

$\Delta F = 176,300 - 78.35T$ for absolute temperatures between 1600 and 1800°. From this it follows that the heat-content increase ΔH is 176,300 calories in this temperature range. The function shows also that at an absolute temperature of 2250° (assuming it to hold up to this temperature) the free-energy increase becomes zero and therefore that the dissociation pressure becomes one atmosphere at this temperature.

Summary

The pressure of nitrogen at which equilibrium prevails between silicon nitride, Si_3N_4 , and its elements at absolute temperatures ranging from 1606 to 1802°K. has been determined by an experimental method previously described. This pressure is 0.27 mm. at 1606°K. and 5.5 mm. at 1802°K. Within this temperature interval the free-energy increase ΔF at one atmosphere attending the reaction $\text{Si}_3\text{N}_4 = 3\text{Si} + 2\text{N}_2$ was found to be expressed by the function $\Delta F = 176,300 - 78.35 T$ calories. From this it follows that the heat-content increase ΔH at 1700°K. is 176,300 cal.; also that the dissociation pressure of the nitride becomes one atmosphere at about 2250°K.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 225]

THE RATE OF REACTION IN A CHANGING ENVIRONMENT

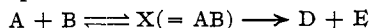
BY GEORGE SCATCHARD

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In the study of the reaction rates described in the following paper¹ there were developed methods which are of general applicability to the treatment of rates in non-ideal solutions in which the deviations change during the course of the reaction. Graphical methods applicable to this problem were presented in an earlier paper;² the present method is analytical and therefore much easier to apply. Although approximate, it is in most cases as accurate as the rate measurements.

The treatment is based upon the theory of Brönsted³ that the mechanism of the reaction is the formation and decomposition of a "critical complex," so that for the simple bimolecular reaction



the rate is given by

$$-\frac{dC_A}{dt} = K C_A C_B \frac{f_A f_B}{f_X} \quad (1)$$

¹ Ashdown, *THIS JOURNAL*, **52**, 268 (1930).

² Scatchard, *ibid.*, **48**, 2259 (1926).

³ Brönsted, *Z. physik. Chem.*, **102**, 169 (1922), and many later papers. The method is more general than this theory, however. For example, it may be applied to the simple activity theory merely by replacing f_X by 1.

where C represents concentration and f activity coefficient. It makes no difference, except for convenience, whether the concentrations are expressed as mole fractions, or weight or volume concentrations, for the units of the C and f terms cancel.⁴ The rate expression should contain the concentration and activity coefficient of every molecule which enters into the complex, whether it be reactant, catalyst or solvent. If the reaction may proceed by more than one mechanism, there should be a term on the right-hand side, each with its own value of K , for each critical complex formed. It is certain that those reactions proceed by more than one mechanism which occur both with and without a catalyst, or with two different catalysts. It is probable that the phenomenon is much more general. The fact that the effect of changing solvent on the rate is much larger than the change of activities of the reactants, so much larger that it is extremely improbable that any change in the activity coefficient of a critical complex can explain it, is most simply accounted for by assuming that the solvents enter into the complexes, so that the mechanism is not the same in different solvents.

Dilute Electrolytes.—Except from the rate measurements themselves, the activity coefficient of the critical complex can be determined only for electrolyte solutions so dilute that the activity coefficient of an ion depends only upon its valence. The Debye-Hückel expression for the activity coefficient of an ion in water at 25° is

$$-\ln f_i = \frac{1.16z_i^2 \sqrt{\mu}}{1 + 0.328a \sqrt{\mu}} \quad (2)$$

where f_i is the activity coefficient, z_i the valence of the ion, negative for a negative ion, and μ is the ionic strength in moles per liter. The numerical constants vary with the temperature and the dielectric constant of the solvent, a is the apparent diameter of the ion in Ångström units, and is generally between 0 and 5. In very dilute solutions it may be neglected to give the Debye-Hückel limiting law.

If the same size be attributed to all the ions

$$\ln \frac{f_A f_B}{f_X} = \frac{-1.16 \sqrt{\mu}}{1 + 0.328a \sqrt{\mu}} [z_A^2 + z_B^2 - (z_A + z_B)^2] = \frac{2.32z_A z_B \sqrt{\mu}}{1 + 0.328a \sqrt{\mu}} \quad (3)^5$$

For a more complicated complex, the valence term, $z_A z_B$, is replaced by the sum of all the cross products of the z 's. This equation shows immediately the conclusions drawn by Brönsted that the rate should have no primary salt effect for a reaction between an ion and a neutral molecule, that the rate should increase with increasing salt concentration for reac-

⁴ The equation may be written so that the f and C terms occur only as products, $f C$ (f_X and dC_A occurring together), which, like activities, are ratios and so pure numbers. The numerical value of K does depend on the conventional definition of unit activity.

⁵ A similar expression using the Debye-Hückel limiting law is given by Brönsted and Livingstone, *THIS JOURNAL*, **49**, 435 (1927).

tions between two ions of the same sign, and should decrease for reactions between ions of opposite signs. Within the range of its applicability it gives quantitatively the magnitude of these changes. Brönsted's application is limited to reactions where the ionic strength and therefore the activity coefficients are constant during the course of the reaction.

When the ionic strength varies, the use of Equation 3 introduces a variable exponential which leads to difficulty in integration. The activity of an ion may also be expressed by

$$f_1 = \frac{1}{1 + 1.16z_1^2 \sqrt{\mu}} \quad (4)^6$$

For small values of $z_1^2 \sqrt{\mu}$, Equation 4 gives the same result as Equation 3, with $a = 1.77z_1^2$. The corresponding value of a decreases slowly with increasing concentration, becoming 1.54 when $z_1^2 \sqrt{\mu}$ is 1. This expression represents the data as well as any which does not introduce specific constants.

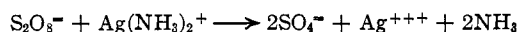
Then

$$\frac{f_{A}f_{B}}{f_X} = \frac{1}{1 - 2.32z_A z_B \sqrt{\mu}} \text{ when } z_A z_B \text{ is negative, and} \quad (5a)$$

$$\frac{f_{A}f_{B}}{f_X} = 1 + 2.32z_A z_B \sqrt{\mu} \text{ when } z_A z_B \text{ is positive} \quad (5b)$$

Since the ionic strength is a linear function of the extent of the reaction, it can be expressed as $\sqrt{\mu} = \sqrt{\mu_0} \sqrt{1 + gx}$, where x is the extent of the reaction, μ_0 is the initial ionic strength, and $\mu_0(1 + g)$ is the ionic strength when the reaction is complete ($x = 1$). Simplification in integration without significant loss in accuracy may be obtained by replacing $\sqrt{1 + gx}$ by $1 + gx/2$. The difference between the two expressions is less than 10% even when the ionic strength is doubled or halved.

Not many reactions have been studied with a large change in ionic strength and without complicating factors such as the formation of unknown amounts of complex ions or of weak electrolytes. The studies of Yost⁷ on the oxidation of ammonia by persulfate ion indicate that the slow reaction is



Since the complex silver ion is regenerated in the subsequent rapid reaction, the reaction is apparently unimolecular, and $z_A z_B = -2$. The expression for the rate is then

⁶ Two ways of expressing Equation 2 as a power series are

$$f_1 = 1 - 1.16 z_1^2 \sqrt{\mu} + (0.673 z_1^4 + 0.380 z_1^2 a) \mu + \dots$$

$$1/f = 1 + 1.16 z_1^2 \sqrt{\mu} + (0.673 z_1^4 - 0.380 z_1^2 a) \mu + \dots$$

Since a is positive the two coefficients of μ compensate in the second expression, but add in the first. This is true also in the higher terms, so the first two terms of the second expression (Equation 4) give a much more accurate expression of Equation 2 than the corresponding terms of the first.

⁷ Yost, THIS JOURNAL, 48, 374 (1926).

$$\frac{dx}{dt} = KC_{A_0}(1-x) \frac{f_A f_B}{f_X} = \frac{KC_{A_0}(1-x)}{1 + 4.64\sqrt{\mu_0}\sqrt{1+gx}}$$

$$\frac{dx}{1-x} (1 + 4.64\sqrt{\mu_0}\sqrt{1+gx}) = KC_{A_0} dt \quad (6)$$

or, approximately

$$\frac{dx}{1-x} [1 + 4.64\sqrt{\mu_0}(1+gx/2)] = KC_{A_0} dt \quad (7)$$

Integrating between the limits $t = 0$ and $t = t$ gives, in the two cases

$$\ln \frac{1}{1-x} + 4.64\sqrt{\mu_0} \left[\sqrt{1+g} \ln \frac{(\sqrt{1+g} + \sqrt{1+gx})(\sqrt{1+g}-1)}{(\sqrt{1+g}-\sqrt{1+gx})(\sqrt{1+g}+1)} - 2(\sqrt{1+gx}-1) \right] = KC_{A_0} t \quad (8)$$

$$[1 + 4.64\sqrt{\mu_0}(1+g/2)] \ln \frac{1}{1-x} - 2.32g\sqrt{\mu_0}x = KC_{A_0} t \quad (9)$$

Neglecting the change of environment during the reaction (putting $g = 0$), gives

$$(1 + 4.64\sqrt{\mu_0}) \ln \frac{1}{1-x} = KC_{A_0} t \quad (10)$$

Table I shows the application of these equations to two measurements of Yost starting with 0.0138 M $(NH_4)_2S_2O_8$ and 0.0059 M $AgClO_4$. The initial ammonia concentrations are 0.0687 M and 0.1123 M . The ionic strength changes from 0.0473 to 0.0887, so that $g = 0.875$. The first column gives the time, the second the fraction of persulfate ion converted, and the last three columns give the values of the constants computed by Equations 10, 8 and 9. Comparison of the last two columns shows that the error introduced by the approximation of Equation 7 is negligible. By Equation 10 or by the ideal solution law the constant decreases about 20%. By either of the other two equations there is no trend up to 90% conversion. As shown by the figures in parentheses, the decrease beyond this point may be prevented by decreasing the observed values of the persulfate-ion concentration by one unit in the last place given, which should be within the experimental error.

TABLE I
OXIDATION OF AMMONIA BY PERSULFATE ION

$NH_3 = 0.0687 M$					$NH_3 = 0.1123 M$				
Time	x	$K_{(10)}$	$K_{(8)}$	$K_{(9)}$	Time	x	$K_{(10)}$	$K_{(8)}$	$K_{(9)}$
5.5	0.18	12.4	12.6	12.6	5	0.22	16.7	17.1	17.1
15.5	.41	11.7	12.3	12.3	17	.54	15.4	16.4	16.4
26	.59	11.8	12.7	12.7	26	.70	15.6	16.9	17.0
40	.73	11.2	12.2	12.3	39.5	.83	15.1	16.7	16.8
57	.84	11.0	12.2	12.3	57.5	.91	14.5	16.2	16.5
91	.94	10.2	11.5	11.7 (12.2)	91	.97	13.2	15.2	15.4 (16.6)
125	.97	0.95	11.0	11.3 (12.1)	125	.99	11.6	13.5	13.6 (15.9)

It is possible, however, that this decrease is due to the fact that Equation 5 gives too small a correction for the changing activity coefficients in this case. Yost found that with 0.0086 *M* K₂S₂O₈, 0.005 *M* AgClO₄ and 0.383 *M* NH₃, a change in KOH concentration from 0.0170 *M* to 0.0904 *M* decreased *K* by 32%. According to Equation 5 the decrease should be 23%, while according to the Debye-Hückel limiting law it should be 45%.

The measurements of King⁸ on the same reaction are affected by some disturbing factor at the start. Integrated from the first reading rather than from zero time, however, Equations 8 or 9 give values of *K* without a trend.

Non-Electrolytes.—There are in the literature descriptions of many reactions between non-electrolytes whose rates change during the course of the reaction, so that they do not give constants for a reaction of any order. Although the term $f_A f_B / f_X$, or its equivalent for reactions of other types, cannot be determined independently, an approximate expression can be derived so that it may be determined from the rate measurements themselves.

The activity coefficient of a non-electrolyte in dilute solution in another non-electrolyte may be expressed by

$$\ln f_1 = gm_1 \text{ or } f_1 = e^{gm_1} \quad (11)$$

in which m_1 is the molality and g a constant.⁹ Where gm_1 is large, this gives only a very rough approximation. As for the electrolyte solutions, we will substitute an expression which is the same as (11) for small values of gm_1 , and which for larger values agrees as well with the experimental data.

$$-\ln f_1 = \ln(1 - gm_1) \quad 1/f_1 = 1 + gm_1 \quad (12)^{10}$$

Figure 1 shows the values of the activity coefficients, $f = a/m$, for iso-amyl alcohol and for propionic acid in dry nitrobenzene, two examples of very large deviations, computed by Brown and Bury¹¹ from their freezing point measurements. The broken lines are for Equation 11 and the full lines for Equation 12, the constants in both cases being selected to give agreement at 1 *M*. For the alcohol the agreement of the two equations

⁸ King, *THIS JOURNAL*, 49, 2689 (1927). Dr. King has been kind enough to send me the manuscript of his article with Mr. F. L. Griswold which indicates that under these conditions the reaction does not go quantitatively to nitrogen but part of the ammonia is oxidized to nitrate ion. We are agreed that this finding has no effect on the conclusions of this paper. The constants should be increased, but not more than 0.2%.

⁹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 275. In their notation, $g = -2h$.

¹⁰ Equation 12 may be derived from Equation 11 by expansion of $1/f_1$ as a power series.

¹¹ Brown and Bury, *J. Phys. Chem.*, 30, 696 (1926). The values there tabulated are the activity divided by the mole fraction.

is about the same. For the acid, Equation 12 fits much better, although still only fairly well.

The reaction mixtures are not binary, however, and a term must be added to our expression to include every substance whose concentration varies, giving for our type reaction

$$1/f_A = 1 - g_{AA}m_A - g_{BA}m_B - g_{DA}m_D - g_{EA}m_E \quad (13)$$

Since the concentration of each substance is a linear function of the extent of the reaction, we may write

$$1/f = 1 - G_A - G'_A x \quad (14)$$

where G_A and G'_A are functions of the initial composition of the solution. If the ratios of the concentrations are constant, the G 's are proportional to

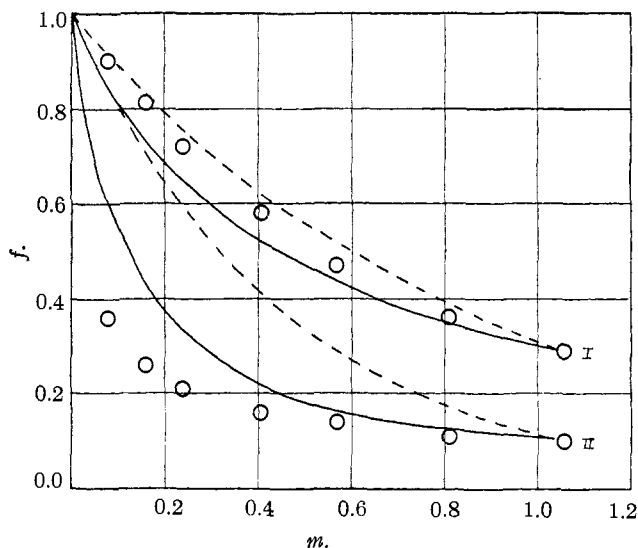


Fig. 1.—Activity coefficients in dry nitrobenzene: I, *iso*-amyl alcohol, $g=1.17$ (Eq. 11), $=2.32$ (Eq. 12); II, propionic acid, $g=2.18, 8.51$.

the concentrations. Equation 14 with similar expressions for f_B and f_X permits integration, but it is generally desirable to simplify first by ignoring relatively small terms in Equation 13.

The Magnitude of the Deviations.—The value of g in Equation 11 or 12 is closely related to the change of activity of the solute as the medium changes from pure solute to pure solvent. This may be seen by expanding Margules' equation in terms of activities instead of partial pressures¹²

$$RT \ln \frac{f}{f_0} = \frac{\beta}{2} (1 - N)^2 + \frac{\gamma}{3} (1 - N)^3 = \left(\frac{\beta}{2} + \frac{\gamma}{3} \right) - (\beta + \gamma)N + \left(\frac{\beta}{2} + \gamma \right)N^2 - \frac{\gamma N^3}{3} \quad (15)$$

¹² See Hildebrand, "Solubility," Chemical Catalog Co., Inc., New York, 1924, p. 48.

In this equation N is the mole fraction, and f the activity divided by the mole fraction; β and γ are constants; f_0 is the activity coefficient of the pure substance. When $N = 0$, $f = 1$ and $\ln f = 0$, so

$$RT \ln 1/f_0 = \left(\frac{\beta}{2} + \frac{\gamma}{3}\right)$$

$$RT \ln f = -(\beta + \gamma)N + \left(\frac{\beta}{2} + \gamma\right)N^2 - \frac{\gamma N^3}{3} \quad (16)$$

For dilute solutions we may neglect the terms in N^2 and N^3 and replace the mole fraction by the concentration in moles per thousand grams of solvent or per liter of solution, with the appropriate change of constant. For the former this gives Equation 11. The neglected terms give deviations in the same direction as does Equation 12.

For binary mixtures it is possible to predict the value of $g_{11} = \frac{-N(\beta + \gamma)}{mRT}$ by the methods of Hildebrand or of Mortimer.¹³ For mixtures of two non-polar substances, for which the γ term in Equation 15 is generally small, these methods are quite precise. For one non-polar and one polar component they are only approximate. For both these cases g_{11} is negative. For mixtures of two polar substances these methods may fail completely because such mixtures have a tendency to chemical reaction. If there is chemical combination between the solute and the solvent g_{11} is positive, but Equation 12 still holds approximately.

If a second solute forming an ideal solution in binary mixture with the solvent ($g_{22} = 0$) is added to a solution containing a non-ideal solute,

its effect will be the same as diluting with the solvent and $g_{21} = -\frac{n_1}{n_0} g_{11}$,

where n_1/n_0 is the mole ratio of the first solute to the solvent. For dilute solutions g_{21} will be small relative to g_{11} . Moreover, $g_{12} = g_{21}$. This is

most simply obtained from the expression, given by Bjerrum,¹⁴ $\frac{d \ln f_1}{dn_2} =$

$\frac{d \ln f_2}{dn_1}$, but it may also be obtained from the fact that the change must be

the same for the ideal solute as for the solvent.

If there is a third solute which forms an ideal solution with the first, and so does not with the solvent, $g_{31} = g_{13} = g_{11} = g_{33}$, and, of course, $g_{32} = g_{23} = g_{12} = g_{21}$.

If the added solute does not form an ideal solution with either the solvent or the first solute, there are two possibilities. If the solution is intermediate in its properties between the two solutes, $g_{41} = g_{14}$ will be positive; if it is not, $g_{41} = g_{14}$ will be negative and will lie between g_{11} and g_{44} . There is then a possibility that g_{41} may change sign with changing concen-

¹³ See Hildebrand, Ref. 12, pp. 99-116.

¹⁴ Bjerrum, *Z. physik. Chem.*, **104**, 423 (1923).

tration instead of remaining constant, but it is improbable that this should happen in dilute solution unless g_{41} is always small enough to be negligible.

If two of the components are polar, the situation may be very considerably complicated. If the two solutes react together their effect on each other may be very much greater than that of either on itself. If either or both react with the solvent, it may be very much less.

It is possible to make some tentative conclusions regarding the effect of changing environment on the activity coefficient of the critical complex. Since the complex formation may be assumed to involve the more active groups, and therefore to screen them, the complex may be taken as less polar than its most polar component, and possibly less polar than either. If the complex also contains solvent molecules, which is probably quite often the case, it may be a more ideal solute than any of its components other than the solvent. This term will tend to make the deviations from ideality less than would be predicted from the simple activity theory.

Illustration.—As an example of the application of the method we may take the action of *p*-nitrobenzoyl chloride with some of the simpler alcohols in ether solution, which is considered in detail in a paper which follows.¹ Not many ether solutions have been studied accurately, but the freezing points of benzene from solutions of ether are almost identical with those from solutions of toluene, which are known to be nearly ideal. Therefore ether may be taken as not much different from benzene as a solvent. Figure 2 shows the freezing-point curves of ether, toluene, benzoyl chloride and propyl alcohol in benzene.¹⁵ The freezing points of solutions of ethyl acetoacetate¹⁶ are identical with those of ether or toluene up to 1 molal (the limits of the measurements), so the esters should behave as ideal solutes and have little effect on the activity coefficients of the other solutes. Benzoyl chloride does not differ very greatly from the ideal solutes, so we may assume, with considerable probability, that the activity coefficient of nitrobenzoyl chloride is near unity and equal to that of the critical complex. The acid chloride should also have little effect on the activity coefficient of the alcohol. The alcohols, however, should show large deviations depending largely on their own concentration. The hydrogen chloride formed in the reaction shows a great tendency to chemical combination; it forms stable compounds with ether. Its effect on the activity coefficients appears to depend upon its relative reactivity with the solute and with the solvent, which is most easily determined from the rate measurements themselves. For butyl alcohol the rate was found to be unchanged when one mole of hydrogen chloride was added to one mole of alcohol and one of chloride in a thousand grams of ether. Further confirmation was obtained from the fact that the curves

¹⁵ "International Critical Tables," Vol. 4, pp. 112, 116, 177.

¹⁶ Auwers, *Z. physik. Chem.*, **12**, 693 (1893).

for initial concentrations of one molal and of one-half molal fit together smoothly as functions of the alcohol concentration, showing that one-half mole of hydrogen chloride plus one-half of ester have no effect on the rate. So only the change of the activity coefficient of the alcohol due to changes in its own concentration need be considered. The higher alcohols behave as does butyl. Not enough measurements were made on propyl alcohol to determine the effect of the hydrogen chloride.

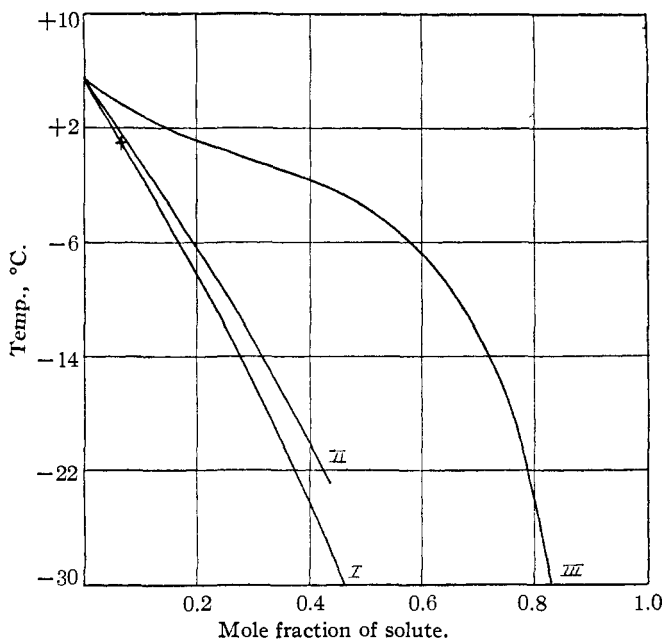


Fig. 2.—Freezing points of benzene solutions: I, toluene, ether; ethyl acetoacetate to +; II, benzoyl chloride; III, propyl alcohol.

For ethyl alcohol, an excess of one mole of ester shows no effect on the rate, but half a mole of ester and half of hydrogen chloride retard the action considerably. It seems that hydrogen chloride combines with ethyl alcohol more readily than with ether. The existent measurements may be fitted by assuming that the effect of the acid on the activity coefficient of the alcohol is equal to that of an equal concentration of the alcohol itself, or that $g_{31} = g_{11}$, so that the activity coefficient may be regarded as constant during the course of the reaction, but varying with the initial concentration of alcohol. Methyl alcohol behaves similarly but $g_{31} = g_{11}$ is considerably larger than for ethyl alcohol.

Summary

There is given an analytical method for the treatment of reaction rates in non-ideal solutions where the environment changes during the course

of the reaction, based on approximate equations for the change of activity coefficient with concentration.

By use of Brönsted's theory of reaction mechanism, the method is applied to the oxidation of ammonia by persulfate ion in the presence of silver ion.

The principles by which the activity coefficients in non-electrolyte mixtures may be approximately evaluated are given, and illustrated by their application to the reaction of *p*-nitrobenzoyl chloride with certain alcohols.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PHOTOCHEMICAL DISSOCIATION OF TRIATOMIC MOLECULES. HYDROGEN CYANIDE

BY DONALD STATLER VILLARS

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The remarkable success of Franck, Kuhn and Rollefson¹ in explaining the absorption spectra of the Group I halides leads one to the query whether the same mechanism does not hold also in the case of polyatomic molecules. Its importance to photochemistry cannot be neglected, especially in view of the attempt of Franck and Scheibe² to explain in a reasonable manner the photolysis of hydrogen iodide in aqueous and hexane solutions. According to Franck and Kuhn³ an "atomic"⁴ molecule may be dissociated photochemically into a normal atom plus an excited atom. Only two continuous absorption regions in the near ultraviolet should result, depending on which is the one excited. On the other hand, an "ionic"⁵ molecule may be dissociated photochemically into two normal atoms, one way in addition to those in which the "atomic" molecule may dissociate. In this case an extra absorption region is to be found to the red side of the spectrum and at a distance corresponding to the energy difference ${}^2P_{1/2} - {}^2P_{11/2}$ of the halogen ground doublet. The first step toward the application of their theory to polyatomic molecules is the consideration of triatomic molecules. When several of these have been investigated it will be time to take up the more complicated ones. Terenin⁶ has already studied triatomic molecules, two atoms of which are similar. As this is likely to lead to degeneracy complications in the analysis of the spectra, it was thought desirable to choose

¹ Franck, Kuhn and Rollefson, *Z. Physik*, **43**, 155 (1927).

² Franck and Scheibe, *Z. physik. Chem.*, **139A**, 22 (1928).

³ Franck and Kuhn, *Z. Physik*, **43**, 164 (1927).

⁴ An atomic molecule may be defined as one which when given sufficient vibrational energy will dissociate into atoms.

⁵ An ionic molecule may be defined as one which when given sufficient vibrational energy will dissociate into ions.

⁶ Terenin, *Z. Physik*, **44**, 713 (1927); **49**, 882 (1928); *Nature*, **118**, 843 (1926).