCl should be sufficient to produce the observed shift of the equilibrium.

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It is pointed out that chemiluminescent reactions are necessarily nonadiabatic, since emission of radiation can only occur by transition from an upper to a lower potential energy surface. The restriction imposed by the second law of thermodynamics on the photon yield is,

$$\varphi \leqslant \Delta F/E,$$

where φ is the ratio of quanta evolved to molecules reacted, ΔF is the free energy decrease in the reaction, and E is the energy of the photon emitted. Upper potential energy surfaces are reached either by activation by radiation, which may be that of a black body at the temperature of the reaction, or by the "crossing" of potential energy surfaces. From Audubert's data on the radiation produced by the thermal decomposition of sodium azide approximate surfaces which account for the observations are constructed.

INTRODUCTION

THE purpose of the present paper is to treat chemiluminescence as a particular example of the general theory of chemical reactions. A general survey of the field is given along with sufficient examples to illustrate the point of view and the method of treatment.

Chemiluminescent reactions are noteworthy because of the wide variation of the ratio of the number of quanta evolved to the number of molecules reacted. Thus reactions are found experimentally with photon yields ranging from about 0.3 to 10^{-15}. The upper limit of 0.3 for the photon yield is reported for the reaction of sodium

vapor with chlorine, a type of reaction studied by Polanyi and his co-workers.[1] An intermediate value for the yield has been observed by Harris and Parker[2] for the oxidation of 3-aminophthal-hydrazide, while reactions with very low photon yields have been studied by Audubert and his associates.[3] Those with the very high photon yields are plainly visible to the unaided eye, while the rather elaborate and sensitive photon counters employed by Audubert and his associates must be employed to detect the radiation emitted by those with very low yields. There is no apparent reason why reactions with photon yields anywhere between zero and one should not be found, subject to the thermodynamic restriction discussed below.

EFFICIENCY OF RADIATIONLESS TRANSITIONS AND THE SECOND LAW OF THERMODYNAMICS

In this section are discussed certain thermodynamic restrictions applying to the efficiency with which normal or excited atoms or molecules can be further excited by ordinary thermal collision processes. Consider a mole of mercury atoms in the metastable 6^3P_0 state dispersed in a foreign gas. Then the energy, E_1 per mole, corresponding to the transition from the excited state, 6^3P_0, to the normal state, 6^1S_0, is almost exactly equal to the free energy difference between the two states. This is true because if the energy of excitation were emitted, the work which it could be made to do would simply be equal to the energy difference between the two levels. Now suppose that a number, N_1, of the excited mercury atoms are raised by thermal collision from the state, 6^3P_0, to the still higher state, 6^3P_1, where their energy referred to the ground state is E_2. In such a process an amount of energy, $N_1(E_2-E_1)/N$, is converted from the thermal energy of the molecules of the inert gas to the free energy of excitation of the mercury. Clearly this increase in free energy for part of

the atoms must be balanced by a decrease, at least equal in amount, caused by radiationless transitions from the first excited to the ground state of the mercury atoms. The decrease in free energy, caused by N_2 such transitions, is given by, $N_2(E_1/N)$, and we have the inequality,

$$\frac{N_1(E_2-E_1)}{N} \lessgtr \frac{N_2 E_1}{N}. \tag{1}$$

Since N_1 plus N_2 equals N, this leads to the relations,

$$\frac{N_1}{N} \lessgtr \frac{E_1}{E_2} \quad \text{and} \quad \frac{N_2}{N} \gtrless \frac{(E_2-E_1)}{E_2}. \tag{2}$$

Thus we see that the second law of thermodynamics places an upper limit on the efficiency of excitation by radiationless transitions, and it follows that the number of quanta of energy, E_2/N, that can be emitted is restricted in the same way. In reactions of this kind which do not involve the formation of a new kind of molecule no concentration terms should be included in the free energy expression since normal and excited atoms or molecules cannot be regarded as separate components. If they could be, then energy rich molecules could conceivably be separated from those of low energy by a membrane permeable to only one of the species. Such a membrane, however, would be an example of Maxwell's demon.

The above example is a special case of the more general law,

$$(N_1/N) \lessgtr (\Delta F/E), \tag{3}$$

where ΔF is the decrease in free energy in any chemiluminescent reaction, E is the energy per Einstein of the quanta which are emitted, and N_1/N is the photon yield. It may be seen from (3) that in those cases where $\Delta F > E$ these thermodynamic considerations place no restriction on the quantum yield.

The ΔF of Eq. (3) is the decrease in free energy that actually takes place in the reaction vessel; i e., it includes a term for the free energy of mixing. Thus, even if the equilibrium constant is unity, and consequently the free energy difference of the *pure* products and reactants is

[1] Beutler and Polanyi, Zeits. f. Physik **47**, 379 (1928); Zeits. f. physik. Chemie, **B1**, 3 (1928). Bogdandy and Polanyi, Zeits. f. physik. Chemie **B1**, 3 (1928). Polanyi and Schay, ibid. **B1**, 30 (1928).

[2] Louis Harris and Almon S. Parker, J. Am. Chem. Soc. **57**, 1939 (1935).

[3] See, for example, R. Audubert, J. Chim. Phys. **33**, 507 (1936).

zero, there is still a free energy decrease in the reaction due to the mixing of reactants and products. As an example let us consider the problem of how much radiation can be evolved if a mole of A reacts to form $\frac{1}{2}$ mole of its optical isomer, B, in ideal solution with A. Here the equilibrium constant is certainly unity and the free energy change is due entirely to the entropy of mixing. This is equal to $R \ln 2$, which corresponds to a free energy decrease of 0.415 kcal. at 300°K. The maximum photon yield from such a reaction is found by application of Eq. (3) to be about 1 percent for a wave-length of 6900A and correspondingly different for other wave-lengths. Since actual reactions in general have much larger free energy decreases, as well as photon yields much below this value, it is obvious that the restriction imposed by Eq. (3) will rarely, if ever, be the factor limiting the yield. When pure A first forms B the free energy decrease per molecule is extremely large so that initially there is no thermodynamic restriction on the quantum yield. As the concentration of B approaches equality with that of A the thermodynamically allowed φ drops to zero. Our definition has been couched in terms of the over-all ΔF and φ.

The question has sometimes been asked whether or not it is possible for an endothermal reaction to be chemiluminescent. The answer given here is that if the reaction is spontaneous, i.e., if it involves a free energy decrease, then it can be chemiluminescent with a maximum photon yield given by Eq. (3). How nearly this maximum efficiency is approached is purely a question of mechanism and can only be solved by reaction rate theory.

ACTIVATION BY BLACK-BODY RADIATION

Since chemiluminescent reactions must necessarily involve the transition of molecules from upper to lower potential energy surfaces, the theory of these reactions must provide some mechanism for reaching an upper level. One such possible mechanism is activation by means of absorption of black-body radiation originally proposed by Perrin and W. C. McC. Lewis as the mechanism for the activation of molecules
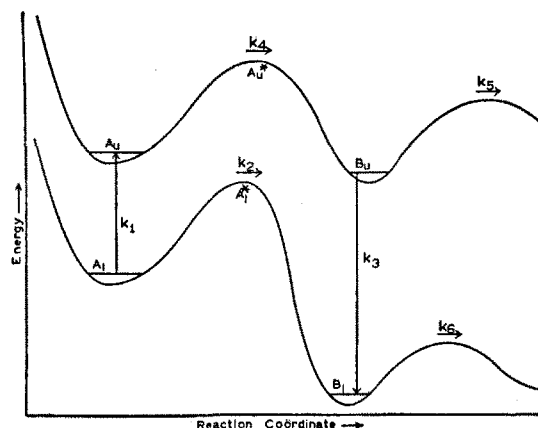

FIG. 1. Schematic energy diagram on which a chemiluminescent reaction could take place by means of activation by black-body radiation.

undergoing ordinary chemical reactions. There is abundant evidence showing that the reaction rates via this mechanism are ordinarily slower by a factor of about 10^5 than the rates resulting from activation by thermal collision when the activation energies are the same. However, activation by black-body radiation may be of importance in chemiluminescent reactions.

Figure 1 illustrates a potential energy surface on which it would be possible for a chemiluminescent reaction to take place by means of the black-body mechanism of activation.

Here A_l (lower) and A_u (upper) refer to the species that are reacting in the normal and excited states respectively; B_l and B_u have the same significance for the products of reaction. A_l^* and A_u^* indicate the activated molecules for the lower and upper surfaces respectively. When enclosed in parentheses, these symbols refer to concentrations. The k's indicate the specific reaction rate constant for a process proceeding in the direction indicated by the arrow. When the reaction rate constants refer to directions opposite to that indicated by the arrow, they will be primed.

At equilibrium between A_u and A_l, the rates in the two directions will be the same and a discussion applying to k_1' will be applicable to k_1. An expression for k_1' can be written in terms of the Einstein coefficient for spontaneous transition, $\mathbf{A}_{ul}$, from the upper state corresponding to

A_u, to the lower state, A_l. We have[4]

$$k_1' = \sum_u \sum_l \left\{ \omega_u \frac{\mathbf{A}_{ul}}{1 - \exp(-h\nu_{ul}/kT)} \right.$$

$$\left. \times \exp(-\epsilon_u/kT) \right\} \left\{ \sum_u \omega_u \exp(-\epsilon_u/kT) \right\}^{-1}. \quad (4)$$

Here ω_u is the usual statistical weight, ν_{ul} is the frequency of the emitted radiation, and ϵ_u is the energy in the excited state referred for convenience to the lowest state of the normal molecule, A_l. If the radiation density is equal to that of a black body at the temperature of the reaction, the states u and l will be in equilibrium and we have the relation,

Equilibrium constant

$$\frac{k_1'}{k_1} = \frac{\sum_l \omega_l \exp(-\epsilon_l/kT)}{\sum_u \omega_u \exp(-\epsilon_u/kT)}. \quad (5)$$

Equations (4) and (5) may be combined to give an expression for k_1.

$$k_1 = \sum_u \sum_l \left\{ \omega_u \frac{\mathbf{A}_{ul}}{1 - \exp(h\nu_{ul}/kT)} \exp(-\epsilon_u/kT) \right\}$$

$$\times \left\{ \sum_l \omega_l \exp(-\epsilon_l/kT) \right\}^{-1}. \quad (6)$$

The expressions for k_4' and k_4 are identical with those for k_1' and k_1 except that in this case the summations are made over the energy levels of B_u and B_l, respectively.

Since expressions (4) and (6) represent the total transition probability between states we expect that a satisfactory approximate expression can be secured by taking a transition probability averaged over all states, and an averaged energy of activation secured in the same way. This gives for the rate expression,

$$k_1 = (1/\tau) \exp(-E/kT). \quad (7)$$

Here $1/\tau$ and E are interpreted as being the reciprocal mean lifetime and energy difference

[4] See for example, Condon and Shortley, *The Theory of Atomic Spectra*, (Cambridge Press, 1935), Chap. IV, or Tolman, *Statistical Mechanics with Applications to Physics and Chemistry* (Chemical Catalog Co., 1927), Chaps. 16 and 21.

between the two states, respectively, and the difference in entropy between the upper and lower states has been neglected. When sufficient information is available the exact expression (6) will be used. For many atomic transitions, $1/\tau$ is of the order of 10^8 and is probably not greatly different for transitions in molecules. For forbidden transitions it may drop to values as small as 10^{-2}.[5]

We now go on to develop a general theory of chemiluminescent reactions involving as one step the transition from a lower to an upper level by means of black-body radiation. This can be done conveniently by referring to the schematic energy diagram in Fig. 1. When there is not too much difference between the free energy of the activated complex, $A_u{}^*$ on the upper surface and $A_l{}^*$ on the lower surface, an appreciable fraction of the reaction will proceed by way of the upper surface and will therefore emit radiation in the transition, $B_u \to B_l$. At equilibrium this will just be balanced by the absorption $B_l \to B_u$, but in a system containing more than the equilibrium amount of reactant, A_l, more energy of this wave-length will in general be emitted than absorbed.

As an example we set up the rate and photon yield expressions for the particular case where all the reactions are first order with respect to the substances indicated in Fig. 1. Any dependence on other substances is implicitly included in the k's. We can write in the usual way.

$$d(A_u)/dt = k_1(A_l) + k_4'(B_u) - (A_u)(k_1' + k_4) = 0, \quad (8)$$

$$d(B_u)/dt = k_4(A_u) - (B_u)(k_4' + k_5 + k_3) = 0. \quad (9)$$

Here the processes with specific rate constants, k_3' and k_5' have been neglected. Combining Eqs. (8) and (9) so as to eliminate (A_u) we have,

$$(B_u) = \frac{k_4 k_1 (A_l)}{(k_1' + k_4)(k_4' + k_5 + k_3) - k_4 k_4'}. \quad (10)$$

Then if dN/dt is the rate of emission of light we have,

$$\frac{dN}{dt} = \frac{k_3 k_4 k_1 (A_l)}{(k_1' + k_4)(k_4' + k_5 + k_3) - k_4 k_4'} \quad (11)$$

[5] Condon and Shortley, reference 4, p. 282.
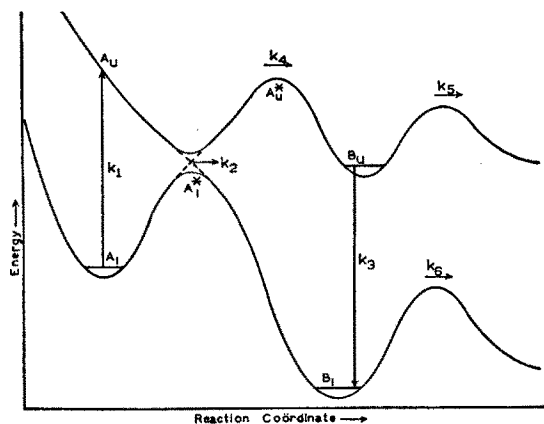
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FIG. 2. Schematic energy diagram illustrating the "crossing" mechanism of activation. The separation of the two surfaces at the point corresponding to A_l^* is exaggerated.

and for the photon yield, φ, we obtain,

$$= \frac{(dN/dt)}{-d(A_l)/dt}$$

$$= \frac{k_3}{k_3 + k_5 + \dfrac{k_2[(k_1'+k_4)(k_4'+k_5+k_3) - k_4 k_4']}{k_1 k_4}} \quad (12)$$

if we note that $d(A_l)/dt$ is given by

$$-d(A_l)/dt = dN/dt + k_5(B_u) + k_2(A_l). \quad (13)$$

We will consider three limiting cases for the rate dN/dt, in each case neglecting the quenching process involving k_5.

Case I.—When the rate determining step is the transition $A_l \rightarrow A_u$ then $k_1' \ll k_4$ and

$$\varphi = k_1/(k_1 + k_2). \quad (14)$$

Case II.—When the rate determining step is the transformation $A_u \rightarrow B_u$ then $k_4 \ll k_1'$, $k_4' \ll k_3$ and,

$$\varphi = \frac{k_4(k_1/k_1')}{k_4(k_1/k_1') + k_2}. \quad (15)$$

Case III.—Finally, when the rate determining step is the transition $B_u \rightarrow B_l$ then $k_3 \ll k_4'$ and

$$\varphi = \frac{k_3(k_1 k_4/k_1' k_4')}{k_3(k_1 k_4/k_1' k_4') + k_2}. \quad (16)$$

The quantities in parentheses in Eqs. (15) and

(16) are equilibrium constants between upper and lower levels.

From Fig. 1 it may be seen that a photon yield approaching the thermodynamically allowable maximum given by Eq. (3) is not to be expected unless the upper surface at the point marked A_u^* approaches close to the lower surface. For higher temperatures where the rate corresponding to k_1 is the slow step, a high yield will be obtained if the energy difference between A_u and A_l is very small.

ACTIVATION WITHOUT BLACK-BODY RADIATION

In this case chemiluminescence will arise because of the nonadiabatic "crossing" of energy levels. This is illustrated in the schematic diagram (Fig. 2).

The essential difference between Figs. 1 and 2 is that in the latter case the two potential surfaces come very close together and to a first approximation they may be said to cross making possible a nonadiabatic jump of the system from the lower to the upper surface without absorbing radiation. The approximate expression for the probability of this process happening has been given by Zener[6] and by Landau[7] and the expression has been applied in a treatment of the nonadiabatic decomposition of N_2O.[8] This expression is

$$P = \exp\left\{\frac{-4\pi^2 \varepsilon_{12}^2}{hV|s_1 - s_2|}\right\}. \quad (17)$$

Here $|s_1 - s_2|$ is the absolute difference in slope between the two dotted lines in Fig. 2 while $2\varepsilon_{12}$ is the difference in energy between the upper and lower surfaces at the activated point corresponding to the species, A_l^*. V is the velocity along the reaction coordinate at this point.

The transmission coefficient,[9] κ, may be related to P in the following way. If, of the number of molecules that reach the activated point corresponding to A_l^*, a fraction P jump to the upper surface, then $1 - P$ will be the fraction that remains on the lower surface. Those on the

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[6] C. Zener, Proc. Roy. Soc. **A137**, 696, (1932); **A140**, 660 (1933).
[7] Landau, Physik. Zeits. Sowjetunion **2**, 46 (1932).
[8] A. E. Stearn and H. Eyring, J. Chem. Phys. **3**, 778 (1935).
[9] H. Eyring, J. Chem. Phys. **3**, 10[7] (1935).

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upper surface may return to the lower surface in two ways, one corresponding to reaction and the other corresponding to a return to the initial configuration, A_l. κ, the probability that the system will react after having once reached the activated configuration, is given by,

$$= 1 - P + P^2[(1-P) + (1-P)^3$$
$$+ (1-P)^5 + \cdots] = 2(1-P)/2 - P, \quad (18)$$

which reduces to $2 - 2P$ when P is almost equal to unity. Further, when this is the case, the exponential in Eq. (17) may be expanded and the higher powers of $(4\pi^2\epsilon_{12}^2)/(hV|s_1 - s_2|)$ dropped so that we have as an approximate expression for κ,

$$\kappa = (8\pi^2\epsilon_{12}^2)/(hV|s_1 - s_2|), \quad (19)$$

which is valid for values of P that are not too far from unity.

One other possible mechanism for reaching the upper surface is that corresponding to the transition with the specific rate constant, k_1. This will in general, however, not be of importance for the case of activation by black-body radiation unless the upper surface comes very close to the lower one at a point directly above the one corresponding to A_l on the lower surface. However, if activation is brought about by illuminating the system with radiation of the proper wave-length this mechanism for reaching the upper surface may become the important one. This would be a case of photoreaction which might be accompanied by fluorescence. The general considerations discussed above also apply in this case.

Considering now the rate determining step for the luminescent reaction we see that it can be either the process with specific rate constant, k_4, or the one with specific rate constant, k_3. When the mean life of B_u is of the order of 10^{-8} sec., then the rate corresponding to k_4 will be the slow step if the energy of activation for k_4' is less than about $23T$ cal. or 6900 cal. at room temperature. For energies of activation greater than $23T$ cal., k_3 will become the slow process. These approximate computations neglect any difference in entropy between B_u and A_u^*.

There is, however, an important group of reactions which involve the possibility of emitting radiation, but where the mean life of the excited

molecules may be of the order of minutes. This is the case for those instances where the "crossing" of potential energy surfaces is due to a change in multiplicity. The general expression for the Einstein transition probability $\mathbf{A}(a, b)$ between level a and b can be written as the sum of three terms, i.e., one for the electric dipole, one for the magnetic dipole and one for the quadrupole radiation, respectively. The transition probability can be written in the form :[10]

$$\mathbf{A}(a, b) = (64\pi^4\sigma^3/3h)[|(a|\mathbf{P}|b)|^2$$
$$+ |(a|\mathbf{M}|b)|^2 + (3/10)\pi^2\sigma^2|(a|\mathbf{N}|b)|^2].$$

Here σ is the wave number of the emitted radiation;

$$\mathbf{P} = -e\sum_i \mathbf{r}_i; \quad \mathbf{M} = -(e/2\mu c_i)\sum_i (\mathbf{L}_i + 2\mathbf{S}_i);$$

$$\mathbf{N} = -e\sum_i \mathbf{r}_i\mathbf{r}_i;$$

where e is the charge on the ith electron whose vector distance is $\mathbf{r}_i$; μ is the mass of the electron; $\mathbf{L}_i$ the orbital angular momentum, and $\mathbf{S}_i$ the spin angular momentum. For forbidden lines $|(a|\mathbf{P}|b)|$ equals zero due to a change in multiplicity and $\mathbf{A}(a, b)$ instead of being about 10^8 is much smaller. For example the interpretation of the nebular lines of $OIII$ as given by Condon[11] leads to an Einstein transition probability of $\mathbf{A} = 0.018$ sec.$^{-1}$ for the $D_2 \rightarrow 3P_2$ transition and an $\mathbf{A} = 0.006$ for the transition $D_2 \rightarrow 3P_1$. The transition probabilities for quadrupole radiation are found to be about 1000 times smaller. For transitions involving a change in multiplicity the magnetic dipole transition probabilities are known to be proportional to $(\epsilon_{12}/(E_1 - E_2))^2$ where ϵ_{12} is the spin orbital interaction between the upper and lower state and $E_1 - E_2$ is the energy emitted in the transition. Now this ϵ_{12} is formally the same as the ϵ_{12} occurring as a factor in the transmission coefficient for k_2 discussed above. The difference in the two ϵ_{12}'s is that they are the spin orbital interactions calculated for different configurations but an examination of multiplet widths (which enables one to calculate ϵ_{12} for atoms)[12] indicates that the value for ϵ_{12}

[10] Condon and Shortley, reference 4, p. 90 etc.
[11] Condon, Astrophys. J. **79**, 217 (1934). Condon and Shortley, reference 4, p. 282.
[12] See Condon and Shortley, reference 4, p. 268.

often changes only slightly when an atom becomes a part of a diatomic hydride molecule. There are notable exceptions to this rule among nonhydride molecules.[13] Thus for forbidden magnetic dipole transitions of $B_u \rightarrow B_l$ we expect $(\kappa_2(kT/h))$ often to be proportional to $1/\tau_3$, the former being about 10^{10} times the latter. Thus if k_3 is to be of the same order as k_2 we must then have $(E_1 - E_2)/RT \approx 10^{10}$; or $E_1 - E_2 \approx 46T$ cal., i.e., if the reactions are to proceed at about the same rate at room temperature then the energy of B_u should be about 14 kcal. lower than $A_l{}^*$. From this one sees that there are types of "crossing" potential surfaces which can lead to high photon yields even when the emission process involves a change of multiplicity and is consequently forbidden in the electric dipole approximation. For "crossing" potential surfaces which, however, do not involve forbidden transitions for $B_u \rightarrow B_l(\kappa_2(kT/h))$ will probably be more nearly 10^5 than 10^{10} times $1/\tau_3$. This case has already been discussed.

The quenching of radiation can in general be expected to proceed by reaction over the potential hills marked k_5 in Figs. 1 and 2. If this is the case the amount of quenching for a given activation energy can be expected to be proportional to the mean life of B_u. Quenching can thus be expected to be a much more important factor for cases involving forbidden transitions than for other instances where the mean lifetimes are very short.

In Fig. 2 a particular manner of "crossing" of the two surfaces is shown. Clearly the photon yield for radiation will be higher the higher the activation energy hill for the nonluminescent reaction is in comparison to the luminescent one. If, instead of "crossing" before the system reaches the activation hill, $A_l{}^*$, the "crossing" occurs afterwards, the chemiluminescent efficiency should approach the thermodynamic maximum. In this case there would be no difference in activation energy for the luminescent and nonluminescent reactions, and the entire difference in rate would arise from the difference in the transmission coefficients for the two alternative processes.

It is of some interest to note that the thermodynamic considerations discussed in Section II

place a lower limit on the transmission coefficient corresponding to the reaction rate constant, k_2 of Fig. 2. Thus, κ cannot become so small that the condition imposed by Eq. (3) will be violated.

CHEMILUMINESCENT REACTIONS OF METALLIC AZIDES

As an example of the interpretation of data that may be obtained, we consider a series of chemiluminescent reactions studied by Audubert,[14] the decomposition of metallic azides. It appears likely that the potential energy surface for these reactions is similar to that given in Fig. 1, although a surface of the type illustrated by Fig. 2 is not entirely precluded. However, evidence will be presented tending to show that if the luminescent reaction proceeds by way of "crossing" of potential energy surfaces, the crossing cannot be due to a change of multiplicity.

Audubert finds that the azides of silver, lead, sodium and potassium all emit radiation lying in the neighborhood of 2000A, about 140 kcal. per mole. This we interpret as corresponding to the transition, B_u to B_l of Figs. 1 or 2, and the fact that all the different azides emit light of about the same frequency seems to indicate that the same molecule is radiating in all cases.

The decomposition of NaN_3 furnishes an example of what might be expected to be a fairly common phenomenon, a chemiluminescent reaction in which the activation energy for photon emission show two quite different values. The rate determining step at low temperatures is due to the reaction, $A_l \rightarrow B_u$, proceeding with an activation energy of about 48 kcal. The activation energy of 23 kcal. given in column four of Table I may be either that for the reaction of B_u going to B_l shown in Figs. 1 or 2 or that for the transition, A_l to A_u, of Fig. 1. However, the following consideration will throw some light on the question. If the mechanism for the reaction is that illustrated by Fig. 2, then the "crossing" of the two surfaces cannot be due to change of multiplicity. For transitions involving change of multiplicity the value of τ in Eq. (7) is greater by a factor of about 10^{10} than for other transitions which are not forbidden. But the temperature at which the two rates corresponding

[13] See R. S. Mulliken, Rev. Mod. Phys. **4**, 37 (1932).

[14] Audubert, J. Chem. Physique **34**, 29 (1937).

to the two activation energies become equal is the point at which the two straight lines obtained by plotting ln k against $1/T$ intersect. By referring to Fig. 3 of Audubert's paper this temperature is found to be 640°K for the case of NaN_3. We can then set up the equation,

$$\frac{kT}{h}\exp\left(\frac{-48\pm2\text{ kcal.}}{RT}\right)=\frac{1}{\tau}\exp\left(\frac{-23\pm2\text{ kcal.}}{RT}\right)$$

and solve for τ. For this case we get values for τ of approximately 3×10^{-10} and 10^{-13} sec. for upper and lower limits, respectively. These values are even smaller than the value of about 10^{-8} sec. that would be expected for most allowed transitions, and are *very* much smaller than would be expected for transitions involving change of multiplicity. We accordingly draw the conclusion that if the potential energy surface for the decomposition of the azides is similar to that illustrated in Fig. 2, the "crossing" does not involve a change in multiplicity.

It is not possible to decide from the evidence at hand whether the process with the activation energy of 23 kcal. corresponds to the reaction of B_u going to B_l of Figs. 1 and 2 or to the reaction of A_l going to A_u of Fig. 1. This point could, however, be decided experimentally by increasing the density of radiation at the wave-length corresponding to 23 kcal., about 12,000A. This would speed up the transition A_l to A_u, but would alter the velocity of B_u going to B_l by only a negligible amount.

In confirmation of our suggestion that the

decomposition reactions of the azides all proceed by the same mechanism, it will be noted that the activation energies for the reaction A_l going to B_u are the same for the three cases recorded in Table I. Likewise the activation energies for the other step in the luminescent reaction are essentially the same for the two cases recorded. It appears probable that if the decomposition reaction of $Pb(N_3)_2$ could be followed to a low enough temperature an activation energy for the reaction of A_l going to B_u would be found. Conversely, if the decomposition reactions of AgN_3 and KN_3 could be studied at high enough temperatures another activation energy should be found with the value of about 25 kcal.

We now attempt to construct as complete a potential energy surface for the decomposition of NaN_3 as is possible by using the data at hand. A possible surface that accounts for most of the facts is shown in Fig. 3.

The amount of free energy, 26 ± 2 kcal./mole, by which the maximum of the upper curve lies above the maximum point of the lower one is obtained from Audubert's value of the photon yield. He states that the order of magnitude of this quantity is 10^{-9} to 10^{-10} for the azides which leads to the equation:

$$\exp -(\Delta F_4\ddagger-\Delta F_2\ddagger)/RT=10^{-9}\text{ to }10^{-10},$$

$$\Delta F_4\ddagger=\Delta F_2\ddagger+26\pm2\text{ kcal./mole.}$$

To the approximation to which we can neglect $T(\Delta S_4\ddagger-\Delta S_2\ddagger)$ this is also the difference in energy of activation for the two reactions.

The difference in energy between the $A_l{}^*$ and $A_u{}^*$ can be obtained by a second method. This energy difference is found to be $(48\pm2)-34=14\pm2$ kcal./mole from the temperature coefficient of the photon yield. The disagreement indicates either that the value of about 10^{-9} for the photon yield is too low, or that it is not a good approximation to neglect the difference in entropy between the activated complexes on the lower and upper surfaces.

The emission of radiation of a frequency corresponding to an energy of 140 kcal. per Einstein presents an interesting problem. The energy difference between A_l and B_u according to the data cannot be greater than about 23 kcal., and may be less than this depending on whether the

TABLE I.

SUB-STANCE	HEAT OF REACTION[15a]	ENERGIES OF ACTIVATION FOR THE REACTIONS, (See Fig. 1 or 2)		
		k_2 $A_l\rightarrow B_l$[15b]	k_1 $A_l\rightarrow A_u$[15c] or k_3 $B_u\rightarrow B_l$	k_4 $A_l\rightarrow B_u$[15c]
AgN_3	$-$ 67.3 kcal.			47 ± 1 kcal.
$Pb(N_3)_2$	$-$103.0	38 kcal.	25 ± 1 kcal.	
NaN_3	$-$ 5.0(?)	34.4	23 ± 2	48 ± 2
KN_3	$-$ 0.5(?)	36.1		48 ± 2

15a Data quoted by Audubert. For AgN_3 and $Pb(N_3)_2$ the reference to the original work is, Wöhler and Martin, Zeits. ges. Schiess Sprengstoffen, 12, 1 (1918). For the alkali azides Audubert gives no reference and we have been unable to find one.
15b Garner and Mark, J. Chem. Soc. 657 (1936).
15c Audubert apparently omitted the factor of 2.3 in calculating his activation energies from the slope of the curves in which log₁₀ k is plotted against $1/T$.

transition A_l to A_u or B_u to B_l is the slow process. Audubert quotes the figure 5 kcal./mole for the heat emitted during the decomposition of NaN_3 into solid sodium and gaseous nitrogen. If this figure is correct and if there is no energy difference between the stable final product and the product obtained immediately after emission of the photon, then 23 molecules of NaN_3 would each have to contribute their energy of reaction in order to build up an excited molecule capable of emitting a photon of the required energy. On the other hand, this difficulty is not encountered in the case of AgN_3 and $Pb(N_3)_2$. In these cases it is only necessary to assume that two azide groups are involved in the steps leading to the emission of each photon in order to have sufficient energy available.

Since all the reactions proceed with about the same quantum yield it does not appear to be probable that the luminescent reaction for the azides of silver and lead involve only two azide radicals per quantum emitted while the same reaction for the azides of the alkali metals involves twenty molecules or more. What appears to us to be more probable is that the quoted values for the heats of decomposition of the alkali azides are incorrect.

The work of Sklar[15] on the theory of color of organic compounds makes it possible to offer a tentative suggestion concerning a possible structure of the excited molecule that emits the quanta of wave-length 2000A. Sklar expresses the energy levels corresponding to the absorption of light of different frequencies in terms of the resonance energy of the benzene molecule. He finds the first strong absorption band to be at a wave-length of about 2000A, just the same wave-length as the light that is emitted during the decomposition of the azides. This fact, along with the observation that in the case of the azides of lead and silver the energy of two azide radicals is necessary to furnish the energy emitted in one photon, leads us to suggest that a cyclic nitrogen compound with six nitrogen atoms arranged in a ring may be the molecule emitting the radiation. Although the total energy difference between cyclic N_6 and $3N_2$ must be very much less than that between C_6H_6 and $3C_2H_2$, it is not unreasonable to assume that the reso-

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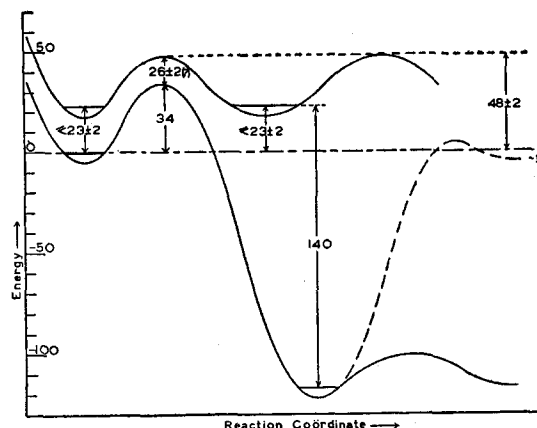[15] Alfred L. Sklar, J. Chem. Phys. **5**, 669 (1937).

FIG. 3. Schematic energy diagram for the chemiluminescent decomposition of sodium azide. The energy units are kcal./mole. A surface similar to Fig. 2 is not completely excluded.

nance energy of the cyclic N_6 would be about the same as that of benzene. If this were the case the absorption bands according to Sklar's theory would be expected to be about the same.

It should be pointed out that the energy of the reacting system immediately after emitting a photon is not necessarily greater than the energy of the final products. This, of course, is not true of the free energy which must be lower for the stable products than for any intermediates. In this connection it may be pointed out that if the value of 5 kcal. for the heat of decomposition of NaN_3 is accepted and if the cyclic N_6 molecule is the immediate product after the radiation is emitted, then the N_6 molecule would be expected to be thermodynamically stable up to about 1300°K. This estimate is based on the assumption that the difference between the entropy of N_6 and $3N_2$ is about the same as the difference in entropy between C_6H_6 and C_2H_2. Even if the reaction mechanism is quite different from that proposed here, an energy difference of the order of magnitude of that shown by the dotted curve of Fig. 3 seems to be entirely unreasonable.

CONCLUSION

Although quenching processes play an important role in most reactions involving radiation, they have been only briefly mentioned above. There are many data available on the quenching of excited atoms in the gas phase by collision with foreign atoms or molecules. These

data have generally been interpreted in terms of an effective cross-sectional area, but a more rational explanation is to be found in the "crossing" of potential energy surfaces. For many simple cases the surfaces could be constructed for direct comparison with experiment, and work along these lines is planned. Aside from these cases, there are quantitative data on quenching for only a few cases. Anderson[16] has obtained data on the effect of dissolved salts on the chemiluminescence of cypridine luciferin, and has found increases in the photon yield in some cases. This result is understandable either as a change in the activity coefficients of the reactants or activated complexes for some of the reactions or as a change in the important mechanisms. One possible example of the latter type would be the removal of a quenching agent originally present.

The phenomenon of mitogenetic ray emission has been very extensively studied with rather contradictory results, and a review has been written by Hollaender and Claus.[17] Although we do not attempt to express an opinion regarding the physiological effects of such radiation, the occurrence of many weak chemiluminescent reactions in living organisms is to be expected in the light of the mechanism for their occurrence discussed above.

Audubert and Victorin[18] have investigated the ultraviolet luminescence occurring at aluminium anodes showing an electric valve effect. While it is difficult to assign the precise mechanism from the available experimental material it apparently is possible to understand these results in terms of "crossing" potential surfaces.

The following general considerations regarding chemiluminescence in flames may be mentioned. Figs. 1 and 2 show only a single upper potential energy surface. For complicated molecules there will be many such surfaces and if the activated complex on any such surface is denoted by $A_u^*(n)$, the concentration of $A_u^*(n)$ is determined by the temperature and by the free energy difference between A_l and $A_u^*(n)$ and for sufficiently high temperatures many of these upper levels will contribute chemiluminescent reactions. On the other hand the frequency of the emitted light is determined by the energy difference between $B_u(n)$ and B_l. Here $A_u^*(n)$ and $B_u(n)$ are denoted by simply A_u^* and B_u on the lowest excited surface represented in Figs. 1 and 2. Since reactions proceed with a free energy decrease, the free energy of B_l will be lower than that of A_l. We thus expect that in general the energy of the light emitted will be greater than the free energy of activation of A_l going to $A_u^*(n)$, but that the amount of radiation of the corresponding frequency will, in the absence of quenching processes, be governed by the energy of activation. Quenching processes may, however, destroy any correspondence of this kind, especially if the excited molecule, $B_u(n)$, has a long mean life. The black-body spectrum corresponding to the temperature of the flame will, of course, form a background on which is superimposed the radiation from chemical reactions.

In a recent paper dealing with the interpretation of alkali halide-thallium phosphors, Dr. Frederick Seitz[19] has concluded that it is possible for a particular phosphor containing an excited electron to pass less readily over a potential barrier by an adiabatic process than it does over a higher barrier which can only be reached by absorption of radiation. This case, if correctly interpreted, is of great interest in providing the only known type of reaction in which the rate by the radiation mechanism is actually faster than the rate resulting from a collision mechanism involving a lower energy of activation.

[16] R. S. Anderson, J. Am. Chem. Soc. **59**, 2115 (1937).
[17] A. Hollaender and W. D. Claus, J. Opt. Soc. Am. **25**, 270 (1935).
[18] Audubert and Victorin, J. Chim. Phys. **34**, 18 (1937).
[19] F. Seitz, J. Chem. Phys. **6**, 150 (1938).