TABLE IV

PHYSICAL PROPERTIES OF SUBSTANCES IN THE REACTION

	M.p., °C.	Calcd. temp. of self-diffusion,[20] °C.	Ionic size, Å.[18] Cation	Anion	Crystal form
Ferric sulfate	Dec.[4]	At least 225	0.67	*ca.* 2.23	Rhombohedral–orthorhombic[19]
Ferric chloride	306[15]	30	0.67	1.81	Hexagonal[4]
Calcium chloride	772[5]	250	1.0	1.81	Cubic[4]
Calcium sulfate	1450[5]	590	1.0	*ca.* 2.23	Rhombic–monoclinic[4]

formation of a eutectic mixture involving ferric chloride could possibly give rise to a liquid phase.

Many reactions between solids proceed with high velocity because the crystals have a certain amount of disorder.[14] Diffusion of disordered ions is an exchange reaction which is capable of a transfer of ions over distances which are much greater than the mean free path. No data are available on the extent of crystalline defects in either ferric sulfate or calcium chloride but there is some evidence that ferric sulfate is the active constituent of the reaction mixture. Ferric sulfate will also react with sodium chloride,[16] a substance which has been prepared with almost a perfectly ordered lattice.[17]

A solid phase reaction can proceed at the temperature of self-diffusion of one of the reactants, or at a crystallographic transition point.[21] Self-diffusion is not appreciable in calcium chloride under 250° (Table IV), and the crystal has only one modification. Hence, diffusion in this substance cannot proceed below 250°. Diffusion would appear to be more probable in the ferric sulfate crystals which do exhibit two rather indefinite modifications.

Crystals of ferric sulfate exhibit an ideal situation for a high degree of Frenkel disorder.[14,22] The small size of the ferric ion and the large ionic radius of the sulfate ion (Table IV) are favorable for the removal of the cation to an interstitial position. It is suggested that the sulfate ion in ferric sulfate is tightly held in its lattice position while the ferric ion is free to migrate. Neither calcium ion nor chloride ion in calcium chloride has a high rate of diffusion since the temperature is well below the temperature of self-diffusion.

The supposition of rigidity of the sulfate lattice is strengthened by the fact that the particle size of the calcium sulfate formed in the reaction is approximately the same as the ferric sulfate involved. If large particles of ferric sulfate react, the calcium sulfate crystals are large, and if fine powders are used the product is finely divided. Ferric sulfate and calcium sulfate have been reported to exist in the form of rhombic crystals. Therefore, it is possible that the sulfate lattice is undisturbed and the ferric and calcium ions are exchanged.

(16) K. H. Oenicke, *Chem. Centr.*, [1] **11**, 447 (1840).

(17) R. M. Barrer, "Diffusion in and Through Solids," Cambridge University Press, New York, N. Y., 1941, p. 264.

(18) H. A. Lange, "Handbook of Chemistry," Handbook Publishing Company, Sandusky, Ohio, 1944.

(19) E. W. Posnjak and H. E. Merwin, THIS JOURNAL, **44**, 1965 (1922).

(20) G. Tammann and Q. A. Mansuri, *Z. anorg. Chem.*, **126**, 119 (1923).

(21) J. A. Hedvall, "Reacktionfahigkeit fester Stoffe," Barth, Leipzig, 1938, p. 128.

(22) J. Frenkel, *Z. Physik*, **35**, 652 (1926).

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WESTERN AUSTRALIA]

The Diffusion Coefficients of Calcium Chloride and Ammonium Chloride in Concentrated Aqueous Solutions at 25°

BY J. R. HALL,[1] B. F. WISHAW AND R. H. STOKES

RECEIVED AUGUST 20, 1952

A Goüy diffusiometer is described and measurements on calcium chloride and ammonium chloride solutions up to high concentrations at 25° are reported and discussed.

Introduction

The Goüy diffusiometer, as developed by Ogston and co-workers[2] and simultaneously by Kegeles, Gosting and Longsworth,[3] is probably the most accurate and convenient method for determining diffusion coefficients in solutions of moderate and high concentrations. Over its chief rival in this concentration range, the magnetically-stirred porous diaphragm cell,[4] it offers the advantages of being an absolute instead of a relative method, of somewhat greater intrinsic accuracy and of requiring shorter times for runs (though the latter advantage is somewhat offset by the time required for measuring the photographic records). In this Laboratory we have therefore transferred our program of diffusion studies in aqueous electrolytes to a Goüy instrument, and are now reserving the porous diaphragm cell for studies involving organic solvents and strongly colored solutions, for which optical methods employing a plastic diffusion cell are inapplicable.

The Goüy diffusiometer which we have built for this purpose combines some of the features of

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(1) The sections of this paper dealing with the construction of the apparatus and the measurements on calcium chloride are abstracted from a thesis presented by J. R. Hall in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours in the University of Western Australia.

(2) C. A. Coulson, A. G. Ogston, *et al.*, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).

(3) G. Kegeles and L. J. Gosting, THIS JOURNAL, **69**, 2516 (1947); L. G. Longsworth, *ibid.*, **69**, 2510 (1947).

(4) R. H. Stokes, *ibid.*, **72**, 763 (1950).

both the American and the English versions, and differs sufficiently from both to justify some detailing of its construction. Data for calcium chloride and ammonium chloride up to high concentrations are then presented.

The Optical System.—A 2-meter optical bench is mounted on two concrete pillars which rise from the ground without contact with the laboratory floor. The light source is a 100 watt mercury arc focused onto the source slit by a double plano-convex condenser of 7.5 cm. focal length. A heat filter of Chance O.N.20 glass and an Ilford No. 807 (mercury green) filter are interposed between the condenser and slit. The source-slit, though primitive, is entirely successful; it was constructed by lightly ruling across a blackened "process" photographic plate with a new razor-blade, using a good quality engineers' straight-edge. It is about 10 μ in width, which gives adequate resolution and intensity for patterns of the dimensions obtained with this apparatus. The slit is focused onto a photographic plate at the other end of the bench by means of a Kodak Aero Ektar camera lens of 17.5 cm. focal length and maximum aperture f. 2.5. The plate-holder takes 3.25 × 2.25" dark-slides and is preceded by a mask which covers all but 1 cm. width of the plate, so that about 8 exposures can be taken on each plate. The dark slide can be moved horizontally to a new position after each exposure. The time at each exposure is automatically recorded along with the pattern photograph as follows: the image of an illuminated stopwatch is projected onto the plate below the interference pattern, by means of a small 45° mirror and a microscope objective of 2.5 cm. focal length. Movement of the focal-plane shutter simultaneously exposes the pattern and the stopwatch. Exposures, on Kodak Ortho X plates, are of about one second duration; in this time the stopwatch second-hand moves appreciably, but is clearly visible as a blur over a small angle, which can be bisected with an accuracy of 0.1 sec. To obtain satisfactory images of the second-hand, it has proved necessary to use a watch with a black dial and white hands.

The Diffusion Cell.—For forming the sharp boundary we have employed the technique of flowing both liquids from a fine slit; in this respect the cell design is based on that described by Ogston and co-workers.[2] It is, however, much larger, as economy of solution is not a prime consideration, and experience has shown that prolonged flushing of the diffusion channel with the appropriate solutions above and below the slit is essential to reproducibility. Clear evidence of this was found by filling the cell with solutions of ferric chloride and ammonium thiocyanate and observing the rate of removal of the red color from the cell walls by flushing. (The same two solutions, one inside and one outside the cell, are invaluable aids to the detection of minute leaks due to inadequate sealing of the optical flats.) The cell is shown in isometric projection in Figs. 1 and 2. It is constructed of sheet Perspex, the parts forming the diffusion channel A being ground and lapped by hand to a tolerance of about 2 μ. The boundary-sharpening slit S was formed by butting the two components B against a piece of feeler-gage steel 0.005 cm. in thickness, which was removed after the parts B had been cemented to the collecting channel C. The whole face of the diffusion channel carrying the slit was then lapped flat. The less dense solution enters the diffusion channel from the reservoir R_1, while the denser solution from R_2 passes down through the reference channel D and hole H into the bottom of the diffusion channel. The hole H can be closed by a sliding gate valve V controlled by a wire (which lies in the groove G to avoid blocking the light passing through the reference channel). This facilitates filling the reservoirs. The optical flats O are sealed to the Perspex faces by a trace of rubber solution, and are held in place by the pressure of the thermostat jacket round their outer edges. The thermostat jacket, which is also of Perspex, surrounds the entire cell and the reservoirs, except the outermost faces of the optical flats, and has holes cut in its walls to expose the outer surfaces of the optical flats, which are sealed to it by rubber gaskets. Thermometers can be mounted in both reservoirs and also in the thermostat jacket. The cell is mounted on leveling screws on the optical bench, connections being made from the jacket to the main thermostat by thin rubber tubing to avoid communicating vibrations.

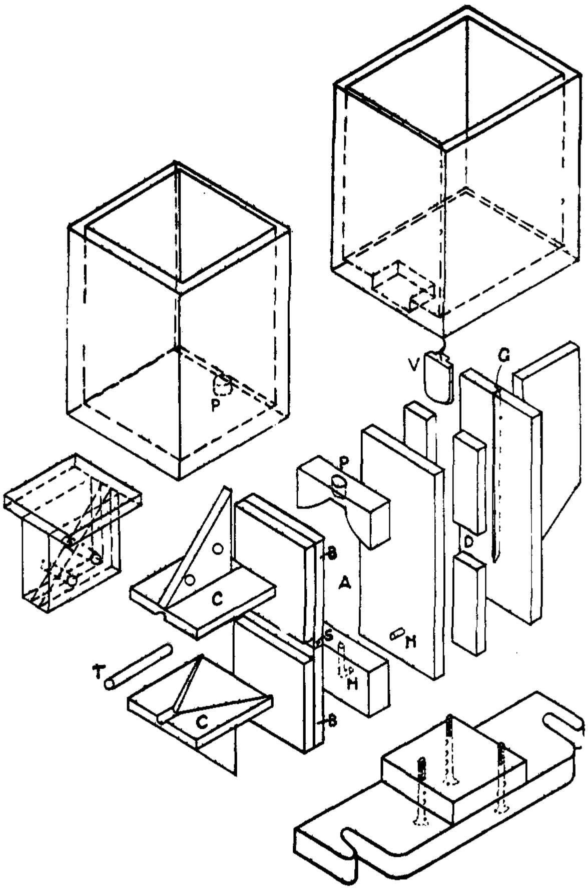

Fig. 1.—Cell for Goüy diffusiometer, exploded view.

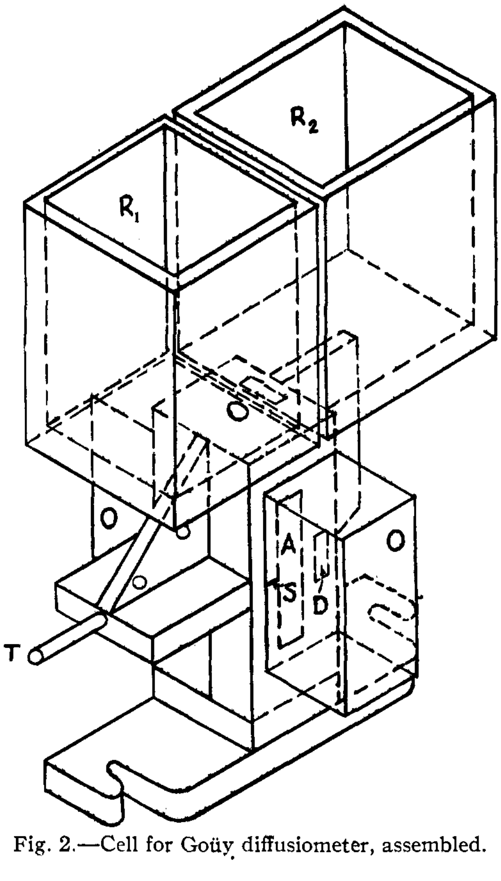

Fig. 2.—Cell for Goüy diffusiometer, assembled.

The outflow tube T from the slit is connected to a small stopcock mounted rigidly nearby. A double stop consisting of two 1.5 mm. square holes 1.5 mm. apart is fixed permanently in front of the reference channel, and on the other side of the cell a tilted optical flat displaces the light from this stop upwards to form a fixed reference mark on the plate as described by Ogston, *et al.*[2] The diffusion channel can be covered either by a pair of slits 4 mm. apart and centered on the boundary which are used for determining the fractional part of the refractive index difference in wave lengths between the two solutions, or by a vertical slit 4 mm. wide and adjustable to any desired gap in the vertical direction. This serves to stop down the diffusion channel to a convenient width to reduce over-exposure near the optic axis in the early exposures. The length of the diffusion channel along the optic axis is 2.372 cm.; its width and height are 0.65 and 3.2 cm., respectively. The "optical distance" from the center of the cell to the photographic plate was 93.60 cm. during the work reported in this paper, but has now been increased to 141.32 cm.

Manipulation.—The procedure follows that of the Oxford workers: At the beginning of a run denser solution from R_2 is allowed to fill the diffusion channel to the bottom of the hole P, and double-stop exposures are made to determine the distance from the optic axis to the reference mark. The reservoir R_1 is then filled, the gate valve opened, and solution is flowed out from the slit. The flow is allowed to continue slowly for half an hour or so to flush the channel out and to establish temperature equilibrium. The total amount of each solution passed through the diffusion channel during the boundary-sharpening process is about 30 to 40 ml. Toward the end of this process the flow-rate is increased to about 25 drops per minute. Another double-stop exposure is made while the flow continues; the double-stop is then replaced by the 4 mm. vertical slit, the tap is turned off, and the stopwatch started simultaneously. For solutions with diffusion coefficients of the order of 10^{-5} cm.^{2} sec.$^{-1}$ the Goüy interference pattern is photographed at intervals from about 3 minutes to 30 minutes after the closing of the tap attached to T.

The measurement of the plates and the calculation of the results follows the lines established by Kegeles, Gosting and Longsworth. The cell proves to have a satisfactory zero-time error of about 6 to 10 seconds; excellent straight lines are obtained in the plots of apparent diffusion coefficient *versus* reciprocal time, so that no serious attempt has been made to reduce the zero-time error below this level, though a preliminary model of the cell, with a wider sharpening slit, appeared to have a zero-time error of perhaps only 2 or 3 seconds. The observed spacing of the pattern lines agrees well with the theoretical, the ratio C_t (see ref. 3) seldom varying by 0.1% throughout the pattern, except in the case of exposures taken less than 3 minutes after the start of the process. Usually about 8 to 10 fringes are measured on each pattern, starting with $j = 1$ and proceeding toward the optic axis at equal intervals of j, *e.g.*, in a 70-line pattern the fringes $j = 1, 5, 10, 15, \ldots, 50$ would be measured, the cross-wire being set on the center of the minimum. No lines less than 1 mm. from the optic axis are measured, as the reading error of $\pm 2\ \mu$ on the measuring microscope is too serious in such cases.

The instrument has been tested by measurements on potassium chloride at 25°, the results agreeing within 0.1% with those reported by Gosting,[5] and with those of Harned and Nuttall.[6] Further confirmation of its accuracy is provided by the measurements on calcium chloride solution which follow: these may be compared over part of the concentration range with those of Lyons and Riley.[7]

Materials.—The calcium chloride and ammonium chloride were B.D.H. "Analar" materials, made into stock solutions which were analyzed gravimetrically for chloride and also by accurate density measurements. Pairs of cell solutions were prepared by dilution of these stocks. The usual concentration difference between the upper and lower solutions in a run was 0.1 molar (giving about 100 lines in the Goüy pattern) for calcium chloride, and 0.15 molar (giving about 70 lines) for ammonium chloride. A few measurements were made on calcium chloride at low concentrations using concentration differences as low as 0.02 molar; these were proportionately less accurate, but were considered worth attempting in order to approach the region of concentration studied by Harned and Levy,[8] who used concentrations up to 0.005 molar. In the case of ammonium chloride the curve in the region up to a few tenths molar lay so close to that for potassium chloride that it appeared unnecessary to carry the measurements below 0.1 molar.

The experimental results are given in Table I; in Table II diffusion coefficients are presented at round molarities.

TABLE I

DETAILS OF DIFFUSION EXPERIMENTS WITH CALCIUM CHLORIDE AND AMMONIUM CHLORIDE SOLUTIONS AT 25°

$\bar{c}$, mean molarity of pair of solutions in cell; Δc difference in molarities of pair; D, differential diffusion coefficient for concentration $\bar{c}$ (strictly, its average value over range Δc).

Calcium chloride			Ammonium chloride		
$\bar{c}$	Δc	$D \times 10^5$	$\bar{c}$	Δc	$D \times 10^5$
0.0152	0.0202	1.155	0.0698	0.1396	1.857
.0255	.0307	1.143	.0760	.1519	1.848
.0710	.0604	1.113	.1042	.0990	1.838
.1516	.1008	1.109	.2258	.1465	1.837
.3036	.1008	1.118	.3768	.1556	1.848
.4994	.0995	1.140	.5121	.1258	1.865
.6426	.0872	1.160	.6756	.1867	1.883
.9989	.0984	1.203	.8626	.1874	1.902
1.2965	.0730	1.236	1.4050	.1851	1.976
1.5962	.0697	1.275	1.8759	.1705	2.030
1.9765	.1040	1.306	2.8182	.2030	2.151
2.452	.0920	1.307	3.640	.2351	2.210
2.748	.0990	1.288	4.558	.2097	2.258
3.248	.1074	1.234	5.285	.1929	2.264
3.530	.1025	1.192			

Discussion

For calcium chloride the results agree satisfactorily with those obtained by the same method by Lyons[7] in the range 0.05 to 1.0 molar. The curve of D *vs.* $\sqrt{\bar{c}}$ (Fig. 3) prepared from our data also joins up smoothly with that for the work of Harned and Levy[8] in solutions below 0.01 molar. This eliminates any doubt about the correctness of their results in dilute solution, and makes it clear that the lack of agreement with the Onsager–Fuoss theory in this region, to which Harned and Levy drew attention, is not due to experimental error.

Since the theory of Onsager and Fuoss, though highly successful for 1:1 electrolytes, breaks down even for very dilute calcium chloride solutions, it is useless to attempt to apply it at the concentrations of the present experiments. It is however worthwhile attempting an approximate explanation of the form of the curve at higher concentrations, which is remarkable for the rather sharp maximum at 2.7 molar.

There can be little doubt that the diffusing species are hydrated calcium ions and (probably unhydrated) chloride ions in the one direction, and single water molecules[9] in the other. The very complex situation arising from the diffusion in binary non-electrolyte solutions at high concentrations has been analyzed by Hartley and Crank,[10] who arrive at an expression for the diffusion co-

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[5] L. J. Gosting, THIS JOURNAL, **72**, 4418 (1950).

[6] H. S. Harned and R. L. Nuttall, *ibid.*, **71**, 1460 (1949).

[7] P. A. Lyons; we are indebted to Prof. H. S. Harned of Yale University for his courtesy in making these data from his laboratory available to us before publication.

[8] H. S. Harned and A. L. Levy, THIS JOURNAL, **71**, 2781 (1949).

[9] J. H. Wang, *ibid.*, **73**, 510, 4181 (1951).

[10] G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

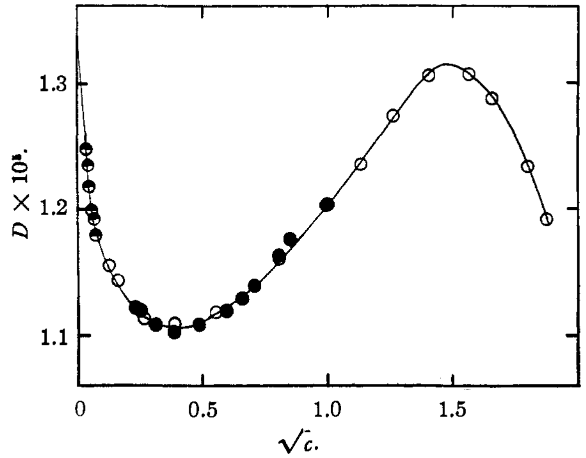

Fig. 3.—Diffusion coefficient of calcium chloride at 25°: ○, this research; ●, Lyons and Riley (Goüy method); ◐, Harned and Levy (conductance method). Note: open circles and filled circles coincide at $\sqrt{c} = 0.7$ and $\sqrt{c} = 1.0$.

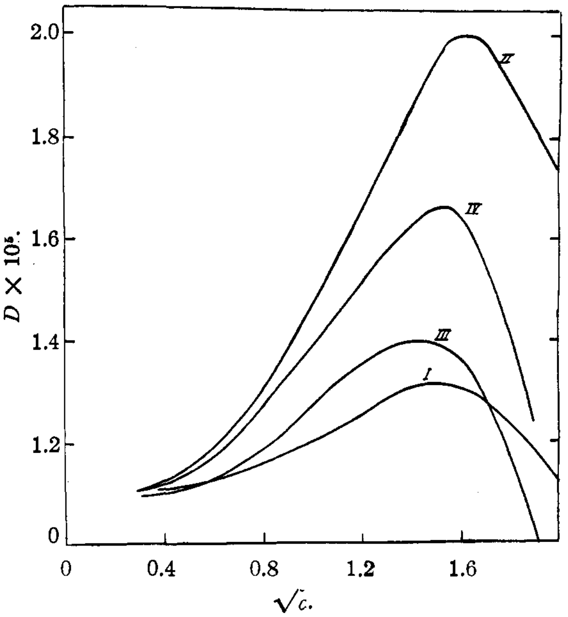

Fig. 4.—Observed and calculated diffusion coefficients of calcium chloride at 25°: curve I, experimental; curve II, equation 1 with $n = 0$; curve III, equation 1 with $n = 4$; curve IV, equation 1, with $n = 9$ but omitting the factor $\eta°/\eta$.

efficient in terms of the thermodynamic properties of the solution and the frictional coefficients of the diffusing species. Dr. J. N. Agar[11] has modified this expression to apply to the case of a diffusing aqueous electrolyte whose ions are hydrated, the resulting equation being

$$D = D_0 \left(1 + m \frac{\mathrm{d} \ln \gamma}{\mathrm{d}m}\right) (1 - 0.018\, nm) [1 + 0.018m(\nu D^*/D_0 - n)] \frac{\eta_0}{\eta} \quad (1)$$

where η and η_0 are the viscosities of solution and pure solvent, respectively, m is the molality, γ the mean molal activity coefficient, n the "hydration number" (number of moles of "bound" water per mole of salt), D^* the self-diffusion coefficient of water (2.1×10^{-5} cm.^{2} sec.$^{-1}$ at 25° [9]), D_0 the Nernst limiting value of the diffusion coefficient, and ν the number of ions formed by one stoichiometric molecule of salt. It is probable that the value D_0 in this equation should be replaced by the Onsager–Fuoss mobility including the electrophoretic corrections,[12] but these corrections seldom exceed a few per cent. of D_0, so that for approximate purposes equation (1) should suffice. In Fig. 4 we plot the function given by equation (1) with various values of the hydration parameter n. There is some doubt about the validity of including the viscosity factor η_0/η for particles as small as ions, but it is noteworthy that by including it, even with neglect of hydration, a curve of the same general form as the experimental one is obtained, having a maximum at nearly the right concentration. A reasonable value of the hydration parameter is also sufficient to introduce a maximum in approximately the right position, even if the viscosity factor is omitted from equation (1). By including both the measured viscosity of the solution and a smaller hydration parameter, a nearer approach to the experimental curve can be made. None of these alternatives is quantitatively successful, but the proposed equation is at least able to account for the major features of the experimental curve. A simple explanation of the failure of any one curve to follow the experimental one up to the highest concentrations may well be that the hydration parameter n is decreasing (owing to shortage of water) at the higher concentrations.

TABLE II

DIFFERENTIAL DIFFUSION COEFFICIENTS AT 25°

c in moles/liter; D in units of cm.^{2} sec.$^{-1}$ $\times 10^{-5}$

c	D_{CaCl_2}	D_{NH_4Cl}	c	D_{CaCl_2}	D_{NH_4Cl}
0.015	1.155	...	1.5	1.263	1.986
.025	1.143	...	2.0	1.307	2.051
.070	1.113	...	2.5	1.306	2.113
.1	1.110	1.838	3.0	1.265	2.164
.2	1.111	1.836	3.25	1.233	2.184
.3	1.118	1.841	3.5	1.195	2.203
.5	1.140	1.861	4.0		2.235
.7	1.166	1.883	4.5		2.257
1.0	1.203	1.921	5.0		2.264

TABLE III

COMPARISON OF DIFFUSION COEFFICIENTS FOR NH_4Cl AND KCl AT EQUAL MOLALITIES

m	D_{NH_4Cl}	D_{KCl}	m	D_{NH_4Cl}	D_{KCl}
0.1	1.838	1.840	2.0	2.032	1.986
.3	1.841	1.840	2.5	2.089	2.036
.5	1.862	1.850	3.0	2.138	2.084
.7	1.884	1.864	3.5	2.173	2.128
1.0	1.914	1.889	4.0	2.199	2.165
1.5	1.974	1.935			

Ammonium Chloride.—We have already remarked[13] on the extremely small differences between the activity coefficients (and between the ionic conductances) of ammonium chloride and of potassium chloride. As might be expected, the diffusion coefficients are also nearly equal, as Table

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[11] J. N. Agar, private communication, 1951.

[12] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[13] B. F. Wishaw and R. H. Stokes, *Trans. Faraday Soc.*, in press.

III demonstrates. In this table we compare diffusion coefficients at equal molalities rather than at equal molarities, since the resemblance between the activity coefficients is most marked when the molal scale is used for the comparison.

In view of the close similarity in effective ionic sizes for these two electrolytes, it is highly probable that the Onsager–Fuoss electrophoretic effects on the diffusion mobilities are nearly equal. Thus, even if the mathematical theory which Onsager and Fuoss presented for the magnitude of these effects is inapplicable at high concentrations, a comparison of diffusion data at equal concentrations for the two salts should eliminate most of the uncertainty due to the electrophoretic terms. Hence, by comparing values of $D' = D/(1 + m \text{ d} \ln \gamma/\text{d}m)$ for the two salts, we might expect to estimate the difference in the hydration factors of equation (1). We have, using this equation, and provided that $0.018nm$ is small compared to unity

$$\begin{aligned} D'_{\text{NH}_4\text{Cl}}/D'_{\text{KCl}} &\cong \frac{\eta_{\text{KCl}}}{\eta_{\text{NH}_4\text{Cl}}} [1 + 0.036m(D^*/D_0 - n_{\text{NH}_4\text{Cl}})]/ \\ &\qquad [1 + 0.036m(D^*/D_0 - n_{\text{KCl}})] \\ &\cong \frac{\eta_{\text{KCl}}}{\eta_{\text{NH}_4\text{Cl}}} [1 + 0.036m(n_{\text{KCl}} - n_{\text{NH}_4\text{Cl}})] \qquad (2) \end{aligned}$$

When these calculations are carried out, we find that if the quantity $(n_{\text{KCl}} - n_{\text{NH}_4\text{Cl}})$ is given the value 0.3, the values of $D'_{\text{NH}_4\text{Cl}}/D'_{\text{KCl}}$ can be reproduced within 1% up to 4 molal, though the function $D'_{\text{NH}_4\text{Cl}}/D'_{\text{KCl}}$ *vs. m* shows some curvature which cannot be reproduced by the linear equation (2). A much better straight line is obtained by omitting the viscosity factors; the quantity $(n_{\text{KCl}} - n_{\text{NH}_4\text{Cl}})$ then requires the value 0.53, but the equation thus modified gives a considerably better fit. However, it is difficult to decide between these two courses, for the viscosities of both potassium chloride and ammonium chloride change little with concentration, and the viscosity factors are therefore small.

The difference of 0.3 to 0.5 in the hydration parameters obtained by this treatment is entirely consistent with that obtained by applying the one-parameter form of the hydration-corrected Debye–Hückel equation developed by Stokes and Robinson. There, the values $n_{\text{KCl}} = 1.9$[14] and $n_{\text{NH}_4\text{Cl}} = 1.6$[13] fit the experimental activity coefficients up to $4m$ and $7m$, respectively.

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[14] R. H. Stokes and R. A. Robinson, THIS JOURNAL, **70**, 1870 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Extraction of Zirconium and Hafnium with Various β-Diketones[1]

BY EDWIN M. LARSEN AND GLENN TERRY

RECEIVED APRIL 7, 1952

Distribution coefficients for the partition of zirconium and hafnium between perchloric acid solution and a β-diketone-containing benzene phase were determined for 2-thenoyltrifluoroacetone (HTTA), 2-furoyltrifluoroacetone (HFTA), 2-pyrryltrifluoroacetone (HPTA) and trifluoroacetylacetone (HCTA). The ratios of $D_{\text{Zr}}/D_{\text{Hf}}$ at constant hydrogen ion and constant diketone activity were: HTTA, 23; HFTA, 24; HCTA, 13; HPTA, 12.

Certain β-diketones[2,3] have been used for the fractional separation of zirconium and hafnium. It seemed desirable to make a comparison of the β-diketones which could be used for this purpose and to compare the efficiency of the processes under similar conditions.

The diketones selected were acetylacetone (HCCA), trifluoroacetylacetone (HCTA), 2-furoylacetone (HFCA), 2-furoyltrifluoroacetone (HFTA), 2-thenoylacetone (HTCA), 2-thenoyltrifluoroacetone (HTTA) and 2-pyrroyltrifluoroacetone (HPTA).

The experimental conditions selected were those established in the work of Connick and Reas.[4] The aqueous solutions were 2 *M* HClO_4 (except in the HCTA runs) and had equilibrium metal ion concentrations of 3×10^{-3} *M* or less. Under these conditions it was assumed that the metal ion species was mainly M^{+4} and the polymer concentration was negligible. The equilibrium studied was, then

$$\text{M}^{+4} + 4\text{HK} \rightleftharpoons \text{MK}_4 + 4\text{H}^+ \qquad (1)$$

and at constant hydrogen ion concentrations the equilibrium constant was expressed by the equation

$$\log K' = \log D - 4 \log [\text{HK}] \qquad (2)$$

where D was the metal distribution coefficient $[\text{MK}_4]/[\text{M}^{+4}]$, and [HK] the diketone activity.

Under the conditions selected only HTTA, HFTA and HPTA gave a reasonable degree of metal extraction. For the HCTA studies, the hydrogen ion concentration was reduced to 0.5 *M* H^+ although it was realized that as a consequence the nature of the metal ion species was different than in the preceding cases, and the K' values could then not be compared directly. The ratio $K'_{\text{Zr}}/K'_{\text{Hf}}$ could be compared with the others, however. The HCCA did not give metal extraction at hydrogen ion concentrations as low as 0.4 *M* and diketone concentrations as high as 0.1 *M*, while the HTCA did give a slight metal extraction at 0.1 *M* diketone concentration.

Experimental

Materials.—The β-diketones were all synthesized. The crude trifluoroacetylacetone[5] was dried over phosphorus

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[1] Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy and carried out under Task Order 4 of Contract N7onr-28504 between the office of Naval Research and the University of Wisconsin.

[2] E. H. Huffman and L. J. Beaufait, THIS JOURNAL, **71**, 3179 (1949).

[3] B. G. Schultz and E. M. Larsen, *ibid.*, **72**, 3610 (1950).

[4] R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

[5] A. Henne, M. Newman, L. L. Quill and R. Staniforth, *ibid.*, **69**, 1819 (1947).