three times the mass of hydrogen, the equilibrium ortho-para concentrations for tritium correspond to those for hydrogen at one-third the temperature. Therefore, for partial conversion liquid hydrogen or liquid neon is satisfactory, but for total conversion liquid helium is necessary. The rate of conversion of tritium on charcoal was faster than expected with a half-life time of one minute compared with 24 minutes for hydrogen. Preliminary results on the rate of conversion in the solid state indicate an abnormally high rate of conversion with a half-life of 15 minutes.

It would appear from the present work that ion reactions do not interfere in the conversion on the charcoal. Further experiments will clarify the effect of ions in the solid phase.

Ionic Association

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Dedicated to Prof. Dr. K. Clusius *on his sixtieth birthday*

Theories of ionic association due to Bjerrum, Fuoss and Kraus, and Ramsey are briefly reviewed. A statistical theory is developed and shown to be not in conflict with them or with recent experimental results.

The picture of a positive ion surrounded by a diffuse and continuous cloud of negative electricity has mathematical advantages but physicochemical deficiencies. When two ions of opposite sign get close together, the "cloud" surrounding either ion is simply the charge on the other ion, and the region occupied by the pair is, on an average, electrically neutral. Allowance for the existence of such ion-pairs was recognised by Bjerrum[1] as a necessary correction to those theories of electrolytes that treat the solute as being completely ionic. His theory has been criticised because of the artificiality of one of its assumptions and because of its failure to account for the variation of the association constant, K_{A}, with respect to the dielectric constant, D, of the solvent, and has now been superceded by a theory which is mathematically simpler and in closer agreement with experiment[2, 3].

The equilibrium constant governing the association of univalent ions:

$$\mathrm{A^+ + B^- \rightleftarrows A^+B^-}$$

when extrapolated to infinite dilution is given in terms of concentrations, c, by the equation

$$K_{\mathrm{A}} = C_{\mathrm{A^+B^-}} / C_{\mathrm{A^+}} C_{\mathrm{B^-}} . \tag{1}$$

Denison and Ramsey[2] and Fuoss and Kraus[3] have independently argued that K_{A} must be given, to a first approximation, by the expression:

$$K_{\mathrm{A}} = K_{\mathrm{A}}^0 \cdot \exp\{\varepsilon^2/(D\,a\,k\,T)\} \tag{2}$$

when ε is the protonic charge, and a is the distance apart of the two charges in the ion-pair. K_{A}^0 is a constant which is discussed later.

The fraction of the solute which is unassociated may be determined from the electrical conductivity of the solution[4], and the logarithm of the association constant derived therefrom may be plotted as a function of $1/D$. If a is a true constant, the plot should be linear, since

$$\log_{10} K_{\mathrm{A}} = \log_{10} K_{\mathrm{A}}^0 + \frac{\varepsilon^2}{2.303\,a\,k\,T} \cdot \frac{1}{D} , \tag{3}$$

or

$$\log_{10} K_{\mathrm{A}} = \log_{10} K_{\mathrm{A}}^0 + B/D , \tag{4}$$

where B is an isothermal constant, whose value depends on the nature of the solute but not on that of the solvent. When applied to a temperature of 298.16 °K, we have

$$\log_{10} K_{\mathrm{A}} = \log_{10} K_{\mathrm{A}}^0 + 243/(\mathring{a}\,D) , \tag{5}$$

where $\mathring{a}$ is the value of a expressed in Ångström

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[1] N. Bjerrum, Erg. exakt. Naturw. **6**, 125 [1926].

[2] J. T. Denison and J. B. Ramsey, J. Amer. Chem. Soc. **77**, 2615 [1955].

[3] R. M. Fuos and C. A. Kraus, J. Amer. Chem. Soc. **79**, 3304 [1957].

[4] C. W. Davies, The Conductivity of Solutions, 2nd Ed., Chapman & Hall, London 1934. — H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York 1943. — R. M. Fuoss, J. Amer. Chem. Soc. **79**, 330 [1957]. — C. W. Davies, Ion Association, Butterworths, London 1962.

units. A typical graph, due to Inami, Bodenseh and Ramsey[5], is reproduced in Fig. 1. Further data, summarised in the form of equation (4), are given in Table 1. They differ from one another in their accuracy, and in the ranges of dielectric constants covered. The data for silver nitrate refer to solutions in water, methanol and ethanol: those for tetrabutylammonium picrate to pure solvents; and those for tetra*iso*amylammonium nitrate to dioxane-water mixtures of different compositions, with dielectric constants varying from 2 to 80. Further details are to be found in the monographs and papers cited.

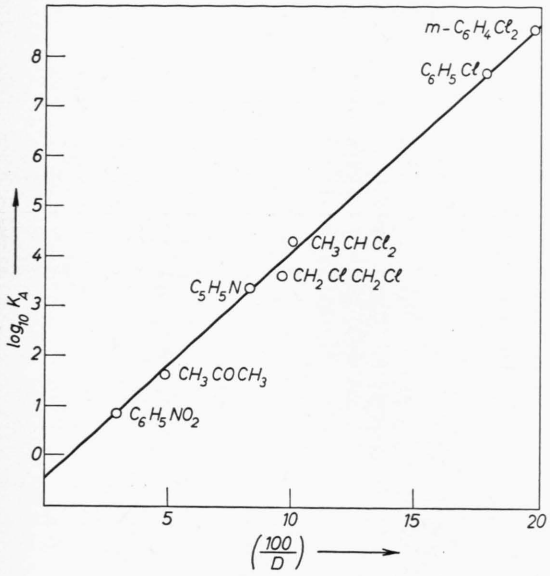

Fig. 1. Association constants of tetrabutylammoniumpicrate at 25 °C (after Inami, Bodenseh and Ramsey[5]).

Ramsey[2] finds that, whereas this linear relationship holds for a given solute in a variety of pure solvents, points fall off the straight line when they refer to solvents, such as ethylene dichloride, which exist in two forms of differing polarity. To explain the divergence, he suggests that the effective dielectric constant for such solvents is greater than the macroscopic value. Subject to this limitation, equation (3) appears to be obeyed with considerable accuracy, yielding reasonable values for the separation of the charges in the various ion pairs (column 4 of Table 1).

The term K_A^0 can be interpreted as the association constant of a pair of uncharged particles. An approximate expression for it can be found by considering a solution containing, per c.c., n_A spheres of radius r_A and n_B spheres of radius r_B. The probability that a sphere of type A shall be in contact with one of type B is the ratio of the sum of the shell volumes $(4/3)\pi[(r_A+r_B)^3-r_B^3]N_B$ to the total volume V of the solution. Here N_B is the total number of B particles in the system. The probability is thus $(4/3)\pi(a^3-r_B^3)n_B$, where $a=r_A+r_B$. The number of contacting pairs in unit volume is n_A times as great, and is thus $(4/3)\pi(a^3-r_B^3)n_A n_B$. Had we started the argument in the other order, we would have found the number to be

$$(4/3)\pi(a^3-r_A^3)n_A n_B .$$

The mean value is $(2/3)\pi a^3[1+(3r_A r_B/a^2)]n_A n_B$. The association constant is $n_{AB}/n_A n_B$ ccs./molecule or

$$K_A^0 = \frac{N_0}{1000}\,\frac{2}{3}\,\pi a^3\left[1+\frac{3r_A r_B}{a^2}\right] \tag{6}$$

litres/mole. If the spheres have equal radii,

$$K_A^0 = \frac{N_0}{1000}\cdot\frac{7}{6}\,\pi a^3 . \tag{7}$$

On this assumption, we have calculated from the experimental values of K_A^0 the ion-pair separations

Electrolyte	$\log_{10} K_A^0$	B	a[Å]		
			From B	From K_A^0	Mean
$AgNO_3$	$\bar{2}$,802	88.5	2.75	3.06	2.91 ± 0.16
$(C_4H_9)_4NBr$	$\bar{1}$.041	56.4	4.31	3.68	4.00 ± 0.31
$(C_4H_9)_4NI$	$\bar{1}$.892	43.9	5.55	7.06	6.31 ± 0.76
$(C_4H_9)_4NC1O_4$	$\bar{1}$.755	50.2	4.85	6.37	5.61 ± 0.76
$(C_4H_9)_4NPic$	$\bar{1}$.543	46.0	5.29	5.41	5.35 ± 0.06
(*iso*$C_5H_{11})_4N.NO_3$	$\bar{1}$.549	41.7	5.83	5.43	5.63 ± 0.20

Table 1. Temperature = 25 °C. $\log_{10} K_A$ (litres/mole) $= \log_{10} K_A{}^0 + B/D = \log_{10} K_A{}^0 + \varepsilon^2/(2.303\,D\,a\,k\,T)$.

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[5] Y. H. Inami, H. K. Bodenseh and J. B. Ramsey, J. Amer. Chem. Soc. **83**, 4745 [1961].

shown in column 5 of Table 1. The agreement between the two sets of a values is satisfactory for the last two electrolytes listed, and is as reasonable as may be expected for the remaining solutes. Greater internal consistency would result from the use of equation (7), but this requires a knowledge of at least one individual ionic radius; and recent work[6] has cast doubt on the applicability of STOKES' law and on the validity of radii obtained by its means.

Equation (3) though admittedly oversimplified, accounts for the principal features of ionic association in solution, and has been amended in many ways. For example, the COULOMBIC energy term $\varepsilon^2/(D\,a_1)$ must be increased by an ion-dipole term $\varepsilon\,\mu/(D\,a_2^2)$, when one of the ions is asymmetric and contains a dipole of magnitude μ. This correction has been shown by FUOSS and KRAUS[3] to account for the otherwise anomalous ionic association of sodium bromate. Induction energies and still further terms will doubtless have to be incorporated in formulating a refined theory capable of accounting for all the facts. The energy of intrinsic repulsion can be introduced as follows in a simple statistical treatment[7].

An elementary statistical treatment of ion-pair formation involving repulsive forces

If ions repel one another with a force varying as the inverse $(s+1)$th. power of their distance, a, apart, the energy of interaction of a pair of univalent ions with charges of opposite signs in a medium of dielectric constant, D, is

$$\Phi = \frac{A}{a^s} - \frac{\varepsilon^2}{D\,a}. \tag{8}$$

The interaction energy has the following minimum value when $a = a_e$:

$$\Phi_e = -\frac{\varepsilon^2}{D\,a_e}\left(1 - \frac{1}{s}\right). \tag{9}$$

Small displacements from the equilibrium separation are attended by a harmonic vibration of frequency

$$\nu_e = \frac{\varepsilon}{2\,\pi\,a_e}\left[\frac{s-1}{m^*\,D\,a_e}\right]^{1/2}, \tag{10}$$

where m^* is the reduced mass of the pair. In deriving the partition functions for the ions, it is assumed that their internal motions are the same in the free and associated states, so that only the translational components of their total partition functions need be considered. In terms of the masses, m_+ and m_-, of the ions, whether free or solvated, of their numbers, N_+ and N_-, in a total volume V and of their average potential energies, u_+ and u_-, these are:

$$f_+ = \frac{(2\,\pi\,m_+\,k\,T)^{3/2}\,V\,e}{h^3\,N_+}\cdot e^{-u_+/k\,T},$$

and

$$f_- = \frac{(2\,\pi\,m_-\,k\,T)^{3/2}\,V\,e}{h^3\,N_-}\cdot e^{-u_-/k\,T}. \tag{11}$$

The motions of the ion pair can be resolved into (i) translation throughout the total volume V, (ii) rotation of the pair, with moment of inertia $I = m^*\,a_e^2$, about its centre of gravity, and (iii) vibration along the line of centres. The magnitude of the vibration frequency ν_e is such that $h\,\nu_e$ is ordinarily much less than $k\,T$, so that the classical partition function may be used for this motion. The total partition function of the pair thus becomes

$$f_+ = \frac{[2\,\pi\,(m_+ + m_-)\,k\,T]^{3/2}\,V\,e}{h^3\,N_+}\cdot\frac{8\,\pi^2\,I\,k\,T}{h^2}\cdot\frac{k\,T}{h\,\nu_e}\cdot e^{-u_{+-}/k\,T}. \tag{12}$$

The condition of equilibrium is

$$\mu_+ + \mu_- = \mu_{+-},$$

where the chemical potential of each species is given by the equation

$$\mu_i = -k\,T\left[\ln f_i + \frac{\mathrm{d}\ln f_i}{\mathrm{d}\ln N_i}\right]_{T,V}.$$

It follows that

$$K_A = \frac{n_{+-}}{n_+\,n_-} = 4\,\pi\,a_e^3\left[\frac{2\,\pi\,D\,a_e\,k\,T}{(s-1)\,\varepsilon^2}\right]^{1/2}\cdot\exp\left\{-\frac{u_{+-} - u_+ - u_-}{k\,T}\right\}. \tag{13}$$

According to equation (9), the algebraic sum of the potential energies appearing in the exponent is $(\varepsilon^2/D\,a_e)\,(s-1)/s$. On converting the units of K_A from ccs. per molecule to litres per gram-mole, the association constant becomes

$$K_A = \frac{N_0}{1{,}000}\,4\,\pi\,a_e^3\left[\frac{2\,\pi\,D\,a_e\,k\,T}{(s-1)\,\varepsilon^2}\right]^{1/2}\cdot\exp\left\{\frac{\varepsilon^2}{D\,a_e\,k\,T}\left(\frac{s-1}{s}\right)\right\}. \tag{14}$$

When applied to data at 298.16 °K, the equation

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[6] F. ACCASINA, S. PETRUCCI and R. M. FUOSS, J. Amer. Chem. Soc. **81**, 1301 [1959].

[7] E. A. MOELWYN-HUGHES, Physical Chemistry, 2nd Ed., Pergamon Press, London 1961, p. 911.

may be cast in the form

$$\log_{10}\frac{K_\mathrm{A}}{D^{1/2}} = \bar{4}.905 + \log_{10}\left[\frac{\mathring{a}_\mathrm{e}^{7/2}}{(s-1)^{1/2}}\right] + 243\left(\frac{s-1}{s\,\mathring{a}_\mathrm{e}}\right)\cdot\frac{1}{D}$$
$$= \bar{4}.905 + \log_{10}\beta + 243\,\gamma\,\frac{1}{D}, \qquad (15)$$

where β and γ are specific constants which may be obtained from the intercept and gradient, respectively, of the isothermal plot of $\log_{10}(K_\mathrm{A}/D^{1/2})$ against $1/D$. This treatment allows an evaluation of s and a_e. The former may be obtained from the equation

$$s = \beta^2\,\gamma^7\left(1-\frac{1}{s}\right)^6. \qquad (16)$$

The method is sensitive to uncertainties in β or γ, and yields values of s ranging from 5 for silver nitrate to 50 for tetra-*iso*-amylammonium nitrate. These values of s are reasonable in themselves and when compared with repulsive integers found in the study of crystals and gases.

Two items concering this treatment call for comment.

(1) No appeal has been made to the concept of ionic radius. The term a_e is the average distance apart of the charges in the ion pair when in its state of lowest potential energy. The root-mean-square displacement about the average separation is given by the equation

$$\frac{\bar{\bar{x}}}{a_\mathrm{e}} = \left[\frac{D\,a_\mathrm{e}\,k\,T}{(s-1)\,\varepsilon^2}\right]^{1/2}. \qquad (17)$$

(2) If $\log_{10} K_\mathrm{A}$, rather than $\log_{10}(K_\mathrm{A}/D^{1/2})$ is plotted against $1/D$, a constant gradient is not obtained since

$$\frac{\mathrm{d}\log_{10} K_\mathrm{A}}{\mathrm{d}(1/D)} = \frac{1}{2.303}\left[\frac{\varepsilon^2}{a_\mathrm{e}\,k\,T}\left(\frac{s-1}{s}\right) - \frac{D}{2}\right], \qquad (18)$$

which increases at $1/D$ increases. It is in this direction that deviations from linearity have recently been observed by Bodenseh and Ramsey [8].

I am indebted to Professor C. W. Davies for some fruitful discussions and to Professor J. B. Ramsey for valuable criticisms and the courtesy of letting me have some of his publications in advance.

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[8] H. K. Bodenseh and J. B. Ramsey, in the press.

The Zero Point Energies of Isotopic Homologues and Isomers*

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Klaus Clusius *zum 60. Geburtstag gewidmet*

An explicit formula is derived for the zero point energy of a system of coupled harmonic oscillators. It is shown that for the case of isotopic homologues this leads to an approximate linear relation in the number of equivalent isotopic substituents. It is shown that the zero point energy differences of successive members of an isotopic homologous series increases with further substitution of the heavy isotope. Through a study of the parabolic deviations from the linear rule, it is shown that intermediate members of an isotopic homologous series form a better basis for interpolation and extrapolation than the end members. The appropriate intermediate members are given by the second order sum rule.

It is a well-established empirical fact that the zero point energies of a set of homologous isotopic molecules are approximately a linear function of the number of equivalent isotopic substituents [1]. In this approximation, the zero point energies of equivalent isotopic isomers are the same. In fact, the zero point energies seem to obey the linear sum rule in $\lambda_i = 4\pi^2\nu_i^2$ of Decius and Wilson [2] and Sverdlow [3].

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[1] H. J. Bernstein and A. D. E. Pullin, J. Chem. Phys. **21**, 2188 [1953].

[2] J. C. Decius and E. B. Wilson, jr., J. Chem. Phys. **19**, 1409 [1951].

[3] L. M. Sverdlov, Dokl. Akad. Nauk, SSSR **78**, 1115 [1951].