

## Potential Energy of a Molecule in a Liquid

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tion<sup>3</sup> that succinic acid and its amino substituted derivatives are formed under the conditions of high radical concentration which are obtained<sup>4</sup> in cyclotron irradiations. At lower radical concentrations, e.g., in x-ray irradiation it is assumed that  $\text{CH}_2\text{COOH}$  is removed via (3). Radiation yields  $G$ , obtained<sup>1</sup> in x-ray radiolysis of oxygen-free 1-M glycine solutions, are compared in Table I with the corresponding values calculated on<sup>5</sup> the basis of reactions (1)–(6). The reported<sup>6</sup> yields  $G_R=3.0$ ,  $G_F=0.8$  were used for the primary processes<sup>7</sup>: (R),  $\text{H}_2\text{O}\rightarrow\text{H}+\text{OH}$ , and (F),  $\text{H}_2\text{O}\rightarrow\frac{1}{2}\text{H}_2+\frac{1}{2}\text{H}_2\text{O}_2$ . The observed  $G$ -values for acetic acid and formaldehyde were taken as a measure of reactions (2a) and (6a), respectively.

Ammonia yields from oxygen-free and oxygen-saturated solutions are essentially the same.<sup>2,8</sup> The  $G$ -value for ammonia is approximately 4.0 in 1-M glycine solution. Since this is greater than the radical pair yield  $G_R$ , and since H in the presence of oxygen reacts to form  $\text{HO}_2$ , it has been assumed that ammonia formation involves the reaction of both OH and  $\text{HO}_2$  with glycine. It can be shown,<sup>3</sup> however, that this assumption does not lead to the observed<sup>1</sup> product stoichiometry. Recent studies<sup>9,10</sup> of the effect of certain solutes on the yield of hydrogen peroxide from the primary reaction (F) are considered to be of significance here. Bromide ion, for example, has been found to suppress the "molecular" yield of hydrogen peroxide by reaction with OH radicals in the regions of high ionization density. If glycine in 1M solution reacts in a similar manner, a  $G$ -value of  $3.8(G_R+G_F)$  for ammonia would be anticipated on the assumption that all  $\text{NH}_2\text{CHCOOH}$  radicals formed by OH attack on glycine react with  $\text{O}_2$  (or  $\text{HO}_2$ ) to form imino acetic acid,  $\text{NHCHCOOH}$ . This proposal regarding the total number of OH radicals available for reaction with glycine is stoichiometrically equivalent to the reaction sequence (1), (5) in the foregoing. A detailed report on glycine radiolysis is forthcoming.

\* This work was performed under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> Maxwell, Peterson, and Sharpless, *Radiation Research* 1, 530 (1954).

<sup>2</sup> Sharpless, Blair, and Maxwell, *Radiation Research* 2, 135 (1955).

<sup>3</sup> B. M. Weeks, Ph.D. thesis (to be published). See also B. M. Weeks and W. M. Garrison, paper presented at the 1955 Meeting of the Radiation Research Society, University of California Radiation Laboratory Report No. 3068, 12 pp. (1955).

<sup>4</sup> Garrison, Bennett, Cole, Haymond, and Weeks, *J. Am. Chem. Soc.* 77, 2720 (1955).

<sup>5</sup> Product yields in Table I were calculated on the assumption that reaction between  $\text{NH}_2\text{CHCOOH}$  (or  $\text{NHCH}_2\text{COOH}$ ) radicals results only in disproportionation. Data recently obtained in  $\gamma$ -ray irradiation studies at this Laboratory (BMW) indicate that a dimerization reaction also occurs with  $G\approx 0.4$ . This would account for the fact that the calculated yields for  $\text{NH}_2$  and  $\text{CHOCO}$  are slightly higher than the observed.

<sup>6</sup> E. J. Hart, *J. Am. Chem. Soc.* 76, 4198 (1954).

<sup>7</sup> Allen, Hochanadel, Ghormley, and Davis, *J. Phys. Chem.* 56, 575 (1952).

<sup>8</sup> G. Stein and J. Weiss, *J. Chem. Soc.* 3256 (1949).

<sup>9</sup> T. J. Sworski, *J. Am. Chem. Soc.* 76, 4687 (1954).

<sup>10</sup> E. R. Johnson, *J. Chem. Phys.* 21, 1417 (1953).

## Potential Energy of a Molecule in a Liquid\*

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IN a recent note Girifalco<sup>1</sup> has proposed the following potential energy for use in the cell model of a liquid:

$$\varphi(r) = \frac{2\pi}{v} \int_{R_0}^{\infty} R dR \int_{|R-r|}^{R+r} x \rho(x) \epsilon(x) dx, \quad (1)$$

where  $v$  is the volume per molecule,  $R_0$  is the distance of closest approach between molecules,  $\rho(x)$  is the radial density function,  $\epsilon(x)$  is the intermolecular potential function, and  $r$  is the separation of the molecule from its "mean position." (The absolute value indication on the lower limit of the first integral was not given in the original note, but is plainly demanded by the derivation.)

It is the purpose of this note to point out that  $\varphi(r)$  as defined above is hardly suitable for use as an effective potential. With the usual kinds of  $\rho(x)$  and  $\epsilon(x)$  it merely provides a barrier at distances of the order of  $R_0$ , after which it falls off again and approaches a constant value at large  $r$ . The proof of this is the following.

Let

$$\varphi_0 = \frac{2\pi}{v} \int_0^{\infty} R dR \int_{|R-r|}^{R+r} x \rho(x) \epsilon(x) dx.$$

By following the derivation given by Girifalco, one sees that this is simply an integration over all space in bipolar coordinates  $R, x$  (with poles separated by  $r$ ) of  $v^{-1}\rho(x)\epsilon(x)$ , and, hence, can equally well be written  $\varphi_0 = v^{-1} \int_0^{\infty} \rho(x) \epsilon(x) 4\pi x^2 dx$ , which is manifestly independent of  $r$ . Then  $\varphi(r) = \varphi_0 - \theta(r)$ , where  $\theta(r) = 2\pi/vr \int_0^{R_0} \times R dR \int_{|R-r|}^{R+r} x \rho(x) \epsilon(x) dx$ , and this is just the interaction energy between the given molecule and other molecules within a sphere of radius  $R_0$  whose center is a distance  $r$  from the given molecule. For  $r \gg R_0$ ,  $\theta(r)$  is proportional to  $\epsilon(r)$  and thus vanishes as  $r \rightarrow \infty$ . Also  $\theta(0) = v^{-1} \int_0^{R_0} \rho(x) \epsilon(x) 4\pi x^2 dx$ , from which it may be seen that  $\theta(0)$  is negative (or very weakly positive in unusual cases), because  $\rho(x)$  is exceedingly small except where  $\epsilon(x) < 0$ . This means that  $\varphi(0) > \varphi(\infty)$ , in ordinary cases, and despite a "hump" in  $\varphi$  at intermediate distances,  $\varphi$  cannot provide an effective well for the single-particle model. Furthermore, the partition function deduced by Girifalco [Eq. (3), reference 2] does not exist because the integral by which it is defined does not converge.

If one introduces an arbitrary cutoff, the potential  $\varphi(r)$  can be employed in a formal way, but its physical validity remains questionable. Apart from the difficult problem of justifying Eq. (1), it can be seen that the binding provided by  $\varphi(r)$  is derived from that part of the intermolecular potential near the chief maximum in  $\rho(r)$ , and takes virtually no account of the repulsive part at small  $r$ . With typical intermolecular potential functions both  $\varphi(r_0) - \varphi(0)$  and the vibrational frequency of the caged molecule will tend to be abnormally low. Indeed, for the case of an intermolecular potential which is entirely repulsive it can be shown that the vibrational frequency usually will be zero or imaginary.

\* Work done under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> L. A. Girifalco, *J. Chem. Phys.* 23, 1728 (1955).

## Potential Energy of a Molecule in a Liquid: Calculations for Argon

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(Received November 11, 1955)

THE potential energy function of a molecule in a liquid proposed in a previous letter<sup>1</sup> gives the energy of a molecule within a cell as a function of the distance  $r$  from the center of the cell. This center may be defined as the mean position of the molecule. Although the range of  $r$  was not explicitly stated, it is physically obvious that  $0 \leq r \leq a$  where  $a$  is the distance to the first coordination shell and is approximately equal to  $R_0$ , the distance of closest approach between molecules. If  $r$  is permitted to exceed  $a$ , the molecule is no longer in its original cell, and the potential energy must be referred to the center of the new cell as origin. This is just an alternative statement of the fact that in the cell model of liquid, the potential energy of a molecule must have a three-dimensional periodicity.

In reference 1, the potential energy is given in terms of the radial distribution function and the intermolecular potential function, both of these functions being referred to the central molecule as origin. Streetman<sup>2</sup> has pointed out that if experimental distribution functions are to be used, it is more realistic to refer them to the mean position of the molecule in the cell as origin. With this change the potential energy of a molecule in a liquid is

$$\varphi(r) = \frac{2\pi}{v} \int_{R_0}^{\infty} R \rho(R) dR \int_{R-r}^{R+r} x \epsilon(x) dx. \quad (1)$$

Calculations of  $\varphi(r)$  have been made for argon using the interatomic potential of Jura as given by Hildebrand and Scott<sup>3</sup> and

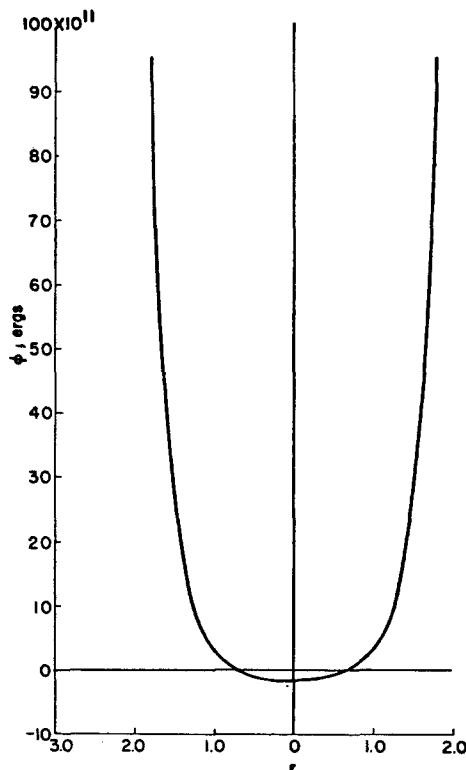


FIG. 1. The potential energy of a molecule in liquid argon at 88.4°K.

the radial distribution function of Eisenstein and Gingrich.<sup>4</sup> A cross section of the potential well for this case is given in Fig. 1 showing that Eq. (1) gives a quite satisfactory potential function for an atom in liquid argon.

The configuration integral in reference 1 was integrated from 0 to  $\infty$ . Since  $\phi(r)$  is defined only from  $r=0$  to  $R=a$ , it is more correct to integrate the configuration integral from 0 to  $a$ . The partition function therefore becomes

$$Z = \left[ \frac{2\pi mkT}{h^2} \right]^{3N/2} \left[ \int_0^a e^{\phi(r)/kT} 4\pi r^2 dr \right]^N. \quad (2)$$

<sup>1</sup> L. A. Girifalco, *J. Chem. Phys.* **23**, 1728 (1955).

<sup>2</sup> J. R. Streetman (private communication).

<sup>3</sup> J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes* (Reinhold Publishing Corporation, New York, 1950), third edition, p. 95.

<sup>4</sup> A. Eisenstein and N. S. Gingrich, *Phys. Rev.* **62**, 261 (1942).

## Ionization Potentials of Ammonia and the Excited States of the $\text{NH}_3^+$ Ion

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(Received December 21, 1955)

THE first ionization potential of ammonia has been variously reported as  $10.5 \pm 0.1$ ,<sup>1</sup>  $10.42 \pm 0.05$ ,<sup>2</sup> and  $10.25 \pm 0.1$ ,<sup>3</sup> ev. This potential obviously represents the energy required to remove one of the electrons from the nonbonding ( $za_1$ ) orbital in the following molecular orbital formula for ammonia.<sup>4</sup>

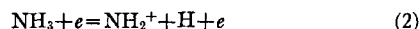
$$(sa_1)^2[\pi e]^4(za_1)^2, \quad {}^1A_1. \quad (1)$$

The removal of an electron from the ( $za_1$ ) orbital results in the formation of a  $\text{NH}_3^+$  ion in its ground  ${}^2A_1$  state (assuming the  $\text{NH}_3^+$  ion to belong to symmetry group  $C_{3v}$ ).

Recent measurements of the absorption cross sections, ionization efficiencies, and ionization cross sections of  $\text{NH}_3$  from the

onset of the ionization continuum to 687 Å have been made by Walker and Weissler.<sup>5</sup> From these results it appears that ionization begins at  $1231 \pm 5$  Å, corresponding to  $10.07 \pm 0.1$  ev. Though this is somewhat lower than the previous experimental values it undoubtedly corresponds to the process discussed above. Walker and Weissler found that at 824 Å both the ionization efficiency and the ionization cross section rose sharply and tentatively ascribed this to the onset of a second continuum at about 15 ev.

Studies of the ionization of ammonia by essentially monoenergetic electrons<sup>6,7</sup> were made some time ago by D. C. Frost and myself at the University of Liverpool. These showed conclusively that there is a second ionization potential of ammonia at  $15.31 \pm 0.04$  ev. This process obviously refers to the removal of an electron from the degenerate  $[\pi e]$  bonding orbital which spans the three N—H bonds, thus forming a  $\text{NH}_3^+$  ion in its  ${}^2E$  first electronically excited state (assuming that the  $\text{NH}_3^+$  ion has symmetry  $C_{3v}$ ). These new results mean, of course, that there should be a second continuum setting in a little above 15 ev, and this is confirmed by the results of the photoionization studies given by Walker and Weissler.<sup>5</sup> It is not possible, however, to attribute the occurrence of this second continuum wholly to this ionization process, for as Walker and Weissler mention, electron impact studies<sup>1</sup> show that the dissociative ionization process



occurs at about 15.7 ev.

In an earlier discussion<sup>8</sup> of the origin of process (2) it was assumed that the  $\text{NH}_2^+$  ion was formed by the dissociation of a vibrationally excited  $\text{NH}_3^+$  ion in one of the two vibronic states  ${}^2A_1$  or  ${}^2E$ , which can arise from the ground  ${}^2A_1$ , electronic state of  $\text{NH}_3^+$  (assuming the ion to have symmetry  $C_{3v}$ ). The new electron impact results mentioned above make it highly likely, however, that the  $\text{NH}_2^+$  ion is formed from one of the vibronic states  ${}^2A_1$ ,  ${}^2A_2$ , or  ${}^2E$ , which can arise from the formation of the parent  $\text{NH}_3^+$  ion in its first excited  ${}^2E$  electronic state. No unequivocal decision seems possible at present. For the stretching (or bending) of an NH bond during the act of dissociation will, of course, destroy the original (assumed)  $C_{3v}$  symmetry of the  $\text{NH}_3^+$  ion. If during the dissociation process the parent  $\text{NH}_3^+$  ion is completely distorted so that it loses all symmetry (which is possible) then one has difficulty in identifying the particular vibronic state of the parent ion from which the  $\text{NH}_2^+$  ion originates. That is because the number of adiabatic correlations between the states of the  $\text{NH}_3^+$  ion and those of its dissociation products is greatly increased as the result of the lack of symmetry in the transition state.

<sup>1</sup> Mann, Hustrulid, and Tate, *Phys. Rev.* **58**, 340 (1940).

<sup>2</sup> J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.* **20**, 1021 (1952).

<sup>3</sup> K. Watanabe, *J. Chem. Phys.* **22**, 1564 (1954).

<sup>4</sup> R. S. Mulliken, *J. Chem. Phys.* **1**, 492 (1933).

<sup>5</sup> W. C. Walker and G. L. Weissler, *J. Chem. Phys.* **23**, 1540 (1955).

<sup>6</sup> Fox, Hickam, Kjeldas, and Grove, *Phys. Rev.* **84**, 959 (1951).

<sup>7</sup> Frost and McDowell, *Proc. Roy. Soc. (London)* **A232**, 227 (1955).

<sup>8</sup> McDowell, *Applied Mass Spectrometry*, Institute of Petroleum, London, 129 (1954).

## Photolysis of Acetone in the Absence of Mercury

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(Received December 22, 1955)

IT has been suggested<sup>1</sup> recently that mercury plays a significant role in all methyl radical reactions through the formation of mercury dimethyl and the subsequent reactions of this compound. Such a conclusion would require a reconsideration of all previous work involving methyl radicals. It is of some interest, therefore, to report some experiments made with acetone in a mercury-free system.

The apparatus is one used for other studies with the 1849 Å mercury-resonance line for which every precaution has necessarily been taken to avoid any contamination with mercury. The