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Conductance of Ions in Light and Heavy Water at 25°[1,2]

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Abstract: Conductances of potassium fluoride, potassium chloride, potassium bromide, potassium iodide, sodium chloride, cesium chloride, potassium benzoate, potassium *p*-toluenesulfonate, and tetra-*n*-butylammonium bromide were determined in the range 5–90 × 10^{-4} *M* in both protium oxide and deuterium oxide at 25°, using 1 l. of solvent for each salt. Limiting ionic equivalent conductance ratios, calculated by combining these data for the salts with the transference numbers of Longsworth, vary from 1.198 for potassium and cesium ions to 1.229 for tetra-*n*-butylammonium and 1.235 for fluoride ions. These limiting conductance ratios are treated as solvent isotope effects arising from changes in zero-point librational energy of the solvating waters upon going from the ground state to the transition state. Assuming four solvating waters in the ground state, the librational frequencies are calculated for various numbers of water molecules around the ion at the transition state. Since the average librational frequency is less for the transition state than for the reactant ions, three waters appears unreasonable. An addition–elimination mechanism for conductance is proposed in which the ion has five solvating water molecules at the transition state.

The conductance of electrolytes in deuterium oxide was first determined in 1933.[3] The measurements were carried out on what was then a considerable fraction of the world's supply of heavy water, 0.3 ml, and constituted some of the first evidence for the distinctive differences in the behavior of an isotopically substituted substance. As heavy water became more available, a number of investigators[4–7] carried out such measurements. Their results established that conductance of salts was about 23% greater in light water than in heavy water and that there was a detectable difference in the ratio of equivalent conductances, Λ^H/Λ^D, for various salts. The measurements were limited by the quantity and, in some cases, by the purity of heavy water available. Because of these limitations, it was impossible to study the change of conductance with concentration in the concentration range in which conductance theories are applicable. Usually the conductance was determined in fairly concentrated solutions (0.01 *M* and higher) and the limiting conductance was calculated from the assumption $(\Lambda/\Lambda_0)^D = (\Lambda/\Lambda_0)^H$.[8]

The recent availability of heavy water in large quantities allows precise techniques to be applied to measurements of the conductance of electrolytes in light and heavy water, a unique system for testing present theories of conductance. In going from light to heavy water, one of the bulk properties upon which the conductance depends, the viscosity, changes by 23%, while the other bulk property, the dielectric constant, changes by only 0.4%. Because of the similarities in structure of light and heavy water, this system holds more promise for analyzing and interpreting the results than other solvents of similar dielectric constant prepared in the past by the use of two-component mixtures.

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(1) Supported in part by the National Institutes of Health through Research Grant GM-3711 and by a predoctoral NIH fellowship to D. F. Evans.

(2) For further details, *cf.* D. F. Evans, Ph.D. Thesis, MIT, May 1963.

(3) G. N. Lewis and T. C. Doody, *J. Am. Chem. Soc.*, **55**, 3504 (1933).

(4) J. P. Chittum and V. K. LaMer, *ibid.*, **59**, 2425 (1937).

(5) L. G. Longsworth and D. A. MacInnes, *ibid.*, **59**, 1666 (1937).

(6) E. Ronaess, *Kgl. Norske Videnskab. Selskabs, Forh.*, **12**, 133 (1939); *Chem. Abstr.*, **35**, 3147 (1941).

(7) O. E. Frivold, O. Hassel, and E. Hetland, *Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Kl.*, No. 3, 14 (1940); *Chem. Abstr.*, **35**, 2055 (1941).

(8) V. K. La Mer and J. P. Chittum, *J. Am. Chem. Soc.*, **58**, 1642 (1936).

Experimental Section

Conductivity Water. Conductivity grade protium oxide was prepared by passing distilled water through a Pyrex column, 55 cm long and 5 cm in diameter, filled with Fisher analytical grade Amberlite MB-1 resin (a mixture of sulfonic acid and quaternary ammonium ion resin). Each time before the column was used, a liter of distilled water was passed through the column to rinse the resin.[2] Conductivity water prepared in this manner had a specific conductance of 1–2.5 × 10^{-7} ohm^{-1} cm^{-1}.

Conductivity deuterium oxide was prepared by passing deuterium oxide (Atomic Energy Commission normal O^{18} content) through 100 ml of MB-1 resin. The resin was deuterated by allowing it to equilibrate with deuterium oxide for 6 months. The exchange was begun on damp resin taken directly from the bottle, since earlier work using protium oxide showed that alternate drying and wetting resulted in disintegration of the beads and evolution of amines of low molecular weight. Periodically the heavy water was filtered and a new batch added. The extent of exchange was determined by density analysis.[2,9] Since the sixth 100-ml batch had 99% deuterium content, the exchange was carried no further. Contaminants were removed from the column before it was used by washing it with 60–80 ml of heavy water.[2] This water was used to rinse the conductivity cell before a conductivity-grade heavy water run was made. The purified deuterium oxide had a density of 1.10449 ± 0.00002 g ml^{-1} and a specific conductance of 0.35–1.04 × 10^{-7} ohm^{-1} cm^{-1}. The accepted density value[9] of pure D_2O is 1.10451 g ml^{-1}.

Purified Nitrogen. Purified nitrogen was obtained by passing prepurified nitrogen through a train consisting of two gas-washing bottles equipped with fritted-glass bubblers and containing concentrated sulfuric acid, a spray trap packed with glass wool, a tube of Drierite (calcium sulfate), two tubes of Ascarite (sodium hydroxide on asbestos), a tube of indicating silica gel, a tube of Drierite, and a tube of Anhydrone (anhydrous magnesium perchlorate). This procedure was found satisfactory for the removal of small traces of carbon dioxide, ammonia, and water.

Inorganic Salts. Potassium chloride, Baker Analyzed reagent, was twice precipitated from a saturated conductivity-water solution by adding an equal volume of reagent grade ethyl alcohol,[10] dried in a 130° oven for 24 hr, ground in an agate mortar, and then dried at 100° (0.01 mm) for 3 days.

Potassium bromide was prepared by adding Mallinckrodt analyzed reagent hydrobromic acid (48%) to Mallinckrodt analyzed reagent potassium carbonate until pH 3 was reached.[11] The solution was cooled, and the crystals were recrystallized twice from conductivity water, dried at 100° at 0.01 mm, fused under carbon dioxide free nitrogen, and ground in an agate mortar.

Potassium iodide was prepared from hydriodic acid and potassium carbonate.[12] The hydriodic acid, Fisher reagent, was distilled three times to free it from the phosphoric acid preservative. Only the middle fraction was collected in each distillation. Mallinckrodt analyzed reagent potassium carbonate was added to the purified acid until pH 3. After the bulk of the water had been removed in a rotary evaporator, the salt was dried in a desiccator connected to a Dry Ice–acetone trap. Fusion of the resulting reddish crystals in a platinum dish under carbon dioxide free nitrogen gave white crystals, which were ground in an agate mortar and used within 24 hr after fusion.

Potassium fluoride was prepared by adding a 10% excess of Baker Analyzed reagent hydrofluoric acid to Mallinckrodt analyzed reagent potassium carbonate in a platinum dish. Drying the resulting potassium fluoride–potassium bifluoride mixture in a desiccator over phosphorus pentoxide at 0.01 mm and then heating at 0.03 mm for 3 days at 195° and 3 days at 500° gave potassium fluoride.[13] The potassium fluoride was stored in a platinum dish in a desiccator over indicating silica gel and, because it is extremely hygroscopic, handled only in a drybox.

Sodium chloride, Mallinckrodt analyzed reagent, was purified by the procedure described above for potassium chloride. Cesium chloride, A. D. MacKay optical grade, was ground in an agate mortar, dried at 100° at 0.01 mm, and used without further purification.[14]

Organic Salts. Potassium *p*-toluenesulfonate, prepared by carefully neutralizing Eastman White Label *p*-toluenesulfonic acid with Mallinckrodt analyzed reagent potassium carbonate, was recrystallized five times from conductivity water, ground in an agate mortar, and dried for 24 hr at 80° at 0.01 mm. The salt was neutral as shown by pH measurements using a Beckman pH meter.

Anal. Calcd for $C_7H_7SO_3K$: C, 39.98; H, 3.36; K, 18.59. Found: C, 40.05; H, 3.38; K (as K_2SO_4 by ash analysis), 18.50.

Potassium benzoate was prepared from Eastman White Label benzoic acid and Mallinckrodt analyzed reagent potassium carbonate. Since it was impossible to neutralize the acid stoichiometrically because of the buffering action, potassium carbonate was added until pH 6 was reached. After the solution had been cooled, the resulting crystals, which contained most of the excess benzoic acid, were removed by filtration and discarded. Conductivity water was added to the filtrate, and the remaining benzoic acid was removed by steam distillation. Concentration of the filtrate, followed by cooling, gave potassium benzoate, which was collected on a filter, recrystallized once from conductivity water and twice from methanol, dried at 80° at 0.01 mm, ground in an agate mortar, and redried. Analysis for K as potassium sulfate gave 24.45% (calcd 24.41%).

Tetra-*n*-butylammonium bromide was prepared by treating *n*-butyl bromide with tri-*n*-butylamine.[2,15] It was recrystallized five times from an acetone–ether mixture, dried at 56° at 0.01 mm, ground in an agate mortar, and redried, mp 117–118°, 24.73% Br by gravimetric analysis (calcd 24.78%).

Conductivity Equipment. A Jones–Joseph bridge manufactured by Leeds and Northrup Co. was used to measure the conductance of the solutions. The recommendations of Dike[16] concerning its calibration and operation were followed. The 1000-ohm ratio arms were matched, and the five 10,000-ohm resistors were checked with a 10,000-ohm resistor from the National Bureau of Standards and found to be within ±0.005% of the stated value. A Jackson Electrical Instrument Co. Model 652 oscillator was used as the power source for the bridge. Both the frequency and power output could be varied. A General Radio Co. Type 1231-B amplifier and null detector and Type 1231-P5 adjustable filter were used to amplify the bridge signal and a DuMont Type 208-B oscilloscope was used to detect the null point of the bridge.[2]

The constant-temperature bath was a steel-framed glass aquarium, 13 in. wide, 30 in. long, and 18 in. high, filled with 30 gal of lightweight transformer oil. A Cenco 0.5-hp pump with a rated capacity of 105 gal of water/min provided adequate stirring. The bath was cooled by circulating water maintained at a constant temperature of 22° by a Tecumseh compressor, Model P611, through a 12-ft coil of 0.5-in. copper tubing. The bath was maintained at 25 ± 0.002° by a Princo Magna-Set thermoregulator, Catalog No. T-260, and an electronic phase-control unit equipped with a 250-w infrared bulb intermittent heater and a 100-w copper tube constant heater. The thermoregulator was mechanically coupled to the stirrer. The sides of the bath were covered with fiber glass insulation. A calibrated platinum resistance thermometer[17] was used to set the thermoregulator. An Eppley Laboratories Mueller-type bridge, Model 393, and a Keithly microvolt ammeter, Model 150, were used for measuring the resistance of the platinum resistance thermometer. The ice point of the thermometer was checked periodically.

The conductance cells were of the erlenmeyer type.[2,10] Contact between the electrodes and the Jones–Joseph bridge was made by platinum wires gold-soldered to the electrode assembly. The electrodes were platinized to a dull gray color so that the frequency correction for a 2 × 10^{-3} *M* potassium chloride solution was less than 0.02%.[2,18] The solutions were stirred with a seamless Teflon-covered magnet and gave resistance readings independent of the rate of stirring.

The conductance cells were used in conjunction with a cup-dropping device of the type developed by Hawes and Kay.[19] This device when placed above the cell enables eight salt-containing cups to be added successively to the solution without exposing the solu-

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[9] I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p 14.

[10] H. M. Daggett, Jr., E. J. Bair, and C. A. Kraus, *J. Am. Chem. Soc.*, 73, 799 (1951).

[11] G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1945).

[12] R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *J. Am. Chem. Soc.*, **75**, 2855 (1953).

[13] E. F. Westrum, Jr., and K. S. Pitzer, *ibid.*, **71**, 1940 (1949).

[14] W. E. Voisenet, Ph.D. Thesis, Yale University, 1951.

[15] H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950).

[16] P. H. Dike, *Rev. Sci. Instr.*, **2**, 379 (1931).

[17] J. Kaminsky, Ph.D. Thesis, MIT, 1937; J. A. Beattie, M. Benedict, and B. E. Blaisdell, *Proc. Am. Acad. Arts Sci.*, **71**, 327 (1936).

[18] G. Jones and D. M. Bollinger, *J. Am. Chem. Soc.*, **57**, 280 (1935).

[19] J. L. Hawes and R. L. Kay, *J. Phys. Chem.*, **69**, 2420 (1965).

tion to the atmosphere. This arrangement permitted solvents of low conductance to be used and assured that the solvent conductance remained constant throughout the experiment.[2]

Procedure. Before each determination, the conductivity cells were steamed for 30 min with nitric acid, and after a thorough rinsing with conductivity water were resteamed for 30 min with conductivity water. The cells were always stored filled with conductivity water.

The salt cups were boiled in nitric acid, cooled, and then repeatedly rinsed with conductivity water. The cleaned cups were wrapped in aluminum foil, baked for 4 hr in an oven at 130°, and then stored in the aluminum wrappers in a desiccator over Drierite. A check of the cleaning procedure was made by noting no change in the solvent resistance upon dropping cleaned cups into a cell filled with conductivity water.

Nonhygroscopic salts were weighed on a microbalance in Pyrex cups made from 10-mm glass tubing, 9 mm high. The hygroscopic salt, potassium fluoride, was weighed in capped cups made from $^{12}/_{30}$ ground-glass joints. The empty capped cups were weighed on the microbalance and transferred to a drybox, where salt was added to all but one cup. The cups were capped, removed from the drybox, and reweighed. The empty cup was weighed first, and not until it had reached its former weight were the salt-filled cups weighed. The weighed cups were uncapped and stored in the cup-dropping device. One of the holes of the device was closed so that the cell could be isolated from the cup chamber to prevent wetting of the salt in the cups before they were dropped into the cell.

To begin a conductance determination, the cleaned cell was rinsed with conductivity water and a 5-cm seamless Teflon-covered magnetic stirring bar placed in the cell. Purified nitrogen was swept through the cell for 20 min. Since reproducible results could not be obtained if the electrodes dried after they had been steamed with nitric acid, the nitrogen was saturated with solvent.

The swept-out cell was filled with 1 l. of conductivity water delivered directly from the column of Amberlite resin by means of polyethylene tubing and a delivery device. During this time, purified nitrogen was introduced through a stopcock on the cell and vented out of a stopcock on the delivery device. After the cell had been filled, the water delivery tube was disconnected, the delivery device removed, and the cell capped. The flow of nitrogen was increased so that the cap was lifted slightly off the cell in order to remove any carbon dioxide that may have been introduced. After the cell had been swept out for 5 min, the stopcock and cap were closed, and the cell was weighed on a 2-kg balance. The weight of the empty cell was determined periodically and found to be reproducible to within ±0.02 g.

The cell was placed in the constant temperature bath, and, with purified nitrogen flowing in through the stopcock on the cell, the cap was replaced by the cup-dropping device. With the stopcock on the cup-dropping device open, the system was swept out with purified nitrogen for 5 min. The stopcocks were then closed, the nitrogen tube was disconnected, the magnetic stirrer was started, and then the cell was allowed to come to thermal equilibrium. The solvent resistance was determined by shunting the cell with 30,000 ohms.

All resistance measurements were made at 0.5, 2.0, and 5.0 kc. After the cell had attained equilibrium and a constant value for the solvent resistance had been obtained, the stirring rate was increased until a large vortex formed in the cell, and then the first cup was dropped. If the cup was dropped directly into the vortex, no solvent splashed on the walls of the cell. The stirring rate was decreased, and the magnetic stirrer moved around so that the cup was thrown against the walls of the cell several times in order to remove air bubbles which occasionally remained inside the cup. These air bubbles often covered small amounts of salt and, if allowed to remain, produced a considerable error in the resistance measurement. The magnetic stirrer was then adjusted so that the magnetic stirring bar was directly in the center of the cell and the cups moved around the bottom of the cell in a circular motion. This prevented the cups, which chipped and cracked easily, from being continually banged against the cell walls. The chips of glass, when they did form, often ended up in the electrode compartment where they effectively changed the cell constant. They were removed from the compartment by gently tipping the cell while it was in the bath. The cell was tipped to remove small air bubbles, which were occasionally introduced when a cup was dropped into the cell. The solution was stirred until a steady resistance value was obtained, the frequency dependence of the resistance was determined, and then the next cup was dropped. At the end, the cell was removed from the bath, washed with pentane to remove the oil, emptied, filled with conductivity water, and then stored.

For measurements in heavy water, the cell was treated in the same manner, except that it was placed in a drybox, washed with four 20-ml portions of heavy water from the deuterated Amberlite column, drained thoroughly, and filled. A fresh liter of heavy water was used for each run.

The above procedure was followed for all salts except potassium fluoride. Solutions of this salt gave resistances which increased with time, possibly because of reaction of the fluoride ion with the glass walls of the conductance cell. To minimize the error resulting from this, the conductance determinations were carried out as rapidly as possible.

Results

The cell constant of 1.7721 ± 0.0001 was obtained from five conductance calibrations at 25° using the equation proposed by Lind, Zwolenik, and Fuoss.[20] The absence of the Parker effect[21] was shown by the constancy of the cell constant over the concentration range employed.

Equivalent conductances (ohm^{-1} cm^{-1} mole^{-1}) of a number of salts in protium and deuterium oxide at 25° are shown in Tables I and II, respectively. Concentrations are expressed in moles per liter of solution and were calculated from the 1958 molecular weight assignment of the International Union of Pure and Applied Chemistry.[22] The specific conductance of the solvent, κ_0, is recorded along with $\Delta\Lambda$, the difference between the measured Λ and Λ calculated as described below.

A buoyancy correction was applied to all weighings. The densities of the alkali halides were taken from the International Critical Tables, and the densities of potassium benzoate and of potassium tosylate were assumed to be 1.7 g ml^{-1}. They were shown to be between the values of 1.5 and 1.7 g ml^{-1} by their buoyancy in chloroform, carbon tetrachloride, and pentachloroethylene. The density value of 1.13 g ml^{-1} was used for tetrabutylammonium bromide.[23] The molarity of the solutions was calculated using equations of the form

$$c = d_0 m - Am^2$$

where m is moles of salt per kilogram of solvent, d_0 is the density of the pure solvent, and A is an empirically determined constant. The A values for the alkali halides were taken from Harned and Owen.[24] The A value for potassium fluoride was assumed to be the same as that for lithium chloride. The values for potassium benzoate (A = 0.0507), potassium tosylate (A = 0.1640), and tetrabutylammonium bromide (A = 0.2791) were determined by pycnometry. The A values in H_2O and D_2O for KCl were measured and found to be the same, within experimental error. The A values for the other salts were assumed to be equal in the two solvents.

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(20) J. E. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1577 (1959).

(21) H. C. Parker, *ibid.*, **45**, 2017 (1923).

(22) E. Wichers, *ibid.*, 80, 4121 (1958).

(23) A. K. R. Unni, L. Elias, and H. I. Shiff, *J. Phys. Chem.*, **67**, 1216 (1963).

(24) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p 725.

Table I. Equivalent Conductances in H_2O at 25°

10^4c	Λ	$\Delta\Lambda$	10^4c	Λ	$\Delta\Lambda$
	KF			KI	
	$10^7\kappa_0 = 1.4$			$10^7\kappa_0 = 1.0$	
10.479	126.04	0.05	7.198	148.22	0.02
24.267	124.48	−0.09	17.654	146.80	−0.02
36.147	123.72	0.02	29.598	145.72	−0.01
49.253	122.95	0.03	39.654	145.01	0.00
61.692	122.30	0.01	51.729	144.28	0.00
74.541	121.71	−0.02	60.884	143.79	0.00
92.192	121.05	0.00	71.746	143.29	0.01
	KCl			NaCl	
	$10^7\kappa_0 = 1.4$			$10^7\kappa_0 = 0.7$	
8.291	147.21	0.00	10.448	123.73	0.00
17.981	145.95	−0.02	22.042	122.48	−0.02
29.956	144.89	0.01	32.943	121.65	0.00
40.782	144.11	0.01	43.952	120.97	0.01
51.579	143.42	−0.02	54.721	120.42	0.05
61.107	142.93	0.01	67.526	119.75	−0.01
			78.201	119.28	−0.03
	KBr			CsCl	
	$10^7\kappa_0 = 0.8$			$10^7\kappa_0 = 1.2$	
7.467	149.19	0.01			
18.399	147.75	−0.01	18.830	149.48	0.02
28.876	146.81	0.00	29.334	148.44	−0.02
39.903	145.99	−0.01	41.309	147.52	−0.01
51.378	145.30	0.01	50.613	146.91	0.00
63.325	144.67	0.01	62.331	146.23	0.00
74.459	144.12	−0.01	74.413	145.60	0.01
	$KOCOC_6H_5$			$(n\text{-}C_4H_9)_4NBr$	
	$10^7\kappa_0 = 1.6$			$10^7\kappa_0 = 1.1$	
9.521	103.00	−0.06	5.684	95.561	0.03
18.374	102.16	0.01	11.528	94.642	0.01
28.839	101.40	0.03	16.195	94.067	0.00
37.154	100.89	0.03	22.022	93.447	−0.01
46.339	100.40	0.02	27.198	92.956	−0.03
55.897	99.943	0.00	32.341	92.515	−0.03
66.399	99.490	−0.04	36.868	92.155	−0.04
			42.290	91.868	0.08
	$KO_3SC_6H_4\text{-}p\text{-}CH_3$				
	$10^7\kappa_0 = 1.0$				
5.364	103.79	0.05			
13.258	102.64	−0.03			
20.975	101.90	−0.02			
30.101	101.20	−0.02			
37.951	100.71	0.00			
47.098	100.20	0.01			
56.230	99.748	0.02			

Table II. Equivalent Conductances in D_2O at 25°

10^4c	Λ	$\Delta\Lambda$	10^4c	Λ	$\Delta\Lambda$
	KF			KI	
	$10^7\kappa_0 = 0.9$			$10^7\kappa_0 = 0.6$	
11.065	103.72	−0.04	7.911	123.13	0.02
26.006	102.54	0.01	19.755	121.88	−0.02
38.982	101.80	0.03	30.541	121.12	−0.01
52.659	101.16	0.04	39.617	120.59	−0.01
69.614	100.44	0.00	50.073	120.07	0.00
82.455	99.982	−0.02	59.887	119.64	0.00
94.090	99.617	−0.02	69.584	119.26	0.01
	KCl			NaCl	
	$10^7\kappa_0 = 0.4$			$10^7\kappa_0 = 0.6$	
9.240	121.87	0.01	10.470	102.11	0.02
19.620	120.80	−0.01	23.993	100.94	−0.01
30.171	120.04	0.00	35.472	100.23	−0.02
42.257	119.32	0.00	48.492	99.589	−0.01
55.336	118.67	0.00	60.539	99.097	0.01
68.508	118.11	0.00	75.146	98.551	0.00
79.832	117.68	0.00	89.156	98.091	0.00
89.917	117.32	0.00	99.910	97.776	0.00
	KBr			CsCl	
	$10^7\kappa_0 = 1.0$			$10^7\kappa_0 = 0.8$	
8.163	123.84	0.01	8.367	125.00	0.03
19.111	122.70	0.01	18.140	123.88	−0.02
31.011	121.81	−0.01	29.432	122.99	−0.01
43.160	121.11	−0.01	39.487	122.35	0.00
56.294	120.49	0.01	52.394	121.64	−0.01
67.494	120.01	0.00	64.049	121.09	0.00
78.097	119.61	0.00	74.723	120.65	0.02
	$KOCO_6H_5$			$(n\text{-}C_4H_9)_4NBr$	
	$10^7\kappa_0 = 0.6$			$10^7\kappa_0 = 0.6$	
8.068	85.643	−0.02	5.474	78.758	0.01
19.453	84.677	0.00	10.452	78.082	0.00
30.288	84.037	0.02	16.515	77.439	−0.01
41.503	83.497	0.02	22.601	76.901	−0.01
48.762	83.189	0.01	27.516	76.511	−0.01
56.443	82.888	0.00	33.440	76.092	0.00
68.596	82.471	−0.02	39.045	75.736	0.02
	$KO_3SC_6H_4\text{-}p\text{-}CH_3$				
	$10^7\kappa_0 = 0.7$				
5.116	86.061	0.03			
14.256	85.012	−0.01			
22.297	84.397	−0.02			
31.870	83.829	−0.01			
40.089	83.415	0.00			
49.585	83.002	0.01			
56.775	82.722	0.01			

The data shown in Table III were analyzed using the Fuoss–Onsager equation.[25]

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec\log c + (J - B\Delta_0)c \qquad (1)$$

The universal constants employed in the equation have been given in convenient form.[25] The values employed for the dielectric constant were 78.37[26] and 78.05[27] for light and heavy water, respectively. The viscosity of heavy water, 0.01096 poise, was obtained by multiplying the ratio of the viscosities for light and heavy water[28] times the value, 0.008903 poise,[29] used for light water.

A least-squares treatment[30] was used to obtain the values of the parameters Λ_0 and a and the standard deviations of Λ_0, a, and Λ, given in Table III. The program was written in Fortran, and the calculations were performed on an IBM 7090 computer. To start the calculation, estimated values of Λ_0 and a were given, but the final parameters were independent of the initial estimates and minimized $\Sigma(\Lambda - \Lambda_{\text{calcd}})^2$. A subprogram was added which calculated the equivalent conductance and the concentration from the weights of salt and solvent, resistance, densities, and specific conductance of the pure solvent.

Two sets of parameters are shown for the Bu_4NBr results. The first was calculated with the viscosity correction, B, equal to 0.0 and the second with the measured value[31] of $B_{H_2O} = 1.34$. Using a weighting factor of c for each conductance value gave results which were almost identical with those without weight-

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(25) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

(26) G. A. Vidulich and R. L. Kay, *J. Phys. Chem.*, **66**, 383 (1962).

(27) G. A. Vidulich, R. L. Kay, and D. F. Evans, to be published.

(28) R. C. Hardy and R. L. Cottington, *J. Res. Natl. Bur. Std.*, **42**, 573 (1949).

(29) J. R. Coe, Jr., and T. B. Godfrey, *J. Appl. Phys.*, **15**, 625 (1944); J. F. Swindells, J. R. Coe, Jr., and T. B. Godfrey, *J. Res. Natl. Bur. Std.*, **48**, 1 (1952).

(30) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

(31) R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957).

Table III. Conductance Parameters for H_2O and D_2O Solutions at 25°

Salt	Solvent	Λ_0	a	$\sigma\Lambda$	J
KF	H_2O	128.86 ± 0.04	3.3 ± 0.1	0.05	189.4
KF	D_2O	106.19 ± 0.03	3.1 ± 0.1	0.03	146.3
KCl	H_2O	149.94 ± 0.01	3.08 ± 0.05	0.01	195.2
KCl	D_2O	124.23 ± 0.006	2.99 ± 0.02	0.008	157.4
KBr	H_2O	151.78 ± 0.009	3.24 ± 0.03	0.01	207.3
KBr	D_2O	126.07 ± 0.007	3.15 ± 0.03	0.009	168.1
KI	H_2O	150.73 ± 0.01	3.34 ± 0.04	0.02	213.1
KI	D_2O	125.29 ± 0.01	3.38 ± 0.05	0.01	179.5
NaCl	H_2O	126.59 ± 0.03	3.24 ± 0.09	0.03	181.9
NaCl	D_2O	104.45 ± 0.01	3.14 ± 0.03	0.01	145.8
CsCl	H_2O	153.63 ± 0.02	2.53 ± 0.05	0.02	161.6
CsCl	D_2O	127.27 ± 0.02	2.50 ± 0.06	0.02	132.6
KOBz[a]	H_2O	105.58 ± 0.03	4.2 ± 0.2	0.04	207.2
KOBz[a]	D_2O	87.59 ± 0.02	4.0 ± 0.1	0.02	162.4
KOTos[b]	H_2O	105.69 ± 0.02	3.1 ± 0.1	0.03	152.6
KOTos[b]	D_2O	87.59 ± 0.02	3.2 ± 0.1	0.02	131.9
Bu_4NBr[c]	H_2O	97.58 ± 0.03	0.3 ± 0.1	0.04	−17.9
Bu_4NBr[c]	H_2O[d]	97.58 ± 0.03	2.3 ± 0.2	0.04	107.7
Bu_4NBr[c]	D_2O	80.41 ± 0.009	0.08 ± 0.01	0.01	−51.0
Bu_4NBr[c]	D_2O[d]	80.41 ± 0.009	1.4 ± 0.1	0.01	52.5

[a] Potassium benzoate. [b] Potassium *p*-toluenesulfonate. [c] Tetra-*n*-butylammonium bromide. [d] Calculated with $B = 1.34$.

ing, showing that there were no increased errors in the low concentration range.

Discussion

Comparison with Previous Values. The limiting conductances and a values for the alkali metal halides in protium oxide shown in Table III agree well with those reported in the literature after recalculation with the Fuoss–Onsager equation.[30] The only exception to this is potassium iodide for which Λ_0 values centering around 150.55 and a values ranging from 3.5 to 3.9 have been reported.[30] Repeated attempts to purify this salt so as to give results in agreement with the literature values were unsuccessful. The salt sample finally used for the results quoted here was that which gave a Λ_0 closest to 150.55, the accepted value. Since the same salt samples were always used in both solvents, the absolute error in the conductance ratios between H_2O and D_2O will tend to cancel; and it is the conductance ratios which are the important quantities.

Recalculation of the previous data[32] for tetra-*n*-butylammonium bromide using eq 1 and setting $B = 1.34$ gives $\Lambda_0(Bu_4NBr) = 97.53 \pm 0.01$ and $a = 1.9 \pm 0.3$, which is in agreement, within a standard deviation, with the results shown in Table III. After recalculation of previous data[33] for potassium benzoate so as to bring them into conformity with eq 1 and the Jones–Bradshaw conductance standard,[34] the values of $\Lambda_0(KOBz) = 105.90 \pm 0.01$ and $a = 4.2 \pm 0.1$ are obtained. Their higher values of Λ_0 might result from hydrolysis since they used a somewhat more dilute concentration range (1 to 55×10^{-4} *M*) than was used here. However, recalculation of their data with and without the points below 6×10^{-4} *M* gave the same result, indicating the absence of any appreciable amount of hydrolysis. They obtained the same a value as we did, which is indicative of the same concentration dependence. It would appear that the discrepancy in Λ_0 of 0.32 conductance unit has no clear explanation.

The following values for the limiting conductance Λ_0 of potassium chloride in deuterium oxide at 25° have been reported: 123.8,[4] 124.05,[5] 124.54,[6] and 124.05.[7] The values reported for sodium chloride are 104.8,[4] 104.54,[5] and 104.50.[7] The results are those quoted in the original literature. No attempt has been made to re-evaluate them in terms of eq 1 because the experimental points are too few for meaningful analysis or covered too high a concentration range for the theory to be applicable. In general, considering the methods of extrapolation required and the small quantities of D_2O available, the agreement with our results is satisfactory.

The Ion-Size Parameter. The a values for the salts (distances of closest approach between cation and anion centers) in light and heavy water are the same within experimental error.[35] This result is evidence that the Fuoss–Onsager equation contains the correct viscosity dependence since one of the macroscopic properties upon which the equation depends, the viscosity, changes by 23%, while the other, the dielectric constant, remains essentially constant. Accascina and Petrucci[36] have measured the conductance of potassium chloride in water–glycerine mixtures, a system in which the viscosity increases by a factor of 1000, but in which the dielectric constant decreases by a factor of two. They obtained a parameters which showed some scatter ranging from 3.1 to 4.6 with an average of 3.8 ± 0.4. They concluded that their results, which covered such an enormous range of viscosity, confirmed the validity of the Fuoss–Onsager equation viscosity dependence and justified the use of the macroscopic viscosity of the solvent in theoretical calculations. Our results corroborate this conclusion.

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(32) P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **41**, 1033 (1955).

(33) F. G. Brockman and M. Kilpatrick, *J. Am. Chem. Soc.*, **56**, 1483 (1934).

(34) Reference 24, p 197.

(35) The sensitivity of a to small experimental errors is illustrated by the following calculation. The change of J with a, $\partial J/\partial a$, is approximately 40 for the salts studied here. Two determinations on the same salt which differed in a by 0.2 would differ at 0.01 *M* concentration by ($c\Delta a \partial J/\partial a$) or 0.08 conductance unit. The discrepancy of 0.9 in a obtained for Bu_4NBr in H_2O and D_2O indicates a difference of 0.16 conductance unit at the highest concentration used ($c = 4 \times 10^{-3}$ *M*). Further conductance studies on Bu_4NBr in H_2O and D_2O have shown this to be experimental error (R. L. Kay and D. F. Evans, in press).

(36) F. Accascina, *J. Am. Chem. Soc.*, **81**, 4995 (1959); F. Accascina and S. Petrucci, *Ric. Sci.*, **29**, 1640 (1959).

The a values obtained for the alkali metal halides in water have been discussed by Kay.[30] He proposed that the consistent decrease of the a parameters from lithium to cesium for all salts, in contrast to the increasing crystallographic size, could be accounted for by a small amount of association which increased in the order Li < Na < K < Cs. The same pattern of behavior is evident in heavy water.

The results for potassium fluoride and tetra-n-butylammonium bromide require further comment. The a value obtained for potassium fluoride may be slightly too large because of the slow increase of the measured resistances at each concentration. We attribute this increase to reaction of fluoride ion with the glass of the cell walls. It was more pronounced in the more concentrated solutions, and therefore would affect primarily the a values. The a parameters obtained for tetra-n-butylammonium bromide in light and heavy water are unrealistically low possibly because of some association. The association of this salt in water has been discussed;[31] however, correction for this effect in our results is not possible without more extensive measurements.

Ionic Conductances. The transference numbers and conductances of sodium, potassium, and deuterium chloride in heavy water have been measured by Longsworth and MacInnes[5] at 0.09, 0.05, and 0.02 M. They extrapolated the resulting ion conductances using the Shedlovsky conductance equation[37] to obtain limiting chloride conductances of 62.74, 62.86, and 62.79 from KCl, NaCl, and DCl, respectively. The agreement for the chloride ion limiting conductance from NaCl and KCl in D_2O can be improved considerably and checked independently of their conductance measurements by using an extrapolation procedure for transference numbers. Kay and Dye[38] have shown that transference numbers depend on only the electrophoretic effect and can be extrapolated with considerable accuracy using

$$t_0 = t + \frac{(0.5 - t)}{\Lambda_0}\Lambda_e \qquad (2)$$

where Λ_e is the electrophoretic contribution to conductance. They used eq 2 to calculate the electrophoretic effect from transference numbers in protium oxide. The experimentally determined value was then compared to the theoretical value given by the Fuoss–Onsager equation

$$\Lambda_e = Bc^{1/2}/(1 + \kappa a) \qquad (3)$$

and found to be the same up to at least 0.03 M if the same a is used, as is required to fit the conductance data. From eq 2 and 3 and the values of a and Λ_0 from Table III, the values of t_0 can be calculated. The results, which are now in conformity with the Fuoss–Onsager equation, give 62.81 and 62.86 for the limiting conductance of chloride ion in D_2O from KCl and NaCl, respectively. This is as good agreement as can be expected considering the rather high concentration involved.

The transference numbers of KCl in D_2O have also been redetermined by D. F. Evans and R. L. Kay at 0.02, 0.01 and 0.005 M by the moving boundary method using a dc probe technique (data being prepared for publication). Extrapolation of the transference numbers by eq 2 gave $t_0 = 0.4946$ for K^+, in good agreement with the value of 0.4943 obtained from Longsworth's data[5] by the same method.

The limiting ionic conductances in Table IV were calculated on the basis of $\lambda_0(Cl^-) = 76.40$ in water and 62.83 in D_2O. Also shown are the ratios of the limiting ion conductances in the two solvents, λ_0^H/λ_0^D, and the ratios of the Walden products for the ions in the two solvents.

Table IV. Limiting Equivalent Ionic Conductances in H_2O and D_2O at 25°

Ion	λ_0^H	λ_0^D	λ_0^H/λ_0^D	$(\lambda_0\eta_0)^H/$ $(\lambda_0\eta_0)^D$
F^-	55.32	44.79	1.235	1.003
Cl^-	76.40	62.83	1.216	0.988
Br^-	78.24	64.67	1.210	0.983
I^-	77.19	63.89	1.208	0.981
OBz^{-a}	32.04	26.19	1.223	0.993
Tos^{-b}	32.15	26.19	1.228	0.997
Na^+	50.19	41.62	1.206	0.980
K^+	73.54	61.40	1.198	0.972
Cs^+	77.23	64.44	1.198	0.973
Bu_4N^{+c}	19.34	15.74	1.229	0.998

[a] Benzoate. [b] p-Toluenesulfonate. [c] Tetra-n-butylammonium.

The Walden Product. The Walden product is not perfectly constant, since Λ_0^H/Λ_0^D is not exactly equal to the ratio of viscosities of H_2O and D_2O, for all salts and ions. It is most constant from light to heavy water for ions that are intrinsically large, like the tetra-n-butylammonium ion, or that, on the basis of mobility data, appear large because of hydration, like fluoride or lithium. For ions that meet neither of these conditions, the Walden product often shows considerable variation from one solvent to another. For example, the Walden product for K^+ ion changes by a factor of two upon going from water to methanol. The Walden product variation from light to heavy water is small by comparison, the largest difference being 2.5% for the potassium and cesium ions.

The near constancy of the Walden product from H_2O to D_2O shown in Table IV is in accord with Fuoss–Boyd–Zwanzig modification[39] of the Stokes equation, which allows for relaxation of solvent molecules around a moving ion

$$\lambda_0 = \frac{|Z_i|F_2}{6\pi\eta(r + C/r^3)} \qquad (4)$$

where $C = (^2/_3)(^1/_9\pi)(\tau/\eta)(Z_i^2e^2)(\epsilon_S - \epsilon_\infty)/\epsilon_S^2$, r is the Stokes ionic radius, F the Faraday, Z_i is the charge of the ion, η the viscosity, τ the dielectric relaxation time of the solvent, ϵ_S the static dielectric constant, and ϵ_∞ the dielectric constant at infinite frequency. Both τ/η and $(\epsilon_S - \epsilon_\infty)/\epsilon_S^2$ are the same, within experimental error, in light and heavy water.[40] Consequently, the factor C is the same for light and heavy water, and eq 4 for the ratio

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(37) T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1405 (1932).

(38) R. L. Kay and J. L. Dye, *Proc. Natl. Acad. Sci. U. S.*, **49**, 5 (1963).

(39) R. Zwanzig, *J. Chem. Phys.*, **38**, 1603 (1963).

(40) C. H. Collie, J. B. Hasted, and D. M. Ritson, *Proc. Phys. Soc.* (London), **60**, 145 (1948); J. B. Hasted and S. H. M. El Sabeh, *Trans. Faraday Soc.*, **49**, 1003 (1953).

$(\lambda_0\eta)^H/(\lambda_0\eta)^D$ reduces to the classical Stokes equation in this special case.

The small deviations of λ_0^H/λ_0^D from the viscosity ratio, 1.23, may reasonably be attributed to a special mechanism of conductance in which the ion exchanges water molecules with the solvent as it moves, instead of simply dragging its intact hydration shell with it through the solution. Such exchange evidently provides the dominant mechanism for conductance of most alkali metal and halide ions because the limiting conductance increases (instead of decreasing) from sodium (50 in water) to cesium (77) and from fluoride (55) to bromide (78). The precise mechanism of this water exchange is of special interest. In fact, this work was begun originally because it was hoped that the isotope effects obtained would help to distinguish between possible mechanisms for this exchange.

Mechanism of Conductance. In this section we will consider only the special mechanism of conductance of alkali and halide ions which involves exchange of solvating water molecules at every step. This mechanism must have isotope effects very close to the ones observed, in view of its evident dominant importance, noted in the paragraph above. It is remarkable but helpful that the isotope effects λ_0^H/λ_0^D are all so close to 1.23. As a consequence, the arguments which follow are essentially unchanged whether we use 1.23 throughout, or the observed values (as are actually used below), or values deviating several times as much from 1.23 (as would be required if there were dominant conductance by another mechanism not involving exchange of water).

Inferences drawn from experimental results generally depend on the model used to represent the real physical system. The following discussion combines the simplest tetrahedral model for liquid water and water solutions[41] with absolute rate theory, in an effort to elucidate this mechanism of conductance. The tetrahedral model assumes that each water molecule or ion is surrounded by exactly four water molecules and that all force constants and potential energies are unchanged from light to heavy water.

From measured infrared frequencies but with *no* adjustable parameters, all of the following differences between light and heavy water are calculable[41] from the model in good agreement with experiment: difference in heat, entropy, free energy, heat of vaporization, and heat capacity of the pure liquid waters, difference in heat, entropy, and free energy for solution of alkali metal and halide ions, relative solubility of lithium fluoride in the two waters, and relative autoprotolysis constants. The only misfit is iodide ion, for which six coordinated waters are required to obtain agreement with experiment; for all the other water molecules, alkali ions and halide ions, four gives agreement and other integral numbers do not. Thus in one sense the solvation number is an adjustable parameter, yet the only number that fits is the physically reasonable value of four in every instance except for iodide. The only significant variable is the observable average librational (restricted rotational) frequency of water, which depends on whether the water is bonded to other waters only (667 cm^{-1}) or to fluoride ion (698 cm^{-1}), chloride ion (598 cm^{-1}), sodium ion (635 cm^{-1}), or some other ion; all of the solvent isotope effects mentioned above are calculable from it alone, since the internal frequencies do not change appreciably. The model has also been applied to many kinetic situations, organic reactions involving water, hydroxide ion, or hydronium ion as reactants, to distinguish between different kinds of transition states and mechanisms and to ascertain just how late along the reaction coordinate the transition state comes.[42] This has led to two complementary general rules about the effect of structure of reactants on the structure of transition states.[43]

For the present application, we will attribute all of $\ln(\lambda_0^H/\lambda_0^D)$ to the decreased average librational frequency and zero-point kinetic energy of the solvating water molecules at the transition state, assuming, as in the applications above, that the more remote waters not adjacent to an ion maintain their normal frequencies as in pure water. Therefore

$$\ln(\lambda_0^H/\lambda_0^D) = (-3hb/2kT)[n^*\Delta\omega^* + (n - n^*)\Delta\omega_w - n\Delta\omega]$$

$$\Delta\omega = \omega^H - \omega^D = \omega^H - (\omega^H/1.3815)$$

$$\Delta\omega_w = 667 \text{ cm}^{-1}$$

where *h* is the Planck constant, *b* the velocity of light, *k* the Boltzmann constant, *T* the absolute temperature, *n* the number of coordinated waters, and ω the librational frequency in cm^{-1}; * refers to the transition state, no * to reactant, subscript w to pure water, H to H_2O, and D to D_2O. Table V gives the resulting calculated librational frequencies ω^* for various assumed numbers n^* of water molecules coordinated to the ion at the transition state.

Table V. Librational Frequencies for H_2O

Ion	n	ln (λ_1/λ_2)	ω, cm^{-1}	ω^*, cm^{-1} n^* = 3	 n^* = 4	 n^* = 5
F^-	4	0.2098	698	675	673	672
Cl^-	4	0.1952	598	543	574	592
Br^-	4	0.1920	573	510	549	572
I^-	4	0.1884	546	476	524	552
I^-	6	0.1884	587	529	564	584
Na^+	4	0.1881	635	592	611	622
K^+	4	0.1812	625	579	602	615
Cs^+	4	0.1812	613	564	590	605

Two extreme mechanisms are conceivable for moving an alkali or halide ion through a water solution from left to right with exchange of solvation shell water molecules as it moves: it might first release one of its waters on the left to become solvent water, then move slightly right to include a new solvent water on the right in its solvation shell (an elimination–addition mechanism); or it might first move right, expanding its solvation shell to include the extra water, then cast off an original water on the left (an addition–elimination mechanism). If the former mechanism were correct and the number of bound water molecules were three

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[41] C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960).

[42] C. G. Swain, R. F. W. Bader, and E. R. Thornton, *ibid.*, **10**, 200 (1960); C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 3884, 3890 (1961); C. G. Swain and A. S. Rosenberg, *ibid.*, **83**, 2154 (1961); C. G. Swain and E. R. Thornton, *ibid.*, **84**, 822 (1962).

[43] C. G. Swain and E. R. Thornton, *ibid.*, **84**, 817 (1962); C. G. Swain, D. A. Kuhn, and R. L. Schowen, *ibid.*, **87**, 1553 (1965).

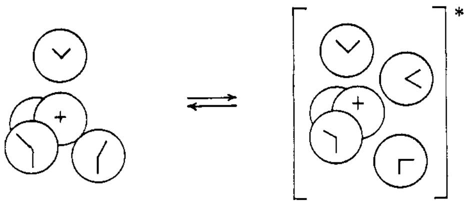

Figure 1. Reactant and transition state structures for conductance of an alkali metal ion in aqueous solution.

in the transition state in contrast to four in the reactant state, the correspondingly stronger bonding to each at the transition state should lead to an increased librational frequency. The restriction to rotation, due to ion–dipole attraction or hydrogen bonds, is primarily electrical, because even with four attached the surrounding water structure is open and uncrowded. The fact that the calculated average librational frequency for the solvating waters *drops* for all these ions (*cf.* Table V for $n^* = 3$) seems to exclude this mechanism. On the other hand, if the addition–elimination mechanism is correct and a larger number of water molecules is attached at the transition state, the bonding to each should be weaker and the frequency should drop, as calculated (*cf.* Table V for $n^* = 5$). This looser bonding in the transition state can also be viewed as resulting in formation of free volume around the ion, which allows the ion to move through the solution in small discrete steps. In summary, the migration of an alkali or halide ion through water is a process involving making and breaking solvation bonds to the ion. The coordinated water molecules at the transition state are each more loosely bound than those of the reactant, whether one assumes three, four, or five. This seems unreasonable for three (initial decrease in number of solvating water molecules), but consistent with prior or incipient coordination of an *additional* water (Figure 1).

Theory of Controlled Potential Electrogeneration of Chemiluminescence[1]

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Abstract: Several workers have reported chemiluminescence produced by electrogeneration at a single electrode of anion and cation radicals of a large number of aromatic hydrocarbons. Light emission probably results from a radical-annihilation reaction, followed by radiative decay: (1) $R^+ + R^- \xrightarrow{k} R + R^*$; (2) $R^* \rightarrow R + h\nu$. The purpose of this paper is to relate quantitatively the light intensity produced in electrogenerated chemiluminescence to the current, time, and kinetic parameters. These relationships have been calculated for a double potential step mode of generation. In a solution containing only the organic species R, the electrode potential is initially set so that zero current flows. A sufficiently positive potential pulse of duration t_f is applied to the electrode so that the concentration of species R at the electrode surface instantaneously becomes zero as R is oxidized to the cation radical R^+. The positive pulse is immediately followed by a negative potential pulse of duration t_r so that the surface concentrations of both species R and R^+ are zero as the anion radical R^- is generated. During the negative pulse the annihilation and light emission reactions (see above) occur in the diffusion layer. The calculations are made using an IBM 7094 digital computer.

Hoijtink and co-workers[2] were the first to report chemiluminescence resulting from the reaction between the cation and anion radicals of anthracene. Subsequently, several workers have produced chemiluminescence by the electrogeneration of the anion and cation radicals of various organic aromatics at a single electrode surface using alternating current[3] and alternating potential techniques.[4]

Nearly all workers have suggested the formation of an excited singlet state, which undergoes radiative and nonradiative decay to the ground state. The following generalized mechanism may be written

$$R \longrightarrow R^+ + e^- \quad \text{oxidation at electrode surface} \qquad (1)$$

$$\left.\begin{aligned} e^- + R &\longrightarrow R^- \qquad (2) \\ 2e^- + R^+ &\longrightarrow R^- \qquad (3) \end{aligned}\right\} \quad \text{reduction at electrode surface}$$

$$R^+ + R^- \xrightarrow{k_4} R^* + R \quad \text{in bulk of solution} \qquad (4)$$

$$R^* \xrightarrow{k_5} R + h\nu \quad \text{radiative decay} \qquad (5)$$

$$R^* \xrightarrow{k_6} R \quad \text{nonradiative decay} \qquad (6)$$

$$R + R^* \xrightarrow{k_7} 2R \quad \text{self-quenching} \qquad (7)$$

where R is the organic molecule, R^+ and R^- are the cation and anion radicals, and R^* is the molecule in the excited state. Chandross, Longworth, and Visco[5]

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) Private communication by Professor Hoijtink to E. A. Chandross and F. I. Sonntag, Bell Telephone Laboratories, Inc., Murray Hill, N. J.; see E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

(3) D. M. Hercules, *Science*, **145**, 808 (1964).

(4) (a) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964); (b) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965).

(5) E. A. Chandross, J. W. Longworth, and R. E. Visco, *ibid.*, **87**, 3259 (1965).