sities of 3130 Å. radiation (data of Table I). The photolysis cells were made from fused quartz test-tubes containing an optically flat quartz window fused into the side wall. Light intensities obtained from the monochromator were measured with an Eppley line thermopile together with a high sensitivity galvanometer calibrated with standard radiation lamps provided by the N. B. S. The intensities refer to the quanta/sec. striking a fixed area of the zinc oxide suspension. Uranyl oxalate actinometry[13] was employed to measure the intensity of the beam from the chemical filter system. Light intensities were measured before and after each run. The mixture in the photolysis cell containing 0.20 g. of ZnO/25 ml. of solution was stirred magnetically to form a fairly uniform suspension and was continually saturated with oxygen by bubbling the gas through the solution at atmospheric pressure for a 5-min. period before irradiation and during the run. Flow rates of about 15 and 100 ml./min. were used for experiments at low and high light intensities, respectively. The peroxide yield was independent of both the flow rate of oxygen (at flow rates above 10 ml./min.) and the time of initial oxygen saturation (at periods above 5 min.) for the light intensities used in the quantum yield work (1×10^{13} to 1×10^{15} quanta/sec.). Other conditions being equal, amounts of ZnO above 0.2 g./25 ml. of solution gave no increase in peroxide quantum yield, evidencing complete light absorption. The H_2O_2 product was analyzed as described. The absorption, coefficient of zinc oxide at wave lengths less than 4000 Å. is extremely great, so the reasonable assumption was made in the calculation of the quantum yields given in Table I that all quanta entering the cell were absorbed by the ZnO. Correction for the dark reaction was made, assuming the photochemical and thermal rates to be additive. In the case of the oxalate solutions the corrections were most serious; they amounted to as much as 20% of the net amount

of H_2O_2 formed in the long experiments necessary at the very low light intensities. The data of Fig. 1 were obtained at different intensities of incident radiation, but all intensities were below 4×10^{14} quanta/sec. In this range the quantum yield of H_2O_2 formation at 3130 Å. (and probably at the other wave lengths) is independent of the incident intensity as shown in Table I. At the conditions used in this research the quantum yield decreases at intensities above 1×10^{16} quanta/sec. At 1×10^{17} quanta/sec. the net quantum yield of H_2O_2 formation in the region of 3130–3660 Å. is about 0.3 (0.6 M NaO_2CH solution and O_2 flow rate of 100 ml./min.). **(b) Effect of Oxygen Pressure on Peroxide Yield.**—A water-cooled, Pyrex-jacketed General Electric A-H6 arc, operated on a stabilized a.c. voltage, was used as the light source. ZnO (0.20 g.) in 20 ml. of 0.2 M NaO_2CH solution was stirred magnetically in a heavy Pyrex test-tube connected to a high pressure oxygen flow system. Oxygen was bubbled through the mixture at 100 ml./min. at the pressures indicated in Fig. 2 for a preliminary period of 5 min. and then irradiated for a period of 1 min. The intensity was approximately constant during this series of runs. H_2O_2 was determined as before. **(c) Reactant and Product Ratio Determination.**—A water-cooled A-H6 arc was suspended in the constant temperature bath of the Warburg apparatus. A 0.10-g. sample of ZnO, 7.00 ml. of solution and several glass beads were placed in a Warburg reaction flask. The solution was saturated with O_2 and pure O_2 was placed over the solution and in the connecting and manometer tubes. The shaking of the irradiated system provided by the Warburg apparatus supplied the means of mixing. The usual procedures were utilized to determine the amount of oxygen uptake. Following irradiation and separation of the ZnO, aliquots of the solution were analyzed as described for H_2O_2 and oxalate. Usually duplicate simultaneous runs were made.

COLUMBUS, OHIO

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The Differential Diffusion Coefficient of Rubidium Chloride in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND MILTON BLANDER

The differential diffusion coefficient of rubidium chloride between 0.001 and 0.01 M concentrations at 25° has been determined by the conductometric method previously employed in this Laboratory. Good agreement with the prediction of the Nernst–Onsager and Fuoss equations has been obtained.

Determinations of the differential diffusion coefficients of potassium chloride from 4 to 30°,[1,2] sodium chloride[3] and lithium chloride[3] at 25° in water at concentrations less than 0.01 M have achieved three purposes. They have supplied definite objective evidence for the validity of the Nernst equation for the diffusion coefficient of an electrolyte at infinite dilution. This result lends confidence to an analogous limiting equation for the self-diffusion coefficients of ions at infinite dilution.[4] Secondly, the concentration dependences of these diffusion coefficients confirm the validity of the thermodynamic term which results from the general theory of irreversible processes.[5] Finally, the re-

sults seem to indicate that the mobility term of the theory[6,7] which corrects for the effect of electrophoresis on the limiting ionic mobilities is of the right order of magnitude and sign. The proof of this contention requires a high order of accuracy in the determination of the diffusion coefficients and one hesitates to give a final verdict until a large amount of evidence is available. As a further contribution to this subject, the diffusion coefficient of rubidium chloride from 0.0015 to 0.011 M concentration has been measured by the conductometric method. These determinations form the subject of the present communication.

Theoretical Considerations

The concentration and temperature dependences of the diffusion coefficient of 1–1 electrolytes

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(3) H. S. Harned and C. L. Hildreth, Jr., ibid., **73**, 650 (1951).

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(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y.

according to the theory[6] are

$$\mathfrak{D} = 10.629 \times 10^{10} T \frac{\overline{M}}{c} \left(1 + c \frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

where the mobility term, $\overline{M}/C$, is given by

$$\frac{\overline{M}}{c} \times 10^{20} = 1.0748 \left(\frac{\lambda_1^0 \lambda_2^0}{\Lambda^0}\right) -$$
$$\frac{22.148}{\eta_0(DT)^{1/2}} \left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0}\right) \frac{\sqrt{c}}{1 + A'\sqrt{c}} +$$
$$\frac{9.304 \times 10^7}{\eta_0(DT)^2} c\phi(A'\sqrt{c}) \quad (2)$$

and the thermodynamic term $(1 + c\partial \ln y_\pm/\partial c)$ may be evaluated from the equations

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{1.1514\, S_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} +$$
$$4.606Bc + c\psi(d) \quad (3)$$

$$\psi(d) = \frac{\partial d}{\partial c} + \frac{0.001\,(2M_1 - M_2)}{d + 0.001\,(2M_1 - M_2)} \quad (4)$$

$$d = d_0 + \frac{(M_2 - d_0\phi_v^0)c}{1000} - \frac{S_v d_0 C^{3/2}}{1000} \quad (5)$$

In equation (1), $\mathfrak{D}$ is the differential diffusion coefficient in cm.^{2}, sec.$^{-1}$, T is the absolute temperature, c is the concentration in moles per liter and $y_\pm$ is the activity coefficient of the chloride on the molar concentration scale. In equation (2), λ_1^0 and λ_2^0 are the equivalent limiting ionic conductances, $\Lambda^0 = \lambda_1^0 + \lambda_2^0$, η_0 is the viscosity of water, and D its dielectric constant.

$$A = a35.559 \times 10^8/(D\Gamma)^{1/2}$$

in which κ is the Debye and Hückel reciprocal radius, a, the mean distance of approach of the ions and Γ is the ional concentration. The quantity $\phi(A'\sqrt{c})$ is an exponential integral function which may be obtained from tables.[8]

In equation (3), $S_{(f)}$ represents the limiting theoretical slope of the Debye and Hückel theory for activity coefficients, B is an empirical constant and $c\psi(d)$ is the term required to convert the expression from rational to molar activity coefficient. Equations (4) and (5)[9] are used to evaluate $\psi(d)$. In them, d is the density of the solution, d_0 is the density of solvent, M_1 is the molecular weight of solvent, M_2 the formula weight of the salt, ϕ_v^0 is the apparent molal volume at infinite dilution and S_v is the experimental slope of the apparent molal volume versus $\sqrt{c}$.

From equations (1) and (2), the limiting value of the diffusion coefficient, $\mathfrak{D}_0$, may be computed by the equation

$$\mathfrak{D}_0 = 17.872 \times 10^{-10} T \left(\frac{\lambda_1^0 \lambda_2^0}{\Lambda^0}\right) \quad (6)$$

Equations (1), (2) and (3) may be used to evaluate the slope $S_{(\mathfrak{D})}$, of the limiting law

$$\mathfrak{D} = \mathfrak{D}_0 - S_{(\mathfrak{D})} \sqrt{c} \quad (7)$$

with the result that

$$S_{(\mathfrak{D})} = \frac{3.754 \times 10^{-3}}{D^{3/2}T^{1/2}} \frac{\lambda_1^0 \lambda_2^0}{\Lambda^0} + \frac{3.683 \times 10^{-8}}{\eta_0 D^{1/2}T^{-1/2}} \left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0}\right)^2 \quad (8)$$

In Table I, the constants, parameters and specific quantities required for the calculations are com-

(8) Reference 7, p. 130.
(9) See ref. 7, p. 250.

piled. Substitution of these data in equations (6) and (8) yields

$$\mathfrak{D} \times 10^5 = 2.0566 - 1.2055 \sqrt{c} \quad (9)$$

for the limiting equation (7).

TABLE I
CONSTANTS AND PARAMETERS EMPLOYED IN THEORETICAL CALCULATIONS

T	298.16	λ_1^0	78.05[10]
$S_{(f)}$	0.5091[a]	λ_2^0	76.34[a]
η_0	8.949×10^{-3a}	$a \times 10^8$	3.6[a]
D	78.54[a]	$4.606B$	0.0368[a]
d_0	0.99707	S_v	2.219[a]
M_1	18.016	ϕ_v^0	31.87[a]
M_2	120.94		

[a] Ref. (7).

Experimental Results

The experimental results were obtained by the conductance method described in detail by Harned and Nuttall[1] and are of the same order of accuracy as those obtained for lithium, sodium and potassium chlorides. The sample of rubidium chloride of high purity used in these experiments was prepared by Dr. Walter E. Voisenet, Jr., in this Laboratory. The value of the limiting equivalent conductance of the rubidium ion, λ_1^0 used in the calculation of the diffusion coefficient was determined by him from the same sample.

The second column in Table II contains the results obtained at the concentrations designated in the first column. The values calculated by equations (1) to (6) are recorded in the third column. The sum of the differences between the observed and calculated results divided by their number is 0.0035 or approximately 0.17% while the maximum difference is 0.007 or 0.35%. The last column contains values of $\mathfrak{D}' = \mathfrak{D}_{obs.} + (\mathfrak{D}_0 - \mathfrak{D})_{calcd.}$ which should be constant and equal to $\mathfrak{D}_0$. It is to be observed that the mean value of $\mathfrak{D}'$ is 2.059 which differs by 0.1% from the limiting result 2.057. These considerations and the conclusions derived from similar results with lithium, sodium and potassium chlorides leave little doubt of the validity of the theory at concentrations below 0.01 M for these 1–1 type electrolytes.

TABLE II
OBSERVED AND CALCULATED VALUES OF THE DIFFUSION COEFFICIENT OF RUBIDIUM CHLORIDE AT 25°

c, mole/l.	$\mathfrak{D} \times 10^5$ (obs.)	$\mathfrak{D} \times 10^5$ (calcd.)	$\mathfrak{D}' \times 10^5$
0.0	...	2.057	(2.057)
.00176	2.012	2.014	2.055
.00255	2.008	2.007	2.058
.00408	2.001	1.996	2.062
.00446	1.988	1.994	2.051
.00449	1.998	1.994	2.061
.00460	1.998	1.993	2.062
.00677	1.986	1.983	2.060
.00687	1.989	1.982	2.064
.00797	1.979	1.978	2.058
.01110	1.969	1.968	2.058
		Mean	2.059

(10) W. E. Voisenet, Jr., Dissertation, Yale University, June, 1951.

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NEW HAVEN, CONN.

The Conductance at 25° of Lithium Chloride, Sodium and Potassium Bromides and Potassium Iodide in Methanol, and of Lithium Chloride, Sodium Bromide and Potassium Iodide in Water

BY R. E. JERVIS, D. R. MUIR, J. P. BUTLER AND A. R. GORDON

The conductance of lithium chloride, sodium and potassium bromides and potassium iodide has been determined in anhydrous methanol by the direct current method, and as a check on the purity of the salts similar measurements with lithium chloride, sodium bromide and potassium iodide have been carried out in aqueous solution. The methanol data were extrapolated to zero concentration by two different methods; combined with the known limiting conductances for sodium, potassium and chloride ions recently determined in this Laboratory, they provide limiting conductances for lithium, bromide and iodide ions in this solvent. For the two bromides, the Kohlrausch rule is obeyed within experimental precision. As might be expected, the Walden rule fails completely to correlate the methanol data with those for water. The significance of the limiting conductance ratio for a pair of ions of like charge and sign in different solvents is discussed.

This research is a sequel to the earlier transference[1] and conductance measurements[2] for potassium and sodium chlorides in anhydrous methanol. Its purpose was to provide reasonably precise limiting conductances for lithium, bromide and iodide ions in this solvent.

Experimental

The measurements were effected by the direct current method[2,3] previously employed in this Laboratory, and are based on the Jones and Bradshaw 25° 0.01 Demal standard.[4] It was found that the silver-silver iodide probe electrodes gave somewhat larger bias potentials than was the case with chloride and bromide electrodes; such bias potentials were, however, independent of the current passing, and agreed within experimental precision (0.01 mv.) with the static bias measured in the absence of current. The preparation of the stock solutions, the dilution procedure, the technique of solution transfer to the cell (including the precautions taken to avoid evaporation losses) and the determination of solvent conductance have been previously described[2]; the only change in the methanol measurements lay in flushing the empty cell with methanol-saturated nitrogen before filling, thus eliminating the small evaporation correction previously employed.

Lithium Chloride.—Analar grade lithium nitrate was crystallized three times from water, making use of the difference in solubility between 0 and 60°. A concentrated, twice distilled solution of ammonium carbonate containing excess ammonia was added dropwise to the nitrate solution, and the precipitated carbonate was digested for several hours at 80°, filtered and washed until the washings were free from nitrate.[5] The carbonate was dissolved in three times distilled constant boiling hydrochloric acid, and the chloride was finally crystallized from slightly acid solution and centrifugally dried. The salt was fused in platinum in dry HCl, cooled in dry CO₂-free nitrogen, and weighed by means of a bottling apparatus. The product was neutral and spectroscopically pure.

Potassium Bromide.—Two methods of preparation were used. B. D. H. Analar grade KBr was three times crystallized from conductivity water containing a trace of HBr, and centrifugally dried. Alternatively, analytical grade constant boiling hydrobromic acid was three times distilled,

only a 50% middle cut being retained in each distillation, and in this three times crystallized K₂CO₃ was dissolved leaving the solution slightly acid; the bromide was then recovered as outlined above. The salt was dried at 600° in purified nitrogen, and the resultant material was neutral and spectroscopically pure. Gravimetric analysis, in which the precipitation[6] was effected very slowly at a concentration of 0.01 N to minimize occlusion, gave (after allowing for the small solubility correction) 0.63370 ± 0.00003 for the KBr/AgBr ratio as compared with the theoretical 0.63375. Determinations of the conductance in aqueous solution showed no difference in the two methods of preparation, and the measured equivalent conductances were in good agreement with the earlier KBr data.[3d,7]

Sodium Bromide.—After a lengthy investigation, the procedure described below was adopted. Three times crystallized Na₂CO₃ was suspended in carefully purified methanol, and a slight excess of redistilled constant boiling hydrobromic acid was added; the solution was then concentrated under reduced pressure at temperatures below 40°, and the crystals (after being vacuum-dried) were dissolved at 40° in the minimum amount of methanol which had been slightly acidified with HBr. Carefully purified peroxide-free ether was then distilled in dropwise under an atmosphere of nitrogen until a crop of very fine crystals had formed, and the solution was then chilled to 0°; after standing, the crystals were filtered, washed in methanol and dried under vacuum. With reasonable precautions against exposure to moisture, it is possible in this way to obtain the anhydrous salt rather than the dihydrate (see below). The salt was heated to 600° in purified nitrogen, since it was found that this procedure gave results with samples prepared in this way identical with those obtained when the salt was fused in an atmosphere of HBr and subsequently cooled in nitrogen. The salt was finally weighed by means of a bottling apparatus. The material was neutral and spectroscopically pure. Electron diffraction patterns were notably sharp and corresponded to the correct lattice constant for NaBr in contrast to those obtained with samples containing appreciable amounts of chloride; we wish to thank Dr. F. C. Boswell of the Physics Department for making these measurements. Gravimetric analysis (see above) gave 0.54802 ± 0.00004 for the NaBr/AgBr ratio as compared with the theoretical 0.54800.

There are several points to be noted in the preparation of this salt. (1) Any procedure which yields the dihydrate, e.g., recrystallization from aqueous solution, will in our experience yield on heating a slightly basic product even if the heating takes place in an atmosphere of HBr. For example, a 0.005 N aqueous solution gave at 25° Λ = 122.35 when salt prepared as outlined in the preceding paragraph was used. Some of the same preparation, after crystallization

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