TABLE I

POTENTIAL OF THE ELECTROCAPILLARY MAXIMUM IN TENTH-NORMAL SODIUM OR POTASSIUM CHLORIDE RELATIVE TO A TENTH-NORMAL CALOMEL ELECTRODE IN THE SAME ELECTROLYTE

Method	Source	Potential, volts NaCl	KCl
I	This work	0.5585	0.5590
II	This work	.562	.559
III	This work	.560	.560
IV	This work	.5585	.5595
V	This work	.558	.556
V	Paschen	.557	.553
V	Erdey-Gruz and Szarvas	.551	
	Gouy	.58	
I	Gouy + this work	.56	
	Smith		.57
V	Palmaer		.573

chloride. No two authors have done exactly the same thing, and in order to make a comparison, we have made the best conversions we could to a single standard. Values given in Table I for tenth-normal sodium chloride are expressed relative to a calomel electrode in the *same* solution.

Except for the value by Gouy, these measurements are in reasonably good accord. Gouy obtained his result by extrapolation of the diameters of the electrocapillary curve, and close examination of his data reveals that the extrapolation was a long one, especially in this case. If one combines his interfacial tension measurements with our differential capacity data as in method I, thus eliminating the extrapolation, the disagreement with our "best" value disappears to within less than the accuracy to which Gouy's values are reported. This corrected value is entered along with the others in Table I.

Acknowledgment.—We are grateful to the Research Corporation for two grants from the Frederick Gardner Cottrell fund in support of this work.

Summary

1. Three techniques are described for the determination of "isotension potentials," pairs of potentials at which the interfacial tension is the same on the two branches of the electrocapillary curve.

2. A method is described for the determination of the potential of the electrocapillary maximum by combining isotension potential data with measurements of the capacity of the electrical double layer.

3. Values of the potential of the e. c. max. in tenth-normal potassium and sodium chlorides are obtained by these three methods and also by two other methods of which one is new. Good agreement is obtained.

4. A value of 0.559_0 volt is obtained for the e. c. max. potential of tenth-normal potassium chloride relative to a tenth-normal calomel electrode, both at 25°.

5. Essentially the same value is obtained for tenth-normal sodium chloride relative to a tenth-normal calomel electrode in sodium chloride. This value is compared with previously published values.

6. A temperature coefficient of -0.0705 mv./deg. is found for the e. c. max. potential in tenth-normal potassium chloride.

AMHERST, MASS. RECEIVED NOVEMBER 29, 1948

[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLIII. Effect of Ammonia and Water on the Conductance of Lithium, Sodium and Silver Ions in Pyridine at 25°[1]

BY CHARLES J. CARIGNAN[2] AND CHARLES A. KRAUS

I. Introduction

Burgess has shown that the conductance of tetrabutylammonium picrate in pyridine is changed but little on addition of ammonia. The observed effect may be accounted for by the viscosity change of the solvent; the dissociation constant of the salt remains unchanged. However, when ammonia is added to a solution of sodium picrate, the conductance of the salt is greatly increased. In view of the fact that the conductance of the quaternary ammonium picrate remains constant (except for viscosity effect), it may be concluded that the increased conductance of sodium picrate is due to an increase in the conductance of the sodium ion.

It seemed worth while to investigate this phenomenon in somewhat greater detail. Accordingly, we have measured the conductance of lithium picrate at five different concentrations of ammonia, sodium picrate at two concentrations, and sodium iodide and silver nitrate, each at one concentration of ammonia. In addition, we have measured the conductance of sodium picrate at three different concentrations of water.

II. Experimental

1. Materials.—Pyridine was purified according to the procedure of Luder[3] and Burgess[4]

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[1] This paper is based on a portion of a thesis presented by Charles J. Carignan in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1947.

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[3] Luder and Kraus, THIS JOURNAL, **69**, 2481 (1947).

[4] Burgess and Kraus, *ibid.*, **70**, 706 (1948).

except that the treatment with zinc chloride was omitted. The fact that our conductance values for lithium picrate check those of Burgess and that the density and viscosity of our solvent agree with those in the literature indicates that the zinc chloride step is unnecessary.

Ammonia was dried over sodium amide in a special stock cylinder. In making up known solutions of ammonia in pyridine, the ammonia was condensed in a weighed cylindrical tube of 100-cc. capacity containing ammonium nitrate. The vapor pressure of the saturated solution is one atmosphere at 23.6°. The pyridine, about 800 cc., was weighed in a round-bottom flask; it was then attached to the system, cooled to −78° and exhausted to remove all air. The desired amount of ammonia was then condensed on the pyridine, the amount of ammonia being found by weight difference of the ammonium nitrate container. The pyridine was warmed up to 25° in a water-bath, being stirred by means of a magnetic stirrer. After noting the pressure of ammonia above the solvent, dry air was admitted to bring the pressure to one atmosphere. The solvent was transferred from the stock flask to the cell as needed, the stock flask being connected to a supply of an air–ammonia mixture having the same composition as the atmosphere in the flask.

The conductance of pure pyridine was of the order of 5×10^{-10}. On addition of ammonia or water, the conductance was increased approximately tenfold. The conductance of these solvent mixtures usually ranged from 1 to 1.5×10^{-8}; it was necessary to apply a solvent correction in the case of the more dilute solutions.

1. Salts.—Lithium picrate was recrystallized from nitromethane; sodium picrate was recrystallized from ethanol. Both salts were dried *in vacuo* at 80°. Care should be exercised not to overheat the picrates. Sodium iodide and silver nitrate were recrystallized from water; the former was dried at 100°, the latter *in vacuo* at room temperature in the dark.

2. Physical Constants.—Densities were determined with a pycnometer of 30-cc. capacity with a capillary 5 cm. long and 1.0 mm. diameter. This pycnometer was provided with a ground-glass cap. Values are given in the tables.

Viscosities were determined with a modified Ostwald viscometer. An atmosphere of ammonia and air was maintained above the liquid with which it was in equilibrium. Values are given in the tables.

Dielectric constants were determined with a special cell and the parallel arm bridge that was also used for measuring the conductance of the pure solvents. The cell was calibrated with pyridine, using the value 12.01 for the dielectric constant of pure pyridine. With a 0.4798 *N* solution of ammonia, the dielectric constant was found to be 12.06. The difference with respect to pure pyridine is negligible for present purposes. With water, a marked increase of the dielectric constant was found. Values are given in Table II.

3. Experimental Techniques and Procedure.—Conductance measurements were carried out at 25 ± 0.01° as described in earlier papers.[4] The conductance cell was provided with gray platinum electrodes and had a capacity of 60 cc. It was well filled so as to reduce the vapor space to a minimum. Dilution was made as already

TABLE I

CONDUCTANCE OF SALTS IN PYRIDINE–AMMONIA MIXTURES AT 25°

A. Lithium Picrate

c, NH_3 = 0.0; d = 0.97801; η_0 = 0.008827

$C \times 10^4$	Λ
1.4724	31.98
0.78358	37.74
.41304	43.32
.21674	48.22
.12145	51.61

c, NH_3 = 0.1009; d = 0.97655; η/η_0 = 0.987

$C \times 10^4$	Λ
3.8084	27.92
1.8247	34.90
1.0039	41.06
0.42081	48.83
.23643	53.09
.14800	55.79

c, NH_3 = 0.2169; d = 0.97534; η/η_0 = 0.971

2.0186	39.68
0.92759	47.39
.46282	53.55
.22722	58.48
.12277	61.60

c, NH_3 = 0.2922; d = 0.97442; η/η_0 = 0.963

2.0142	40.51
1.0244	47.75
0.53857	54.02
.26277	59.55
.12886	63.14

c, NH_3 = 0.3408; d = 0.97455; η/η_0 = 0.958

2.0905	40.69
0.86685	50.39
.63120	53.63
.25967	60.65
.10281	65.87

c, NH_3 = 0.3716; d = 0.97362; η/η_0 = 0.955

5.5596	30.81
1.9409	41.55
0.96736	48.80
.41633	57.86
.21028	62.63
.09994	65.91

B. Sodium Picrate

c, NH_3 = 0.0954; d = 0.97671; η/η_0 = 0.986

$C \times 10^4$	Λ
33.328	8.97
5.0785	18.66
2.5396	24.13
1.1306	31.62
0.46056	41.13
.27380	46.21
.13622	52.51

c, NH_3 = 0.2230; d = 0.97543; η/η_0 = 0.970

$C \times 10^4$	Λ
5.321	21.17
1.620	31.95
1.149	34.26
0.7750	38.27
.2326	52.58

C. Sodium Iodide

c, NH_3 = 0.2299; d = 0.97501; η/η_0 = 0.969

3.3813	55.73
1.1672	68.15
0.59343	74.42
.33533	78.74
.16969	83.06

D. Silver Nitrate

c, NH_3 = 0.3415; d = 0.97379; η/η_0 = 0.958

6.8843	59.35
3.7403	66.77
1.8421	74.74
0.97121	80.84
.48290	86.03
.20259	90.69

described except that an atmosphere of air and ammonia was maintained above the liquid which was in equilibrium with it. When water was used, an atmosphere of dry carbon dioxide-free air was maintained over the solution.

III. Results

The results for the lithium and sodium picrates, for sodium iodide and silver nitrate in the presence of ammonia are presented in Table I. The concentration of ammonia and values of the density and relative viscosity, η/η_0, are given at the head of the several tables.

Results for sodium picrate in the presence of water are given in Table II. At the head of the several tables are given the concentration of water, the density, the relative viscosity and the dielectric constant.

TABLE II

CONDUCTANCE OF SODIUM PICRATE IN PYRIDINE–WATER MIXTURES

c, H_2O = 0.1018; d = 0.97783; η/η_0 = 1.004; D = 12.32

$C \times 10^4$	Λ
7.5151	21.12
3.4469	27.52
0.90357	39.96
.45399	46.07
.19335	52.23
.12088	54.65

c, H_2O = 0.2048; d = 0.97795; η/η_0 = 1.011; D = 12.44

$C \times 10^4$	Λ
9.4212	23.51
3.5930	31.70
1.5512	39.42
0.72532	46.00
.32705	51.64
.17025	55.03

c, H_2O = 0.3148; d = 0.97815; η/η_0 = 1.019; D = 12.52

$C \times 10^4$	Λ
11.626	25.51
4.9599	32.79
2.2814	39.82
0.95102	47.42
.38970	53.44
.15429	57.59

IV. Discussion

The data presented in Tables I and II have been analyzed by the method of Fuoss and values of the limiting conductance, Λ_0, and the dissociation constant, K, have been determined. Fuoss plots are shown for lithium picrate in Fig. 1 and for sodium picrate, sodium iodide and silver nitrate in Fig. 2 (all in the presence of ammonia).

Plots for sodium picrate in the presence of water are shown in Fig. 4.

It will be noted that all the plots are linear, conforming to the Bjerrum–Fuoss relation. It is of particular interest to point out that our values for lithium picrate in pure pyridine are in good agreement with those of Burgess, although we used a simpler method in the purification of the solvent. Evidently, the treatment with zinc chloride is unnecessary.

1. Salts in Presence of Ammonia.—Values of Λ_0 and K as derived from the plots for ammonia–pyridine mixtures are listed in Table III (columns

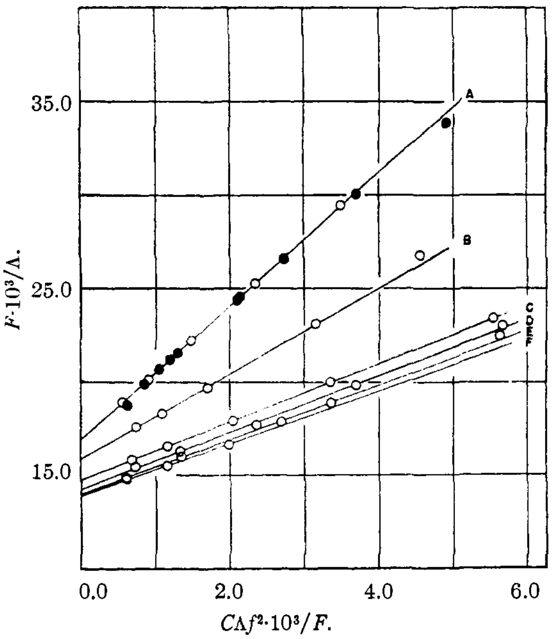

Fig. 1.—Fuoss plots for lithium picrate in pyridine–ammonia mixtures: concentration of ammonia: (A), 0.00; (B), 0.1009 m; (C), 0.2169 m; (D), 0,2922 m; (E), 0.3408 m; (F), 0.3716 m.

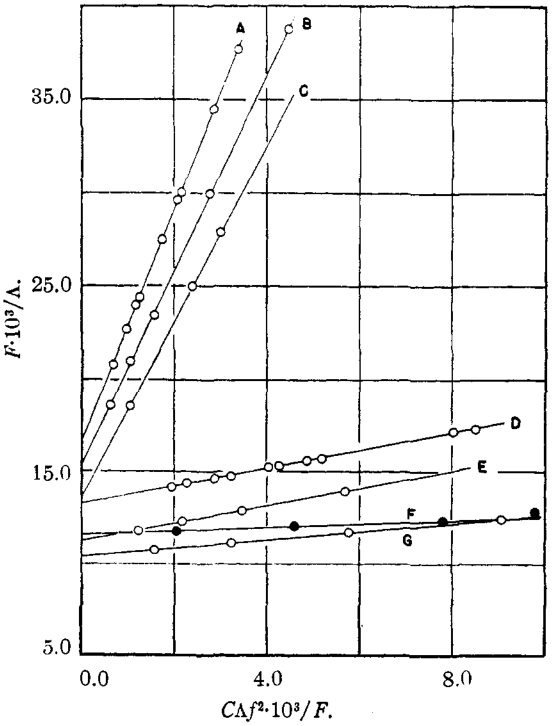

Fig. 2.—Fuoss plots for sodium picrate, sodium iodide and silver nitrate in pyridine–ammonia mixtures: concentration of ammonia: NaPi (A) 0.00 (B) 0.0954 m; (C) 0.2230 m; NaI (D) 0.00, (E) 0.2299 m; $AgNO_3$ (F) 0.00, (G) 0.3415 m.

TABLE III

LIMITING EQUIVALENT CONDUCTANCES, ION CONDUCTANCES AND DISSOCIATION CONSTANTS OF ELECTROLYTES IN PYRIDINE–AMMONIA MIXTURES

NH_3 concn. moles/liter	Λ_0	Λ_0^- [a]	Λ_0^+	% Increase in Λ_0^+	Dissoc. const. $K \times 10^4$
			A. Lithium Picrate		
0.0	58.45	33.68	24.77	..	0.81
0.1009	63.17	34.12	29.05	17.3	1.09
.2169	67.70	34.69	33.01	33.2	1.40
.2922	70.18	34.97	35.21	42.1	1.35
.3408	71.22	35.15	36.07	45.6	1.38
.3716	72.20	35.26	36.94	49.1	1.25
			B. Sodium Picrate		
0.0	60.5	33.7	26.8	..	0.43
0.0954	65.3	34.2	31.1	16.0	.45
.2230	73.8	34.7	39.1	45.9	.39
			C. Sodium Iodide		
0.0	75.20	48.4	26.8	..	3.7
0.2299	88.50	49.9	38.6	44.1	2.70
			D. Silver Nitrate		
0.0	86.9	52.6	34.3	..	9.3
0.3415	95.6	54.9	40.7	18.7	4.96

[a] Corrected for change in solvent viscosity on addition of ammonia.

2 and 6). In the third column is given the anion conductance corrected for viscosity change, in the fourth column, the cation conductance, and in the fifth column, the percentage increase of cation conductance over that in the pure solvent.

As may be seen from Table III as well as from Fig. 3, the conductance of the lithium ion is greatly increased on addition of ammonia. The conductance evidently approaches a limiting value with increasing ammonia concentration; for an ammonia concentration of 0.37 molar, the conductance increase is 49%. In the limit, the increase must be considerably greater than this.

With sodium picrate, the cation conductance increases more rapidly than with the corresponding lithium salt. For an ammonia concentration of 0.22 molar, the (ion) conductance increase is 46%. It is of interest to note that the conductance increase of the sodium ion is the same for the iodide as for the picrate. It is also of interest to note that the conductance increase of the silver ion is much smaller than that of the lithium or the sodium ion.

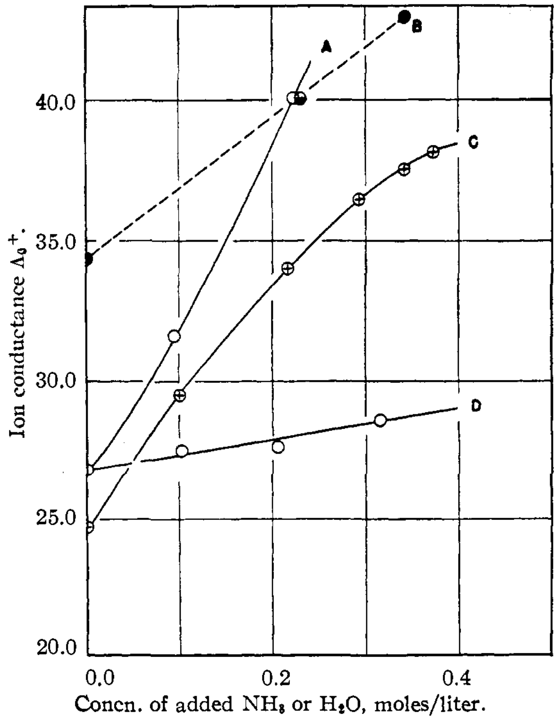

Fig. 3.—Conductance of lithium, sodium and silver ions in pyridine–ammonia mixtures and sodium ion in pyridine–water mixtures: (A) NaPi ○, NaI ⊖; (B) $AgNO_3$ ●; (C) LiPi ⊕; (D) NaPi with H_2O ○.

TABLE IV

LIMITING EQUIVALENT CONDUCTANCE, ION CONDUCTANCES AND DISSOCIATION CONSTANT OF SODIUM PICRATE IN PYRIDINE–WATER MIXTURES

H_2O concn. moles/liter	Λ_0	Λ_0^- (cor.)	Λ_0^+	% Increase in Λ_0^+	Dissoc. const. $K \times 10^4$
0.0	60.5	33.7	26.8	...	0.43
0.1018	61.2	33.5	27.7	3.3	1.01
.2048	61.3	33.3	28.0	4.5	1.61
.3148	62.3	33.1	29.2	9.0	2.29

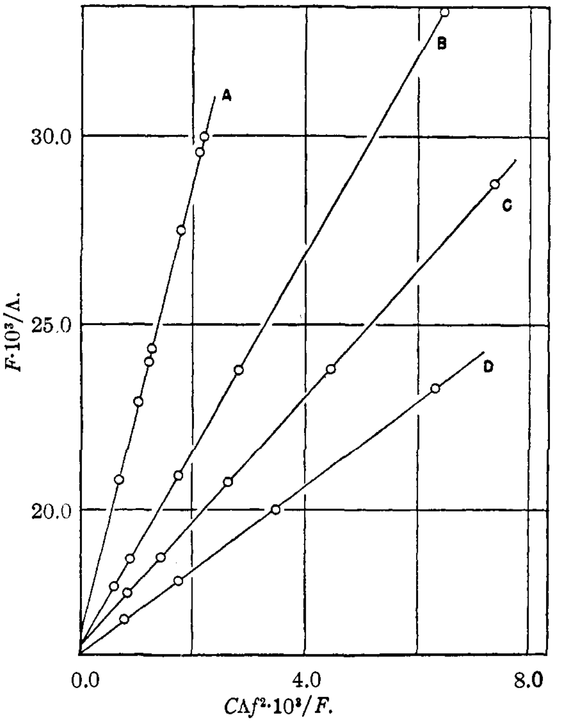

Fig. 4.—Fuoss plots for sodium picrate in pyridine–water mixtures: water concentration: (A) 0.00; (B) 0.1018 *m*; (C) 0.2048 *m*; (D) 0.3148 *m*.

The dissociation constant, on addition of ammonia, may increase, decrease or remain unchanged. Thus, for lithium picrate, there is an increase, for sodium iodide and silver nitrate, a decrease, while for sodium picrate there is no change. It appears that although free ions of lithium, sodium and silver become effectively smaller due to the presence of ammonia, in their ion pairs they may become either larger or smaller or undergo no change. Ion conductances are shown as a function of ammonia concentration in Fig. 3.

2. Sodium Picrate in Presence of Water.—In Table IV are given values for the constants of sodium picrate in the presence of water. Graphs are shown in Fig. 4.

As may be seen from Table IV, the conductance of the sodium ion in pyridine is increased on addition of water, but much less than on addition of ammonia. The increase is only 9% with 0.32 molar water. On the other hand, there is a marked increase of the dissociation constant, approximately six times for 0.32 molar water. This increase may be due, in part, to the higher dielectric constant of the water mixtures. At the concentration mentioned above, the dielectric constant is 7% greater than that of pyridine.

V. Summary

1. The conductance of lithium and sodium picrates and of sodium iodide and silver nitrate have been measured in pyridine solutions to which ammonia had been added.

2. The conductance of sodium picrate has been similarly measured in pyridine to which water had been added.

3. Values of the limiting conductance and the dissociation constant have been derived for the salts in these solutions by the Fuoss method and ion conductances have been determined.

4. The conductance of the three cations increases markedly on addition of ammonia. At an ammonia concentration of 0.2 molar, the conductance increase for the lithium, sodium and silver ions is, respectively, 33, 42 and 15%.

5. The conductance increase for the sodium ion on addition of 0.2 molar water is 4.5%.

6. On addition of ammonia, the dissociation constant of lithium picrate increases somewhat. Those of sodium iodide and silver nitrate decrease and that of sodium picrate remains unchanged. The dissociation constant of sodium picrate is increased markedly on addition of water.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Effect of Centrifugal Force on Galvanic Potentials: (a) The Transference Numbers of Potassium Iodide, (b) The Iodide–Iodine Ion

BY D. A. MACINNES AND B. ROGER RAY[1a]

The effect of gradients of centrifugal force on the potentials of simple galvanic cells has been studied by Des Coudres[1] and more extensively by Tolman,[2] and some preliminary measurements have been reported by MacInnes.[3] Tolman and MacInnes used galvanic cells of the type

$$\underset{r_2}{(\mathrm{Pt})};\ \mathrm{I_2},\ \mathrm{KI},\ \mathrm{I_2};\ \underset{r_1}{(\mathrm{Pt})} \qquad \text{(A)}$$

in which two, otherwise identical, iodide–iodine electrodes with a uniform solution between them are placed at radii r_1 and r_2 in a centrifugal field. These researches have been interpreted by the equation

$$EF = 2\pi^2 n^2 (r_2^2 - r_1^2)[t_\mathrm{K}(M_\mathrm{KI} - \bar{V}_\mathrm{KI}\rho) - (M_\mathrm{I} - \bar{V}_1\rho)] \qquad (1)$$

in which F is the faraday, n is the number of revolutions per second, t_K is the transference number of the cation constituent, ρ is the density of the solution, M_KI and $\bar{V}_\mathrm{KI}$ are the molecular weights and partial molal volumes of potassium iodide, and M_I and $\bar{V}_\mathrm{I}$ are the atomic weight and partial atomic volume of iodine. It will be shown below that this is a limiting form of an equation which is based on more complete knowledge of the mechanism of cell A.

Studies of the closely related effect of differences of height on the potentials of galvanic cells have been made by Des Coudres[4] and more recently by Grinnell and Koenig.[5]

The results to be described below are the outcome of a long research undertaken to develop the centrifugal e. m. f. procedure into a precision method for obtaining transference numbers. It is of particular importance in that it can be used, as has been demonstrated by experiments already made, in the determination of transference numbers in non-aqueous solvents, where, due to Joule heat, the Hittorf and moving boundary methods encounter difficulties.

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(1) Des Coudres, *Ann. Physik*, **49**, 234 (1893).

(2) Tolman, *Proc. Am. Acad. Arts Sci.*, **46**, 109 (1910); THIS JOURNAL, **33**, 121 (1911).

(3) MacInnes, *Ann. New York Acad. Sci.*, **43**, 243 (1942).

(4) Des Coudres, *Ann. Physik*, **57**, 232 (1896).

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