Summary

The heat of neutralization of acetic acid and sodium hydroxide was found to be 54,324 joules at 20° at concentrations of $HC_2H_3O_2 \cdot 100H_2O$ and $NaOH \cdot 100H_2O$. The heat of neutralization at other concentrations is calculated with the aid of thermochemical data presented in previous publications. By extrapolation, upward for acetic acid and downward for strong acids, the heat of reaction $H^+ + OH^- = H_2O$ was found to be 57.07 kj. or 13.65 Cal. at 20°.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

A STUDY OF THE THERMOCHEMICAL BEHAVIOR OF WEAK ELECTROLYTES[1]

BY THEODORE W. RICHARDS AND BEVERIDGE J. MAIR

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Introduction

Within the past few years the thermochemical behavior of aqueous solutions of many strong electrolytes has been investigated in this Laboratory.[2] The present investigation is a continuation of that work, particularly with weak electrolytes. Heats of dilution at 16 and 20° of aqueous solutions of citric acid, sodium citrate and the acid citrates were measured and from these values the heat capacities of the resulting solutions calculated by means of the Person–Kirchhoff equation.[2d] The heats of neutralization of citric acid and its acid salts were also measured and from the heats of dilution of factors and products the heat of neutralization at various concentrations was calculated. The significance of such measurements in connection with solution theories needs no explanation. The heats of dilution and resulting heat capacities will be considered first.

Apparatus and Method

The apparatus and experimental procedure have been adequately described elsewhere.[2d,e] The large absorption of heat on dilution of the citrates, however, necessitated one minor modification. A reservoir for ice and water, supported four feet above the apparatus, was connected to a circular rose in the outer bath. The rose, made out of glass tubing with small apertures three inches apart, encircled the "submarine" and

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[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author under the general direction of Dr. Lawrence P. Hall.

[2] (a) Richards and Rowe, THIS JOURNAL, **42,** 1622 (1920); (b) **43,** 771 (1921); (c) **44,** 684 (1922); (d) Richards and Gucker, *ibid.*, **51,** 712 (1929); (e) Richards, Mair and Hall, *ibid.*, **51,** 727 (1929).

permitted the addition of ice water to take place throughout the bath rather than at any one spot. This, together with the efficient stirrer already in the bath, made it possible to add water rapidly without appreciable thermal inhomogeneity. Since the calorimeter system was identical with that used by Richards, Mair and Hall[2e] its heat capacity was taken as 76.4 mayers, the value previously obtained by them from the heat capacity of its constituent parts.

Purification and Analyses of Solutions Used in the Dilution Experiments

Sodium Citrate Solution.—Sodium citrate, the best obtainable, was further purified by a single crystallization with centrifuging, dried in the oven at 100° and dissolved to make a solution approximately $Na_3C_6H_5O_7 \cdot 50H_2O$. The solution was then analyzed by digesting a weighed quantity with sulfuric acid in a long-necked quartz flask of about 100 cc. capacity. The digestion mixture, when clear, was transferred to a weighed platinum crucible and evaporated to dryness on a ring burner. It was fused to constant weight and weighed as Na_2SO_4. The residues were examined for SiO_2, tested for excess SO_3 with methyl orange, and showed no signs of either. Four analyses showed the solution to be of the concentration $Na_3C_6H_5O_7 \cdot 49.35 \pm 0.01H_2O$.

Citric Acid Solution.—The best obtainable citric acid was further purified by a single crystallization with centrifuging and dissolved to make a solution of approximately the desired concentration. Two analyses with carbonate-free sodium hydroxide, using phenolphthalein as an indicator, showed the solution to be of the concentration $H_3C_6H_5O_7 \cdot 25.07H_2O$. 0.07 g. of thymol was added to three liters of solution. This quantity, insufficient to alter the heat capacity of the solution, adequately prevented the formation of mold.

Monosodium Dihydrogen Citrate and Disodium Monohydrogen Citrate Solutions.—These solutions were made up determinate to the concentrations $NaH_2C_6H_5O_7 \cdot 50H_2O$ and $Na_2HC_6H_5O_7 \cdot 50H_2O$, using the citric acid and sodium citrate solutions which had been previously analyzed.

Reference to the papers previously mentioned will show how the results were calculated. The rise in temperature, Δt, was the average of two or more experiments agreeing within 0.0003°. In a few cases, where there was a larger discrepancy caused by some temporary minor difficulty, a greater number of experiments were performed so that the average deviation from the mean was in no case greater than ±0.0004°. The heat capacities of the most concentrated solutions used in the calculation of the first stage of the heat of dilution were the instantaneous values at 16 and 20°, directly determined by Richards and Gucker,[3] while for the subsequent dilutions the heat capacity at 18° (calculated by means of the Person–Kirchhoff equation) was used to compute the heat of dilution at both 16 and 20°. This approximation was adequate for the accuracy desired.

The experimental data, corrected to integral stages where necessary, are summarized in the following tables.

The values given in Table II for the heats of dilution are depicted graphically in Fig. 1, in which ordinates represent heats of dilution and abscissas

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[3] Richards and Gucker, THIS JOURNAL, **47**, 1876 (1925).

TABLE I

HEAT CAPACITIES PER GRAM AT 18° IN MAYERS

	$50H_2O$	$100H_2O$	$200H_2O$	$400H_2O$	$800H_2O$	$1600H_2O$
$H_3C_6H_5O_7$	3.7326	3.9313	4.0487	4.1134	4.1470	....
$NaH_2C_6H_5O_7$	3.6700	3.8778	4.0124	4.0915	4.1348	4.1579
$Na_2HC_6H_5O_7$	3.5921	3.8187	3.9734	4.0683	4.1222	4.1512
$Na_3C_6H_5O_7$	3.4987	3.7443	3.9241	4.0388	4.1057	....

TABLE II

HEATS OF DILUTION AND THEIR TEMPERATURE COEFFICIENTS

	Total moles of water in final solution					
	$50H_2O$	$100H_2O$	$200H_2O$	$400H_2O$	$800H_2O$	$1600H_2O$
		$H_3C_6H_5O_7 \cdot 25H_2O$				
ΔH at 16°, joules	511	900	1178	1393	1605	1838
ΔH at 20°	465	818	1072	1282	1475	1714
ΔC_p, mayers	11.5	20.5	26.5	27.8	32.5	31.0
		$NaH_2C_6H_5O_7 \cdot 50H_2O$				
ΔH at 16°		2066	3449	4256	4688	....
ΔH at 20°		1896	3138	3847	4210	4380
ΔC_p		42.5	77.8	102.3	119.5	....
		$Na_2HC_6H_5O_7 \cdot 50H_2O$				
ΔH at 16°		3129	5378	6721	7405	7711
ΔH at 20°		2851	4857	6019	6584	6812
ΔC_p		69.5	130.2	175.5	205.3	224.5
		$Na_3C_6H_5O_7 \cdot 50H_2O$				
ΔH at 16°		2948	5226	6595	7234	7400
ΔH at 20°		2509	4409	5484	5924	[6180]
ΔC_p		109.8	204.2	277.8	327.5	....

fractions of a mole of salt per mole of water. It is worthy of note that there is no regularity between the heats of dilution of these substances due to the replacement of hydrogen by sodium.

In Table III the heats of dilution, ΔH, of acetic and citric acids are compared with their degrees of ionization.[4] The first two rows represent the concentration and corresponding degree of dissociation, while the third and fourth rows give the change in ionization and corresponding heat of dilution between the concentrations given in the first row.

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[4] The only one of the substances investigated in this research on which data necessary for the calculation of the degree of ionization are available is citric acid. Acetic acid, for which accurate data for the heats of dilution have been published in a recent paper of this series (Richards and Gucker, THIS JOURNAL, **51,** 712 (1929), is the classical example given for the Ostwald dilution law and is consequently particularly suitable for this comparison. The degree of ionization was calculated by the approximate formula $\alpha^2 = K/c$, where α = fraction ionized, c = concentration in moles per liter and K is the equilibrium constant. The dissociation constants used for acetic and citric acids were 1.8×10^{-5} and 0.082×10^{-5}, respectively (Creighton and Fink, "Electrochemistry," **1924,** Vol. I, p. 309). Accuracy adequate for the present purpose was obtained by neglecting the dissociation of the secondary and tertiary hydrogens of citric acid.

Table III

Comparison of Heat of Dilution and Ionization

Acetic acid	$25H_2O$		$50H_2O$		$100H_2O$		$200H_2O$		$400H_2O$		$800H_2O$
$\alpha \times 10^{-3}$	3.04		4.16		5.78		8.13		11.46		16.14
$\Delta\alpha \times 10^{-4}$		11.2		16.2		23.5		33.3		46.8	
ΔH, joules		−296.6		−164.8		−83.7		−42		−22	
Citric acid	$25H_2O$		$50H_2O$		$100H_2O$		$200H_2O$		$400H_2O$		$800H_2O$
$\alpha \times 10^{-4}$	7.25		9.46		12.76		17.69		24.6		34.5
$\Delta\alpha \times 10^{-5}$		22.1		33.0		49.3		69.4		98.7	
ΔH, joules		464		353		254		210		193	

An examination of the third and fourth rows shows immediately that the heat change evolved does not parallel the increase in ionization, the heats of dilution decreasing while the change in degree of ionization increases. These results indicate that some other factor or factors must be largely responsible for the heat of dilution (in the range studied), although they do not preclude the possibility that there is a heat effect due to ionization masked by some larger effect. Other factors besides ioniza-

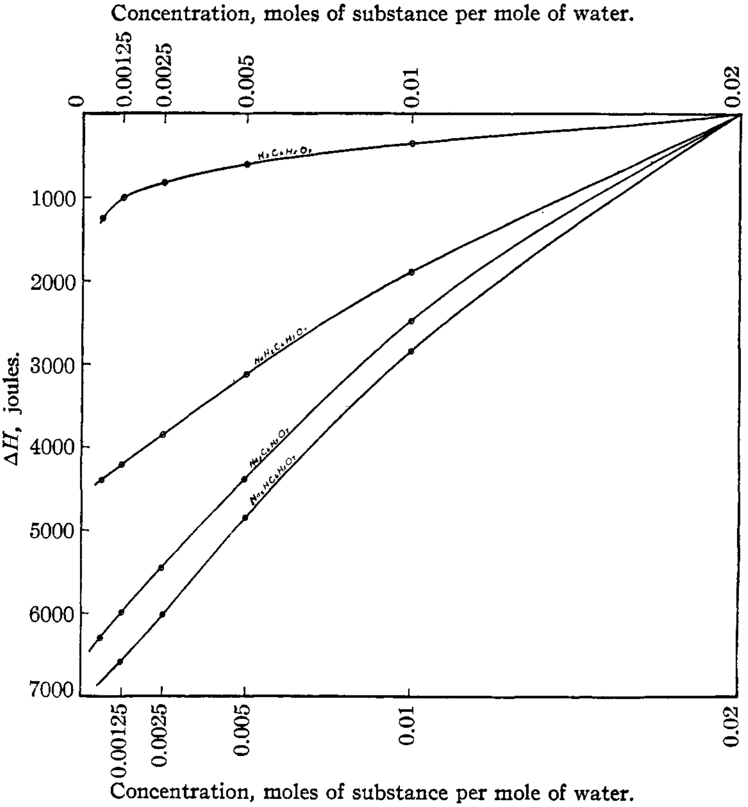
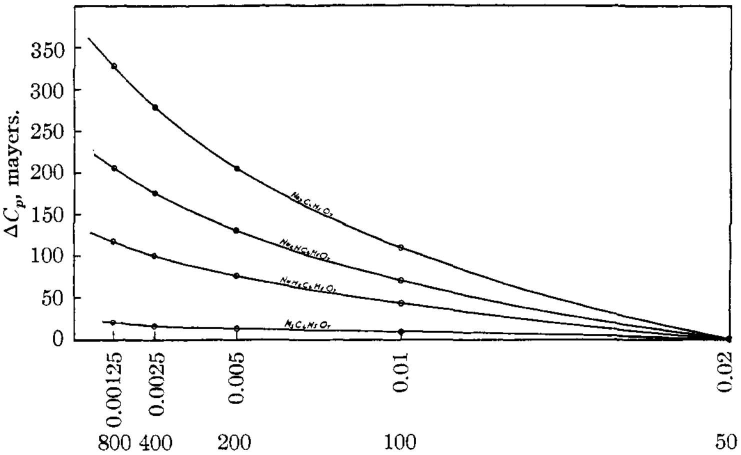


Fig. 1.—Heats of dilution.

tion responsible for the heat effect might be polymerization or depolymerization of solvent and solute molecules and solvation of molecules or ions of solute.

Another series of quantities worthy of consideration is loss of heat capacity on dilution. These values are depicted graphically in Fig. 2 in a manner identical with that employed for the heats of dilution. An examination of the curves shows that each hydrogen replaced by sodium in the citrates produces an increase in the loss of heat capacity which is almost regular. As was pointed out, no such regularity existed with the heat of dilution. This may be taken to indicate that loss of heat capacity is a function of fewer variables than heat of dilution. Richards and Rowe[2b] have pointed out that ionization should be accompanied by a decrease in heat capacity since the neutralization of strong acids and bases in which H^+ and OH^- are de-ionized is accompanied by an increase in heat capacity. It is interesting to see whether differences in degree of ionization can explain the regularity observed in the loss of heat capacity of the citrate solution. The strength of these substances as electrolytes increases from citric acid to sodium citrate and the percentage increase in ionization over the range investigated probably increases in the same order. Since this is the order in which the loss of heat capacity increases, it is apparent that the loss of heat capacity in these solutions depends to a large extent on the number of ions formed.



Concentration, (a) moles of substance per mole of water. (b) Moles of water per mole of substance.

Fig. 2.—Loss of heat capacity.

The total molal heat capacities are tabulated in Table IV.

These values (in the dilute solutions, at least) exhibit some regularity, heat capacity decreasing as hydrogen is replaced by sodium. This is

Table IV

Molal Heat Capacities at 18° in Mayers

	$50H_2O$	$100H_2O$	$200H_2O$	$400H_2O$	$800H_2O$
$H_3C_6H_5O_7$	4079.5	7837.7	15366	30433	60566
$NaH_2C_6H_5O_7$	4091.5	7816.3	15316	30361	60479
$Na_2HC_6H_5O_7$	4083.6	7781.1	15255	30278	60385
$Na_3C_6H_5O_7$	4054.4	7711.9	15152	30147	60234

exactly contrary to the behavior of strong inorganic acids, in which Richards and Rowe found the replacement of hydrogen by sodium to be accompanied by an increase in heat capacity. At infinite dilution it might be expected that the replacement of each hydrogen by sodium would produce the same change in heat capacity, since in such a condition the solution would be completely ionized and the difference in heat capacities would be simply the difference between the heat capacities of the hydrated sodium and hydrogen ions. The above solutions do not show a constant difference nor could it be expected that they would, since citric acid even in $800H_2O$ solutions is but slightly ionized. Some tendency toward a constant difference is noticeable as the solutions become dilute.

Heats of Neutralization.—The heat of neutralization of citric acid and its acid salts was determined with the same apparatus and in a manner identical to that previously employed to determine the heat of neutralization of acetic acid.[5]

The purification and analysis of the sodium hydroxide were performed with all the precautions previously described in publications from this Laboratory.[2c,6]

The citric acid was purified and analyzed in the same manner as in the dilution experiments. The acid salt solutions were made up determinate from standard sodium citrate (analyzed as described in the dilution experiments) and citric acid solutions.

By titration with standard sodium hydroxide a direct comparison of the solutions thus prepared was obtained. The results of the direct analyses and the determinate values agreed satisfactorily in all cases.

With disodium monohydrogen citrate a slight excess of base was used to eliminate as far as possible any uncertainty caused by traces of carbonate in the sodium hydroxide. Since this procedure was not possible with citric acid and monosodium dihydrogen citrate, exactly equivalent quantities were used.

The essential experimental data are recorded in Table V. ΔT is the average of at least five experiments which agreed within 0.003° in the cases of citric acid and disodium monohydrogen citrate. The results were not as concordant with monosodium dihydrogen citrate, in which case

[5] Richards and Mair, This Journal, **51**, 737 (1929).

[6] Ref. 3, p. 1882.

the average deviation from the mean was 0.004°. Δh refers to the heat absorbed by the quantities used in the actual experiment, while ΔH refers to molal quantities. A and B refer to acid and base, respectively.

TABLE V

HEATS OF NEUTRALIZATION OF CITRIC ACID AND ITS ACID SALTS

Weight, g.	Ht. cap. per g., mayers	Total heat cap. incl. Cal. (mayers)	ΔT, av.	Final T	Δh Joules	ΔH Joules
Citric Acid (Series I). $NaOH \cdot 100.99H_2O + H_3C_6H_5O_7 \cdot 100.79H_2O$						
630.00A	3.9330	4918.9	3.400	19.95	−16726	−53310
583.42B	4.0537	Average at 20° = −53305				
(Series II). $NaOH \cdot 100.99H_2O + H_3C_6H_5O_7 \cdot 100.00H_2O$						
630.00A	3.9313	4934.5	3.413	19.80	−16844	−53309
587.53B	4.0537	Average at 20.00° = −53291				
Monosodium Dihydrogen Citrate. $NaOH \cdot 99.75\ H_2O + NaH_2C_6H_5O_7 \cdot 100H_2O$						
640.60A	3.8778	4925.7	3.428	19.88	−16884	−53136
583.73B	4.0523	Average at 20° = −53130				
Disodium Monohydrogen Citrate. $NaOH \cdot 99.75H_2O + Na_2HC_6H_5O_7 \cdot 100H_2O$						
640.62A	3.8187	4875.2	3.524	20.05	−17180	−54664
580.60B	4.0523	Average at 20.00° = −54663				

The temperature coefficients of the heats of neutralization were calculated from the heat capacities of the factors and products with the aid of the Person–Kirchhoff equation and are given in the following table.

TABLE VI

TEMPERATURE COEFFICIENT OF HEAT OF NEUTRALIZATION

	Molal heat cap. of fac. at 18°, mayers	Total mayers, K	Molal heat cap. of prod. at 18°, mayers, K	Average $\frac{\Delta(\Delta H)}{\Delta T}$ or ΔC_p
$H_3C_6H_5O_7 \cdot 100H_2O$	7837.7	15301.0	15391.0	+90.0
$NaOH \cdot 100H_2O$	7463.3			
$NaH_2C_6H_5O_7 \cdot 100H_2O$	7816.3	15279.6	15329.9	+50.3
$NaOH \cdot 100H_2O$	7463.3			
$Na_2HC_6H_5O_7 \cdot 100H_2O$	7781.1	15244.4	15226.7	−17.7
$NaOH \cdot 100H_2O$	7463.3			

The molal heat capacity of the product was obtained by adding to the molal heat capacity of the $200H_2O$ solution the heat capacity of one mole of H_2O and correcting this value for loss of heat capacity on dilution with the aid of curves for ΔC_p given in Fig. 2.

It is interesting to note that two of these acids show a much smaller increase in heat capacity on neutralization than the strong inorganic acids investigated by Richards and Rowe, while one of them actually shows a decrease in heat capacity. This is fully in accord with what has been noted previously with regard to loss of heat capacity and ionization. The degree of ionization of weak acids being less, the total decrease of ions in the solution on neutralization is less also, so that a smaller increase in heat capacity is to be expected. Even the behavior of $Na_2HC_6H_5O_7$ is not so very abnormal. The concentration of hydrogen ions from $Na_2HC_6H_5O_7 \cdot 100H_2O$ is probably quite small, so that it is quite conceivable that there actually are more ions present in $Na_3C_6H_5O_7 \cdot 200H_2O$ than in equivalent quantities of $NaOH \cdot 100H_2O$ and $Na_2HC_6H_5O_7 \cdot 100H_2O$. Whether this is true is not of great significance since examples of a decrease in heat capacity may be expected in such border cases in which changes of solvation of molecules and polymerization of solvent mask the effect produced by increase in the number of ions formed.

The heats of neutralization of these acids with changing concentration are recorded in Table VII. The results were calculated from the heats of dilution of factors and products with the aid of the well-known thermochemical equations.

TABLE VII

HEAT OF NEUTRALIZATION AT VARIOUS CONCENTRATIONS IN JOULES

(TEMPERATURE, 20°)

Moles of H_2O in factors	50 + 50	100 + 100	200 + 200	400 + 400	800 + 800
In products	101	201	401	801	1601
$H_3C_6H_5O_7$ + NaOH	53881	53298	52965	52825	52806
$H_2NaC_6H_5O_7$ + NaOH	52934	53130	53332	53489	53582
$HNa_2C_6H_5O_7$ + NaOH	53406	54663	55716	56441	56680

The values for the heat of neutralization of these acids are much smaller than those obtained by Richards and Rowe for strong inorganic acids. Furthermore, they do not approach the value 57.07 kj. to which these stronger acids tend at infinite dilution. These substances are, however, only slightly ionized even in the most dilute solutions investigated, so that it is probable that heat effects due to their ionization continue into solutions infinitely dilute.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

Summary

1. The heats of dilution of citric acid, the acid citrates and sodium citrate have been measured at 16 and 20° over the concentration range of 50 moles to 1600 moles of water per mole of substance.

2. The heat capacities over the same range have been calculated with the aid of the Person–Kirchhoff equation.

3. No relationship has been found to exist between the degree of ionization and heat of dilution. Hence some factor or factors other than ionization play a predominant part in the heat of dilution of these solutions.

4. The regularity in the decrease of heat capacity of these solutions has been explained as due to the number of ions formed.

5. The heat of neutralization of citric acid and the acid citrate has been measured. The values found are much less than for strong acids. The temperature coefficient of the heat of neutralization of these acids is decidedly smaller than for inorganic acids and, indeed, in one case, is of opposite sign. These results are discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE VAPOR PRESSURE AND VAPOR DENSITY OF INTENSIVELY DRIED AMMONIUM CHLORIDE[1]

BY WORTH H. RODEBUSH AND JOHN C. MICHALEK

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The anomalous behavior of intensively dried ammonium chloride was first reported in the literature by Baker,[2] who found that the vapor density as determined by a Victor Meyer method indicated no dissociation into ammonia and hydrogen chloride. Baker's work was repeated by Gutmann,[3] who obtained results indicating complete dissociation. Baker[4] again repeated his measurements and remained convinced that the vapor density of intensively dried ammonium corresponds to no dissociation. Two determinations of vapor density were made upon dried ammonium chloride by Johnson[5] with contradictory results. Smith, Eastlack and Scatchard[6] report that Smith and Lombard found no dissociation for dry ammonium chloride vapor but these results have not been published. Most investigators have found the vapor of moist ammonium chloride to be completely dissociated, but here again there is lack of complete agreement and Smith and Lombard[7] in an extensive investigation found only partial dissociation for undried ammonium halides.

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[1] This manuscript was prepared for publication some months ago but publication has been delayed because of the appearance of a preliminary report by A. Smits [*Rec. trav. chim.*, **46**, 445 (1927)] of a similar series of experiments, with results differing from those here reported. A note was published by the authors [*Proc. Nat. Acad.*, **14**, 131 (1928)] commenting on the discrepancies between the two series of experiments. Since a detailed report of Smits' experiments has not appeared, it seemed advisable to submit the manuscript for publication as originally prepared. Meanwhile a paper has appeared by Braune and Knoke [*Z. physik. Chem.*, **135**, 49 (1928)] reporting measurements on undried ammonium chloride which are in substantial agreement with those described in this paper.

[2] Baker, *J. Chem. Soc.*, **65**, 611 (1894).

[3] Gutmann, *Ann.*, **299**, 267 (1898).

[4] Baker, *J. Chem. Soc.*, **73**, 422 (1898).

[5] Johnson, *Z. physik. Chem.*, **61**, 458 (1908).

[6] Smith, Eastlack and Scatchard, THIS JOURNAL, **41**, 1961 (1919).

[7] Smith and Lombard, *ibid.*, **37**, 48 (1915). These authors give references to previous determinations.