Ortho and Paratritium[1]

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Klaus Clusius *zum 60. Geburtstag gewidmet*

Normal tritium was partially and totally converted to paratritium by adsorption on charcoal at liquid neon and liquid helium temperature. The experimentation was performed with 300 millicuries of tritium sealed in a small glass apparatus where the transformation could be performed and the paratritium concentration measured by thermal conductivity. In the adsorbed phase the conversion half-life time was one minute, about 24 times faster than normal hydrogen. In the solid phase the conversion half-life was in the order of 15 minutes. Both processes were much faster than expected.

Introduction

Eucken's measurement of the specific heat of hydrogen at low temperature in 1912[2] was particularly important in retrospect[3], because his work was the impetus for many subsequent interesting investigations and discoveries. The departure of the rotational specific heat of hydrogen as observed by Eucken from that expected from classical theory was not explained until fifteen years later when Dennison[4] made an entirely unexpected approach. Dennison, using the quantum mechanical considerations of Heisenberg[5], found an explanation for the peculiar rotational specific heat of hydrogen at low temperatures. By Dennison's treatment the anomalous behavior of hydrogen could be explained by assuming that hydrogen actually consisted of two distinct forms which do not interchange. One form, orthohydrogen, was characterized by molecules in which the nuclear spins are parallel, while the other form, parahydrogen, possessed spins which are antiparallel. For the ortho modification only the rotational states with $J = 1, 3, 5 \ldots$ are allowed and for the para modification only $J = 0, 2, 4, 6 \ldots$. The ortho modification, as easily can be shown, has the statistical weight of 3; the para modification, the weight of 1[6]. Consequently, as Dennison showed, the heat capacity of normal hydrogen is given by

$$C = \tfrac{3}{4} C_{\text{ortho}} + \tfrac{1}{4} C_{\text{para}} . \qquad (1)$$

Using the above expression, agreement between theory and experiment left little to be desired.

With the preparation of pure parahydrogen by Bonhoeffer and Harteck[7] and the subsequent calorimetric determination of the specific heat of almost pure parahydrogen by Clusius and Hiller[8], the validity of Dennison's theory was established beyond doubt.

Immediately following the discovery of deuterium by Urey, Brickwedde and Murphy[9], the normal deuterium was successfully converted into ortho deuterium by A. Farkas, L. Farkas and P. Harteck[10] using a technique similar to the one employed for preparing parahydrogen. The specific heat for HD which exists in only one modification has been measured calorimetrically by Clusius and Bartholome[11].

In the bombardment experiments of Oliphant, Harteck and Rutherford[12] with deuterons impinging on deuterated ammonium sulfate the following nuclear reactions occurred:

$$ {}_1D^2 + {}_1D^2 \longrightarrow \begin{cases} {}_1T^3 + {}_1H^1 \\ {}_2He^3 + {}_0n^1 . \end{cases} \qquad (2)$$

[1] The research reported in this document has been sponsored by the National Aeronautics and Space Administration, Washington, D.C.

[2] A. Eucken, S.B. Preuß. Akad. Wiss. **41** [1912].

[3] At this time Eucken was an assistant of W. Nernst in Berlin.

[4] D. M. Dennison, Proc. Roy. Soc., Lond. A **115**, 483 [1927].

[5] W. Heisenberg, Z. Phys. **38**, 411 [1926].

[6] For details see the excellent monograph by A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen, Cambridge University Press 1935.

[7] K. Bonhoeffer u. P. Harteck, S.B. Preuß. Akad. Wiss. **103** [1929]; Naturwiss. **17**, 182 [1929]; Z. phys. Chem. B **4**, 113 [1929].

[8] K. Clusius and K. Hiller, Z. phys. Chem. B **4**, 158 [1929].

[9] H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev. **39**, 164, 864 [1932].

[10] A. Farkas, L. Farkas and P. Harteck, Proc. Roy. Soc., Lond. A **144**, 481 [1934].

[11] K. Clusius and E. Bartholome, Naturwiss. **22**, 297 [1934]; Nachr. Ges. Wiss. Göttingen, III. 1 [1934]; Z. Elektrochem. **40**, 524 [1934].

[12] M. L. Oliphant, P. Harteck and E. Rutherford, Proc. Roy. Soc., Lond. A **144**, 692 [1934]; Nature, Lond. **133**, 413 [1934].

As can be seen, a third hydrogen isotope, tritium, is formed. In addition to establishing the exsistence of tritium, reaction (2) constitutes the basis for thermal fusion. ALVAREZ [13] found that tritium is radioactive with a half-life of 12.4 years. Since the tritium nucleus has the same spin [14] as normal hydrogen (1/2) the same statistics apply. Furthermore, since tritium has a long half-life for radioactive decay, one should also be able to transform the ortho-para modifications of this hydrogen isotope. If one takes into consideration that the rotational constant, B, of tritium is one-third that of normal hydrogen [15] then the rotational specific heat of tritium is equivalent to that for hydrogen at one-third the temperature. This relationship results since both molecules follow the same statistics, and the specific heats for rotation are given as:

$$C_{\mathrm{rot}} = f(B/T).$$

Therefore C_{rot} is the same for hydrogen or tritium when B/T is the same. Calculated values for the rotational specific heat and equilibria of the tritium system have been reported by JONES [16].

The conversion of hydrogen to parahydrogen was accomplished by adsorption on charcoal at low temperatures [7]. This technique was extended to the conversion of deuterium. The present work has used the analogous experimental techniques with some modifications to obtain enriched paratritium.

Experimental

Because of the radioactive nature of tritium, it was not possible to follow exactly the same technique as with hydrogen, since for hydrogen virtually each measurement required a new sample of gas which was subsequently discarded. With tritium this was impractical and one charge of tritium had to be used for a series of measurements. Therefore a sealed Pyrex manifold had to be fabricated as a single unit within which one could convert the tritium to paratritium and back again to normal tritium, measuring the degree of conversion by the heat conductivity method as used by BONHOEFFER and HARTECK [8]. A schematic drawing is shown in Fig. 1. The small bulbs D and J contained the catalyst (about one-tenth gram) for the conversion. Bulb D contained a coconut charcoal and bulb J an animal charcoal with a coating of gadolinium chloride to increase the number of paramagnetic centers substantially over that of ordinary charcoal. These tiny bulbs were connected with the apparatus by one-millimeter capillary tubing (C) to minimize back diffusion, because otherwise at room temperature the tritium might have equilibrated on the catalyst rapidly and interfered with the measurements. Appreciable back diffusion of tritium to the catalysts in the bulbs D and J at room temperature might result in reconversion of paratritium to normal tritium interfering with concentration measurements.

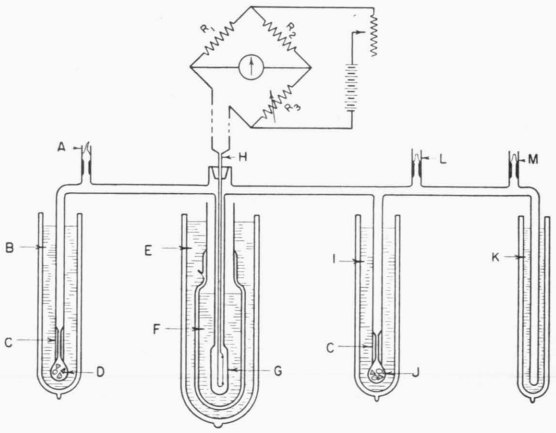

Fig. 1.

The overall size of the apparatus was approximately 280 mm × 250 mm × 20 mm. The heat conductivity cell, G, was cooled with liquid neon, F, which was jacketed with liquid nitrogen E. The heat conductivity cell was made of 19 mm O.D. medium-wall Pyrex. The lead-in wires, H, were 22 gauge tungsten. A platinum filament, approximately 100 mm in length and 10 microns in diameter, was soldered to the tungsten. At this point it should be emphasized that certain concessions had to be made with regard to the construction of the heat conductivity gauge, i. e., the selection of a relatively thick 10-micron diameter wire was made not only to insure stability in shipment of the apparatus from Cambridge, Mass., to Troy [17] after charging with tritium, but also to minimize the possibility of breakage during the course of the measurements. The total volume of the apparatus was 100 cm^3.

Prior to filling the apparatus with tritium, it was baked out at 170 °C under vacuum for sixteen hours.

[13] L. ALVAREZ and R. CORNOG, Phys. Rev. **56**, 613 [1939]; **58**, 197 [1940].

[14] H. L. ANDERSON and A. NOVICK, Phys. Rev. **71**, 372 [1947]. — F. BLOCH, A. C. GRAVES, M. PACKARD and R. W. SPENCE, Phys. Rev. **71**, 373, 551 [1947]. —E. B. NELSON and J. E. NAFE, Phys. Rev. **75**, 1194 [1949].

[15] $B=h/(8\pi^2 c I)$, where h is PLANCK's constant, c is light velocity, and I equals the moment of inertia [for H_2: $B_e=60.809$, $\alpha_e=2.993$; for T_2: $B_e=20.3243$, $\alpha_e=0.59222$ where $B=B_e-(v+1/2)\,\alpha_e$] (cf. G. HERZBERG, Molecular Spectra and Molecular Structure, Vol. I, D. Van Nostrand Company, Inc., New York 1950).

[16] W. M. JONES, J. Chem. Phys. **16**, 1077 [1948].

[17] By the New England Nuclear Corp.

Tritium was then admitted until the final pressure reached 1 mm, which corresponded to 300 millicuries. This was the maximum allowed under the license for these experiments. With a higher filling pressure (about 50 mm Hg) more exact measurements of the paratritium concentration could have been made.

Initially, the conductivity gauge was cooled with liquid nitrogen (77.4 °K) and the platinum filament heated electrically to a temperature around 95 °K. The resistance of the filament was measured with a WHEATSTONE bridge. This method is not very sensitive as may be seen in Fig. 2 since the maximum difference in the specific heat of ortho and paratritium occurs at about 55 °K. Nevertheless this method did show that the conversion of normal tritium into paratritium on charcoal at very low temperatures does occur.

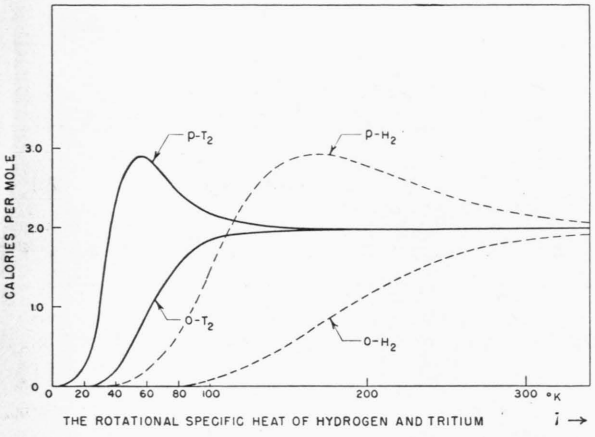

Fig. 2. The Rotational Specific Heat of Hydrogen and Tritium.

In order to improve the sensitivity and thereby study the finer details of the conversion, the heat conductivity cell was cooled with liquid neon. From Fig. 2 it may be seen that liquid neon with a boiling point of 27.16 °K will be as effective as a cooling bath for the thermal conductivity cell for paratritium concentration measurements as liquid nitrogen (77.4 °K) in the case of parahydrogen measurements [18]. Alternately liquid hydrogen could be used as an effective coolant, but liquid neon has certain advantages. No extreme safety precautions are needed. Also the liquid neon has a substantially longer lifetime than liquid hydrogen when contained in a DEWAR flask jacketed with liquid nitrogen, thus providing the temperature and pressure stability needed for this work.

To obtain data of the rate of conversion, the tritium was first always equilibrated to the normal tritium of 3 parts orthotritium to one paratritium [19] by absorbing it on the coconut charcoal at liquid nitrogen temperature. After a few preliminary measurements it was apparent that ten minutes was sufficient for equilibration. The tritium was then desorbed by heating the cell quickly with boiling water, followed by measurements of the resistance with the WHEATSTONE bridge to obtain the reference point of normal tritium on the thermal conductivity cell. For the conversion into paratritium the charcoal was first precooled with liquid nitrogen for two minutes which was then quickly replaced with liquid neon at which point the conversion was assumed to start. At the end of the predetermined time, the neon was removed and the tritium rapidly desorbed from the charcoal bulb with boiling water. The thermal conductivity of the tritium was then measured to determine the extent of conversion. The tritium was then re-equilibrated to normal tritium by adsorption for 10 minutes on charcoal at the temperature of liquid nitrogen as described before and the process repeated for different times to obtain the results in Fig. 3. Equilibrium conversion at neon temperature was assumed to correspond

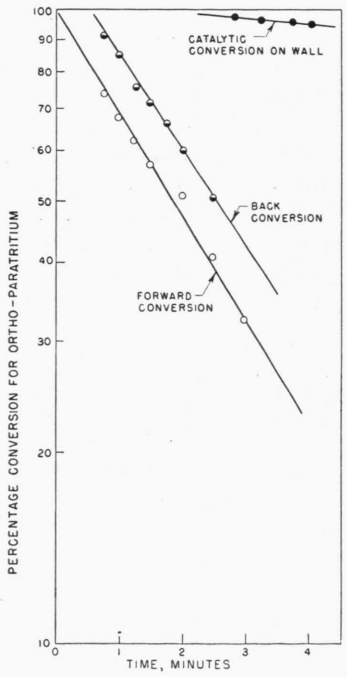

Fig. 3.

to the resistance change observed for long cooling times (ten minutes or more). It should be noted that tritium is almost at the normal equilibrium of 75% ortho to 25% para at liquid nitrogen temperature (77.4 °K) and 52.5% ortho to 47.5% para at equilibrium for neon temperatures (27.16 °K). See Table 1.

It would be of interest, if the necessary amounts of tritium were available, to measure the specific heat of paratritium calorimetrically in the gas phase directly

[18] A. FARKAS, reference [6].

[19] Theoretically 2.95 to 1 at 77.4 °K.

as was done for parahydrogen [9]. Measurements with a thermal conductivity cell assume the validity of the rotational specific heat curves for ortho-paratritium.

T, °K	% Ortho	% Para
0	0.0	100.0
5	0.0	100.0
10	2.8	97.2 9
15	16.4	83.6
20	33.8	66.2
25	47.4	52.6
30	56.7	43.3
40	66.8	33.2
50	71.3	28.7
75	74.5	25.5
100	74.9	25.1

Table 1. Equilibrium Ortho-Paratritium Concentrations.

Results

The precision of the measurements with the thermal conductivity cell for the determination of the concentration of paratritium were comparable to those made previously with hydrogen [7]. The paratritium concentration was measured to $\pm 0.5\%$ meaning that the limit of error for the kinetic data was not due to the concentration measurements, but the uncertainty of the effective time for the conversion, since adsorbing, cooling, heating and desorbing times were not negligible.

In Fig. 3 the kinetic data for the forward and back conversions on coconut charcoal are shown; the half-life for the forward process at 27.16 °K being 0.92 minutes and for the reverse at 77.4 °K about 1.0 minute. The forward process was measured by adsorbing the tritium gas at the temperature of liquid nitrogen, where it becomes equilibrated to its normal ratio of 3 : 1. In transferring from liquid nitrogen to liquid neon, the neon temperature was reached in a few seconds. In the subsequent heating with hot water, the tritium gas was desorbed in a few seconds. The fact that the forward conversion data goes through the origin for time, $t = 0$, indicates that these transient times must have been negligible.

A substantial correction, however, occurs for the back conversion because the adsorption on charcoal at liquid nitrogen temperatures takes about one minute as was readily observed using the heat conductivity cell as a PIRANI gauge. From Fig. 3, in agreement with these considerations it can be seen that the curve for the back conversion is displaced from the origin by about one minute. By changing the experimental procedure this time could be minimized, but such changes would involve other more serious problems.

, In the heating and cooling processes described above, the equilibrium temperature was attained rapidly because of the presence of the helium resulting from the decomposition of the radioactive tritium.

The catalytic conversion on the wall is shown at the top of Fig.3 for the normal tritium, with a half-life time of about one hour. The tritium was converting in the thermal conductivity cell which was cooled with neon. The conversion may have occurred on the wall, or actually on the electrical lead-in wires, or by some other means, but was not fast enough to interfere with the measurements.

When the apparatus was designed it was expected that the rate of conversion of tritium on the charcoal would be slow and therefore a second catalyst, gadolinium chloride coated charcoal, was included. It turned out that the conversion rate on this second catalyst was very fast. In fact practically no forward conversion was observed by cooling with liquid neon. It was found that the catalyst was so effective, that during the desorption process it was re-equilibrated to practically normal tritium. This indicated that the equilibrium was established in seconds, and the tritium re-equilibrated during the short period of desorption. Since the plain coconut charcoal was satisfactory, all the reported kinetic data were obtained with its use.

Discussion

Looking back, BONHOEFFER and one of the authors in 1928 were very fortunate that charcoal at low temperature was such an effective and convenient catalyst for the ortho-para conversion of hydrogen [7]. It was found later by L. FARKAS and H. SACHSSE [20] that the paramagnetic centers on the charcoal were the reason for the fast conversion. To achieve this catalysis the hydrogen molecules had to diffuse freely even at low temperatures (20.4 °K) on the inhomogeneous charcoal surface in order to interact with the paramagnetic centerus of the charcoal.

[20] L. FARKAS and H. SACHSSE, S.B. Preuß. Akad. Wiss. 268 [1933]; Z. phys. Chem. B **23**, 1, 19 [1933].

According to WIGNER [21] the ortho-para transition probability is given for the gas phase by:

$$W_{01} = \frac{8\,\mu_i^2\,\mu_j^2\,I\,\pi^2}{h^2\,r_s^6\,k\,T} \qquad (1)$$

where μ_i and μ_j are the magnetic moments of the interacting species; I, the moment of inertia of the converting species; h, PLANCK's constant; k, BOLTZMANN's constant; r_s, the collision distance between the i-th and j-th particles; and T, the absolute temperature. A similar relation can be assumed as a first approximation for the heterogeneous conversion. The rate of conversion, therefore, should increase inversely with the sixth power of the distance between the hydrogen molecule and these paramagnetic centers, and proportional to the moment of inertia of the molecule and the square of the magnetic moments. The temperature dependence for conversion of the adsorbed hydrogen is at present not well known. It appears that the conversion is temperature independent which could mean that the effective distance to the paramagnetic centers is not a function of temperature. This point should be investigated further.

Since the conversion of hydrogen and tritium follow the same statistics, the difference in the rates of conversion should be due to the different moments of inertia, and any difference in the nuclear magnetic moments. Since the ratio $I(H_2)/I(T_2)$ is one-third and the ratio of the magnetic moments of tritium and hydrogen is about unity [14], the ratio of rates of conversion for tritium should be three times faster in the gas phase compared with normal hydrogen according to equation (1), if converted with a paramagnetic gas such as O_2 or NO. For practical reasons we could not make the conversion experiments in the gas phase with a paramagnetic gas, but only on charcoal. The conversion of one minute which was twenty-four times faster than the conversion of normal hydrogen [22] or eight times faster than expected if eq. (1) for the gas phase were applicable. Three possible reasons for this fast conversion rate are immediately apparent. The term r_s^6 could be smaller for tritium than for hydrogen because the tritium has a zero point energy which is $(1/3)^{1/2}$ smaller than that of hydrogen. But it seems unlikely that the distance r_s for tritium would be smaller by $(1/8)^{1/6}$ (or a factor 0.7) than the distance r_s for hydrogen. The factor 8 can not be explained by this effect, but it could contribute to a minor extent.

In the second place a major increase in rate by ion interaction or by ion exchange mechanisms produced by the radioactivity of the tritium is unlikely because carbon is a semi-conductor and any highly efficient chain mechanism is not likely. Long chains of exchange between hydrogen and deuterium under extremely clean conditions had been observed, however, by THOMPSON and SCHAEFFER [23]. In this connection the same apparatus was filled with deuterium and the rate of conversion was measured using the liquid neon. After taking into consideration the differences in the magnetic moments and the different statistics, the rate appeared to be faster than expected compared with the parahydrogen conversion by a factor six. Since this is also faster than anticipated and no ions are present (deuterium is stable), the effect of ions in the case of tritium conversion on the charcoal should be at the most only minor.

In the third place, another factor which must be considered is a more favorable energy transfer occurring between tritium (or deuterium) and the charcoal than that with hydrogen. This energy transfer may unexpectedly enhance the overall transition probability. This mechanism will be investigated in the near future by using other type adsorbents *.

A few preliminary experiments indicate a relatively fast conversion rate for tritium at liquid helium temperatures where the tritium is solid. The half-life appears in the order of 15 minutes, which is much faster than would be expected. In this case, however, the ions may have a major effect. A faster rate is not observed in the case of deuterium [24].

Conclusion

Conversion of orthotritium to paratritium and reverse can be made by experimental procedures analogous to those for conversion of parahydrogen from normal hydrogen. Because the mass of tritium is

[21] E. P. WIGNER, Z. phys. Chem. B **19**, 203 [1932].

[22] Such conversion experiments with hydrogen were performed in the same apparatus.

[23] S. O. THOMPSON and O. A. SCHAEFFER, J. Amer. Chem. Soc. **80**, 553 [1958].

* We appreciated the opportunity to discuss this problem with E. WIGNER.

[24] K. MOTIZUKI, J. Phys. Soc., Japan **12**, 163 [1957].

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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(Z. Naturforschg. **18 a**, 202—205 [1963]; eingegangen am 2. Dezember 1962)

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:

$$A^+ + B^- \rightleftarrows A^+B^-$$

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

$$K_A = C_{A^+B^-}/C_{A^+}C_{B^-}. \qquad (1)$$

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:

$$K_A = K_A^0 \cdot \exp\{\varepsilon^2/(D\,a\,k\,T)\} \qquad (2)$$

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

$$\log_{10} K_A = \log_{10} K_A^0 + \frac{\varepsilon^2}{2.303\,a\,k\,T} \cdot \frac{1}{D}, \qquad (3)$$

or

$$\log_{10} K_A = \log_{10} K_A^0 + B/D, \qquad (4)$$

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

$$\log_{10} K_A = \log_{10} K_A^0 + 243/(\mathring{a}\,D), \qquad (5)$$

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

[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.