very low,[20] it is possible that the impact value is in error. We have made an independent estimation of the ionization potential from thermochemical data. The method follows essentially the calculation made for SF_6.[21] The beginning of continuous absorption (14.99 e.v.) is interpreted as dissociation into $CF_3^+ + F^-$. Adding the electron affinity (EA_F) of F, we have

$$CF_4(g) = CF_3^+(g) + F(g) + e^- - (14.99 + EA_F) \quad (2)$$

The energy of dissociation of CF_4 into its elements is[22,23]

$$CF_4(g) = C(g) + 4F(g) - (14.65 \text{ e.v.} + 2D_{F_2}) \quad (3)$$

where D_{F_2} is the heat of dissociation of F_2. For breaking a single bond it is assumed that

$$CF_4(g) = CF_3(g) + F(g) - (14.65 \text{ e.v.} + 2D_{F_2})/4 \quad (4)$$

It is also assumed that the energy of the process

$$CF_4^+(g) = CF_3^+(g) + F(g) - (14.65 \text{ e.v.} + 2D_{F_2})/4 \quad (5)$$

is the same as in process (4). On subtracting (5) from (2) we obtain for the desired ionization potential

$$CF_4(g) = CF_4^+ + e^- - 11.33 - (EA_F - D_{F_2}/2) \quad (6)$$

The difference ($EA_F - D_{F_2}/2$) is obtained from a cycle which involves theoretically computed crystal energies and other thermochemical data.[23] Using a value of 2.88 e.v. for this difference[21] the ionization potential is about equal to 14.21 e.v., which is in more satisfactory agreement with the limit of continuous absorption.

ROCHESTER, N. Y.

---

[20] V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **40**, 25 (1948).

[21] Ta-Kong Liu, G. Moe and A. B. F. Duncan, *J. Chem. Phys.*, **19**, 71 (1951).

[22] H. von Wartenberg, *Nachr. Akad. Wiss. Goettingen, Math.-phys. Klasse*, 57 (1946); W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **22**, 1472 (1954).

[23] J. E. Mayer and L. Helmholz, *Z. Physik*, **75**, 19 (1932).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Free Energy, Enthalpy and Entropy of Dissociation of Some Perchlorates in Ethylene Chloride and Ethylidene Chloride

BY J. T. DENISON[1] AND J. B. RAMSEY

RECEIVED JANUARY 3, 1955

From electrolytic conductance measurements at each of the four temperatures, 20, 25, 30 and 35° the values of $\widetilde{\Delta F}^\circ$, $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$, accompanying the dissociation (at 25°) of nine systematically substituted phenyltrimethylammonium perchlorates in ethylene chloride and of six of these in ethylidene chloride, have been determined. The dielectric constant of ethylidene chloride at each of these four temperatures has been determined. Values of ΔH° and ΔS° have been calculated from relations derived (1) from the Bjerrum–Fuoss expression for the dissociation constant, K, and (2) from an expression for K obtained by assuming that only those oppositely charged ions which are in contact constitute associated ion-pairs. The latter simplified treatment is shown to give values of $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$ in better agreement with the experimental values. Interpretations (1) of the uniformly negative values of ΔH° and ΔS° in both solvents, and (2) of the uniformly greater K values in ethylene chloride are presented.

In an investigation[2] of the effect of systematically varying the electrical asymmetry of the cations of nine substituted phenyltrimethylammonium perchlorates on the dissociation constant (K value at 25°) in ethylene chloride, the dissociation constant of one of the salts, namely, *o*-chlorophenyltrimethylammonium perchlorate was determined in ethylidene chloride. The K value of this salt in ethylidene chloride was found to be much less than (about one-tenth) its value in ethylene chloride. This was unexpected since the difference in the accepted values of the dielectric constants of these two liquids is not great enough to cause such a large difference in the K values ($D_{25}°$ of ethylene chloride, 10.23, and of ethylidene chloride, 10.00[3]).

In 1950 preliminary K values of two other of the nine salts (the *o*- and the *p*-methoxyphenyl salts) were determined[4] and found to be from one-seventh to one-tenth their respective values in ethylene chloride. An interpretation of these results was proposed. More recently Healey and Martell[5] found that a number of tetraalkylammonium picrates and a perchlorate have considerably lower K values in ethylidene chloride (from one-fifth to one-tenth less) than in ethylene chloride.

Additional information regarding the thermodynamic behavior of salts in these two solvents seems desirable. In this investigation the K values of the nine perchlorates, previously used,[2] were determined from conductance measurements in ethylene chloride at 20, 25, 30 and 35°, and those of six of the perchlorates (which were sufficiently soluble) in ethylidene chloride. The standard changes in enthalpy and entropy (at 25°) accompanying dissociation in each of the solvents were derived therefrom. The values of $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$ are calculated (a) from the theoretical expression for K obtained by Bjerrum[6] and Fuoss and Kraus,[7] and (b) from an expression for K obtained from a simpler model. An interpretation of the sign of the values of ΔH° and ΔS° is given.

---

[1] Polychemicals Dept., E. I. du Pont de Nemours and Co., Wilmington, Del.

[2] J. B. Ramsey and E. L. Colichman, THIS JOURNAL, **69**, 3041 (1947).

[3] Private communication from Arthur E. Martell, Chemical Laboratories, Clark University, Worcester, Massachusetts. Measured at Brown University, Providence, Rhode Island.

[4] J. T. Denison and J. B. Ramsey, *J. Chem. Phys.*, **18**, 770 (1950).

[5] F. H. Healey and A. E. Martell, THIS JOURNAL, **73**, 3296 (1951).

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

[7] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

Experimental

Purification of Solvents.—Each of the two solvents was fractionally distilled in presence of calcium hydride through a three-foot vacuum-jacketed column filled with glass helices. The middle fraction was collected directly in a three-liter round-bottom Pyrex flask equipped with protecting calcium chloride and soda lime tubes and with an outlet tube for delivering the solvent directly into the conductance cells with the least possible exposure of the solvent to the air during transfer. No contact with rubber or cork occurred at any time. It was found necessary to store the ethylidene chloride over silica gel in order to maintain low conductance. To prevent transfer of silica gel, the delivery tube was fitted with a fine filter of Pyrex wool. The conductance of the ethylene chloride, so obtained, was in no case greater than 5×10^{-10} ohm.$^{-1}$ cm.$^{-1}$, and that of the ethylidene chloride, less than 2×10^{-9} ohm.$^{-1}$ cm.$^{-1}$.

Salts.—All of the nine perchlorates were freshly prepared[8] by methods previously described.[2] Each salt was purified by recrystallization, at least five times, from absolute ethanol. The melting points, previously obtained,[2] and those observed by Bloom,[8] are given in Table I. Agreement with previous values is quite satisfactory except for that of the higher melting modification of the *m*-methyl salt. Recrystallization from absolute ethanol gave the higher melting form. One recrystallization of this solid from 95% ethanol or from water yielded the salt melting at 123°, which agrees satisfactorily with that obtained previously. Resistance of the solution of the higher melting salt in ethylene chloride behaved anomalously in that it did not attain a constant value over a period of several days. The lower melting salt was used in this investigation. The results of microanalysis for carbon and hydrogen were not such as to provide conclusive evidence of a difference in composition between the two modifications of this salt.

Table I

Melting Points of Phenyltrimethylammonium Perchlorates

Substituent and position	Obtained previously, °C.	Obtained by Bloom, °C.	Substituent and position	Obtained previously, °C.	Obtained by Bloom, °C.
o-Methyl	195	196.5	*p*-Chloro	225.5	225.7
m-Methyl	124	123 and 151.7	*o*-Methoxy	220	230.0
p-Methyl	202	202.5	*m*-Methoxy	153.5	153.2
o-Chloro	184	185.0	*p*-Methoxy	192.5	193.1
m-Chloro	166.5	165.0			

Conductance Measurements.—The shielded, alternating current bridge, constructed according to Shedlovsky's specifications,[9] was the one used previously.[2] A Hewlitt-Packard audio oscillator, which gave an excellent sinusoidal wave form, was the source of alternating current. All measurements were made at a frequency of 2500 cycles/second. The output from the bridge was fed into a three-stage, resistance coupled amplifier, provided with a Kay-Lab Model 503 A, 60-cycle rejection filter to eliminate power-line pick-up interference. The output of the amplifier was applied to the vertical plates of a three-inch oscilloscope which was used instead of earphones to establish the null-point as described by Jones.[10]

The conductance cells were of the erlenmeyer type described by Kraus and Fuoss.[11] The platinum electrodes, approximately one centimeter square, were unplatinized. Three cells were used and their cell constants, determined by the method previously described,[2] were 0.1545, 0.1480 and 0.1734 cm.$^{-1}$. These constants were found to be independent of the temperature over the range, 20 to 35°. Measurements were made with the cells immersed in an oil filled thermostat maintained at constant temperature to within 0.005°.

Preparation of Solutions.—Between 10 and 20 mg. of each salt, previously oven-dried for at least ten hours and cooled in a vacuum desiccator, were weighed to within 10 μg. and introduced into the cell. The desired amount of solvent was then added and the cell and contents weighed with an accuracy of one milligram. After a small correction for the weight of solvent in the vapor phase was made, the volume concentration was calculated by taking the density of the very dilute solution to be that of the pure solvent. Each successive dilution was made by rapidly extracting a portion of the solution by means of an evacuated pipet of the type described by Mead, Fuoss and Kraus.[12] After the weight of the solution remaining in the cell was obtained, the desired quantity of the pure solvent was added and the weight of the more dilute solution determined. From these data the concentration of the more dilute solution was calculated.

The resistances at each concentration at each of the four temperatures were measured in the order: 25, 30, 35, 20 and finally at 25°, as a check on the value previously obtained.

Dielectric Constant Measurements.—Values of the dielectric constant of ethylidene chloride over the temperature range of interest were not available in the literature. These were therefore determined by the well-known heterodyne beat, substitution method. A complete discussion of the apparatus, including the capacitance cell, and the procedure is given by Smyth.[13] Two Colpitz radio-frequency oscillators were used, one of which, the beat-frequency oscillator, was of fixed frequency (about 1.3 megacycles), the other, of variable frequency, having provision for external capacitance in the oscillator circuit. The capacitance cell containing the liquid was inserted in the circuit of the variable frequency oscillator. By means of the internal condenser of the latter oscillator, it was tuned until its frequency was exactly 1000 c.p.s. above that of the fixed frequency oscillator. To assure this exact difference, the beat-frequency picked up by the detector is applied to the vertical plates of a three-inch oscilloscope and compared with the pure 1000 c.p.s. note from the Hewlitt-Packard oscillator, the output of which is applied to the horizontal plates.

A standard calibrated variable condenser was then substituted for the cell in the circuit of the variable frequency oscillator and this standard condenser was adjusted until the frequency of the oscillator was again 1000 c.p.s. greater than that of the fixed frequency oscillator. Thus the capacitance registered by the standard oscillator was equal to that of the cell.

For calibrating the capacitance cell purified benzene ($D_{25^\circ} = 2.274$), obtained by distillation of a C.P. grade from sodium ribbon through the same fractionating column employed in purifying the solvents, was used, and was collected directly in the carefully dried capacitance cell. To check the calibration of the cell, the dielectric constant of purified ethylene chloride was measured at 25° and found to be 10.21 which agrees with the generally accepted value, 10.23. The values obtained for ethylidene chloride are given in Table II. It may be noted that the value at 25° is somewhat lower than those previously used, 10.20 by Ramsey and Colichman[2] and 10.00 by Denison and Ramsey[4] and by Healey and Martell.[5]

Results

The values of the dissociation constants (K) and the limiting equivalent conductances (Λ_0) were obtained by use of the relations developed by Shedlovsky.[14] The two basic equations involved are

$$\Lambda = \theta\Lambda_0 - \alpha(\Lambda/\Lambda_0)(c\theta)^{1/2}$$

where θ is the fraction dissociated and $\alpha = 8.15 \times 10^5\ \Lambda_0/(DT)^{3/2} + 82/(DT)^{3/2}$
and

$$1/\Lambda S(z) = c\Lambda f_{\pm} S(z)/K\Lambda_0^2 + 1/\Lambda_0$$

where $S(z) = 1 + z + z^2/2 + z^3/8^- \ldots$, and $z = \alpha(c\Lambda)^{1/2}/\Lambda_0^{3/2}$. The function $S(z)$ is rapidly convergent for small values of z and it is very seldom

---

[8] Murray Bloom, a graduate student in chemistry at the University of California, Los Angeles, prepared and purified the nine perchlorates used in this investigation.

[9] T. Shedlovsky, This Journal, **52**, 1793 (1930).

[10] G. Jones, K. J. Mysels and W. Juda, *ibid.*, **62**, 2919 (1940).

[11] C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933).

[12] D. J. Mead, R. M. Fuoss and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

[13] C. P. Smyth in A. Weissberger, "Physical Methods of Organic Chemistry," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1949, pp. 1633–1649.

[14] T. Shedlovsky, *J. Frank Inst.*, **225**, 739 (1938).

necessary to use more terms than the cubic in z. A table of values of $S(z)$ is unnecessary since its value is readily calculated. The values of the physical constants used are those given by Beardon and Watts.[15]

After visual inspection of the points obtained by plotting $1/\Lambda S(z)$, as ordinates, and $c\Lambda f_{\pm}S(z)$, as abscissas, showed no apparent deviation from a straight line, the best values of the slope, $1/K\Lambda_0^2$, and of the intercept, $1/\Lambda_0$, were obtained by treatment of the data by the method of least squares. A recalculation of the previously obtained results by this method showed that the Λ_0-value at 25° of each of the nine salts in ethylene chloride was within 2 units of 76.0. This value was therefore used as initial trial value of Λ_0 at 25°. Since previous work had shown that Walden's rule ($\eta\Lambda_0$ = constant) held, within experimental error, for the *o*-chloro substituted salt in the two solvents an initial trial value of Λ_0 at 25° in ethylidene chloride could thereby be obtained. In that preliminary results[4] had shown that value of $\Lambda_0\eta$ of a given salt was substantially constant independent of the temperature (from 20 to 35°) and of the solvent, initial trial values of Λ_0 at each of the other three temperatures were obtainable. In all cases the values of Λ_0 obtained by use of these trial values were within experimental error of the trial value and a second approximation was unnecessary.

The densities of ethylene chloride at the four temperatures were calculated from the equation given in the "International Critical Tables,"[16] and those of ethylidene chloride from the critical compilations of Boas.[17] The viscosities of ethylene chloride were obtained from a graph of the values given in the "International Critical Tables,"[18] and those of ethylidene chloride likewise from the results of Timmermans and Martin.[19]

To obtain the needed values of the dielectric constant of ethylene chloride the results reported by two groups of investigators were plotted (*D vs. T*), *viz.*, those of White and Morgan[20] and of Smyth, Dornte and Wilson.[21] Although the two curves obtained have the same shape, neither give a value of 10.23 at 25°, the value reported and used by C. A. Kraus and co-workers in all their work with ethylene chloride (the one giving a value 0.6% above and the other 0.9% below 10.23). A curve of the same shape was therefore drawn through the point D = 10.23 and t = 25° and the desired values were obtained therefrom. To check the reliability of this curve the dielectric constant of ethylene chloride was measured (as described above) at 20° and the value obtained, 10.50, was within 0.01 unit of that given by this curve.

In Table II are given the values of the dielectric constants of ethylene chloride, thus obtained, and those of ethylidene chloride, measured, along with the densities and viscosities of these solvents.

TABLE II

Temp., °C.	Density, g./ml.	Viscosity, millipoise	Dielectric constant
	ETHYLENE CHLORIDE		
20	1.253	8.30	10.52
25	1.246	7.78	10.23
30	1.238	7.30	9.96
35	1.231	6.85	9.67
	ETHYLIDENE CHLORIDE		
20	1.176	4.80	10.15
25	1.168	4.55	9.90
30	1.160	4.30	9.67
35	1.153	4.08	9.44

From these results the values of the derivative, d ln D/d ln T, at 25° (to be used later) are for ethylene chloride, −1.63, and for ethylidene chloride, −1.44.

The conductances of five to eight concentrations of each salt in each solvent were determined, covering the range from about 10^{-5} to 4×10^{-4} volume formal (normal).

The values of K and Λ_0 are given in Table III. The perchlorates are designated by the nature and position of the substituent in the phenyl group in the phenyltrimethylammonium cation.

It is noted that results are not given for three of the perchlorates, having the substituents, *m*-methyl, *m*-chloro and *p*-chloro, in ethylidene chloride. These salts were not sufficiently soluble in ethylidene chloride to permit accurate resistance measurements even though extreme means were employed to bring about dissolution. The unique behavior of these three salts seems quite anomalous.

The K values of the other six salts are seen to be from seven to ten times greater in ethylene chloride than their corresponding values in ethylidene chloride. That the K value of the *o*-methoxy salt is greater (and appreciably so) than that of the *m*- or *p*-methoxy salt is consistent with the relative magnitudes of the K values of the *ortho*, *meta* and *para* salts of a given substituent in ethylene chloride. A probable interpretation of the relative magnitudes of these three K values was suggested by Ramsey and Colichman.[2]

It readily can be shown from the viscosity values in Table II and the Λ_0-values in Table III that the Walden's rule product, $\Lambda_0\eta$, for any of the salts in either solvent is a constant within the experimental error in the value of Λ_0. In addition the value of $\Lambda_0\eta$ of each of the six salts, with the exception of the *o*-methyl salt, is, within experimental error, the same in the two solvents. The apparent deviation from Walden's rule of this salt may be attributable to the statistical error in the Λ_0-value which is seen to be considerably greater than the average deviation of the other five salts.

Since, for each of the salts used in each of the solvents, the points obtained on plotting the values of $\widetilde{\Delta F}^\circ_{\text{diss.}}$, as ordinates, against the temperatures, T, as abscissas, did not deviate from the most probable straight line by more than experimental error (showing that $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$ have constant values over the temperature range 20 to 35°) and since these values could thereby be derived more readily than by the more common procedure of plotting ln K *vs.* $1/T$ (whence $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$), this procedure was used.

---

[15] J. A. Beardon and H. M. Watts, *Phys. Rev.*, **81**, 73 (1951).

[16] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 28.

[17] A. Boas, *Ind. Eng. Chem.*, **40**, 2202 (1948).

[18] Reference 16, Vol. VII, p. 213.

[19] J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 733 (1926).

[20] A. H. White and S. O. Martin, *J. Chem. Phys.*, **5**, 655 (1937).

[21] C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr., THIS JOURNAL, **53**, 42 (1931).

TABLE III

IN ETHYLENE CHLORIDE

Substituent and position	20°		25°		30°		35°	
	$K \times 10^5$	Λ_0	$K \times 10^5$	Λ_0	$K \times 10^5$	Λ_0	$K \times 10^5$	Λ_0
o-Methyl	5.16 ± 0.02	70.9 ± 0.1	4.74 ± 0.02	75.8 ± 0.1	4.28 ± 0.02	81.1 ± 0.1	3.89 ± 0.03	86.4 ± 0.2
m-Methyl	4.60 ± .03	70.8 ± 0.2	4.21 ± .02	75.7 ± .1	3.81 ± .02	81.0 ± .1	3.45 ± .02	86.5 ± .1
p-Methyl	4.31 ± .12	73.3 ± 1.0	3.97 ± .06	78.3 ± .5	3.62 ± .07	83.6 ± .7	3.28 ± .06	89.3 ± .6
o-Methoxy	8.90 ± .05	70.3 ± 0.13	8.10 ± .04	75.4 ± .11	7.34 ± .05	80.6 ± .15	6.76 ± .06	85.7 ± .23
m-Methoxy	4.30 ± .05	71.1 ± 0.4	3.89 ± .04	76.5 ± .4	3.62 ± .04	81.0 ± .4	3.22 ± .03	87.3 ± .5
p-Methoxy	4.36 ± .32	71.0 ± 1.8	3.91 ± .31	76.7 ± 1.9	3.66 ± .29	81.0 ± 2.0	3.26 ± .25	87.3 ± 2.3
o-Chloro	4.52 ± .02	70.4 ± 0.2	4.06 ± .06	75.7 ± 0.4	3.66 ± .06	81.0 ± 0.4	3.35 ± .04	86.1 ± .4
m-Chloro	2.81 ± .02	70.3 ± 0.15	2.53 ± .02	75.6 ± .2	2.30 ± .02	80.8 ± .2	2.10 ± .02	86.1 ± .2
p-Chloro	2.28 ± .05	72.8 ± 0.6	2.08 ± .05	77.9 ± .7	1.89 ± .04	83.3 ± .7	1.70 ± .04	89.2 ± .9

IN ETHYLIDENE CHLORIDE

Substituent and position	20°		25°		30°		35°	
	$K \times 10^5$	Λ_0	$K \times 10^5$	Λ_0	$K \times 10^5$	Λ_0	$K \times 10^5$	Λ_0
o-Methyl	0.613 ± 0.12	115.3 ± 2.0	0.582 ± 0.11	121.1 ± 2.0	0.561 ± 0.08	125.7 ± 0.8	0.518 ± 0.08	133.0 ± 0.8
p-Methyl	0.506 ± .02	123.6 ± 2.0	0.481 ± .02	129.7 ± 0.5	0.463 ± .02	134.9 ± 2.2	0.433 ± .02	142.1 ± 1.6
o-Methoxy	1.19 ± .02	120.0 ± 0.6	1.12 ± .02	126.1 ± .6	1.04 ± .02	133.2 ± 0.7	.953 ± .02	141.2 ± 0.7
m-Methoxy	0.430 ± .007	120.1 ± 0.7	0.414 ± .005	125.5 ± .5	0.382 ± .005	133.4 ± 0.5	.352 ± .005	141.3 ± 0.6
p-Methoxy	0.434 ± .016	125.5 ± 1.0	0.429 ± .005	129.5 ± .2	0.390 ± .007	138.4 ± 0.2	.358 ± .007	146.8 ± 0.2
o-Chloro	0.447 ± .009	120.6 ± 0.9	0.414 ± .008	128.0 ± .9	0.377 ± .008	136.4 ± 1.0	.344 ± .007	144.9 ± 1.0

The method of least squares was used to obtain the slope ($-\widetilde{\Delta S}^\circ$) and the intercept ($\widetilde{\Delta H}^\circ$) and the long extrapolation to $T = 0$°K. was avoided by a shift in the axes.

The values of $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$ thus obtained are given in Table IV, along with those of $\widetilde{\Delta F}^\circ$.

TABLE IV

IN ETHYLENE CHLORIDE

Substituent and position	$\widetilde{\Delta F}^\circ_{298}$, cal.	$-\widetilde{\Delta H}^\circ_{298}$, cal.	$-\widetilde{\Delta S}^\circ_{298}$, cal./deg.
o-Methyl	5899 ± 5	3429 ± 88	31.3 ± 0.3
m-Methyl	5970 ± 5	3450 ± 67	31.6 ± .2
p-Methyl	6004 ± 8	3509 ± 54	31.9 ± .2
o-Methoxy	5583 ± 5	3303 ± 39	29.8 ± .2
m-Methoxy	6017 ± 6	3534 ± 138	31.5 ± .5
p-Methoxy	6015 ± 6	3355 ± 158	31.4 ± .5
o-Chloro	5990 ± 7	3642 ± 121	32.3 ± .4
m-Chloro	6272 ± 5	3511 ± 37	32.8 ± .1
p-Chloro	6387 ± 12	3480 ± 61	33.1 ± .2

IN ETHYLIDENE CHLORIDE

Substituent and position	$\widetilde{\Delta F}^\circ_{298}$, cal.	$-\widetilde{\Delta H}^\circ_{298}$, cal.	$-\widetilde{\Delta S}^\circ_{298}$, cal./deg.
o-Methyl	7142 ± 12	2013 ± 300	30.7 ± 1.0
p-Methyl	7255 ± 13	1811 ± 132	30.4 ± 0.5
o-Methoxy	6755 ± 5	2600 ± 200	31.4 ± .7
m-Methoxy	7344 ± 7	3033 ± 122	34.8 ± .5
p-Methoxy	7323 ± 12	3257 ± 210	35.5 ± .7
o-Chloro	7344 ± 12	3142 ± 140	35.2 ± .5

It is to be noted that the values of $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$ of all the salts in both solvents are negative. Also the total variation in the $\widetilde{\Delta H}^\circ$ values for all nine salts in ethylene chloride is only slightly greater than the probable error, calculated by the least square method. The same is true of the $\widetilde{\Delta H}^\circ$ values of the last four of the six salts in ethylidene chloride. The appreciably lower values for each of the first two salts is difficult to understand in view of their apparently normal behavior in ethylene chloride. Some unknown and consistent experimental error in the determination of their K values seems the most probable explanation.

With the exception of the *o*- and *p*-methyl salts it is seen that the average value of $\widetilde{\Delta S}^\circ$ in ethylidene chloride is slightly, but significantly, greater negatively than that in ethylene chloride.

Discussion

Negative Values of $\widetilde{\Delta H}^\circ_{\text{diss}}$ and $\widetilde{\Delta S}^\circ_{\text{diss}}$.—Consideration of the following stepwise process leads to a recognition of the factors determining the signs of these thermodynamic quantities.

$$\begin{tikzcd}
\begin{array}{l}\text{Ion-pair at } r_1\\ \text{in medium}\end{array} \arrow[r, "\text{IV}"] \arrow[d, "\text{I}"] & \begin{array}{l}\text{Separated ions at } r_2\\ \text{in medium}\end{array} \\
\begin{array}{l}\text{Ion-pair at } r_1\\ \textit{in vacuo}\end{array} \arrow[r, "\text{II}"] & \begin{array}{l}\text{Separated ions at } r_2\\ \textit{in vacuo}\end{array} \arrow[u, "\text{III}"']
\end{tikzcd}$$

The free energy change accompanying the charging of a pair of ions having charges, $+\epsilon$ and $-\epsilon$ and radii, a_1 and a_2, at an interionic distance, r, and in a medium of dielectric constant D, is given by the expression

$$(\bar{F}\,(\text{charged ions}) - \bar{F}\,(\text{uncharged ions})/N = \int_0^{\epsilon} (q/a_1D + q/a_2D - 2q/rD)\,\mathrm{d}q = \epsilon^2/2a_1D + \epsilon^2/2a_2D - \epsilon^2/rD$$

By use of this relation it can be readily shown that

$$\widetilde{\Delta F}_{\mathrm{I}}/N = (\epsilon^2/2a_1 + \epsilon^2/2a_2 - \epsilon^2/r_1)(1 - 1/D) - \widetilde{\Delta F}_{\mathrm{s}}/N \quad (1)$$

where $\widetilde{\Delta F}_{\mathrm{s}}/N$ is the free energy of solution per pair of uncharged ions at distance of separation, r_1; and

$$\widetilde{\Delta F}_{\mathrm{III}}/N = (\epsilon^2/2a_1 + \epsilon^2/2a_2 - \epsilon^2/r_2)(1/D - 1) + \widetilde{\Delta F}_{\mathrm{s}}/N$$

where $\widetilde{\Delta F}_{\mathrm{s}}/N$ has the same meaning as in equation 1 except that the distance of separation is r_2. It may be noted that if r_2 is large relative to a_1 and a_2 and if $\widetilde{\Delta F}_{\mathrm{s}}/N$ is zero, the value of $\widetilde{\Delta F}_{\mathrm{III}}/N$ becomes $(\epsilon^2/2a_1 + \epsilon^2/2a_2)\,(1/D - 1)$ which is the expression obtained by Born[22] for the free energy of solution of ions of radii a_1 and a_2 in a medium of dielectric constant D.

The free energy change for step II is simply the coulomb work of separation of a pair of ions in a vacuum from r_1 to r_2, *viz.*

$$\widetilde{\Delta F}_{\mathrm{II}}/N = \int_{r_1}^{r_2} (\epsilon^2/r_2)\mathrm{d}r = \epsilon^2/r_1 - \epsilon^2/r_2 \quad (3)$$

Summation of these three values gives

---

(22) M. Born, *Z. Physik*, **1**, 45 (1920).

$$\widetilde{\Delta F}_{\mathrm{IV}}/N = (\epsilon^2/r_2 - \epsilon^2/r_1)(1 - 1/D) + (\epsilon^2/r_1 - \epsilon^2/r_2) = (\epsilon^2/r_1 - \epsilon^2/r_2)/D \quad (4)$$

since the value of $\widetilde{\Delta F}_{\mathrm{s}}/N$ is independent of the distance of separation of the uncharged ions. It is evident that the free energy change accompanying the separation of two oppositely charged ions from r_1 to a greater distance, r_2, in a medium of dielectric constant, D, as calculated by Coulomb's law, includes the free energy change accompanying the solvation of the ions at r_2, and that of desolvation at r_1. The first term on the right of equation 4 represents that contribution to $\Delta F_{\mathrm{IV}}/N$ which is due to the increase in the solvation of the ions with increase in their distance of separation. If now r_2 is considerably greater than r_1, then

$$\widetilde{\Delta F}_{\mathrm{IV}} = N\epsilon^2/r_1D \quad (5)$$

and $\widetilde{\Delta S}_{\mathrm{IV}} = -(\partial\widetilde{\Delta F}/\partial T)_{\mathrm{p}} = (N\epsilon^2/r_1D)(\partial \ln D/\partial T) \quad (6)$

also $\widetilde{\Delta H}_{\mathrm{IV}} = \widetilde{\Delta F}_{\mathrm{IV}} - T\widetilde{\Delta S}_{\mathrm{IV}} = (N\epsilon^2/r_1D)(1 + \partial \ln D/\partial \ln T) \quad (7)$

Since the value of $\partial \ln D/\partial \ln T$ is negative and less than -1 for each of the two solvents used, it is seen from equations 6 and 7 that in these solvents negative values of $\widetilde{\Delta H}_{\mathrm{diss}}$ and $\widetilde{\Delta S}_{\mathrm{diss}}$ are to be expected. This means that the heat evolved during ion-solvation, when at the greater distance of separation, r_2, $(\Delta H_{\mathrm{III}})$, must be greater than the combined heat absorbed during ion-desolvation at r_1 (ΔH_{I}) and that absorbed during separation of the ions *in vacuo* (ΔH_{II}). Also, that the entropy decrease accompanying ion-solvation at r_2, $(-\Delta S_{\mathrm{III}})$, must be greater than the entropy increase accompanying ion-desolvation at r_1 (ΔS_{I}), since ΔS_{II} is zero. Both of these conclusions are a consequence of greater ion–solvent interactions at greater distance of separation of the oppositely charged ions.

Theoretical Evaluation of $\widetilde{\Delta H}^{\circ}_{\mathrm{diss}}$ and $\widetilde{\Delta S}^{\circ}_{\mathrm{diss}}$; (a) By Means of the Bjerrum–Fuoss Treatment.—According to this treatment the value of K is given by the relation

$$K^{-1} = (4\pi N/1000)(\epsilon^2/DkT)^3Q(b) \quad (8)$$

From this relation expressions for $\widetilde{\Delta S}^{\circ}$ and $\widetilde{\Delta H}^{\circ}$ may be derived by well-known thermodynamic relations. Differentiation with respect to temperature gives

$$\mathrm{d}K^{-1}/\mathrm{d}T = 4\pi N/1000\{(3Q(b)(\epsilon^2/DkT)^2[\epsilon^2/k(-1/DT^2 - 1/D^2T\,\mathrm{d}D/\mathrm{d}T)] + (\epsilon^2/DkT)^3\,\mathrm{d}Q(b)/\mathrm{d}T\} \quad (9)$$

By expressing the derivative, $\mathrm{d}Q(b)/\mathrm{d}T$, as an explicit function of b, the evaluation of $\mathrm{d}K^{-1}/\mathrm{d}T$ is more readily accomplished. Thus

$$\mathrm{d}Q(b)/\mathrm{d}T = [\mathrm{d}Q(b)/\mathrm{d}b][\mathrm{d}b/\mathrm{d}T] \quad (10)$$

Since $Q(b) = \int_2^b Y^{-4}\exp(Y)\,\mathrm{d}Y$, where $Y = \epsilon^2/rDkT$ and $b = \epsilon^2/aDkT$, then

$$\mathrm{d}Q(b)/\mathrm{d}b = b^{-4}\exp b \quad (11)$$

With the approximation that the value of a, the distance of closest approach of the two ions of a salt, does not change with the temperature, the derivative, $\mathrm{d}b/\mathrm{d}T$, is given by the expression

$$\mathrm{d}b/\mathrm{d}T = -b(1/T + \mathrm{d}\ln D/\mathrm{d}T) \quad (12)$$

That this approximation is justifiable was shown by the fact that the a value of a given salt in ethylidene chloride, calculated at each of the four temperatures by means of equation 8, was found to increase only slightly with increase in temperature. It follows from equations 10, 11 and 12, that

$$\mathrm{d}Q(b)/\mathrm{d}T = -b^{-3}\exp b\,[1/T + \mathrm{d}\ln D/\mathrm{d}T] \quad (13)$$

Substitution of this value of $dQ(b)/\mathrm{d}T$ into equation 9 and division of the resulting equation by equation 8 gives

$$-\mathrm{d}\ln K/\mathrm{d}T = [3 + b^{-3}\exp b/Q(b)][1/T + \mathrm{d}\ln D/\mathrm{d}T] \quad (14)$$

Substitution of this value of $\mathrm{d}\ln K/\mathrm{d}T$ into the expression for ΔS°, namely

$$\widetilde{\Delta S}^{\circ} = \mathrm{d}(RT\ln K)/\mathrm{d}T = R(\ln K + T\,\mathrm{d}\ln K/\mathrm{d}T)$$

gives

$$\widetilde{\Delta S}^{\circ} = R\{\ln K + [3 + b^{-3}\exp b/Q(b)][1 + \mathrm{d}\ln D/\mathrm{d}T]\} \quad (15)$$

Since $\widetilde{\Delta H}^{\circ} = \widetilde{\Delta F}^{\circ} + T\widetilde{\Delta S}^{\circ} = -RT\ln K + T\widetilde{\Delta S}^{\circ}$, it follows that

$$\widetilde{\Delta H}^{\circ} = RT[3 + b^{-3}\exp b/Q(b)][1 + \mathrm{d}\ln D/d\ln T] \quad (16)$$

A simplification of the Bjerrum model permits a less rigorous derivation of expressions for $\widetilde{\Delta S}^{\circ}$ and $\widetilde{\Delta H}^{\circ}$ and is presented before giving the values of these quantities obtained from both treatments.

(b) By Means of a Simplified Treatment.—A justifiable simplification of the Bjerrum model is suggested, namely, that two oppositely charged ions exist *either* in contact ($r = a =$ the sum of the van der Waals radii), in which state they constitute an associated ion-pair, *or* at such a large distance apart that the Coulombic force between them is negligible (*viz.*, in the state of free ions). Then the $\widetilde{\Delta F}^{\circ}$ accompanying the dissociation of one mole of ion-pairs ($r = a$) to two moles of free ions ($r > a$) is seen, from equation 5, to be given by

$$\widetilde{\Delta F}^{\circ} = N\epsilon^2/aD \quad (17)$$

from which it follows that

$$-\ln K = \epsilon^2/aDkT \quad (18)$$

It should be noted that this simplification would not be justified if $\widetilde{\Delta F}^{\circ}/N$ approaches kT in value since, under these conditions, the relative population of pairs of ions at intermediate distances of separation (between $r = a$ and $r = q$) would become appreciable. On the other hand when conditions are such that $\widetilde{\Delta F}^{\circ}/N$ is considerably greater than kT (as is true for the salts and solvents used in this investigation), fair agreement between the results of the two treatments is expected.

It is seen that equation 17 restricts $\widetilde{\Delta F}^{\circ}$ to positive values, which requires that K approach unity as a or D increases in value.

The following expressions for $\widetilde{\Delta S}^{\circ}$ and $\widetilde{\Delta H}^{\circ}$ accompanying dissociation, are readily derived from equation 17, again with the approximation that the a value is independent of the temperature.

$$\widetilde{\Delta S}^{\circ} = (\widetilde{\Delta F}^{\circ}/T)(\mathrm{d}\ln D/\mathrm{d}\ln T) \quad (19)$$

$$\widetilde{\Delta H}^{\circ} = (\widetilde{\Delta F}^{\circ})(1 + \mathrm{d}\ln D/\mathrm{d}\ln T) \quad (20)$$

In Table V the values of $-\Delta S^{\circ}_{298}$ (in calories per degree) obtained from experimental data are designated by $-\widetilde{\Delta S}^\circ_{\text{exp}}$, those derived from the Bjerrum–Fuoss treatment by $-\widetilde{\Delta S}^\circ_{\text{B}-\text{F}}$ and those from the simplified treatment by $<-\widetilde{\Delta S}^\circ>$. The salts are indicated by the substituent and its relative position in the benzene ring. They are listed in the order of increasing K values at 25°.

TABLE V

IN ETHYLENE CHLORIDE

Salt	$K \times 10^5$	In calories per degree		
		$-\widetilde{\Delta S}^\circ_{\text{exp}}$	$-\widetilde{\Delta S}^\circ_{\text{B}-\text{F}}$	$<-\widetilde{\Delta S}^\circ>$
p-Chloro	2.08	33.1 ± 0.2	36.4	34.9
m-Chloro	2.53	32.8 ± .1	35.7	34.3
m-Methoxy	3.89	31.5 ± .5	33.7	32.9
p-Methoxy	3.91	31.4 ± .5	33.7	32.9
p-Methyl	3.97	31.9 ± .2	33.6	32.8
o-Chloro	4.06	32.3 ± .4	33.6	32.8
m-Methyl	4.21	31.6 ± .2	33.4	32.7
o-Methyl	4.74	31.3 ± .3	33.0	32.3
o-Methoxy	8.10	29.8 ± .1	30.6	30.5
IN ETHYLIDENE CHLORIDE				
m-Methoxy	0.414	34.8 ± 0.5	37.7	35.6
o-Chloro	.414	35.2 ± .5	37.7	35.6
p-Methoxy	.429	35.5 ± .7	37.6	35.5
p-Methyl	.481	30.4 ± .5	37.5	35.1
o-Methyl	.582	30.7 ± 1.0	36.5	34.6
o-Methoxy	1.123	31.4 ± 0.7	34.1	32.7

It is seen that the experimentally determined values of $-\widetilde{\Delta S}^\circ$ for the *o*- and *p*-methyl salts in ethylidene chloride are from 3 to 4 entropy units less than expected. It seems probable that some unknown error has been made in these two determinations especially since, as is seen, these two salts behave normally in ethylene chloride.

With the exception of these two salts in ethylidene chloride it is noted that (1) in each solvent the value of $-\widetilde{\Delta S}^\circ_{\text{exp}}$ decreases with increase in the K value as required by both treatments; (2) the greater the K value the less the discrepancy between the experimental and calculated values of $-\widetilde{\Delta S}^\circ$; (3) the values of $-\widetilde{\Delta S}^\circ$ calculated by either of the two methods are uniformly greater than $-\widetilde{\Delta S}^\circ_{\text{exp}}$; (4) the values of $<-\widetilde{\Delta S}^\circ>$ are in better agreement with the $-\widetilde{\Delta S}^\circ_{\text{exp}}$ than are the values of $-\widetilde{\Delta S}^\circ_{\text{B}-\text{F}}$.

The decrease in entropy, observed and calculated in every case, is interpreted to mean that the decrease in entropy of the solvent due to the greater ordering of the solvent molecules by the free ions (relative to that by the associated ion-pairs) exceeds the increase in entropy accompanying the dissociation of the unsolvated ion-pair into free unsolvated ions.

The values of the standard enthalpies of dissociation at 25°, experimental and theoretical, are given in Table VI with the same symbolic representations as those used in Table V. Again salts are listed in the order of increasing K values.

Except for the anomalously low values of $-\widetilde{\Delta H}^\circ_{\text{exp}}$ of the *o*- and *p*-methyl salts in ethylidene chloride the total variation in the values of $\widetilde{\Delta H}^\circ_{\text{exp}}$ in each solvent is but slightly greater than the probable error as calculated by the least square method. It is therefore impossible to say whether its value decreases with increasing K value as both theoretical treatments predict.

TABLE VI

IN ETHYLENE CHLORIDE

Salt	In calories		
	$-\widetilde{\Delta H}^\circ_{\text{exp}}$	$-\widetilde{\Delta H}^\circ_{\text{B}-\text{F}}$	$<-\widetilde{\Delta H}^\circ>$
p-Chloro	3480 ± 61	4466	4043
m-Chloro	3511 ± 37	4369	3970
m-Methoxy	3534 ± 138	4050	3809
p-Methoxy	3355 ± 158	4046	3807
p-Methyl	3509 ± 54	4040	3801
o-Chloro	3642 ± 121	4029	3792
m-Methyl	3450 ± 67	3990	3779
o-Methyl	3429 ± 88	3945	3734
o-Methoxy	3303 ± 39	3540	3534
IN ETHYLIDENE CHLORIDE			
m-Methoxy	3033 ± 125	3907	3268
o-Chloro	3142 ± 140	3907	3268
p-Methoxy	3257 ± 210	3886	3259
p-Methyl	1811 ± 132	3838	3228
o-Methyl	2013 ± 300	3754	3178
o-Methoxy	2600 ± 200	3414	3006

As was noted regarding the values of $-\widetilde{\Delta S}^\circ$, those of $-\widetilde{\Delta H}^\circ$, calculated by either of the two methods, are seen to be uniformly higher than the experimental values. Also those calculated by the simpler treatment are in better agreement with the experimental value than those derived from equation 8.

The failure of either treatment to give values of ΔS° and ΔH° within experimental error of the measured values is attributable to the fact that the a value of a given salt in either solvent increase slightly with temperature.

Independent Test of Equation 18.—This equation gives a linear relation between ln K, of a given salt in different solvents at the same temperature and the reciprocal of the dielectric constant, $1/D$, of these solvents. Fuoss and Kraus[7] have obtained the dissociation constants of tetraisoamylammonium nitrate in a series of dioxane–water mixtures having dielectric constants ranging in value from 2.3 to 38.0 at 25°. The value of the parameter, a, is chosen to be 6.67 ångströms instead of 6.40, that used by Fuoss and Kraus[7] in plotting the values of log K *vs.* log D (their Fig. 1, p. 1026). In Fig. 1 the values obtained by Fuoss and Kraus are indicated by circles, those derived from the Bjerrum–Fuoss expression for K (equation 5) give the solid curve, and those derived from equation 18 give the dashed straight line.

It is seen that the solid curve approximates linearity over the wide range of values of $1/D$. It seems probable that the simpler treatment will give, in many cases, as satisfactory an agreement with experimental results as does the more rigorous Bjerrum–Fuoss theory.

Interpretation of the Uniformly Greater K Values in Ethylene Chloride.—The difference in value between the dielectric constant of ethylene chloride ($D_{25^\circ} = 10.23$) and that reported for ethylidene chloride ($D_{25^\circ} = 10.00$) would produce but a very small difference in the K value of a given salt. That there should be an appreciable difference in the a values of a given salt in these two similar solvents seems unlikely. It seems reasonable therefore, to consider the possibility that the dielectric constant, effective in determining the stability of an associated ion-pair, may be considerably different from the macroscopic value in salt solutions in at least one of these two solvents.

From preliminary results obtained with three of the nine perchlorates (the *o*-methoxy, the *m*-methoxy and the *o*-chloro) it has been shown[4] that an effective dielectric constant of 11.9 ± 0.1 for ethylene chloride gives K values of these three salts (calculated by use of equation 8) which agree within experimental error with the measured values. The calculation of the effective dielectric constant of ethylene chloride is based on the assumption that the a value of a given salt in ethylene chloride is the same as its a value in ethylidene chloride. More recently Stern, Healey and Martell[23] have applied this procedure to the K values of six tetraalkylammonium salts (picrates and nitrates) in ethylene chloride and ethylidene chloride and obtain therefrom an effective dielectric constant of 11.8 ± 0.2 for ethylene chloride which gives K values, calculated *via* equation 8, which agree within experimental error with the measured values.

Since the accuracy of the value, 10.00, for the D value of ethylidene chloride was not known, it has been measured (by method described) and found to be 9.90 ± 0.03 at 25°. With this value and the K values in ethylidene chloride (given in Table V), the a values of the six salts (including the three referred to above) are calculated. With these a values and the K values of these six salts in ethylene chloride, a value of 11.77 ± 0.06 is deduced for the average effective dielectric constant of ethylene chloride at 25°. The K values calculated by use of this effective D value and those obtained experimentally are given in Table VII.

TABLE VII

K-VALUES AT 25° IN ETHYLENE CHLORIDE

Salt	$K_{\text{exp}} \times 10^5$	$K_{\text{calc.}} \times 10^5$ (D_{eff} = 11.77)
o-Methoxy	8.10	8.19
m-Methoxy	3.89	3.79
p-Methoxy	3.91	3.87
o-Methyl	4.74	4.99
p-Methyl	3.97	4.20
o-Chloro	4.06	3.79

The agreement between the values of K_{exp} and K_{calc} may be considered quite satisfactory if it is realized that the ion-pairs of these salts deviate somewhat from the model used in the derivation of the Bjerrum–Fuoss equation (equation 8) and that the a value of a given salt may be appreciably different in these two solvents although there is no apparent reason why they should be.

According to accepted dielectric theory the dielectric constant of a polar liquid in an electric field of very high strength should be smaller due to dielectric saturation, than its value in the absence of such a field. The assumption that the dielectric constant of ethylene chloride in the near (not immediate) vicinity of an ion is greater than its macroscopic value may seem purely *ad hoc*. The fact that ethylene chloride consists of a mixture of polar and non-polar molecules, however, suggests an interpretation. It is recognized that there is a greater force of interaction (attraction) between an ion and the molecules of ethylene chloride in the gauche (polar) form than between an ion and those in the *trans* (non-polar) form. As a consequence of this the partial molar free energy of the gauche form of ethylene chloride in the near vicinity of an ion will be less than it would be in the absence of the electric field of the ion. An increase in the mole fraction of the gauche form in this locale is therefore to be expected. Thereby the dielectric constant of ethylene chloride may be greater than its macroscopic value at a distance from an ion where dielectric saturation is negligible but at a sufficiently close distance to effect (decrease) the stability of the associated ion-pair. A theoretical justification for an enhancement of the dielectric constant of ethylene chloride (of the observed magnitude) in the near vicinity of an ion will be given in a separate report.

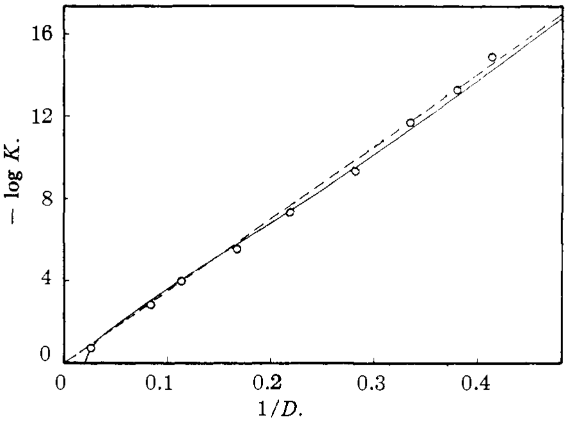

Fig. 1.—Tetraisoamylammonium nitrate in dioxane-water mixtures at 25° from Fuoss and Kraus.[7]

To obtain additional confirmation of the assumption that the a value of a given salt is the same in the two solvents used, a solvent is desired which is closely similar to ethylidene chloride in certain properties, *viz.*, in having nearly the same dielectric constant, in having molecules with a single molecular structure and in being a normal liquid. A liquid which fulfills these requirements is *t*-butyl bromide (b.p. 73.3° and D_{25° = 10.30). Unfortunately none of the nine perchlorates were sufficiently soluble in this purified and dried solvent to permit accurate conductance measurements. Tetraethyl- and tetra-*n*-butylammonium perchlorates were prepared and purified in the expectation that perchlorates, having electrically symmetrical cations, might be more soluble in this solvent. They were also too insoluble. Other salts are being considered for making this test.

We wish to express our gratefulness to Professor W. G. McMillan and R. L. Scott for many very helpful discussions during this investigation; also, to the Atomic Energy Commission for the predoctoral fellowship granted to one of us (J. T. D.) while engaged in this research. We gladly acknowledge our indebtedness to Mr. Murray Bloom for the preparation and purification of the nine perchlorates used.

LOS ANGELES, CALIFORNIA

---

(23) F. Healey, Jr., K. H. Stern and A. E. Martell, *J. Chem. Phys.*, **19**, 1114 (1951).