and silver anode electrodes were adjusted so that they nearly touched the stirred mercury. The coulometer was then connected in series with the cell and the solution electrolyzed at a cathode potential 0.3 to 0.4 v. more negative than that at which the determination was to be run. This preliminary electrolysis, which removed traces of reducible impurities from the solution, was discontinued when the current became negligible. After a few minutes, the current usually decreased to 1 ma. or less.

The applied potential was then reduced until the cathode potential reached the desired value. The electrical circuit was opened; 10 ml. of stock solution, containing 0.5 millimole of ketone in 95% ethanol, was added; the test solution was deoxygenated for 5 min.; the coulometer buret was read; and the run was started. The applied potential was controlled manually to maintain the desired cathode potential until the electrolysis was complete, *i.e.*, the current was 1 ma. or less. In some cases, the current did not drop below 2 ma.; this was due to incomplete reduction, since some of the reducible material was occluded by the resinous by-product previously mentioned, from which it was apparently very slowly released.

Macroscale Electrolysis.—In a typical experiment 2.00 g. (0.0148 mole) of propiophenone was reduced in a manner similar to that used in the coulometric runs at an $E_{\max}$ of 1.35 v. *vs.* the S.C.E., except that the ketone was added in small amounts over a period of *ca.* 10 hr. to the deoxygenated and conditioned base electrolyte (100 ml. of *p*H 4.8 acetate buffer containing 9.5% ethanol). After reduction was essentially complete, the electrolyzed solution was extracted with ether; the ether extract was washed with water, dried over anhydrous sodium sulfate and filtered. Ether, any residual unreduced ketone and any carbinol formed were removed by distillation at atmospheric pressure; the oily yellow residue obtained gave white crystals after cooling for an hour at room temperature. The crystals, purified by washing with petroleum ether, were identified as propiophenone pinacol, m.p. of 132°.[12]

Acetophenone (2.00 g., 0.0166 mole) was electrolyzed under the same conditions except that all of the ketone was added at one time to the deoxygenated and conditioned base electrolyte. The reaction mixture obtained was acidified with hydrochloric acid and steam distilled. The residue was extracted with hot benzene; the extract was washed with water, dried over anhydrous sodium sulfate, filtered, concentrated and then diluted with three parts of Skellysolve B. On cooling this mixture in an ice-bath, acetophenone pinacol crystallized out, m.p., 120.5–121.5°.

Acknowledgment.—The authors wish to thank the U. S. Atomic Energy Commission which helped support the work described.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

Centrifugal Electromotive Force: The Transference Numbers of Lithium, Rubidium and Cesium Iodides. The Iodide–Iodine Complex[1,2]

BY B. ROGER RAY, DONALD M. BEESON AND HAROLD F. CRANDALL

RECEIVED AUGUST 19, 1957

Measurements have been made of the potentials developed in a centrifugal field by galvanic cells of the type (Pt); I_2, MI, I_2; (Pt) in which the two otherwise identical electrodes are at different radii. Lithium, rubidium and cesium iodides, approximately 0.2 *N*, were investigated at 25° over a range of iodine concentrations. The data yielded the following values of the Hittorf transference numbers: $t_{\mathrm{Li}} = 0.317$, $t_{\mathrm{Rb}} = 0.506$, $t_{\mathrm{Cs}} = 0.496$. Utilizing conductivity data, the results are interpreted quantitatively by the previously proposed cell mechanism based upon the presence of the triiodide ion. The partial atomic volumes of the iodine at 25° were found to be 29.82, 30.30 and 30.29 ml./g., at near zero concentration, in solutions of the three iodides.

The simplest type of galvanic cell consists of two identical electrodes immersed in the electrolyte. Examples are M; MX; M, where M is a metal and MX is a salt of the metal, and (Pt); I_2, MI, I_2; (Pt), where MI is an iodide. Such a cell, if reversible and of uniform concentration and temperature throughout, will have no potential unless, as Des Coudres[3] showed, it is placed in a centrifugal field, whereupon a very small e.m.f. develops. Tolman,[4] working with iodide–iodine type cells, achieved the first quantitative results. More recently, Grinnell and Koenig[5] have measured accurately the closely analogous gravitational e.m.f. of the KI–I_2 cell. The latest studies, utilizing improved centrifugal apparatus and techniques, have been carried out by MacInnes and co-workers[6,7] on KI and NaI solutions. Among other things, the work has now shown that centrifugal e.m.f. data are capable of yielding accurate transference numbers and promise to furnish a method applicable to systems in which the established methods are inadequate.

For the iodide–iodine type cell we have the equation

$$-EF = 2\pi^2r^2(x_2^2 - x_1^2)[t_{\mathrm{M}}(M_{\mathrm{MI}} - \bar{V}_{\mathrm{MI}}\rho) - (M_{\mathrm{I}} - \bar{V}_{\mathrm{I}}\rho)] \quad (1)$$

Here E is the centrifugal e.m.f., F is the faraday, r is the revolutions per second, x_1 and x_2 are the electrode distances from the center of rotation, t_{M} is the transference number of the monovalent metal ion, M_{MI} and $\bar{V}_{\mathrm{MI}}$ are the molecular weight and partial molal volume of the salt, M_{I} and $\bar{V}_{\mathrm{I}}$ are the atomic weight and partial atomic volume of iodine and ρ is the density of the solution. This equation states that per faraday of electricity through the cell t_{M} equivalent of salt is transported from the anode region to the cathode region and one equivalent of iodine in the reverse direction.

If, however, the iodine present in the solution complexes to form an I_{j+1} ion, where j is the number of atoms of uncharged iodine per ion, then the applicable equation is

$$-EF = 2\pi^2r^2(x_2^2 - x_1^2)[t_{\mathrm{M}}(M_{\mathrm{MI}} - \bar{V}_{\mathrm{MI}}\rho) - (1 + jt_c)(M_{\mathrm{I}} - \bar{V}_{\mathrm{I}}\rho)] \quad (2)$$

---

[1] A portion of the data was taken from the Ph.D. thesis of D. M. Beeson submitted to the Graduate College of the University of Illinois, 1952.

[2] This work was supported by grants from the American Philosophical Society, the Research Corporation and the National Science Foundation. It is a pleasure for the University and the authors to acknowledge this generous assistance.

(3) Th. Des Coudres, *Ann. Physik*, **49**, 284 (1893).

(4) R. Tolman, *Proc. Am. Acad. Arts. Sci.*, **46**, 109 (1910).

(5) S. Grinnell and F. Koenig, THIS JOURNAL, **64**, 682 (1942).

(6) D. MacInnes and R. Ray, *ibid.*, **71**, 2987 (1949).

(7) D. MacInnes and M. Dayhoff, *J. Chem. Phys.*, **20**, 1034 (1952).

where t_c is the transference number of the complex ion. An equivalent of eq. 2 for the gravitational case has been derived by Koenig and Grinnell[8] in a general theoretical treatment; the equation as written was developed by MacInnes and Ray[7] and shown to be a useful expression for the cell process. (Beginning with the work of Koenig, several generalized treatments of electrokinetic phenomena, including the sedimentation potential, have been carried out using the thermodynamic theory of irreversible processes.)[9,10] Equation 1 is the limiting case of eq. 2 since as the concentration of iodine in the solution approaches zero, t_c must also approach zero. In practice, a very short linear extrapolation of experimental data to zero iodine concentration yields a limiting E/r^2 ratio applicable to eq. 1 that, along with supplementary data, permits the calculation of t_M.

Equation 2 makes possible the elucidation of the nature of the complex ion formed in solution. This can be done by utilizing conductance data and Kohlrausch's law of independent ion mobilities so as to give

$$t_M = \lambda_M/\Lambda_m \qquad (3)$$

$$t_c = \frac{R\lambda_{I^-}}{\Lambda_m} - \frac{\Lambda_{MI}-\Lambda_m}{\Lambda_m} \qquad (4)$$

where Λ_{MI} is the measured equivalent conductance of the salt solution of concentration C_{MI} in the absence of iodine, Λ_m is that quantity for the salt solution after the addition of iodine, λ_M and λ_{I^-} are the ionic equivalent conductances of metal and uncomplexed iodide ions and R is the concentration ratio C_{I^0}/C_{MI} in which C_{I^0} represents original equivalents (gram atoms) of uncharged iodine per liter of salt solution. Thus, with appropriate conductance data, the quantities t_M and t_c can be evaluated and then substituted into eq. 2 in order to calculate values of E/r^2 for any chosen value of j and for different values of R. These E/r^2 values can then be compared with those obtained experimentally in order to establish the correct value of j and, thereby, the form of the actual complex.

Experimental Details

Centrifugal Apparatus.—The vacuum centrifuge was modeled after an earlier design,[11] but with modifications. Essential features of these, to approximate scale, are shown schematically in Fig. 1. The rotor M is suspended from the drive motor A by a small diameter steel shaft. Bolted into the top I of the vacuum chamber is the bearing support H. The top bearing plate F rests on a neoprene ring G. This plate retains the sleeve bearing E and the oil reservoir D that provides lubrication and a vacuum seal.

Both the flexibility and the alignment of the bearing, vital features in this "spinning top" system, are obtained by adjusting the tension of four bolts which press the bearing plate F into the neoprene ring. Experience showed that even with the most careful adjustment a small amount of rotor wobble sometimes occurred at certain critical low speeds. A second bearing was found to be very effective in eliminating this, as well as any rotor precession, yet introduced negligible friction. This small bearing K is pressed into a neoprene disc L that is free to slide loosely about on the studs J, J.

The cell O used in this study is similar to the one developed by MacInnes and Dayhoff.[7] It is made of Jena 16III glass with ring electrodes, R_1 and R_2, of bright platinum wire sealed into the glass. The stopper is of Teflon. The cell is permanently and rigidly seated in an epoxy resin base, cast *in situ*, in the brass casing N; Vaseline fills the space between cell and casing. Although no details are shown, the leads from the electrodes are supported by a plastic ring near the top of the cell—this ring also centers the cell. Brass prongs screw into the ring and down against the leads so as to make positive contact with brass contact pins at the center of the rotor when the cell is inserted. The additional leads, connected in like manner, serve the thermopile used to detect any temperature gradients within the rotor.

In order to achieve microvolt precision in the measurements, it is necessary to avoid, insofar as possible, dissymmetry between the two arms of each circuit and also to avoid even minute thermal differences between pairs of metallic junctions. The circuits are constructed in an identical fashion and connections rely upon friction or screw pressure. The commutator shown in Fig. 1 has four identical copper–mercury contacts of small size. The outside section S, which rotates, consists of four plastic subsections that screw together, each holding a 1/4" diameter copper tube T. The end of each tube rotates in mercury U held in a small plastic cup that is clamped on the stationary insulated shaft V. The commutator is assembled in step-wise fashion. Poor alignment or rotor unbalance produces erratic potentials. The external circuit utilizes a Rubicon precision potentiometer and a Leeds and Northrup 2430C galvanometer.

Speed control, more critical in e.m.f. work than in other applications of centrifuges, is accomplished in a very satisfactory manner as follows. The motor A, in Fig. 1, equipped with special thrust bearings, has an armature excited by 110 v. d.c. and field coils energized by a storage battery. Mounted on the shaft is a small 20 pole generator armature C and nearby are pick-up coils B,B. An oscilloscopic comparison of frequencies is made between the frequency from the pick-up coils, with the proper capacitances and resistances inserted, and the reference frequency from a 1000 cycle calibrated General Radio oscillator. Stationary roulette patterns of simple form are obtained at certain ratios of frequencies. Different speed settings are made by adjusting manually the resistance in the armature circuit of the motor.

The vacuum chamber has two molded Lucite windows that enable one to observe the rotating system. A large diffusion pump keeps the pressure below 50 μ.

Recently Kay and MacInnes[12] have reported on several factors bearing on the precision of the e.m.f. centrifuge. In addition to developing several improvements in design, these workers made a valuable study of the small thermal gradients that tend to be produced in the column of solution during rotation, partly as a result of adiabatic pressure changes and partly from frictional causes. It is evident that small errors due to thermo-potentials are complex in origin and are difficult to eliminate.

Procedure for E.M.F. Measurements.—For accurate results the two electrodes should be, from an electrical standpoint, identical and reversible. Traces of contamination were removed by cleaning the cell in fuming nitric acid followed by thorough soaking in distilled water. At intervals the electrode surfaces were renewed by treatment with aqua regia.

Several hours sometimes were required for the cell to come to equilibrium after being sealed in the rotor. During this time the stationary potential, primarily of thermal origin, generally dropped to a negligible value (less than 1 μv.). However, in some cases a residual potential of up to 10 microvolts remained after permitting the cell and contents to stand or upon carrying out centrifugal runs. This residue, believed due to a slight lack in identity of the electrodes, was sensibly constant for a given cell and solution and was, then, a small constant increment added to, or subtracted from, the true centrifugal potential. In a plot of E *vs.* r^2 this produced a finite intercept but did not change the linear relationship nor the value of the slope E/r^2. It is this slope that is utilized in the calculations.

In a typical centrifugal run the potentials developed at each of five to ten different speeds, in the range up to 5000 r.p.m., were observed. Under satisfactory operating

---

[8] F. Koenig and S. Grinnell, *J. Phys. Chem.*, **44**, 463 (1940).

[9] D. Miller, *Am. J. Phys.*, **24**, 595 (1951).

[10] (a) J. Overbeek, *J. Coll. Sci.*, **8**, 420 (1953); (b) S. DeGrost, P. Mazur and J. Overbeek, *J. Chem. Phys.*, **20**, 1825 (1952).

[11] R. Ray and D. MacInnes, *Rev. Sci. Inst.*, **20**, 52 (1949).

[12] R. Kay and D. MacInnes, *J. Phys. Chem.*, **61**, 657 (1957).

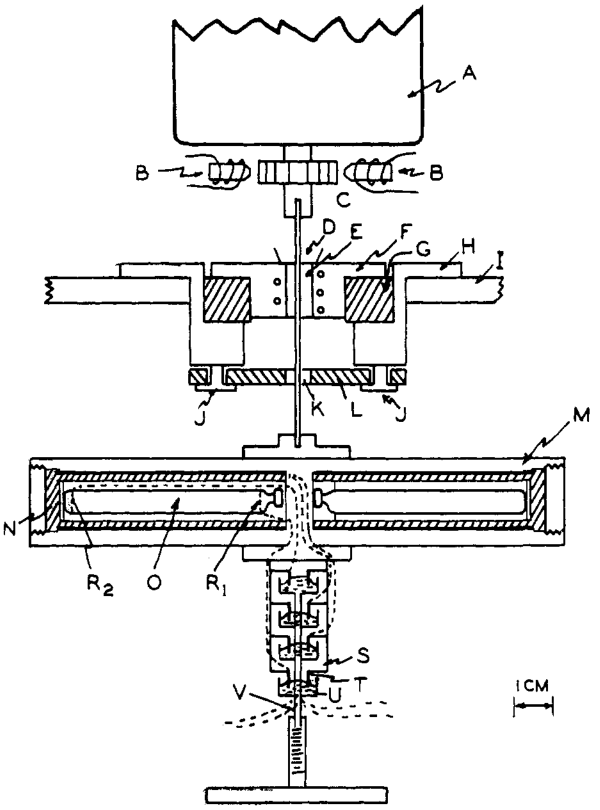

Fig. 1.—Schematic view of the centrifuge used for the measurement of electromotive forces.

conditions, the potentials were essentially independent of the length of time of observation (usually several minutes) and of the order of the speed settings—small initial drifts were sometimes observed, probably due to adiabatic pressure changes.[12]

Determination of Densities and Conductivities.—Density determinations, from which to evaluate the partial atomic volume of iodine, were made using aged Pyrex pycnometers of 20 ml. size and of single capillary design. The customary procedures included calibration of capillaries and weights, application of buoyancy corrections, avoidance of loss of volatile iodine and use of a thermostat regulating to ±0.002°. The reproducibility of runs was better than 0.00002 g./ml.

The electrical conductances of solutions of the alkali iodides containing various amounts of iodine were measured at 25° in a precision conductivity bridge. The cell constant of the Jones type conductivity cell was based upon the data of Jones and Prendergast.[13]

Materials.—In centrifugal e.m.f. work experience has shown that particular care needs to be taken to avoid oily or surface active impurities that can contaminate the electrodes and also to avoid colloidal material which tends to concentrate in the region of one or the other electrode. Solutions containing iodine seem particularly prone to develop, within days, a greasy-like surface film although carefully protected from light and organic matter.

Fresh doubly-distilled water, with portions drawn from the interior, were used to make up the solutions. Merck C.P. potassium iodide was purified by filtration of a hot saturated solution through dense, acid-hardened filter paper, and partial crystallization. This was three times repeated. Finally the dried crystals were heated to 500° for 1 hr. in a stream of purified nitrogen. Baker C.P. iodine was three times resublimed.

The RbI was obtained from City Chemical Corp. and was stated to be better than 99.8% pure with the major impurity consisting of 0.1% K. The CsI was supplied by Dr. V. A. Stenger of Dow Chemical Company; it had been especially purified and by spectrographic analysis contained 0.01% Na and a total of 0.007% Rb, K, Ca, Sr and Ba. The LiI was prepared by treating very pure $LiOH \cdot H_2O$, obtained from Mr. W. F. Luckenbach of Foote Mineral Company, with an excess of HI (Merck reagent for methoxyl determinations), and then vacuum drying. The lithium hydroxide contained 0.1% carbonate and less than 0.005% each of Na, Al, Ca.

A stock solution of a salt (the concentration was determined by the Volhard method) was divided into two portions and iodine added on a weight basis to one; a series of solutions for study consisted of various admixtures by weight of these two portions. After a solution was placed in the centrifuge it was given a short initial centrifugation which served to remove colloidal materials from between the electrodes and, in general, improved the stability of the system.

Results

The Centrifugal E.M.F.'s.—Each solution investigated behaved in accordance with theory in that a linear relationship was found between the observed centrifugal potential, E, and the square of the speed of rotation, r^2. Typical results are illustrated in Fig. 2 where each line connects the data obtained in a single run on a representative iodide–iodine solution.

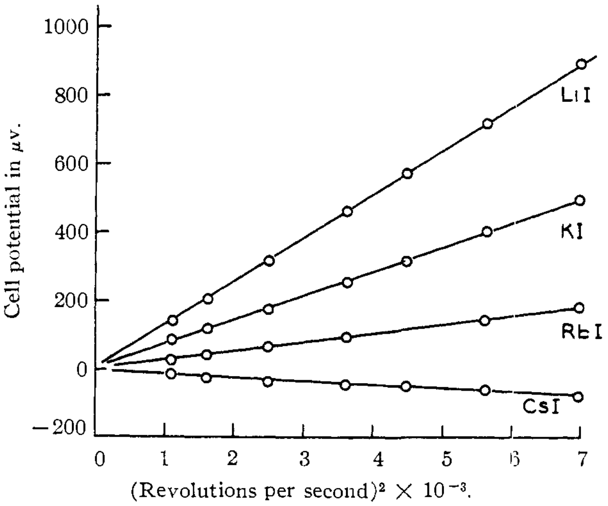

Fig. 2.—Typical results obtained with alkali metal iodides in the e.m.f. centrifuge.

The variation of E/r^2 with iodine concentration for the four alkali iodides is shown in Table I. Average E/r^2 values, by the method of least squares, are given in the last column. When, for each salt, R was plotted against E/r^2 a smooth gentle curve resulted from which, by a very short linear extrapolation, the limiting value of E/r^2 at $R = 0$ was obtained readily. The solid lines in Fig. 3 show these experimental curves. The limiting values of E/r^2 are enclosed in brackets in Table I.

It is interesting that cesium iodide solutions gave potentials which were not only very small (5 to 70 μv.) but reversed sign at an R value of approximately 0.4. Due to a balancing of effects, there is, then, a particular solution of cesium iodide and iodine that will not develop a centrifugal potential.

The Transference Numbers.—The calculation of transference numbers requires accurate knowledge of the electrode distances in the cell and, in addition, values of partial molal volumes and solution densities. The first were obtained by calibration[7] since it was not possible, with the cell design

---

(13) G. Jones and M. Prendergast, THIS JOURNAL, 59, 731 (1937).

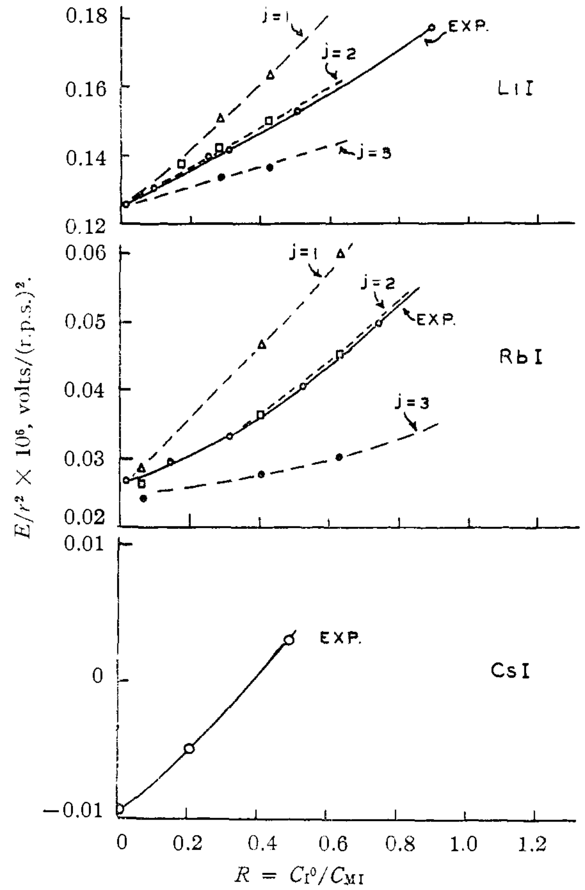

Fig. 3.—Variation of the ratio E/r^2 with the relative concentration of iodine: comparison of experimental and calculated behavior.

used, to measure distances directly to sufficient accuracy. If a cell constant K be defined by

$$K = \frac{F}{2\pi^2(x_2^2 - x_1^2)} \qquad (5)$$

then substitution into eq. 1 followed by rearrangement gives

$$t_M = \frac{-(E/r^2)K + (M_I - \bar{V}_I\rho)}{(M_{MI} - V_{MI}\rho)} \qquad (6)$$

The potassium iodide-iodine system is best for calibration since all the necessary terms in eq. 6 are known to a very satisfactory degree of accuracy. From the work of MacInnes and Dayhoff[14] $\bar{V}_{KI} = 46.12$, $\bar{V}_I = 29.98$ and $\rho = 1.0201$; from the measurements of Longsworth[15] $t_K = 0.4887$. Different cells were used in obtaining the data presented here; the cell constants are given in Table III and were determined in each case by use of 0.185 M KI and the above data.

The partial atomic volume of iodine in each iodide solution was evaluated from the density data that are given in Table II. Each series was based upon a stock solution of the stated concentration. Plots of C_I *vs.* ρ resulted in straight lines and, therefore, it was convenient to use the equation

$$\bar{V} = \frac{M - 1000\,(\mathrm{d}\rho/\mathrm{d}c)}{\rho - C\,(\mathrm{d}\rho/\mathrm{d}c)}$$

TABLE I

THE RESULTS OF CENTRIFUGAL E.M.F. MEASUREMENTS ON ALKALI IODIDE–IODINE SOLUTIONS AT 25°

Salt	C_{MI} Concn. of stock salt soln., moles/l.	$R = C_I^0/C_{MI}$	E/r^2, μv./(r.p.s.)^2
KI	0.192	0.0	(0.0715)
		.0112	.0717
		.0112	.0719
		.0238	.0721
		.0386	.0735
		.0446	.0726
		.0543	.0733
		.0827	.0756
		.3629	.0851
LiI	0.185	0.0	(0.1246)
		.0191	.1253
		.0942	.1300
		.2588	.1391
		.3110	.1415
		.5085	.1523
		.8912	.1770
RbI	0.142	0.0	(0.0264)
		.02927	.0266
		.1447	.0295
		.3133	.0330
		.5268	.0405
		.7451	.0495
CsI	0.161	0.0	(−0.0098)
		.00453	− .0096
		.2073	− .0050
		.4909	+ .0028

TABLE II

DENSITIES OF ALKALI IODIDE–IODINE SOLUTIONS AT 25.200°

Salt	C_{MI} Concn. of stock salt soln., moles/l.	C_I^0 Concn. of iodine, g. atoms/l.	ρ, g./ml.
LiI	0.185	0.0	1.01683
		.01389	1.01812
		.02371	1.01903
		.04680	1.02138
		.1135	1.02775
RbI	0.142	.0	1.02157
		.00977	1.02246
		.0578	1.02706
		.0913	1.03031
CsI	0.161	.0	1.03160
		.02915	1.03440
		.04380	1.03581

TABLE III

DENSITIES, PARTIAL EQUIVALENT VOLUMES AND TRANSFERENCE NUMBERS OF LITHIUM, RUBIDIUM AND CESIUM IODIDES AT 25°

	LiI 0.185 M	RbI 0.142 M	CsI 0.161 M
ρ, g./ml.	1.01683	1.02162	1.03166
$\bar{V}_{MI}$, ml./g.	35.55	51.34	58.33
$\bar{V}_I$, ml./g.	29.82	30.30	30.29
$E/r^2 \times 10^6$ at zero iodine concn.	0.1246	0.0264	−0.0098
$K \times 10^{-6}$	526.38	568.94	344.49
t_M	0.317	0.506	0.496

where $\bar{V}$ is the partial atomic volume, M the atomic mass and $\mathrm{d}\rho/\mathrm{d}c$ the slope of the straight line. The resulting values of $\bar{V}_I$ are 29.82, 30.30 and 30.29 ml./g. for the solutions of lithium, rubidium and

---

[14] D. MacInnes and M. Dayhoff, THIS JOURNAL, **74**, 1017 (1952).

[15] L. Longsworth, *ibid.*, **57**, 1185 (1935).

cesium iodides, respectively. It is not unexpected to find that these values agree closely with those (29.98 and 29.96) found for iodine in potassium and sodium iodide solutions by MacInnes and Dayhoff.[14]

Values for the partial molal volumes of the salts can be calculated from the apparent volume data published by Geffcken.[16] In Table III are given the values of $\bar{V}_{MI}$ we so obtain for the salts at the specified concentrations.

Substitution of the several data for each salt into eq. 6 yields the transference numbers of the lithium, rubidium and cesium ion constituents. The data and results are summarized in Table III.

Discussion

Brought together in Table IV are the transference data now available on the five alkali iodides (for KI only selected values are tabulated). The sparse data on the iodides in contrast to those on the chlorides may partly reflect the difficulties encountered in applying the Hittorf method to iodide salts.

TABLE IV

SUMMARY OF TRANSFERENCE NUMBER DATA ON ALKALI METAL IODIDES

Salt	Temp., °C.	Concn. equiv./l.	t_M	Method	Ref.
LiI	25	1.0	0.267 cor.	Cent. force	Tolman[4]
	25	0.1851	.317	Cent. force	Present work
NaI	18	.05	.380 cor.	Mov. bound.	Denison[17]
	18	.10	.375 cor.	Mov. bound.	Denison[17]
	25	.1911	.3827	Cent. force	MacInnes and Dayhoff[7]
	25	1.0	.384 cor.	Cent. force	Tolman[4]
KI	25	0.20	.4917	E.m.f.	Gelbach[20]
	25	.05	.495	Hittorf	Bein[21]
	18	.1	.485 cor.	Mov. bound.	Denison[17]
	25	.2028	.4887	Mov. bound.	Longsworth[15]
	25	.712	.4887 cor.	Grav. force	Grinnell and Koenig[5]
	25	1.0	.484 cor.	Cent. force	Tolman[4]
	25	0.194	.487	Cent. force	MacInnes and Ray[6]
RbI	18	.02	.498	Mov. bound.	Denison[17]
	18	.1	.497	Mov. bound.	Denison[17]
	25	.142	.506	Cent. force	Present work
CsI	18	.02	.497	Mov. bound.	Denison[17]
	18	.1	.497	Mov. bound.	Denison[17]
	25	.161	.496	Cent. force	Present work

The centrifugal work of Tolman and the gravitational work of Grinnell and Koenig did not include corrections for the influence of the dissolved iodine in the iodide solutions. We have made the necessary corrections, based upon the more complete theory as given by eq. 2. Denison,[17] using an early form of the moving boundary apparatus, obtained values for the cation transference numbers which, as Lewis soon after showed,[18] tended to be too high because no corrections were made for the volume changes accompanying the electrochemical reactions at the electrodes. Using the procedure of Lewis, we have calculated corrections and have applied them, wherever of significant magnitude, to the values of Denison.

The value of $t_{Li} = 0.317$ obtained in the present work can only be compared to the value of 0.267 obtained by Tolman. A small part of the difference lies in the less accurate partial volumes used by Tolman. The difference in salt concentrations is to be noted. (The more extensive data available on alkali chlorides indicate that the concentration dependence of the transference number varies with the different cations. For lithium chloride[19] it decreases from 0.317 to 0.311 in passing from 0.1 to 0.2 *N*.) The only previous results on the rubidium and cesium iodides are those of Denison. His value for RbI is 1.8% lower than ours. Denison worked at 18°, but no appreciable temperature effect would be anticipated. It may be noted that the results of Denison on NaI and KI are 1.6 and 0.9% lower than the best values. In the case of CsI, we agree very well.

As can be seen from Table IV, there are now data for one electrolyte, KI, which permit a comparison to be made of the various methods for determining transference numbers. The value obtained by Longsworth with the moving boundary method can be accepted as the most accurate, and it is gratifying to note the good agreement shown by the centrifugal and gravitational results. The values obtained with the e.m.f.[20] and Hittorf methods[21] are much less accurate.

It is of interest that the transference numbers of the iodides are quite similar to those of the chlorides. For example, the most reliable data[17,19] on the chlorides at 0.1 *N* and at 25° are 0.317, 0.385, 0.490, 0.494 and 0.500, in the order of atomic weights.

The centrifugal e.m.f. method for transference numbers requires accurate values of the partial equivalent volumes of the cell constituents. In the present work it would be desirable to know the values of $\bar{V}_I$ and $\bar{V}_{MI}$ more accurately. The $\bar{V}_{MI}$ values used were calculated from the data of Geffcken[16] yet, for example, his data on KI are in only moderate agreement with recent very careful work.[14]

The Nature of the Complex Ion.—One purpose of the present research was to investigate further the form of the polyiodide ion. How one can do this with the aid of conductance data has been discussed in an earlier section. The equivalent conductances of lithium and rubidium iodide solutions containing varying amounts of iodine are given in Table V. Utilizing these data in eqs. 2, 3 and 4, values of E/r^2 were calculated for $j = 1$ and for the different values of R. Calculations were repeated for $j = 2$ and $j = 3$.

Proof that the correct value of j must be 2 is best seen by reference to Fig. 3 where are plotted values of E/r^2 *vs.* R. The solid curves connect the experimentally measured values; the dashed curves connect the values calculated by the procedure above. It is evident that I_3^- is the ion in solutions of lithium and rubidium iodides, as it is also for sodium and potassium iodides. The e.m.f. results then not only further confirm, by a different method, the existence of the triiodide ion in all the alkali iodides but also lend support to the theoretical treatment given to centrifugal effects.

The complex formation in cesium iodide solutions

---

(16) W. Geffcken, *Z. physik. Chem.*, **155**, 1 (1931).

(17) R. Denison, *Trans. Faraday Soc.*, **5**, 165 (1909).

(18) G. Lewis, THIS JOURNAL, **32**, 862 (1910).

(19) L. Longsworth, *ibid.*, **54**, 2741 (1932).

(20) R. W. Gelbach, *ibid.*, **55**, 4858 (1933).

(21) W. Bein, *Z. physik. Chem.*, **27**, 1 (1898).

TABLE V

EQUIVALENT CONDUCTANCES OF LITHIUM AND RUBIDIUM IODIDE–IODINE SOLUTIONS AT 25°

Salt	C_{MI} Concn. of stock salt soln., moles/l.	$R = C_I^0/C_{MI}$	Λ_m, ohms^{-1}
LiI	0.185	0.0	94.34
		.1736	92.42
		.2827	90.08
		.4221	87.83
RbI	0.142	.0	143.66
		.0687	142.05
		.4089	136.56
		.6367	132.96

was not studied because R values above 0.5 led to the appearance of an insoluble precipitate thought to be cesium triiodide.

It will be noted that in Fig. 3 there is a small deviation of the experimental curves in the direction of the $j = 3$ curves and that this deviation increases with R. This behavior previously has been observed in the cases of KI and NaI. It cannot be due to the slight amount of iodine existing in solution as I_2 since, in all four cases, the calculations leading to the $j = 2$ curves have had corrections (quite small) made for this based upon the equilibrium $I_3^- = I^- + I_2$ for which the mass law constant, according to Jones and Kaplan,[22] is 1.4×10^{-3}. When the percentage deviations are calculated for the Li, K, Na and Rb salts at a large, and approximately equal, value of R (0.6–0.8), one gets 1.0, 1.2, 0.4 and 0.2%, respectively. One possible explanation may be the failure of the law of independent ion mobilities at these concentrations. However, we think it likely that the effect is due to the presence of traces of higher complexes such as I_5^-. Higher complexes have been discussed by several authors.[23,24]

Acknowledgments.—The authors are indebted to Prof. G. R. Peirce for the development of the speed control, to Prof. R. M. Whitney for his assistance with the conductance measurements, to Mr. A. E. Wood for his advice and for his skill in the construction of the centrifuge and to Dr. E. G. Pickels for the specially straightened shafting for the centrifuge.

---

[22] G. Jones and B. Kaplan, THIS JOURNAL, **50**, 1845 (1928).

[23] W. C. Bray and G. M. J. McKay, *ibid.*, **32**, 914 (1910).

[24] G. Jones and B. Kaplan, *ibid.*, **50**, 1600 (1928).

URBANA, ILLINOIS

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

Thermodynamics of Ion Pair Dissociation. Tetrabutylammonium Picrate in Chlorobenzene, *o*- and *m*-Dichlorobenzene[1]

BY PATRICK H. FLAHERTY[2] AND KURT H. STERN

RECEIVED JUNE 5, 1957

The dissociation constant of Bu_4NPi has been measured in chlorobenzene and in *o*- and *m*-dichlorobenzene at 25, 35 and 45°. The corresponding thermodynamic functions have been calculated. The data are used to test the continuum theories of Bjerrum and Denison and Ramsey which are shown to fail in the prediction of ΔS^0 and ΔH^0. The contact distance of the ion-pair is seen to depend on the equation by which it is calculated.

There has been considerable interest in theories of ion-pair dissociation in recent years. The steady accumulation of dissociation constants of salts in a variety of solvents had made it clear that the Bjerrum theory[3] (which considers the electrolyte to exist in a continuous medium distinguished only by its macroscopic dielectric constant D), while adequate for predicting large-scale trends, no longer adequately accounts for all the available data.

It was first suggested by Stern and Martell[4] that a better understanding of electrolyte–solvent interactions might be obtained from a knowledge of the thermodynamic functions for ion-pair dissociation. Shortly thereafter, Denison and Ramsey[5] derived these functions from the Bjerrum theory and also by a simplified treatment which yields essentially the same results for low dielectric constant solvents. For several perchlorates in ethylene chloride and ethylidene chloride the agreement between experimental and calculated values of ΔH^0 and ΔS^0 was very good. Recently, Gilkerson[6] has applied free volume theory to this problem. However, his theory includes several variable parameters and a test of it involves the dipole moment of the solvent. The latter varies considerably with the method of measurement. We shall return to this point later.

The present work was undertaken to provide a further test of the Denison–Ramsey and Gilkerson theories; and to add to the all-too-scanty data in this field. Such a body of data is usually necessary before useful generalizations begin to appear. Tetrabutylammonium picrate (Bu_4NPi) was chosen as the salt because it has been measured in more solvents than any other. The solvents were selected because their chemical similarity makes it likely that any chemical or specific interactions with the salt would be the same for all and because they can be characterized easily by molecular parameters should a theory based on these ever develop; *i.e.*, the molecules are rigid and have well-defined dipole moments and polarizabilities.

---

[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under Contract AF 18(600)-960. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] From the M.S. Thesis of P. H. Flaherty.

[3] N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, **7**, No. 9 (1926).

[4] K. H. Stern and A. E. Martell, THIS JOURNAL, **77**, 1983 (1955).

[5] J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

[6] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).