able discrepancy, although, except for bromobenzene, the results are of the right magnitude. Another way of considering this suggestion is to make use of the known values of p'_α in fitting equation (5) to Danforth's data. We are then left with only one undetermined constant, p'^*. In general it is not possible to fit the results satisfactorily in this way, as is seen from the dotted curves in Fig. 2, .which correspond to the values of p'_α and p'^* given in Table V. It is worth pointing out that the product of $p'-p'_\alpha$, or $p'^*-p'_\alpha$ (it makes small difference which) times the absolute temperature is fairly constant, as may be verified.

TABLE V

Substance	t, °C.	ϵ	l	p'	lp'	$\dot{p}$	p'^*
Carbon disulfide	30	2.61[a]	0.683	0.317	0.216	0.281	0.272
Carbon disulfide	75	2.69[b]	.683	.317	.216	.281	.272
Pentane	30	1.82[a]	.633	.381	.242	.347	.342
Ethyl ether	30	4.15[a]	.831	.774	.644	.303	1.268
Ethyl ether	75	3.82[c]	.823	.753	.620	.303	1.171
Chlorobenzene	30	5.41[a]	.228	1.095	.250	.277	1.047
Chlorobenzene	75	4.90[a]	.25	1.02	.255	.277	0.987
Bromobenzene	30	5.22[a]	.019	0.930	.018	.216	.631
Bromobenzene	75	4.87[a]	.060	.850	.051	.216	.613
Eugenol	0	10.49[a]	.118	2.13	.252	.295	1.98
Hexyl alcohol	30	12.90[a]	.0455	4.10	.187	.306	.60
Hexyl alcohol	75	8.55[a]	.1145	2.50	.286	.306	2.44
i-Butyl alcohol	0	21.1[a]	.0153	7.40	.113	.300	5.94
i-Butyl alcohol	30	17.3[a]	.0313	5.80	.182	.300	5.00
Ethyl alcohol	0	27.8[a]	.0100	10.00	.10	.280	8.10
Ethyl alcohol	30	23.2[a]	.0243	8.03	.195	.280	7.22
Glycerin	0	49.9[a]	.0596	7.05	.420	.223	9.32
Glycerin	30	42.8[a]	.0621	5.95	.370	.223	8.25

[a] At 1 atmosphere. [b] At 1000 atmospheres. [c] At 500 atmospheres.

In conclusion, we must of course admit that the physical meaning of equations (4) and (5) remains uncertain. Such a suggestion as Kerkwood's could be in any case only a very rough approximation to the facts. Indeed, where the molecules were all the same we should expect rather a kind of anomalous dispersion in regard to their interaction, and where the system contained several types of molecules, as in the case of the data described in Part II of this paper, the situation would be more complicated still. Nevertheless, the main point of view developed in this section of the paper appears to be the only reasonable way of explaining what would otherwise remain a rather extraordinary set of numerical coincidences.

Summary

An account is given of measurements of the dielectric constant of solutions of several ampholytes, forming zwitter ions, in a variety of solvents. The results indicate in a rather surprising way that in all these cases the dielectric constant is a nearly additive property of the solutions. A discussion is given of a possible interpretation of this in terms of the internal field, which, if valid, would allow of approximate estimates of polarizations and electric moments in the case of polar solutions.

CAMBRIDGE, MASS. RECEIVED OCTOBER 7, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Thermodynamic Study of Dilute Thallous Chloride Solutions by Electromotive Force Measurements of the Cell Tl-Hg/TlCl(m)/AgCl(s), Ag(s)[1]

BY I. A. COWPERTHWAITE, V. K. LA MER AND J. BARKSDALE

Introduction

Precise measurements of the activity coefficient of thallous chloride in the region of highly dilute solution are of particular interest in view of the interpretations which have been placed upon the existing data as regards the completeness of its dissociation and its obedience to the Debye–Hückel[2] limiting law. Onsager[3] concluded, from an analysis of Kohlrausch's[4] conductivity data in the light of his theoretical equation for conductance, that this salt was incompletely dissociated ($K = 0.31$). Davies[5] reports that the extensive solubility data require, in addition to this dissociation constant, a Debye–Hückel limiting slope of 0.38 instead of the theoretical value, 0.506.[6] Davies finds support for his interpretation in the earlier freezing point measurements of Randall

[1] This paper is from a dissertation submitted in May, 1933, by Jelks Barksdale to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); **25**, 97 (1924).

[3] Onsager, *ibid.*, **28**, 277 (1927).

[4] Kohlrausch, *Z. Elektrochem.*, **8**, 628 (1902).

[5] Blayden and Davies, *J. Chem. Soc.*, 949 (1930); Davies, *ibid.*, 2410 (1930); *Trans. Faraday Soc.*, **23**, 351 (1927).

[6] A similar conclusion in the case of hydrochloric acid has recently been modified [Davies, THIS JOURNAL, **54**, 1698 (1932)].

and Vanselow.[7] These data were interpreted as requiring a limiting slope of 0.412. The freezing point data are inconclusive[8] as they were obtained in a region of concentration (0.0006733 to 0.0067793 molal) where the experimental difficulties attending such determinations are considerable, and are too scattered to define a limiting slope with precision. The computations on solubility are open to the criticism that they have been applied in a range of ionic strengths too concentrated for testing the limiting law without a more adequate recognition of the role played by the ion size parameter "a." This disagreement invites careful reinvestigation of this salt since Davies' conclusions revive the important question of the universal character of the Debye–Hückel limiting slope.[9]

Thallous ions undoubtedly form chloride complexes at higher chloride concentrations.[10] This complication, however, should not affect the *limiting* slope. In fact complex ion formation or incomplete dissociation of any type should actually yield an *experimental* slope somewhat greater, instead of less, than the theoretical value when tested at finite concentrations. It is also a matter of interest to investigate in how far the extended theory of Gronwall, La Mer and Sandved[11] can account for the anomalies ascribed to incomplete dissociation by previous investigators.

Thallium amalgam and silver–silver chloride form highly reproducible electrodes. We have accordingly reinvestigated the behavior of thallous chloride by measuring the e. m. f. of the cell

$$\text{Tl (dilute amalgam)/TlCl}(m)\text{/AgCl(s), Ag(s)} \quad (1)$$

at 0, 12.5, 25, 37.5 and 50° at molalities extending from 0.0005 m to concentrations approaching saturation at these temperatures. This combination has proved to be well suited for investigating the question at issue. Such measurements also permit calculation of the heats of dilution of this salt in dilute solution.[12]

Experimental Methods

A cell was designed to maintain strictly oxygen-free conditions, as oxygen renders the thallium amalgam and silver–silver chloride electrodes[13] unreliable. The novel features of the cell, shown in Fig. 1, are the three thallium amalgam electrodes surrounding a central chamber designed to receive a stopper bearing four silver–silver chloride electrodes. Oxygen was removed from the cell by passing hydrogen in through the three T tubes D D′ D″ and out through the tube Q and trap P. The cell was sealed off without exposure to the air by pushing down the glass rods G G′ G″ and O, thus inserting the collodion covered corks E E′ E″ and M into the four openings of the cell. These corks were then covered with mercury in the cups C C′ C″ and L, and similarly the large stopper K bearing the silver–silver chloride electrodes could be covered with mercury. Details of manipulation are given in the previous paper,[11b] which can readily be adapted to the present cell.

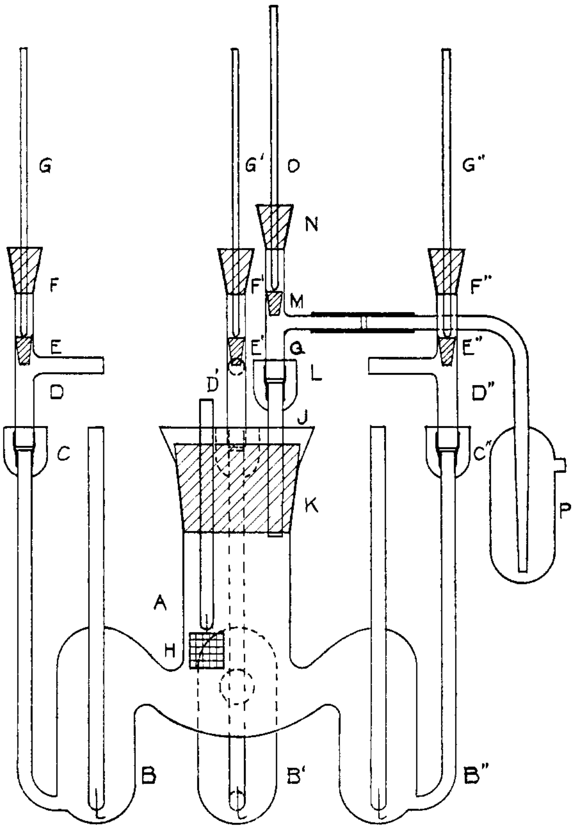

Fig. 1.

The Apparatus.—The type K potentiometer, Eppley standard cell, and thermometers were calibrated and frequently checked during the course of this investigation. The regulation of the water thermostats was maintained to ±0.02°.

Thallous Sulfate.—Commercial thallium metal was dissolved in 9 m sulfuric acid, hydrogen sulfide was passed into the slightly acid solution, the sulfides were filtered

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[7] Randall and Vanselow, THIS JOURNAL, **46**, 2418 (1924).

[8] See Eucken, Jette and La Mer, "Fundamentals of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1925, footnote on p. 331.

[9] Kramers [*Proc. Acad. Sci. Amsterdam*, **30**, 145 (1927)], by an independent theoretical treatment, has confirmed Debye's numerical value of the limiting slope, and an ever increasing volume of experimental work on strong electrolytes supports this value.

[10] La Mer and Goldman, THIS JOURNAL, **51**, 2632 (1929); **52**, 279 (1930); **53**, 473 (1931).

[11] (a) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928); (b) Cowperthwaite and La Mer, THIS JOURNAL, **53**, 4333 (1931); (c) La Mer and Parks, *ibid.*, **53**, 2040 (1931).

[12] La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933).

[13] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

off and the filtrate boiled. The thallium was precipitated as chloride, thoroughly washed by decantation, and reconverted to the sulfate. The sulfate was recrystallized several times and finally dried at 120°.

Thallous Chloride.—Thallous chloride was prepared from purified sulfate and redistilled hydrochloric acid. It was fully washed and dried at 120°.

Thallium Metal.—The thallium metal was electrolytically deposited from a saturated solution of the sulfate. The formation of peroxide was avoided by having the anode in a second beaker of sulfuric acid connected to the first by an inverted U-tube bridge. The crystals of metal were washed, melted in an atmosphere of hydrogen cast into convenient sized sticks, and stored under boiled distilled water.

Hydrogen.—Tank hydrogen was passed over hot copper, through a sodium hydroxide scrubber, and finally through a saturating column.

Thallous Chloride Solution.—The purified thallous chloride was dissolved in water, having a specific conductivity of 0.8×10^{-6} to 1.1×10^{-6} reciprocal ohm, to form a stock solution from which dilutions were made by weight. This solution was analyzed gravimetrically for chloride.[14] Duplicate analyses agreed to within 0.05%. The concentrations of all solutions are expressed in moles per thousand grams of water, weighed *in vacuo*.

The Debye–Hückel equation employs concentrations by volume. However, for solutions of the strength studied in this investigation, the difference between molal and molar concentrations are not significant.

Thallium Amalgam.—Sticks of the purified thallium were warmed under nitrogen with enough mercury, purified by Hulett's method, to form a 5% amalgam. It was filtered through capillary tubing into an evacuated flask and stored under hydrogen. This amalgam is homogeneous through the temperature interval of 0–50°.[15]

All measurements were standardized against solid thallium by measuring the cell

$$\text{Tl (5\% amalgam)}/\text{Tl}_2\text{SO}_4(\text{m})/\text{Tl(s)} \qquad (2)$$

using the same cell and technique.

Thallium Metal Electrodes.—Cast rods were attached to platinum wires sealed through glass tubes. Exposed platinum was covered with paraffin.

Silver–Silver Chloride Electrodes.—Silver–silver chloride electrodes suitable for use in the very dilute solutions studied in this work were produced in the following manner. Fifty-two mesh platinum gauzes one centimeter square welded to pieces of small platinum wire sealed through the ends of glass tubes were cleaned in hot concentrated nitric acid, electroplated in a 0.05 *m* solution of recrystallized potassium silver cyanide for six hours with a current of one milliampere per electrode, washed for five days with frequent changes of distilled water, and chloridized electrolytically in the dark in a tenth molal solution of hydrochloric acid for one-half hour with a current of two milliamperes per electrode. These electrodes agreed among themselves to within three one-hundredths of a millivolt.

Discussion of Results

The observed e. m. f.'s for the dilute thallium amalgam against pure thallium are given in Table I. The precision based upon four thallium electrodes is a. d. = ±0.02 mv.

TABLE I

E. M. F. OF THE CELL

Tl (DILUTE AMALGAM)/$\text{Tl}_2\text{SO}_{4(0.03\text{ m})}$/Tl(s)

T	0	12.5	25	37.5	50
E(obs.)	0.11162	0.11561	0.11959	0.12362	0.12783

If the e. m. f.'s shown in Table I, corresponding to cell 2 above, are added to the values observed for cell 1, the sum is the e. m. f. of the cell

$$\text{Tl(s)}/\text{TlCl(m)}/\text{AgCl, Ag} \qquad (3)$$

The e. m. f.'s of cell 3 are listed in Table II. The precision of the measurements for cell 1 is a. d. = ±0.05 mv. on the basis of from four to ten electrode pairs for each molality. The precision is lower for the most dilute solutions at the higher temperatures. The readings for 0.0005 *m* at 35.7 and 50° and 0.001 *m* at 50° are not in harmony with the other values and have been discarded in the computations to follow.

The observed e. m. f.'s in Table II correspond to the change in free energy due to the reaction

$$\text{Tl(s)} + \text{AgCl(s)} \longrightarrow \text{TlCl(m)} + \text{Ag(s)} \qquad (4)$$

Table II also contains values for the computed function $E^{\circ\prime}$ where

$$E^{\circ\prime} = E + 2RT/F \ln m \qquad (5)$$

or

$$E^{\circ\prime} = E^{\circ} - 2RT/F \ln f \qquad (6)$$

The correction to the observed e. m. f. due to the solubility of the silver chloride was computed, but it was significant only in the cases of the three points that had to be discarded on account of experimental difficulty.

TABLE II

VALUES OF E(OBS.) AND $E^{\circ\prime}$ FOR THE CELL

Tl(s)/TlCl(m)/AgCl(s), Ag(s)

m		0°	12.5°	25°	37.5°	50°
0.0005	E(obs.)	0.89847	0.92487	0.95026	0.97420	0.99790
	$E^{\circ\prime}$	.54074	.55079	.55975	.56727	.57448
.001	E(obs.)	.86627	.89138	.91521	.93803	.95979
	$E^{\circ\prime}$	.54113	.55139	.56031	.56825	.57513
.002	E(obs.)	.83456	.85806	.88047	.90193	.92269
	$E^{\circ\prime}$	.54204	.55218	.56118	.56925	.57663
.004	E(obs.)	.80295	.82491	.84621	.86620	.88567
	$E^{\circ\prime}$	.54309	.55316	.56254	.57064	.57821
.006	E(obs.)	.78484	.80597	.82636	.84554	.86425
	$E^{\circ\prime}$	.54404	.55413	.56352	.57168	.57934
.008	E(obs.)	[a]	.79279	.81245	.83105	.84913
	$E^{\circ\prime}$		.55515	.56438	.57259	.58027
.01	E(obs.)	[a]	[a]	.80173	.81996	.83760
	$E^{\circ\prime}$			.56513	.57344	.58114

[a] Saturation was reached before 0.008 *m* at 0° and before 0.01 *m* at 12.5°.

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[14] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1923, p. 192.

[15] Richards and Daniels, THIS JOURNAL, **41**, 1732 (1919).

The extrapolated values of E° were obtained by means of the Gronwall, La Mer and Sandved extension of the Debye–Hückel theory.[11] The values of E° calculated from the best values of "a" at the different temperatures and concentrations studied are summarized in Table III in which "a" is in Ångström units and x = "a" κ.

TABLE III

VALUES OF x AND E° ASSUMING "a" = 0.93 Å.

m		0°	12.5°	25°	37.5°	50°
0.0005	x	0.00675	0.00679	0.00684	.....	.....
	E°	.53951	.54948	.55835	.....	.....
.001	x	.00954	.00960	.00967	0.00975	.....
	E°	.53937	.54952	.55831	.56610	.....
.002	x	.01349	.01358	.01367	.01379	0.01391
	E°	.53951	.54948	.55829	.56615	.57330
.004	x	.01908	.01920	.01934	.01950	.01968
	E°	.53945	.54927	.55837	.56616	.57338
.006	x	.02338	.02351	.02368	.02388	.02411
	E°	.53952	.54930	.55834	.56611	.57333
.008	x	.....	.02715	.02735	.02757	.02783
	E°	.....	.54952	.55833	.56609	.57325
.01	x	.....	.....	.03058	.03083	.03112
	E°	.....	.....	.55832	.56611	.57322

Plots of $E^{\circ\prime}$ against the square root of the molality at each temperature employed are shown in Fig. 2. The Debye–Hückel limiting slopes are represented by the light solid lines and the theoretical curves calculated from the Gronwall, La Mer and Sandved equation for an "a" value of 0.93 Ångström unit are indicated by the upper heavy lines; the circles designate experimental points. The intercepts of these curves are the extrapolated values of E° obtained as described before. It is evident that the curves are almost straight lines which do not fuse into the limiting slope until concentrations somewhat below 0.001 molal are reached.

The Gronwall, La Mer and Sandved equation fits the data well enough to permit extrapolation for E° when "a" is assigned a value of 0.93 Ångström. This value is hardly a physically reasonable one in view of the fact that crystal structure measurements[16] yield a value of 3.3 Ångströms as the distance of closest approach of the ions in the crystal lattice. Evidently some factors other than the simple Debye–Hückel ion-ion interaction are involved. These factors may be incomplete dissociation or the additional electrical attraction arising from the deformability of the ions when exposed to the intense fields of each other on close approach.

We find, as shown in Table IV, that by employing a value of "a" in the Gronwall, La Mer and Sandved equation equal to three Ångström units which is physically reasonable, in connection with Onsager's mass action constant, K = 0.31, a constant value of E° may be secured. The calculations were performed as follows: as a first approximation, the degree of dissociation in the equation $\alpha^2 f^2 m/(1 - \alpha) = 0.31 = K$ was computed employing the theoretical value of f computed at the molal concentrations. Then new values of f were computed at the concentrations $c = m\alpha$, after which α was computed a second time. These second approximations of f and α were then substituted in the equation

$$E^{\circ\prime} = E^\circ + 0.11830\ (\log f + \log \alpha) \qquad (7)$$

to obtain E°. By employing a series of approximations, a similar method may be used to estimate the dissociation constant of electrolytes from electromotive force data.

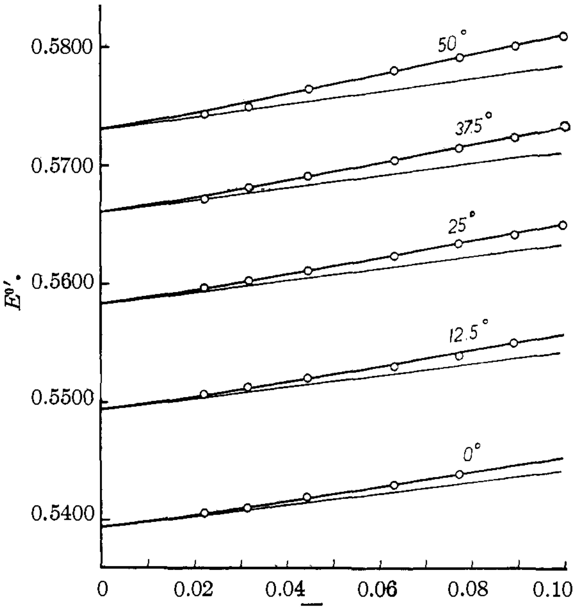

Fig. 2.

In comparing the results of Tables III and IV, it should be recognized that the values in the latter table require two arbitrary parameters,

TABLE IV

VALUES OF E° AT 25° ASSUMING "a" = 3 Å. AND K = 0.31

m	α	$f(c = m\alpha)$	E°
0.0005	0.99848	0.97462	0.55835
.001	.99703	.96456	.55830
.002	.99427	.95076	.55829
.004	.98915	.93222	.55837
.006	.98442	.91870	.55836
.008	.97999	.90780	.55837
.01	.97582	.89850	.55837

(16) Goldschmidt, *Trans. Faraday Soc.*, **25**, 253 (1929).

namely, K and α, whereas in Table III only one arbitrary parameter is employed. It is interesting to note, however, that the two treatments give the same value for $E°$ at 25°.

These computations were performed at 25° only since there are no independently determined values of K for other temperatures.

Table V gives the observed values of the mean activity coefficients of thallous chloride for each experimental point. The theoretical values calculated from the Gronwall, La Mer and Sandved equation agree with the observed values to within 0.001.

Table V

Observed Activity Coefficients of TlCl

m	0°	12.5°	25°	37.5°	50°
0.0005	0.973	0.973	0.973	.....	.....
.001	.965	.961	.962	0.961	.....
.002	.947	.946	.946	.943	0.942
.004	.926	.927	.921	.919	.916
.006	.907	.909	.904	.901	.897
.008	...	.890	.889	.886	.882
.01	...	...	.876	.872	.869

The computations of the heat of the cell reaction ($-\Delta H$) at each concentration and the partial molal heat of dilution of thallous chloride ($\bar{L}_2$) were performed following the procedure of La Mer and Cowperthwaite.[12] Before differentiating with respect to temperature, the values of $E°'$ were smoothed with the aid of the Gronwall, La Mer and Sandved equation to distribute the experimental error more evenly. The corrections for smoothing are equivalent to the deviation in $E°$ in Table III. To facilitate differentiation, these smoothed values were expressed as fourth degree functions of $w = (t - 25)/12.5$

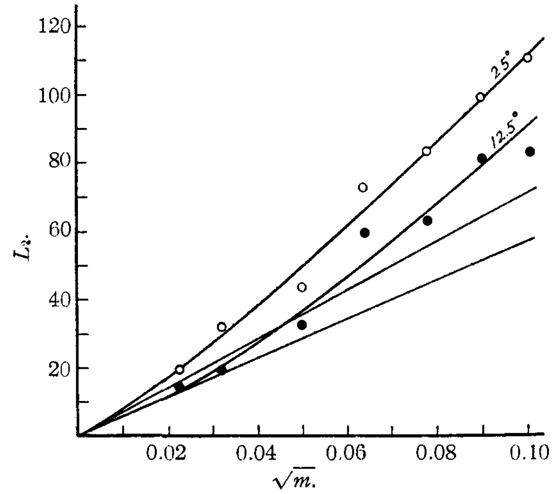

Fig. 3.

$$E°' = A + Bw + Cw^2 + Dw^3 + Ew^4 \quad (8)$$

and the derivatives computed analytically. The values of the coefficients for equation 8 are given in Table VI.

Table VI

$E°' = A + Bw + Cw^2 + Dw^3 + Ew^4$

m	A	$B \times 10^3$	$C \times 10^4$	$D \times 10^5$	$E \times 10^5$
0	0.55833	8.3075	5.7792	3.7500	2.2917
0.0005	.55973	8.4025	5.7292	3.7500	2.2917
.001	.56033	8.4492	5.6708	3.5833	2.2083
.002	.56122	8.5075	5.6792	3.7500	2.2917
.004	.56250	8.6150	5.7667	3.5000	2.6667
.006	.56351	8.6767	5.5833	3.8333	2.3333
.008	.56438	8.7417	5.6583	3.8333	2.5833[a]
.01	.56514	8.7950	5.4750	4.0000[a]	2.2500[a]

[a] Smoothed values of $E°'$ for 0.008 and 0.01 m at 0° and 0.01 m at 12.50° were obtained by extrapolation using the Gronwall, La Mer and Sandved equation and $E°$ as determined.

The heat of the reaction was calculated only at 25 and 12.5° so as to be near the middle of the range of the experimental data where they are most reliable. The results are given in Table VII.

The values of $\bar{L}_2$ at 25 and 12.5° are plotted against the square root of the molality in Fig. 3. The Debye–Hückel limiting slopes are represented by the light solid lines. At 25° the values of $\bar{L}_2$ give no evidence of obeying the limiting slope until concentrations well below 0.0005 molal are reached, although at 12.5° $\bar{L}_2$ obeys the limiting law at about 0.001 molal.

Table VII

m	$E°'$	$-\Delta H$	$\bar{L}_2$
	25°		
0.0	0.55833	8307.5	0.0
.0005	.55973	8287.7	19.8
.001	.56033	8275.9	31.6
.002	.56122	8264.2	43.3
.004	.56250	8234.6	72.9
.006	.56351	8224.3	83.2
.008	.56438	8208.6	98.9
.01	.56514	8196.6	110.9
	12.5°		
0.0	0.54943	7674.2	0.0
.0005	.55074	7659.5	14.7
.001	.55130	7654.6	19.6
.002	.55213	7641.9	32.3
.004	.55330	7614.5	59.7
.006	.55426	7611.0	63.2
.008	.55506	7592.6	81.6
.01	.55578	7590.7	83.5

In conclusion the authors thank Drs. D. A. MacInnes, T. Shedlovsky and A. S. Brown of the Rockefeller Institute for Medical Research for their coöperation in calibrating the instruments used in this research and for their helpful advice in the problems encountered in producing suitable silver-silver chloride electrodes.

Summary

1. The electromotive force of the cell Tl (solid), TlCl(m),AgCl, Ag has been determined by combining measurements on the cells Tl(dilute amalgam), TlCl(m), AgCl, Ag, and Tl(solid), Tl_2SO_4(0.03 M) Tl(dilute amalgam), for temperatures from 0 to 50° employing thallous chloride of molalities from 0.0005 to 0.01 *m*.

2. The logarithms of the activity coefficients of thallous chloride when plotted against the square root of the molality exhibit an *experimental slope* which is somewhat *greater* than the predictions of the Debye-Hückel limiting law in regions of high dilution, although our results indicate that the *limiting slope* is 0.506 at 25° in agreement with the theory. This finding is in contradiction to conclusions drawn by Davies and others based upon determinations by the solubility method at higher concentrations, who report an apparent limiting slope equal to 0.38.

3. The experimental results follow the predictions of the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory when the parameter "*a*" is assigned a value of 0.93 Ångström. This "*a*" value, however, is smaller than the distance of closest approach (3.3 Å.) deduced from crystal structure measurements, and is of doubtful physical significance.

4. The results may be more satisfactorily explained on the basis of incomplete dissociation. The failure of the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory to account for the data when "*a*" is assigned a value of the same order of magnitude as the distance of closest approach of the ions deduced from crystal structure measurements shows that the theory makes no pretense of accounting for incomplete dissociation, a point concerning which there has been some difference of opinion.

5. The values of the partial molal heats of dilution of thallous chloride computed by the aid of the Gibbs-Helmholtz equation have been tabulated.

For the cell Tl(solid), TlCl(m), AgCl, Ag, at twenty-five degrees

$E^\circ = 0.55833$ $-\Delta F^\circ = 12{,}877$ calories
$dE^\circ/dT = 6.646 \times 10^{-4}$ $-\Delta H^\circ = 8{,}307$ calories

NEW YORK, N. Y. RECEIVED OCTOBER 9, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ADELPHI COLLEGE]

Ternary Systems of Urea and Acids. I. Urea, Nitric Acid and Water. II. Urea, Sulfuric Acid and Water. III. Urea, Oxalic Acid and Water

BY LAWRENCE H. DALMAN

Introduction

A study of the literature shows that the salts of urea have received little systematic treatment although the nitrate and oxalate, because of their slight solubility, were utilized as tests for urea almost a century ago. Regnault[1] crystallized these salts and from their analyses derived the formulas now generally assigned to them although the investigations of Marchand[2] appear to indicate that the salts contain water of crystallization. More recently DuToit[3] employed phase rule methods to determine the constitution of the salts formed in aqueous solutions of urea with each of five common acids. In the absence of experimental data, however, his findings cannot be regarded as conclusive.

It seemed desirable therefore to make a systematic study of the solubility relations of urea with the various acids and to determine the constitution and limits of stability of the existing salts. In the present investigation a phase rule study was made of the three ternary systems consisting of urea, water and each of the following: nitric, sulfuric and oxalic acids. Further work on urea-acid systems is now in progress.

Experimental Part

Materials.—The urea and oxalic acid were Mallinckrodt "Analytical Reagent." Analyses of this urea by the stand-

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[1] Regnault, *J. prakt. Chem.*, **16**, 286 (1839).

[2] Marchand, *ibid.*, [1] **34**, 248 (1845); **35**, 481 (1845).

[3] DuToit, *Verslag. Wetenschappen*, **22**, 573 (1913).