

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

THE HEAT OF NEUTRALIZATION OF ACETIC ACID¹

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Introduction

The importance of an accurate determination of the heat of neutralization of acetic acid and its significance in calculating the heat of formation of water from its ions has been emphasized in a recent paper by Richards and Gucker.² In that investigation data were obtained from which the heat of neutralization at various concentrations could be calculated provided the heat of neutralization at any one concentration was known. The data hitherto available for the heat of neutralization of acetic acid were inadequate³ to accomplish this with a degree of accuracy comparable to that of strong acids and bases previously investigated by Richards and Rowe,⁴ for which recalculated values have been presented in a paper of this series.⁵ In this paper are presented accurate data for the heat of neutralization of acetic acid and its change with concentration. From these data, together with those of strong acids and bases, a more probable value for the heat of formation of water from its ions is obtained.

Method and Apparatus

The apparatus was that used by Richards and Gucker for the determination of heats of dilution, modified slightly to make it suitable for the larger temperature changes involved.

The small bottom valve holes (designated a,b, by Richards and Gucker) were enlarged to a diameter of 2.5 mm., while the diameter of the large central valve (designated as c) was reduced to 6 mm. Platinum baffles were soldered over the small valve holes, a,b, in order to deflect the solution from the bottom of the calorimeter into the paths of the stirrers in the annular space.

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 Richards and Gucker, *THIS JOURNAL*, **51**, 712 (1929).

³ Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882, Vol. I, p. 271, gives the value 13.40 Cal. for the heat of neutralization of $\text{HC}_2\text{H}_3\text{O}_2 \cdot 200\text{H}_2\text{O}$ at 20°, and Mathews and Germann, *J. Phys. Chem.*, **15**, 75 (1911), give the value 13.23 Cal. for $N/4$ acetic acid. These values are probably low. Thomsen's results for strong acids are about 2.5% lower than those of Richards and Rowe, while Mathews and Germann used unstandardized thermometers and a Dewar flask as a calorimeter. They disclaimed high accuracy.

⁴ Richards and Rowe, *THIS JOURNAL*, **44**, 684 (1922).

⁵ Richards and Hall, *ibid.*, **51**, 731 (1929).

The experiment was performed by opening the two small bottom valves (a,b), the central valve c about thirty minutes later when mixing was about three-quarters complete and finally five minutes later the side valves. By this procedure the presence of a hot layer on top, with the deleterious effect produced by distillation of water from the solution to the submarine lid was avoided. The temperature difference between the outer bath and calorimeter was well within 0.01° during most of the experiment but rose to 0.04° for about thirty seconds after the central valve was opened. This approach to true adiabacity with the air gap in question was adequate to obtain an accuracy of 0.001° in the measurement of temperature change. Corrections for the temperature drift were applied and the temperature rise was calculated from the resistance change as described by Richards and Gucker.

The heat capacity of the apparatus (76.4 mayers) was calculated from the sum of the heat capacities of its constituent parts in the manner described in the previous publication.²

Preparation and Analyses of Solutions

The sodium hydroxide solution was purified and protected from carbon dioxide in essentially the same manner as that previously employed in this Laboratory.^{4,6} Titration with pure standard hydrochloric acid, using weight burets, showed its concentration to be $\text{NaOH}\cdot 100.99\text{H}_2\text{O}$. The acetic acid solution was prepared from crystallized glacial acetic acid and by comparison with standard sodium hydroxide proved to be of the concentration $\text{HC}_2\text{H}_3\text{O}_2\cdot 100.36\text{H}_2\text{O}$.

TABLE I
HEAT OF NEUTRALIZATION OF ACETIC ACID WITH SODIUM HYDROXIDE^a
 $\text{HC}_2\text{H}_3\text{O}_2\cdot 100.36\text{H}_2\text{O} + \text{NaOH}\cdot 100.99\text{H}_2\text{O}$

Weight, g.	Heat cap./g. mayers	Total heat cap. incl. cal. (mayers)	ΔT	Final T	Δh , Joules	ΔH , Joules
610.63A	4.1338	3.627	19.98	-18413	-56331
610.78B	4.0537	5076.54	3.627	20.02	-18413	-56331
.....	3.625	20.06	-18403	-56300
.....	3.627	20.06	-18413	-56331

Average (ΔH) corrected to $20.00^\circ = -56324$

^a A slight excess of sodium hydroxide was used throughout to avoid as far as possible errors which result from the presence of sodium carbonate.

Δh refers to the heat absorbed by the quantity used in the actual experiment, while ΔH refers to molal quantities. A and B stand for weights of solutions of acid and base, respectively; the rest of the table is self-explanatory.

The specific heats of the solutions were computed from the values at 18° given by Richards and Gucker² for solutions containing exactly 100

⁶ Richards and Gucker, THIS JOURNAL, 47, 1882 (1925).

moles of water per mole of acid or base by correction for the additional water they contained, with the aid of the Person-Kirchhoff equation.

The heats of neutralization of acetic acid with changing concentration are shown in Table II. The results were calculated from the heats of dilution of factors and products⁴ with the aid of the well-known thermochemical equations.

TABLE II
HEAT OF NEUTRALIZATION AT VARIOUS CONCENTRATIONS IN JOULES (20°)
Moles of H₂O

In factors	50+50	100+100	200+200	400+400	800+800
In products	101	201	401	801	1601
HC ₂ H ₃ O ₂ + NaOH	55975	56324	56539	56659	56714

The values given in Table II are depicted graphically in Fig. 1, together with the corresponding values⁵ for hydrochloric and nitric acids. Independent extrapolations of these curves to infinite dilution yield values

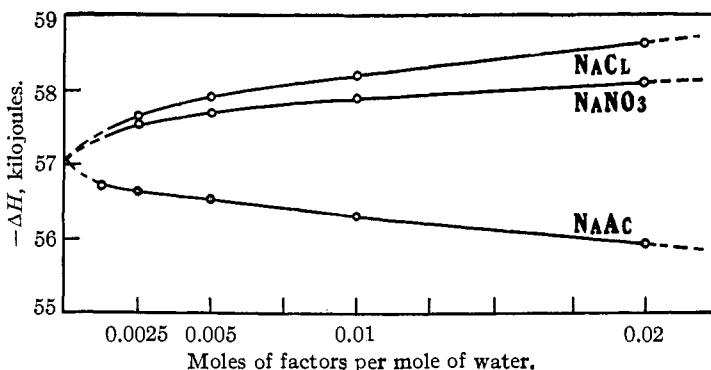


Fig. 1.

ranging from 56.78 to 57.40 kj. Since the reaction at infinite dilution becomes merely $H^+ + OH^- = H_2O$, these curves should approach a common value. Consequently, extrapolation to a point of convergence probably gives a more trustworthy value than the average of the independent extrapolations. Since the curves approach the zero concentration axis from different angles, extrapolation to a point of convergence is less uncertain than was the case with strong acids alone, in which all approached the zero concentration axis from the same direction. A graphical extrapolation to the most probable point of convergence yields the value 57.07 kj, or 13.65 Cal, for the heat of neutralization at infinite dilution.

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Summary

The heat of neutralization of acetic acid and sodium hydroxide was found to be 54,324 joules at 20° at concentrations of $\text{HC}_2\text{H}_3\text{O}_2 \cdot 100\text{H}_2\text{O}$ and $\text{NaOH} \cdot 100\text{H}_2\text{O}$. 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 $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ was found to be 57.07 kj. or 13.65 Cal. at 20°.

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A STUDY OF THE THERMOCHEMICAL BEHAVIOR OF WEAK ELECTROLYTES¹

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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

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).