

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Dependence of Conductance on Field Strength. I. Tetrabutylammonium Picrate in Diphenyl Ether at 50°

BY DARWIN J. MEAD WITH RAYMOND M. FUOSS

I. Introduction

In 1924, Wien¹ showed experimentally that the conductance of electrolytes under high field strengths was abnormal. He first ascribed the effect to a change of the temperature coefficient of conductance with field strength, but subsequent work in his Laboratory² showed that the abnormalities were due to an actual failure of Ohm's law for electrolytes.³ He showed that two effects were present, one quadratic in the field and one linear. The first Wien effect appears in strong electrolytes when the distances the ions move during their relaxation time become of the order of the diameter of the ionic atmosphere. Then the retarding effects on mobility of the atmosphere are diminished, with consequent increase of conductance. In weak electrolytes, the conductance is further increased by increased dissociation in the field. The second Wien effect has been treated theoretically by Onsager,⁴ who showed that the slopes of the conductance-field curves could be predicted from the dielectric constant and temperature of the solvent and the valence type of the electrolyte.

Because the Wien effects are direct experimental evidence for the existence of the ionic atmosphere and for the pairwise association of ions under their mutual coulomb fields, and also on account of general interest in the behavior of dielectrics under high fields, it seemed worthwhile to study by bridge methods several carefully selected systems in some detail.

Diphenyl ether at 50° was chosen as our solvent on account of its ease of purification, low solvent conductance and high solvent power for substituted ammonium salts, which are convenient 1-1 electrolytes for work in non-aqueous solvents. Its dielectric constant at 50° and 60 cycles is 3.53, which is low enough to give marked ion association. In it, the conductance of tetrabutylammonium picrate satisfies the simple binary association law from below millionth normal up to

concentrations of the order of 10^{-4} normal. Consequently the system permitted a test of the theory over a wide range of conductance and concentration. Above 10^{-4} normal, triple ion formation⁵ becomes appreciable; in this range a dependence of the Wien coefficient on concentration was observed.

From the initial part of the conductance-field curves, the activity coefficient of the solute can be determined.⁴ With our present methods, our precision in activity coefficient is not high, because it is determined as a small difference between two large quantities, one of which depends on an extrapolation, but we can show that our experimental coefficients are in approximate agreement with the values calculated by the limiting law of Debye and Hückel. The present results therefore demonstrate the existence of an ionic atmosphere in a solvent of quite low dielectric constant.

From the linear part of the curves, we find at low concentrations an increase in conductance of 1.6% per kilovolt, which is in good agreement with the theoretical value, 1.32%, calculated by Onsager's theory. Since this theory postulates pairwise association of ions, and explains the second Wien effect as a displacement of this equilibrium in the field, our results give experimental proof of the existence of ionic association.

Further work on different types of electrolytes and on solvents of lower dielectric constant, where still higher field strengths can be studied, is in progress. It will be interesting to see whether the shape (electrical and physical) and size of the ions influence the Wien coefficient and also to study the effect in the range of higher association than pairwise.

II. Materials, Apparatus and Method

Diphenyl ether was purified by recrystallization, after which it was dried first with calcium chloride, and finally with activated alumina. Our highest freezing point was 27.1°. The average solvent conductance was 0.3×10^{-12} ; our best value was 0.06×10^{-12} .

Tetrabutylammonium picrate was prepared as described by Fuoss and Kraus,⁶ m. p. 89.2-90.0° (corr.).

(5) Fuoss and Kraus, *THIS JOURNAL*, **55**, 2387 (1933).

(6) Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

(1) Wien, *Ann. Phys.*, **73**, 162 (1924).

(2) Wien, *ibid.*, **83**, 327 (1927).

(3) An excellent bibliography is contained in a review by Eckstrom and Schmelzer, *Chem. Rev.*, **24**, 367 (1939).

(4) Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

Conductance cells of several types were used. Some determinations were made in the cell described by Deitz and Fuoss,⁷ and others in the cell described by Elliott and Fuoss.⁸ The former cell showed a pronounced Parker effect at 1000 cycles and was only used for preliminary 60-cycle work. The second cell (cell no. 2) gave results

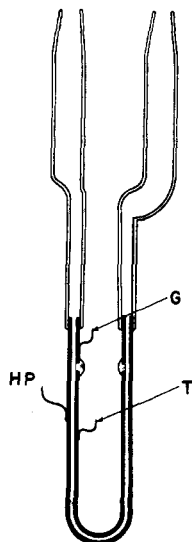


Fig. 1.—Guarded conductance cell.

independent of frequency (except for a normal polarization effect) and was used for about half of the work reported in this paper. For the final work, two platinum cells were used, which had two advantages over Elliott's cell: they could be cleaned with hot nitric acid or chrome-sulfuric acid between runs, and they had no movable parts. Cell no. 3 is shown in Fig. 1. The high potential electrode (8.25 cm. long, 2.540 cm. inside diameter, 0.5 mm. wall thickness) was simultaneously the outer cell wall. It and the guard-test combination (outside diameter 2.060 cm.) were sealed to a hollow ring of soft glass, to which were sealed filling tubes. The volume was 25 cc. A shielded lead ran to the test electrode; the shield was connected to the guard electrode, and the shielding was unbroken from cell to bridge. At final balance, the guard and test electrodes are at the same potential, so that except for an insignificant amount of fringing at the glass joint between the guard and test electrodes, the flux is normal over the entire test electrode. The latter condition is essential, because it was necessary to calculate field strength from cell geometry and the voltage applied to the cell. Cell 4 was similar to cell 3, except that the electrode spacing was 0.491 cm., or about twice that of cell 3.

Cell Comparison and Calculation of Field Strength.—In Fig. 2 are shown conductance-field curves, in which cells 2, 3 and 4 are compared. For convenience in drawing, the ratio of the specific conductance at field strength E to the low voltage conductance is plotted against field strength. Cell 2 had about twice the area and nearly the same spacing as cell 3 (cell constants 0.002727 and 0.004605, respectively), while cells 3 and 4 had about the same area, but quite different spacings (constants 0.004605 and 0.01064). The effect in question is a *linear* field effect; in this case, the average field strength E is given by

$$E = \int_{r_1}^{r_2} E(r) dr / (r_2 - r_1) = V / (r_2 - r_1) \quad (1)$$

where V is the voltage applied to the high potential electrode. It will be seen that the agreement

between the cells checks our calculation of field strength.

Voltage Sources and Scales.—Most of our voltage work was done at 60 cycles; examination with a cathode ray oscilloscope showed that the transformer output was free from harmonics. Some work was done at 500–1500 cycles; here graphical integration of the oscilloscope curves showed the presence of not more than 5% harmonics. The question of harmonics is important, because the second Wien effect is linear in cell voltage and all our voltmeters read mean square voltage. The linear average V was computed from the r. m. s. average V_r by the relations

$$V = (V_{max}/\pi) \int_0^\pi \sin x \, dx = 2 V_{max}/\pi \quad (2)$$

$$V_r = \left[(V_{max}^2/\pi) \int_0^\pi \sin^2 x \, dx \right]^{1/2} = V_{max}/\sqrt{2} \quad (3)$$

whence

$$V = (2\sqrt{2}/\pi) V_r \quad (4)$$

A number of voltage scales were used in order to obtain cross checks. First, the output of the transformer to the cell and bridge network was fed simultaneously to a step-down transformer of known ratio under zero load (potential transformer), and the output voltage of the latter was used as a measure of the cell voltage. The ratio of the potential transformer was determined by

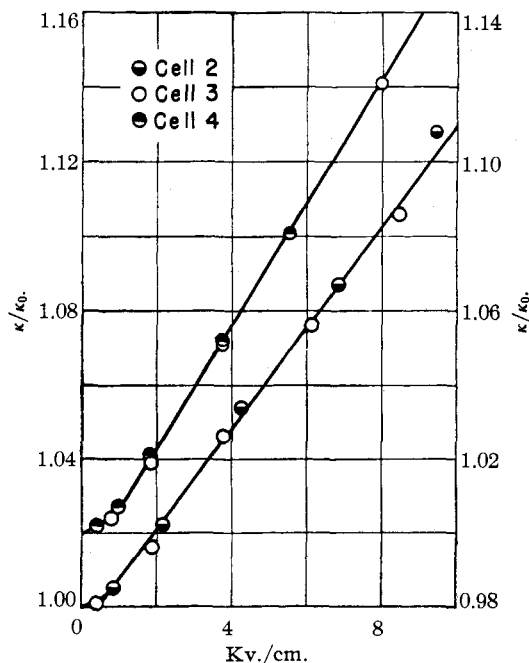


Fig. 2.—Cell comparison: upper curve, $c = 2.376 \times 10^{-5}$; lower curve, $c = 9.64 \times 10^{-5}$.

(7) Deitz and Fuoss, *THIS JOURNAL*, **60**, 2394 (1938).

(8) Elliott and Fuoss, *ibid.*, **61**, 294 (1939).

A. I. E. E. data relating sparking distance with voltage. Second, an electrostatic voltmeter, also calibrated by spark data, was used. Finally, the calibration of the electrostatic voltmeter was checked by direct determination of the current read on a milliammeter through a voltage insensitive resistor. The resistor was the 100,000 ohm wire wound standard used ordinarily as one arm of our resistance bridge.⁹ The voltage calculated from the current and resistance by Ohm's law agreed with that read on the electrostatic voltmeter. The various voltage scales were self-consistent within 2%.

Bridges.—The conductance-field curves were determined using the resistance and Schering bridges which have been described previously.^{9,10} Voltages up to 25 kv. were available at 60 cycles by means of transformers on the shop line. In the range 500–2000 cycles, an alternator was used to supply a tapped transformer, whose maximum output was 10 kv.

Low voltage determinations in the audiofrequency range were made on a parallel bridge. The Wagner ground and guard circuits were combined, so that three terminal cells could be used. Two arms of the bridge were reactance-free 10^5 ohm resistors; the other two arms were 10^5 ohm resistors with about $350 \mu\text{mf}$ capacity in parallel with each. After obtaining zero-balance, the cell was connected parallel to one of the latter arms, and from the changes in resistance and capacity necessary to restore balance, the conductance and capacitance of the cell could be determined.

Procedure.—Solutions were made up by weight in a dilution flask and the density (1.0440 at 50°) of the solvent was used in calculating normality. (Our highest concentration was about $3 \times 10^{-3} N$.) In order to eliminate errors due to sorption effects¹¹ the cell was filled with successive portions of the same solution from the dilution flask, until the conductance of two consecutive fillings differed by less than 0.1%. Several dilution runs were made, covering the concentration range 10^{-6} to $3 \times 10^{-3} N$. For establishing the general conductance concentration curve, the low voltage parallel bridge was used. All electrical measurements were made with the cell in an oil-filled thermostat, maintained at $50 \pm 0.02^\circ$.

At a series of concentrations, the dependence of conductance on field strength was determined. After the cell came to temperature equilibrium in the thermostat, the conductance at 60 cycles and low voltage was determined, low voltage being defined as a voltage so low that doubling it produced no visible change in bridge setting. Then the conductance was determined at a high voltage, and immediately thereafter again at low voltage. By bracketing the high voltage determinations by low, we were always certain that heating by measuring current was not a cause of the increased conductance. An input of one watt in the platinum cells was sufficient to show a drift in conduct-

ance of about 3% per minute. The bridge voltage was applied through a combination of relays and push buttons, and could be turned on or off very quickly; consequently we were able to get reliable readings even at voltages so high that they produced appreciable heating on prolonged exposure. An approximate balance was obtained at high voltage, and then the low voltage conductance was followed until it reached its previous steady state. Then the bridge was set to the approximate high voltage setting first obtained, high voltage was applied for a few seconds, and successive adjustments were made, until a setting was found such that the bridge was in balance when high voltage was flashed on and off. Immediately after this final reading, the low voltage conductance was again checked. A simpler technique was used when the temperature drift caused not more than 1% change in conductance per minute: high voltage was applied at a noted time and the bridge was balanced as quickly as possible. Then the sliding balance was followed and recorded at thirty-second intervals. Extrapolation to zero time gave the true high voltage conductance. For the more dilute solutions, of course, the resistance was so high that temperature drift due to heating by bridge current was negligible.

Polarization.—As anticipated, the apparent conductance varied with frequency. An example is shown in Fig. 3, where the conductance of a $4.22 \times 10^{-4} N$ solution is plotted against reciprocal root of frequency. A straight

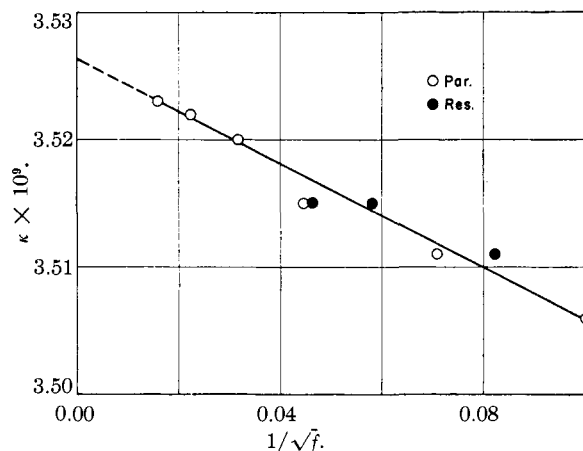


Fig. 3.—Polarization curve for $c = 4.22 \times 10^{-4}$.

line is obtained, which is the normal polarization curve found by Jones and Christian.¹² Several voltage runs were made at 500–1500 cycles. In this range of frequency, the conductance-field curves were less steep than at 60 cycles by about 20% in slope. Further work on the frequency dependence is planned; we expect a decrease of the Wien coefficient with increasing frequency, when the field reverses so rapidly that the ions do not travel far in one cycle, but this effect should not appear until quite high frequencies. The large difference between the slopes at 60 cycles and at 1000 cycles is more likely due to a dependence of polarization on field strength. The question must remain unanswered until more data are available.

Another interesting phenomenon was observed on di-

(9) Fuoss, *THIS JOURNAL*, **60**, 451 (1938).

(10) Fuoss, *ibid.*, **59**, 1703 (1937).

(11) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(12) Jones and Christian, *THIS JOURNAL*, **57**, 272 (1935).

lute solutions placed in a clean cell, that is, on the initial filling before adsorption was saturated. If high voltage at 60 cycles was left on the cell for a short interval, and then the conductance followed at low voltage, a change with time was noted. For example, a millionth normal solution in the platinum cell was subjected to 25 kv. per centimeter for forty seconds. The conductance measured at low voltage was 15% lower than the initial value five minutes after the high voltage was removed; the difference decayed slowly with time, dropping to half value in about twenty minutes. The return behaved like a diffusion mechanism. An increase in cell resistance could not have been produced by heating; these solutions have positive temperature coefficients. Again more information is needed.

Viscosity.—In order to calculate ionic concentrations from conductances, it was necessary to know the limiting mobility. Since extrapolation was impossible, the viscosity of diphenyl ether at 50° was determined, and the limiting conductance calculated by Walden's rule. An Ostwald viscometer was used, whose specifications were as follows: length of capillary 10.0 cm., diameter of capillary 0.0968 cm., average head 20 cm., efflux volume 25 cc. The working volume was 50 cc. Dibenzyl ether (dried over sodium and distilled; b. p. 115–126° at about 1 mm.) was used as the calibrating liquid, and absolute values were based on the data of Bingham and Spooner.¹³ At 50°, the viscosity of diphenyl ether was found to be 0.0209 poise.

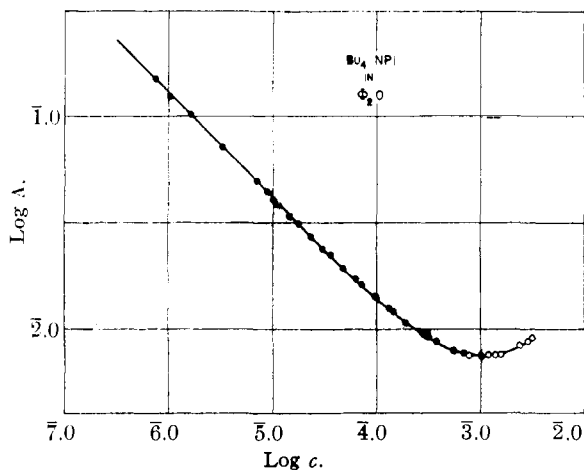


Fig. 4.—Conductance-concentration curve for Bu_4NPI in Ph_2O at 40°.

III. Experimental Results.—In Table I are given the low voltage conductances determined at 1000 cycles on the parallel bridge.

These results are summarized in Fig. 4, where the logarithm of the equivalent conductance is plotted against the logarithm of the concentration. The curve is the normal type expected for a 1-1 salt in a solvent of low dielectric constant.

Typical voltage runs are summarized in Table

(13) Bingham and Spooner, *J. Rheology*, **3**, 221 (1932).

TABLE I
CONDUCTANCE OF TETRABUTYLAMMONIUM PICRATE IN
DIPHENYL ETHER AT 50°, LOW VOLTAGE AT 1000 CYCLES

$c \times 10^4$	$\Lambda \times 10^3$	$c \times 10^4$	$\Lambda \times 10^3$
31.55	0.897	1.308	1.250
28.01	.863	0.941	1.409
23.68	.830	.713	1.614
15.65	.753	.622	1.709
13.82	.746	.4698	1.928
11.74	.750	.3018	2.386
7.745	.749	.2317	2.697
6.729	.764	.1452	3.395
5.771	.792	.0685	4.91
3.781	.853	.0323	7.15
3.116	.908	.01608	10.24
2.737	.954	.01030	12.46
1.446	1.192	.00756	15.06

II. The field strength given is average kilovolts per centimeter, calculated from cell voltage and cell geometry by equations (1) and (4). All data in Table II are for 60-cycle fields; we hope to present data covering higher frequencies in a later paper, after the dependence of polarization on field strength has been studied.

IV. Discussion and Comparison with Theory

It will be noted in Fig. 4 that the $\log \Lambda$ - $\log c$ plot is linear, with slope $(-1/2)$ in the dilute region. This slope corresponds to a simple association of ions pairwise.¹⁴ At about 10^{-3} normal, a minimum appears, due to the association of ion pairs with free ions.⁵ In order to obtain the constants for the system, $\Lambda\sqrt{c} g(c)$ was plotted against c , as shown in Fig. 5. From the slope and intercept, we obtain $\Lambda_0 \sqrt{K} = 1.274 \times 10^{-4}$ and $\lambda_0 \sqrt{K}/k = 0.105$, where Λ_0 and λ_0 are the limiting conductances of the types $\text{A}^+\cdot\text{B}'$ and $\text{A}_2\text{B}^+\cdot\text{AB}_2'$, respectively, and K and k are the corresponding dissociation constants. In ethylene chloride ($\eta_{25} = 0.007853$), Mead¹⁵ found $\Lambda_0 = 57.40$ for tetrabutylammonium picrate at 25°, giving $\Lambda_0\eta = 0.4508$. In tricresyl phosphate ($\eta_{40} = 0.295$), Elliott⁸ found $\Lambda_0 = 1.95$, giving $\Lambda_0\eta = 0.575$. Diphenyl ether is about intermediate in size between ethylene chloride and tricresyl phosphate, so we take the average of the above values of the $\Lambda_0\eta$ product in order to allow for the deviation from Walden's rule due to size and shape of solvent molecules.⁸ Using $\eta(\text{Ph}_2\text{O})_{50^\circ} = 0.0209$, we find $\Lambda_0 = 24.5$ for tetrabutylammonium picrate in diphenyl ether at 50°. Combining this value with the analysis of Fig. 5, and using the value

(14) Fuoss and Kraus, *This Journal*, **55**, 1019 (1933).

(15) Mead, Kraus and Fuoss, *Trans. Faraday Soc.*, **32**, 594 (1936).

TABLE II

WIEN EFFECT FOR TETRABUTYLAMMONIUM PICRATE IN DIPHENYL ETHER AT 50° AND 60 CYCLES

<i>E</i>	$\kappa \times 10^{10}$	<i>E</i>	$\kappa \times 10^{10}$	<i>E</i>	$\kappa \times 10^{10}$
$c = 7.525 \times 10^{-4}$	0.381	26.96	1.83	6.358	
0.038 ^b	55.75	0.755	27.01	3.85	6.550
.094	55.76	1.87	27.28	5.53	6.736
.189	55.77	3.78	27.99		
.378	55.81	6.12	28.78	$c = 1.100 \times 10^{-5}$	
.755	55.84	8.46	29.73	0.189 ^b	4.219
1.888	56.24	11.86	31.23	.378	4.222
3.78	57.34			.755	4.240
5.85	58.69	$c = 9.64 \times 10^{-5}$		1.89	4.309
8.01	60.57	0.042 ^a	13.34	3.78	4.435
10.27	62.34	.211	13.34	5.93	4.584
		.422	13.35	8.01	4.700
$c = 5.407 \times 10^{-4}$.843	13.41	$c = 9.87 \times 10^{-5}$	
0.019 ^b	42.25	2.11	13.63	0.211 ^a	3.996
.094	42.25	4.22	14.06	.422	4.003
.189	42.25	6.83	14.50	.843	4.023
.378	42.28	9.44	15.05	2.11	4.103
.755	42.32	13.24	15.77	4.22	4.228
1.888	42.67	0.038 ^b	13.35	6.83	4.354
3.78	43.67	.189	13.35	9.44	4.549
6.12	44.57	.378	13.36	13.24	4.788
8.46	46.22	.755	13.39	0.189 ^b	3.988
		1.89	13.56	.378	4.002
$c = 5.018 \times 10^{-4}$		3.78	13.95	.755	4.018
0.038 ^b	39.00	6.12	14.36	1.89	4.083
.189	39.00	8.46	14.76	3.78	4.205
.378	39.01	11.86	15.61	6.12	4.325
.755	39.07	15.07	16.42	8.46	4.463
1.888	39.36			11.86	4.702
3.78	40.37	$c = 2.376 \times 10^{-5}$		$c = 1.030 \times 10^{-5}$	
0.018 ^c	39.00	0.094 ^b	6.225	0.094 ^b	1.283
.046	39.00	.189	6.225	.189	1.283
.183	39.01	.378	6.230	.378	1.286
.366	39.01	.755	6.251	.755	1.292
.916	39.11	1.89	6.344	1.89	1.313
1.83	39.40	3.78	6.542	3.78	1.350
2.95	39.92	7.93	6.978	6.12	1.394
3.90	40.41	0.046 ^c	6.229	8.46	1.437
		.092	6.229	11.86	1.505
$c = 2.916 \times 10^{-4}$.183	6.230	15.07	1.582
0.038 ^b	26.94	.366	6.236	18.88	1.685
.189	26.97	.916	6.268		

^a Cell 2. ^b Cell 3. ^c Cell 4.

$\lambda_0/\Lambda_0 = 0.82$ found by Bien¹⁶ for the same electrolyte in anisole, we find $K = 2.70 \times 10^{-11}$ and $k = 1.00 \times 10^{-3}$.

From the values of the dissociation constants, we can calculate the corresponding ion sizes, assuming that the association is due entirely to Coulomb forces.¹⁷ For the binary association of tetrabutylammonium ion and picrate ion, we find $a = 5.33 \times 10^{-8}$ cm. This is somewhat smaller than previous values for this salt ($5.83 \times$

(16) Bien, Kraus and Fuoss, THIS JOURNAL, 56, 1860 (1934).

(17) Fuoss, Chem. Rev., 17, 27 (1935).

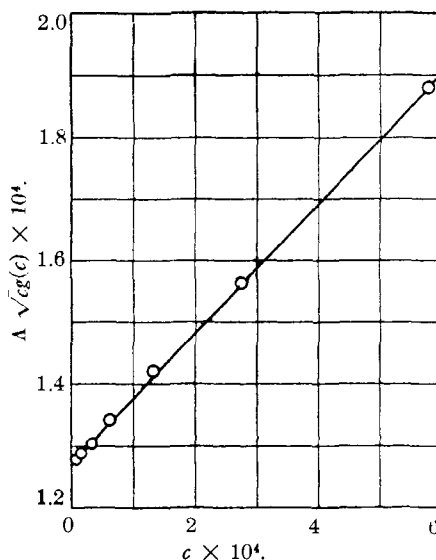


Fig. 5.—Evaluation of dissociation constants by graphical analysis.

10^{-8} in ethylene chloride¹⁵ at 25°, 5.80×10^{-8} in tricresyl phosphate⁸ at 40°, and 5.60×10^{-8} in anisole¹⁶ from -33 to 95.1°); there seems to be a trend of a values with D . For the triple ion equilibrium, we find $a_3 = 7.9 \times 10^{-8}$ cm., which checks Bien's value¹⁶ in anisole at 61.3°. The fact that $a_3 > a$ for picrates has already been discussed.¹⁶

We next consider the conductance-field curves. At low concentrations, where the free ion concentration is extremely small, the curve is substantially linear over the whole voltage range studied, as is shown in Fig. 6 for a millionth normal solution. As the concentration increases, the initial part of the conductance-field curve be-

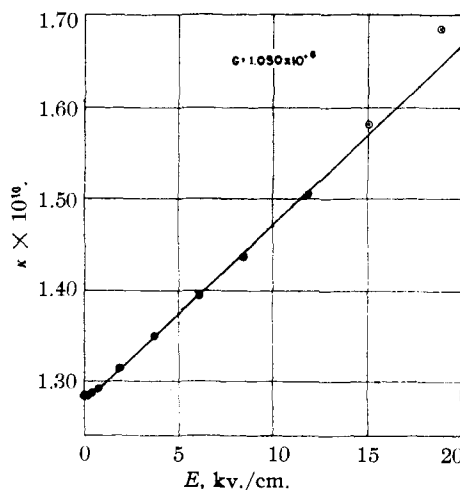


Fig. 6.—Wien effect at low concentration.

comes concave up, and eventually approaches linearity, as is shown in Fig. 7. The curved re-

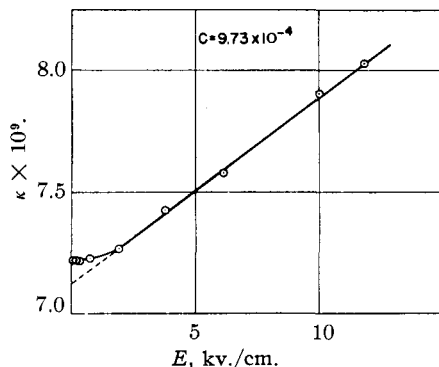


Fig. 7.—Wien effect at high concentration.

gion is due to the presence of an ionic atmosphere and once the ions move so fast in the field that this distribution can no longer be maintained, the curve becomes linear, as predicted by Onsager's theory.⁴ Onsager's result, for the case of small degree of dissociation of 1-1 salts (in our case, $K = 2.70 \times 10^{-11}$) is

$$\kappa/\kappa_0 = 1 + (\epsilon^3/4Dk^2T^2)\bar{X} \quad (5)$$

where κ is the conductance at field strength \bar{X} , κ_0 is the conductance at zero field strength and the other symbols have their usual meaning. For diphenyl ether at 50°, (5) becomes

$$\kappa/\kappa_0 = 1 + 0.0132 E \quad (6)$$

where E is the field strength in kilovolts per centimeter. The data of Table II (see also Figs. 2, 6, 7) all give linear portions at higher field strengths, after the initial concave-up section. The slopes are somewhat higher than predicted by (6), ranging from 1.3 to 1.6% per kilovolt, depending on the concentration. The dependence on concentration is systematic, and therefore, despite the rather large experimental error involved in determining a slope, we believe that it is real. The values of the slope are plotted against concentration in Fig. 8. Below 10^{-4} normal, the slopes are, within our present experimental error, equal to 1.6% per kilovolt, independent of concentration. It is interesting and perhaps significant that the dependence on concentration of the Wien coefficient begins at the concentration where triple ion formation causes the $\log \Lambda - \log c$ plot to start to deviate from linearity. The present theory calls for concentration independence of the Wien coefficient. We plan to study systems in solvents of still lower

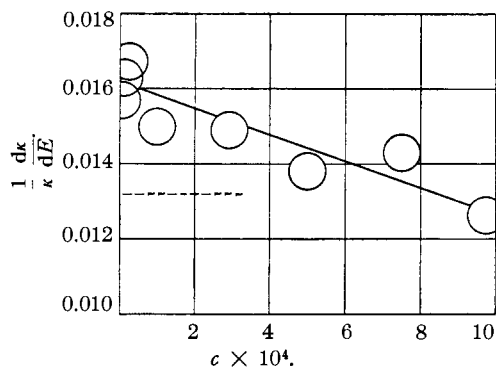


Fig. 8.—Dependence of Wien coefficient on concentration.

dielectric constant, so that the region of complex association can be studied. (It was impossible to work at higher concentrations in diphenyl ether, on account of heating.)

The difference in absolute value between our limiting experimental value of 1.6% at low concentrations and the theoretical value of 1.32% may be due to the dissymmetry of the picrate ion; the theoretical treatment implies a spherical ion. Work in progress on other salts will give information bearing on this question.

If the linear portions of the conductance-field curves are extrapolated to zero field strength, the low voltage conductance is obtained which the ions would have if the activity coefficient were unity.⁴ Consequently the ratio of the actual conductance at low voltage to the extrapolated value measures the activity coefficient for the particular concentration involved. We have made the corresponding calculation for the data of Table II; the results are shown in Fig. 9. As abscissa, we used the square root of total ionic concentration, which was calculated from

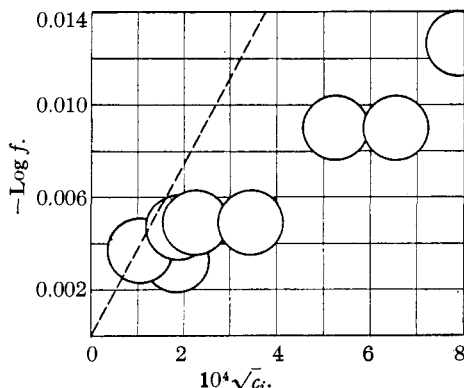


Fig. 9.—Activity coefficients determined by Wien effect.

the stoichiometric concentration and our experimental values of dissociation constants. The dotted line in Fig. 9 is the Debye-Hückel limiting slope, which is given by the following equation for 1-1 salts in diphenyl ether at 50°

$$-\log f = 33.8 \sqrt{c_i} \quad (7)$$

where c_i is total ionic concentration. Considering the large error in the experimental values of f , the results are not disappointing. The fact that we actually find a deviation of the right order of magnitude, which varies in the proper way with concentration, in a solvent of dielectric constant 3.53, is significant, if we recall that K is 2.7×10^{-11} . The highest ionic concentration in Fig. 9 is 6×10^{-7} .

Summary

1. The conductance of tetrabutylammonium picrate in diphenyl ether at 50° has been measured at 1000 cycles and low voltage and at 60 cycles under field strengths up to 15 KV/cm., over the approximate concentration range 10^{-3} to 10^{-6} normal.

2. Onsager's theory of the Wien effect is in good agreement with our data.

3. Deviations of activity coefficients from unity calculated by the limiting law of Debye and Hückel agree in order of magnitude with the experimental values obtained from the conductance curves.

SCHENECTADY, NEW YORK

RECEIVED MAY 16, 1939

[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Reduction of Carbon Dioxide by Graphite and Coke

BY MARTIN A. MAYERS

The rates of reaction of monolithic samples of artificial graphite with carbon dioxide and steam at atmospheric pressure and temperatures from 850° have been reported previously.¹ In that work the limiting effect of the diffusion field adjacent to the surface of the sample was eliminated and the measured reaction rates were considered to be true heterogeneous reaction rates and were referred to unit area of the surface exposed to the action of the gas. Later measurements of the reaction with carbon dioxide of artificial graphite and coke in granular form and of monoliths of both artificial and natural graphite have shown that in artificial graphite and in coke, the reaction rate measured depends not only on the surface exposed, but is the total of the contributions of elementary surfaces reached by the oxidizing gas by its perfusion throughout the body of these porous materials. This result suggests a possible explanation of part of the discrepancy between the measurements by this method and those made under high vacuum.²

Apparatus and Materials.—Carbon dioxide was withdrawn from a cylinder through a reducing valve, passed through a flowmeter and a purifying train consisting of a heated quartz tube containing reduced copper and copper oxide and a drying tower containing calcium chloride

followed by Anhydrone, and then into the furnace. Leaving the furnace the gas stream flowed through a cooling section, and then by way of a three-way stopcock, either direct to the analyzer, or into the large gasometer used in the tests reported before. The gas analyzer was the same one previously described, in which the carbon monoxide is oxidized by iodine pentoxide and its quantity determined by the titration of the iodine liberated which was collected in a condenser cooled by dry ice.

The furnace and sample holder differ from those used in the previous work and are shown in Fig. 1. The smaller diameter of the furnace tube permitted the attainment of high gas velocities without using extremely large volumes of gas. The mullite boat, used as a sample holder, permitted the use of either granular or monolithic samples of carbon. It was streamlined as shown in order to eliminate, as completely as possible, disturbances of the flow across the reacting surface.

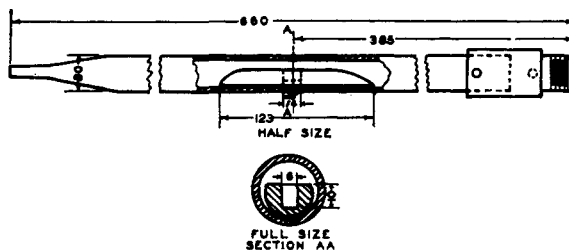


Fig. 1.—Reaction tube and sample boat. All dimensions in millimeters.

Granular samples were prepared for test by crushing coke in a small jaw crusher and by turning off heavy chips of graphite from cylindrical electrodes, and sieving the granular material between standard metal cloth sieves.

(1) M. A. Mayers, *THIS JOURNAL*, **56**, 70, 1879 (1934).

(2) H. Martin and L. Meyer, *Z. Elektrochem.*, **41**, 136 (1935); Lothar Meyer, *Trans. Faraday Soc.*, **34**, 1056-61 (1938).