Summary

1. Several modifications and improvements made in the differential method for the determination of specific heats are presented.

2. The following values were found for specific heats at 18.00°. NaOH·$25H_2O$, 0.9127, thus confirming the recent high value found by Richards and Gucker; NaOH·$50H_2O$, 0.946; NaOH·$100H_2O$, 0.9690 and KOH·$100H_2O$, 0.9567.

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

THE HEATS OF DILUTION OF SODIUM HYDROXIDE, ACETIC ACID AND SODIUM ACETATE, AND THEIR BEARING ON HEAT CAPACITIES AND HEAT OF NEUTRALIZATION[1]

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Introduction

The most convenient and accurate way of studying heats of neutralization at successive concentrations is to determine the heat of neutralization at one concentration and the successive heats of dilution of the factors and products. In previous researches this method has been applied to several strong acids and bases, of which the heat of neutralization was found to *decrease* as the concentration decreased.[2] The present publication presents the first detailed study of an opposite case (acetic acid), in which the heat of neutralization was found to *increase* as the concentration decreased.

Method and Apparatus for Determining Heats of Dilution.—The principles involved in this research are essentially those of the previous dilution experiments.[3] Some differences in experimental detail, however, were applied and the calorimeter was greatly improved. The changes are fully described in the present paper.

The Calorimeter Proper

Figure 1 gives a general idea of the calorimetric apparatus. Two concentric platinum cans were used, the inner, C_2, having half the volume of the outer, C_1. (This assembly was designated Aa by Richards and Rowe.) The inner can always contained the solution and the outer can pure water. The liquids were agitated by two reciprocating stirrers, one, S_2, for the inner can and the other, S_1, for the annular space between the two. A somewhat elaborate mechanism was devised to keep the stirrers rigid (thus

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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] Richards and Rowe, THIS JOURNAL, **44**, 704 (1922).

[3] Richards and Rowe, *ibid.*, **42**, 1621 (1920); **43**, 770 (1921).

avoiding irregular scraping against the sides of the cans). The stroke could be regulated so as to avoid splashing at the surface and still give the maximum permissible stirring.

The calorimeter proper was enclosed in a "submarine" jacket B, which was in turn submerged in a controllable outer water-bath A, described in detail later.

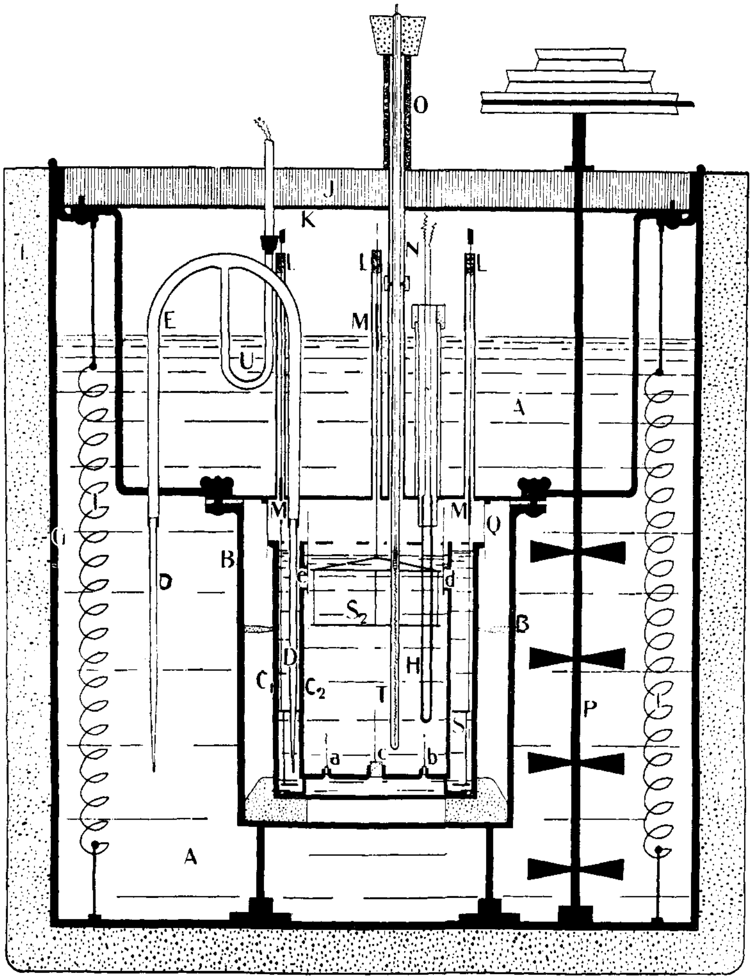

Fig. 1.—Calorimetric apparatus.

Valves between the Concentric Cans.—By opening five valves of different sizes in the inner can, C_2, its liquid could be mixed with that in C_1. The lower valves, a, b, were small platinum plugs, while the upper ones, d, e, were round pieces of thin sheet platinum. Each was sealed with a small quantity of paraffin wax melted into place. The large lower valve, c, was a rubber plug. All the valves were opened by wires passing out of the submarine through fine tubes. Small beads prevented them from being pulled above the level of the solution. The stirrers, moving at the same rate but in opposite directions, helped circulate the liquids and facilitated their mixing.

Thermometric Improvements.—The most important improvements in the present apparatus were (1) the substitution of a platinum resistance thermometer, T, for the mercury thermometer formerly employed to read the calorimeter temperature and (2) the use of a specially constructed thermel, DD, to compare the temperature of the outer water-bath (A) with that of the calorimeter itself. The first of these increased the thermometric sensitivity tenfold, while the second eliminated the necessity of reading two thermometers simultaneously in maintaining adiabatic conditions.

Platinum Resistance Thermometer.—The platinum resistance thermometer was of the Callendar four-lead type, made especially for the purpose by Leeds and Northrup. The pure platinum coil, 10 cm. long, mounted on mica and enclosed in a glass tube, was always completely beneath the level of the liquid in the calorimeter. Its constants were found by the Bureau of Standards (September, 1924) to be: $R_{0°} = 25.301$ international ohms; $R_{100°} = 35.151\omega$; $\delta = 1.51$.

A current of 2.5 m.a. was put through the thermometer coil in these standardizations. During the dilution experiments greater sensitivity was secured by using a current of 5 m.a. A half-dozen careful experiments showed that this increased current raised R_0 by 0.0015ω. This change, though considerable, was constant and a corresponding correction was easily applied.

Resistance Bridge and its Thermostat.—In measuring the resistance of the thermometer coil, a high sensitivity bridge (of the same manufacture) also standardized by the Bureau (August, 1923) was used with many necessary precautions. At the completion of our experiments (April, 1928), a series of ice-points was taken with the thermometer and this bridge and a value $R_0 = 25.304\omega$ was obtained. This showed the magnitude of the change in the thermometer bridge system during the time it was in use. The average value $R_0 = 25.3025\omega$ was taken to compute the isothermal dilution temperatures, which are therefore fixed within ±0.015°. A change of 0.01° in this temperature causes a change as large as 1 joule only in the heat of dilution of sodium hydroxide (which has the largest temperature coefficient). It does not affect at all the *temperature differences* measured or the values of the temperature coefficients and heat capacities.

In order to make thermometer readings significant to 0.0001°, the bridge was enclosed in an efficient air-thermostat, kept constant within 0.01°. The temperature of the resistance coils was undoubtedly yet more constant, since they were enclosed in the wooden and hard rubber box of the bridge.

The thermostat consisted of a large wooden box insulated outside by felt and provided inside with an adequate source of heat, a sensitive thermo-regulator and a fan. The dials and keys of the bridge were operated by extension rods running through the cover of the box.

The bridge was graduated to 0.0001 ohm and the deflections of a high sensitivity galvanometer gave the next decimal place by interpolation. A change of 0.00001 ohm in the resistance of the thermometer (corresponding to a temperature change of 0.0001°) caused a galvanometer deflection of 0.4 mm. External stray currents were kept out of the thermometer and galvanometer circuits by an equipotential shield and parasitic currents in the galvanometer circuit were canceled by a reversing switch.

The Thermel.—One of the chief requisites of precise calorimetry is the maintenance of a really adiabatic condition during an experiment. To compare the temperature of calorimeter and surrounding bath, a thermel connected directly to a galvanometer is more sensitive and convenient than two mercury thermometers. The ordinary glass-encased thermel, however, lags appreciably in registering the temperature difference. Accordingly, for this investigation the thermel was encased in platinum tubes, extending 10 mm. above the surface of the liquid. These were fastened with deKhotinsky cement into the glass tube E, forming the rest of the case. This thermel was compared by Dr. B. J. Mair and Dr. L. P. Hall with a glass-enclosed one similar to that used in the specific heat work[4] and found to respond about three times as rapidly to a change in temperature.

The element itself was of copper-constantan, made in two opposable sections of three couples each. The junctions were made in the usual manner[5] and staggered around the outside of a conical bunch, over a distance of 9 cm., in order to secure a "representative sample" of the temperature of the calorimeter over its whole height. This is one advantage of the thermel over the mercury thermometer, with its small bulb, especially when it is used as a zero instrument with changing temperatures. The cone of insulated wires fitted quite snugly into the metal case but to increase thermal conductivity, the interstices were filled with naphthalene.

The leads were carried inside a small water-proof rubber tube, over which was wound a double spiral strip of copper foil, which formed part of the equipotential shield (including the container of the outer bath, a copper plate under the reversing switch and another beneath the galvanometer). A double-pole double-throw switch, the only one in the circuit, served to reverse the galvanometer and so obtain the true deflection. The sensitivity of the thermel circuit was ample—0.0004° per mm. of scale.

Heating Coil.—A small heating coil H was used to adjust the initial temperature of the calorimeter. It was made from 28 cm. of number 30 B. and S. gage asbestos-insulated constantan wire, threaded through small brass tubing which was bent into a long U and heavily gold plated. The upper ends were cemented into a glass tube which fitted into one of the metal tubes in the "submarine" lid.

Outer Water-Bath.—This bath, of ample size, was thermally insulated by felt (F) and stirred by means of a three-stage propeller P, run at a high speed to insure thorough mixing. It was heated by means of two sets of coils of bare manganin wire, I, I, connected in parallel (each with a resistance of about 22 ohms) and supported on glass frames. To reduce the loss of heat by evaporation, a wooden cover (J) (lined with metal) was fitted over the bath.

Thermal Leakage.—To measure a temperature change with the accuracy of 0.0001°, heat leakage between the calorimeter and its surroundings must be made very small. The three main avenues of thermal leakage are (1) the air gap between calorimeter and jacket, (2) the solid connections bridging this space, and (3) evaporation from the surface of the calorimeter or condensation upon it.

(1) Calculation from Barry's[6] data for a nearly identical calorimeter system showed that an *average* thermal head of not more than ±0.003°, must be maintained during an experiment to avoid appreciable errors from leakage across the air gap. This condition was amply fulfilled during the experiments.

(2) The following precautions were taken to reduce conduction along the necessary solid connections between the calorimeter and the water-bath. The calorimeter was supported on small cork wedges and centered in the submarine jacket by small conical pieces of hard rubber. The platinum wires used to manipulate the valves were terminated just above the surface of the liquid and attached to insulating sections of waxed silk thread (dental floss). The wires supporting the stirrers were fastened into 2-cm. sections of glass tubing MMM to prevent metallic conduction along this avenue. In the small heating coil H the resistance wire was carried across the air gap, since its thermal conductivity was much less than that of the copper leads.

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[4] Richards and Gucker, THIS JOURNAL, **47**, 1883 (1925).

[5] W. P. White, *ibid.*, **36**, 2292 (1914).

[6] Barry, *ibid.*, **44**, 902 (1922).

Heat leakage from the room to the calorimeter over the leads to the temperature indicators was prevented by bringing them to the temperature of the water-bath. The thermel leads passed through a fine copper U-tube (U), which was immersed to the depth of 7 cm. in the water of the outer bath.[7] The protruding portion of the platinum thermometer stem was enclosed in a copper tube N, thermally insulated from the air of the room by a layer of cotton (O). Thus the whole stem was kept very near the temperature of the water-bath. Calculation showed that with the arrangements described the heat leakage by conduction was entirely negligible.

(3) Evaporation affords one of the most important minor possibilities of error in calorimetric work, often insufficiently regarded. One of its effects was pointed out long ago.[8] If the submarine jacket is cooler than the calorimeter, heat is lost from the latter much more rapidly than it is gained if the jacket is the same amount warmer, because in the first case water continuously distils from the calorimeter and condenses upon the jacket.

Barry[9] by careful experiments has also emphasized the importance of this effect. In the present apparatus the paraffined paper collar Q was designed to confine evaporation to the air space immediately above the calorimeter. Supposing this volume of air to be saturated at the beginning of an experiment, the error from additional evaporation, due to the slight change of temperature concerned, could hardly amount to over 0.00001°. Even this small error is at least partly eliminated by noting the temperature drift after the experiment proper. However, if the rise of temperature amounts to 4° (as in many thermochemical determinations) the error involved would be appreciable (0.0006°). If the usual open calorimeter were employed the error might be 0.003° or more.

The thin driving rods of the stirrers were of such cross sections that no significant volume of air was either drawn in or pumped out of the "submarine" during their alternating operation already mentioned. In addition they were packed with cotton (L) at the top of the tubes leading out of the submarine.

Heat Capacity of Apparatus.—The fixed heat capacity of the calorimetric apparatus was calculated as usual (from the weights and heat capacities of all the constituent parts) to be 18.46 (±0.3) cal. per degree, or 77.2 joules per degree (mayers).

The maximum uncertainty (0.03%) of the total heat capacity of the calorimetric system (including the liquids) was unimportant for the present purpose but should be considered in cases where a percentage accuracy of this order is sought.

Materials and Solutions.—The materials were purified and standardized in much the same manner as for the previous research.[4] The most difficult problem was the sodium hydroxide. It was obtained by crystallization from very concentrated solutions with many precautions. The method of standardization of this alkali used in the specific heat experiments and in the first series of dilution experiments has since been shown to be insufficiently exact for the present purpose. Indeed, this would have been suspected at the time, except for the fact that the comparison with "constant boiling" hydrochloric acid and the weighing of sodium chloride had given an identical outcome. The former method, however, is not always trustworthy; the latter is almost certain to yield too high results. It now appears[10] that sodium chloride ob-

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[7] A similar procedure was adopted by Williams and Daniels, THIS JOURNAL, **46**, 905 (1924).

[8] Richards and Burgess, *ibid.*, **32**, 449 (1910).

[9] Barry, *ibid.*, **44**, 899 (1922). W. P. White, likewise, has entirely appreciated the necessity of preventing evaporation.

[10] Richards and Hall, *ibid.*, **51**, 707 (1929). Nearly all the present work was done in 1924–1925 and has been awaiting publication until the subsequent confirmatory work of Richards and Hall could be finished.

tained by evaporation in the particular manner described in our above-mentioned research regularly retains 0.7% of water. The first analysis of the $NaOH \cdot 25H_2O$ solution was, therefore, in error by $0.20H_2O$. All the concentrations in the previous paper are here corrected for this source of error. The final corrected estimate of the concentration of sodium hydroxide employed in the first series of the present work was $NaOH \cdot 25.31H_2O$. That used for the second series was titrated against hydrochloric acid solution, standardized by silver chloride and hence requires no correction.[11]

The acetic acid was a very pure specimen of the glacial acid, which was further purified by three recrystallizations. The composition of the standard acetic acid solution, analyzed by titration against $NaOH \cdot 25.31H_2O$, was found to be $HC_2H_3O_2 \cdot 25.17H_2O$.

We wish to thank Dr. L. P. Hall for the laborious recalculation of the first series of sodium hydroxide dilution experiments and the acetic acid dilution experiments to the true concentrations.

The sodium acetate was a "chemically pure" sample from a responsible firm; it was recrystallized twice from a clear solution as trihydrate and duly centrifuged, etc. The standard solution was made at first somewhat too concentrated; after careful analysis it was diluted quantitatively to the concentration $NaC_2H_3O_2 \cdot 24.99H_2O$. The analysis was conducted by evaporation at 100° and heating to constant weight at 200°. Later experiments (converting the acetate into the anhydrous sulfate in the usual way) showed that the porous powder thus prepared retained only 0.1% of water. This error would affect the heat of dilution by less than 1 joule at the greatest concentration involved and no corrections were made to the observed values.

In calculating the concentrations of these solutions the following atomic weights were used: H = 1.008; O = 16.000; Na = 22.997; C = 12.000 and S = 32.064.

The initial solutions (about $25H_2O$) were kept in stock bottles in the manner already described.[4] For each quantitative dilution the required amounts of solution and of water were weighed out (within 0.01%). Since in the thermochemical determinations the dilutions were made in successive steps, the product of one experiment served as a factor in the next. The products were carefully preserved and protected from evaporation, so that it was unnecessary to analyze the successive more dilute solutions.

Experimental Procedure

The technique of experimentation was planned so as to conserve time and avoid evaporation of the weighed solutions. Description of the individual steps would be helpful to any one repeating the work, but would require too much space for the present record. When all was in place the temperature of the calorimeter system was slowly raised to the desired initial temperature by passing a current through the inner heating coil. The temperature of the outer bath was then made the same (± 0.003°). Finally, the inner heating coil was disconnected and the apparatus kept for at least five minutes under careful adiabatic control before the first accurate reading of the resistance thermometer.

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[11] Richards and Hall (ref. 10), verified these conclusions by making an entirely new solution of sodium hydroxide, analyzing it by titration against a hydrochloric acid solution standardized by precipitation of silver chloride and determining its specific heat with great accuracy. This value exactly agreed with that found by us previously, when allowance was made for the 0.7% of water held by sodium chloride obtained by evaporation. There can thus be no reasonable doubt of the true concentration of sodium hydroxide solution formerly used by us, and of our present solution.

The time of completing the first reading was recorded to the nearest quarter of a minute. Four minutes later a second reading was made, followed by a third, after an equal interval of time. If the temperature trend during these two periods was sufficiently constant, the experiment was started by pulling out the two platinum valves, a,b, (Fig. 1).[12] This was done at the beginning of an upstroke of the inner stirrer so that the first mixing would occur in the center of the apparatus where it was least likely to cause an uneven temperature on the surface of the calorimeters. The temperature change in the latter (as indicated by the thermel) was carefully paralleled in the outside bath by appropriate heating, or cooling by a small stream of ice water dropping directly over the stirrer. The thermal head for the first two minutes was usually about $\pm 0.015°$, but for the rest of the experiment it was less than $\pm 0.003°$. The average temperature of the bath always was kept slightly higher than that of the calorimeter. When about three minutes had passed and the mixing was practically complete, the other valves were opened. Three minutes later the resistance thermometer was again read to determine the temperature change during the experiment. After eight minutes more a final reading was made to determine the temperature trend after the experiment. The temperature of the bridge thermostat was noted after every thermometer reading in order to be sure that it functioned properly.

A Typical Dilution Experiment.—The full data of a typical experiment will show the method of calculating the true rise of temperature and the amount of heat evolved or absorbed in the reaction.

The temperature drift in eight minutes was equivalent to -0.00009 ohm before the experiment; afterward, -0.00005 ohm. The mean drift was, therefore, -0.00007 ohm during eight minutes (the time of the experiment). Hence the change in resistance during the experiment, corrected for this trend, was $+0.00725 - (-0.00007) = +0.00732$ ohm.

The change of resistance was translated into temperature change by means of a difference formula derived from the familiar Callendar equation by Mueller of the Bureau of Standards.[13] It may be written $\Delta T = \Delta\phi R$. The factor ϕ depends upon the mean temperature of the experiment, increasing 0.03% for every degree of temperature rise; in this case it was 10.0613, so that the change in temperature $\Delta T = 0.0737°$. The final temperature of the experiment was 20.09°.

The quantity of heat absorbed in any single experiment (Δh) was calculated from the temperature change and the heat capacity of the system by the equation $\Delta h = -\Delta T c_p$. c_p is the sum of the heat capacities (under constant pressure) of the factors and that of the apparatus. The heat

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[12] When the temperature change was very small (in the experiments at great dilution) the mixing was effected more rapidly by opening the large valves, d, e, first.

[13] Bureau of Standards Bulletin No. 9, reprint 200.

TABLE I

EXPERIMENT NO. 4

May 7, 1925. Dilution: $HC_2H_3O_2 \cdot 25H_2O + 25H_2O = HC_2H_3O_2 \cdot 50H_2O$.

Calorimeters + solution + water, 1557.98 g. Calorimeters + solution, 1008.56 g. Water, 549.42 g. Calorimeters, 387.12 g. Solution 621.44 g.

Resistance Readings of a Single Experiment

Time	Δt, minutes	Bridge reading, ohms[a,b]	Galv. swing, cm.	Corr. reading, ohms[c]	ΔR, ohms
10:14.0		27.2957 (2)	+0.33		
		27.2958 (2)	−0.11	27.29571	
	6.0				−0.00007
10:20.0		27.2957 (2)	+0.04		
		27.2958 (2)	−0.38	27.29564	
	4.0				−0.00004
10:24.0[d]		27.2956 (1)	+0.34		
		27.2957 (2)	−0.11	27.29560	
	8.0				+0.00725
10:32.0		27.3028 (2)	+0.15		
		27.3029 (1)	−0.27	27.30285	
	8.0				−0.00005
10:40		27.3027 (2)	+0.32		
		27.3028 (2)	−0.10	27.30280	

[a] The bridge thermostat read exactly 25.00° before and after the experiment. At no time was the thermal head greater than ±0.008°.

[b] The calibration corrections for the 0.000 R coils (in parentheses) were necessary to interpolate the fifth place correctly, since the change was not exactly 0.0001 ohm in each case.

[c] The interpolated values are corrected by adding the calibration corrections to all coils changed during an experiment (here, 0. R to 0.000 R inclusive).

[d] The upper platinum valves, d, e, were opened at 10:24.0 to start the experiment and the lower rubber valve, c, at 10:27 to ensure complete mixing.

capacity of the factors was determined by multiplying the weight of each by its heat capacity per gram, at the mean temperature of the experiment. The values for the heat capacities of the concentrated solutions were taken from the work of Richards and Gucker,[4] as duly corrected by Richards and Hall.[10]

In this particular experiment (using c_2 to signify the heat capacity of the dilute acetic acid and c_1 that of the water used for further dilution)

$$\begin{array}{lll} c_2 = 622.09 \times 3.9915 & = 2483.1 & \text{mayers (joules per degree)} \\ c_1 = 550.00 \times 4.1836 & = 2301.0 & \text{mayers (joules per degree)} \\ c_a = & \ \ 77.2 & \text{mayers (joules per degree)} \\ \hline c_p = (c_2 + c_1 + c_a) & = 4861.3 & \text{mayers (joules per degree)} \end{array}$$

Hence

$$\Delta h = -\Delta T\, c_p = -(0.737) \times (4861.3) = -358.3 \text{ joules.}$$

The heat absorbed (ΔH) by the dilution of a mole of solute was obtained by dividing the heat absorbed in any experiment (Δh) by the number (N) of moles of solute used.[14]

In this case $N = 1.2114$ and

$$\Delta H = \Delta h/N = -(358.3)/(1.2114) = -295.8 \text{ j.}$$

This value corresponds to isothermal dilution at the *final* temperature, 20.09°, since the heat capacity of the factors was used in the calculation.[15]

From the experimental values of ΔH at approximately 16 and 20° its temperature coefficient was obtained and used to correct the results to exactly 16 and 20°.

Since the data necessary for these calculations are too bulky for publication in complete form, only the results will be presented.

The difference between parallel experiments often was less than 0.5 joule, which corresponded to an error in temperature reading (ΔT) of about 0.0001°. Occasionally (especially in the case of sodium acetate) the difference amounted to four times as much; in such cases more determinations were made. The sodium acetate experiments were chronologically the first; the better agreement in the other cases is to be ascribed to increased experimental efficiency.

Three blank experiments were carried out to determine any temperature change which resulted from pulling out the plugs and mixing the contents of the two calorimeters. The actual experimental conditions were duplicated as closely as possible. In the first case each calorimeter contained water; in the others a $NaOH\cdot 800H_2O$ solution. The results were: $\Delta T = -0.0000_8°$, $\pm 0.0000_0°$, $-0.0000_5°$, making an average of $-0.0000_4°$. This quantity is beyond the limit of experimental accuracy and the experiments show that no appreciable error can have been introduced in mixing the solution.

With sodium acetate the dilutions were carried to $51H_2O$, $101H_2O$, $201H_2O$, etc., in order to measure directly values required to calculate heats of neutralization. The calculation of the heat capacities per gram is discussed later.

The calculations were carried to two doubtful places and only the final results rounded off in order to prevent cumulative errors.

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[14] Attention should be called to a difference between the symbols used in this paper and in previous publications from this Laboratory. Formerly (in conformity with usual practice) U was used to denote diminution of total energy during a reaction (or, where there is no significant change in volume, the heat *evolved*). Unfortunately U recently has been taken to mean the (unknown) total internal energy of a system. $-\Delta U$ in this new notation is identical in meaning to the old U, and ΔH means heat *absorbed* per mole under constant pressure. The new notation, which is now most frequently employed in America, is used herewith; but the whole subject seems to need revision. At present the notation of chemical thermodynamics is in dire confusion, especially because of changes of sign.

[15] Richards, THIS JOURNAL, **25**, 209 (1903).

Note on Sodium Hydroxide.—Two series of determinations were made on the sodium hydroxide solutions. The first series was brought to an abrupt close by a very hot spell in June, 1925. Because of the sudden change of the heat of dilution at the last stage, extrapolation to zero concentration seemed of doubtful value without additional knowledge. Accordingly, in January and February, 1928, the second series was carried out and showed that the heat of dilution actually changed sign at this point. The curve was followed to $NaOH\cdot 3200H_2O$ because, although the percentage accuracy of these figures is not great, they reduce the uncertainty in the final extrapolation to zero concentration.

The diluting water was distilled, then boiled for five to ten minutes to drive out most of the dissolved air and carbon dioxide. Nevertheless, the presence of a minute trace of carbon dioxide would cause the evolution of a relatively large heat of neutralization during the experiment. Tests with barium hydroxide solution gave no precipitate, showing (by comparison with a standard sodium carbonate solution) that the water contained less than 0.00004% carbon dioxide (by weight). The $NaOH\cdot 3200H_2O$ solution, however, showed about 0.00008% of sodium carbonate, which had accumulated during the five dilutions. Estimating that one-eighth of this came from the diluting water and the rest from the air of the room, during the weighing and handling of the solution, a correction, amounting to 0.0002° in each dilution, was applied to the observed heats of dilution in computing the final values and extrapolating to zero concentration. Had this difficulty been fully appreciated at the beginning of the experiments, it might have been avoided by adding to the diluting water enough sodium hydroxide or barium hydroxide to react with the $CO_3^{=}$. The very dilute carbonate solution resulting would probably, as a diluent, be indistinguishable within the limit of accuracy of the present apparatus, from absolutely pure water. To use pure water (containing an amount of carbon dioxide negligible in diluting hydroxide solutions) in such a calorimetric apparatus would be almost impossible.

Heat Capacities.—Knowing the heat capacities of the initial solutions[16] and the heats of dilution at 16 and 20°, the heat capacities of the products of each dilution were calculated by the principle commonly known as Kirchhoff's Law.[17]

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[16] Richards and Gucker, THIS JOURNAL, **47**, 1883 (1925).

[17] $(\Delta H' - \Delta H)/(T' - T) = \Delta C_p$, where $\Delta C_p = C'_p - C_p$. Here C'_p = total heat capacity of products and C_p = total heat capacity of factors. ΔC_p refers to the change in heat capacity at the mean temperature $(T' + T)/2$, in this case 18.00°. Since, however, the change of ΔC_p with temperature may probably be considered negligible over a 4° interval, the same value of ΔC_p was used in calculating specific heats at 16, 18 and 20°.

It is interesting to note that Person in 1851 [*Ann. chim. phys.*, [3] **27**, 250 (1849); [3] **33**, 437 (1851)], from an inductive study of his data on heats of solution and specific

These calculations, like the dilution experiments, were carried out in steps, the heat capacities calculated from one dilution becoming those of the factors of the next. The method is illustrated by the following example involving sodium hydroxide at 16.00°.

Factors	Mol. wt.	c_p (per gram), m.	C_p (per mole), m.	ΔC_p, m.
$NaOH \cdot 25H_2O$	490.41 g.	3.8132	1870.03	
$+ 25H_2O$	450.40 g.	4.1837	1884.34	
			3754.4	−31.4

Product	C_p (per mole), m.	Mol. wt.	c_p (per gram), m.
$NaOH \cdot 50H_2O$	3723.0	940.81 g.	3.9572

From these values in the absolute system those in the 20° calorie system are easily computed by dividing by 4.1805 (the absolute heat capacity of a gram of water at 20°). For the more convenient use of others these heat capacities were reduced to exactly even molal concentrations—for example, those of $25.31H_2O$ to exactly $25H_2O$. In the following tables, II, III and IV, all these data are brought together. They (as well as the other final data in this paper) are, of course, corrected for all known errors.

From the data obtained tables were prepared giving the heats of dilution and the change of heat capacities during dilution of the different solutions of the substances studied (see Tables V, VI and VII).

TABLE II

SODIUM HYDROXIDE

$c_p{}^a$ in mayers (joules/degree) 16°	18°	20°	Solution	$c_p{}^a$ in calories$_{20°}$/degree 16°	18°	20°
3.8132	3.8170	3.8213	$NaOH \cdot 25H_2O$	0.91214	0.91305	0.91408
3.9572	3.9584	3.9599	$NaOH \cdot 50H_2O$	.94659	.94687	.94723
4.0529	4.0526	4.0527	$NaOH \cdot 100H_2O$	.96948	.96941	.96943
4.1127	4.1117	4.1110	$NaOH \cdot 200H_2O$	.98378	.98354	.98338
4.1467	4.1453	4.1442	$NaOH \cdot 400H_2O$	.99191	.99158	.99132
4.1648	4.1633	4.1620	$NaOH \cdot 800H_2O$	.99624	.99589	.99557
4.1741	4.1725	4.1711	$NaOH \cdot 1600H_2O$	.99847	.99809	.99775

[a] Heat capacity (at constant pressure) per gram of substance.

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heats, discovered this same relationship and expressed it in a mathematical equation which can be shown to be identical with the Kirchhoff equation. Since his work predated that of Kirchhoff [Ostwald's "Klassiker der Exakten Wissenschaften," No. 101, reprinted from Kirchhoff, *Pogg. Ann.*, **103**, 77, 206 (1858); **106**, 322 (1859)] by seven years, his priority should be recognized and the principle renamed the "Person-Kirchhoff Law." This would also obviate any confusion between the law just mentioned and the other laws of Kirchhoff in the domain of pure physics.

Other references to the use of this equation follow: Winkelmann, *Ann. Phys. Chem.*, **149**, 1 (1873); Dupre, *Proc. Roy. Soc.*, **20**, 336 (1873); Berthelot, *Ann. chim. Phys.*, [5] **4**, 21 (1875); Pickering, *J. Chem. Soc.*, **57**, 88 (1890); Richards and Lamb, *Proc. Am. Acad.*, **40**, 678 (1905); Brönsted, *Z. physik. Chem.*, **56**, 577–680 (1906); Tucker, *Phil. Trans.*, [A] **215**, 319 (1915); Richards and Rowe, ref. 2.

TABLE III

ACETIC ACID

c_p[a] in mayers (joules/degree)				c_p[a] in calories$_{20°}$/degree		
16°	18°	20°	Solution	16°	18°	20°
3.9900	3.9901	3.9920	$HAc\cdot 25H_2O$	0.95443	0.95446	0.95491
4.0869	4.0853	4.0856	$HAc\cdot 50H_2O$	.97740	.97723	.97730
4.1348	4.1336	4.1330	$HAc\cdot 100H_2O$	.98907	.98878	.98864
4.1592	4.1576	4.1567	$HAc\cdot 200H_2O$	.99491	.99452	.99431
4.1714	4.1698	4.1686	$HAc\cdot 400H_2O$	.99782	.99744	.99715
4.1774	4.1757	4.1743	$HAc\cdot 800H_2O$	.99926	.99885	.99852

[a] Heat capacity (at constant pressure) per gram of substance.

TABLE IV

SODIUM ACETATE

c_p[a] in mayers (joules/degree)				c_p[a] in calories$_{20°}$/degree		
16°	18°	20°	Solution	16°	18°	20°
3.7653	3.7680	3.7712	$NaAc\cdot 25H_2O$	0.90068	0.90133	0.90209
3.9348	3.9355	3.9365	$NaAc\cdot 51H_2O$	.94123	.94140	.94163
4.0447	4.0443	4.0441	$NaAc\cdot 101H_2O$	.96752	.96742	.96737
4.1091	4.1080	4.1075	$NaAc\cdot 201H_2O$	.98292	.98268	.98254
4.1450	4.1435	4.1425	$NaAc\cdot 401H_2O$	.99151	.99115	.99091
4.1637	4.1620	4.1608	$NaAc\cdot 801H_2O$	.99598	.99558	.99529
4.1734	4.1717	4.1704	$NaAc\cdot 1601H_2O$	.99830	.99790	.99758

[a] Heat capacity (at constant pressure) per gram of substance.

The values for infinite dilution were obtained by graphical extrapolation with a Berkeley flexible ruler. The curve for acetic acid was nearly a straight line, which made extrapolation easy. The sodium acetate curve was regular but difficult to extrapolate because it was inclined so obliquely to the axis. The dilute portion of the sodium hydroxide curve was similar to that of sodium acetate.

Considering all the results obtained, including those for the dilution of sodium hydroxide carried out after an interval of two years, it seems probable that the average values for ΔT are not more than 0.0002° from the true value. In considering the accuracy of the tabulated results and the extrapolations, however, it must be remembered that the error in the *molal* heat of dilution is doubled with each step, because the molal heat capacity is doubled. This cumulation of errors is inevitable and should be clearly borne in mind.

The possible error in the molal heat of dilution is increased from about 1.6 j. (in the dilution from $MX\cdot 50$ to $MX\cdot 100H_2O$) to almost 24 j. (in the dilution from $MX\cdot 800$ to $MX\cdot 1600H_2O$). The possible accumulated error in the value for the dilution $MX\cdot 50$ to $MX\cdot 1600$ is therefore about 48 j., and that in any extrapolation to zero concentration might amount to as much as 75 or 100 j.

In the sodium hydroxide solutions the uncertainty of the carbon dioxide correction increases the possible error to 0.0003°, or a possible uncertainty of 150 j. in the extrapolation. The fact that, plotting on a large scale, smooth curves are obtained, makes it probable that the *actual* errors are not as large as the *possible* errors just discussed.

TABLE V

HEATS OF DILUTION (CORRECTED)

Sodium Hydroxide

Moles of water/mole of NaOH		$\Delta H_{16°}$[a]		$\Delta H_{20°}$[a]		$\frac{\Delta H_{20} - \Delta H_{16}}{4}$	
Factor	Product	Joules	20° Cal.	Joules	20° Cal.	Mayers	Cal./Deg.
25	50	587	140.5	461	104.9	−31.4	− 7.5
25	100	1004	240.2	767	183.5	−59.2	−14.2
25	200[b]	1197	285.9	889	212.7	−77.0	−18.4
25	400[b]	1247	298.4	902	215.9	−86.7	−20.7
25	800	1273	292.6	860	205.7	−91.5	−21.9
25	1600	1180	282.3	803	192.1	−95.0	−22.7
25	3200	[1132][c]	[270.8]	749	228.7	[−95.9]	....
25	∞	[1071]	...	[682]	[163.1]	[−97.4]	[−23.2]

[a] All results are corrected for 0.00001% of CO_2 in the diluting water.

[b] The values here recorded are the average of the two series.

[c] Bracketed figures are obtained by extrapolation.

TABLE VI

HEATS OF DILUTION (CORRECTED)

Acetic Acid

Moles of water/mole of HAc		$\Delta H_{16°}$		$\Delta H_{20°}$		$\frac{\Delta H_{20} - \Delta H_{16}}{4}$	
Factor	Product	Joules	20° Cal.	Joules	20° Cal.	Mayers	Cal./Deg.
25	50	−316.1	− 75.6	−296.5	− 71.0	4.9	1.16
25	100	−492.4	−117.7	−461.2	−110.4	7.8	1.95
25	200	−580.7	−138.9	−544.8	−130.4	9.0	2.23
25	400	−624.5	−149.3	−586.9	−140.5	9.4	2.33
25	800	−637.0	−152.3	−608.6	−145.6	7.1	1.53
25	∞	[−653]	[−156]	[−630]	[−151]	[5.8]	[1.4]

TABLE VII

HEATS OF DILUTION (CORRECTED)

Sodium Acetate

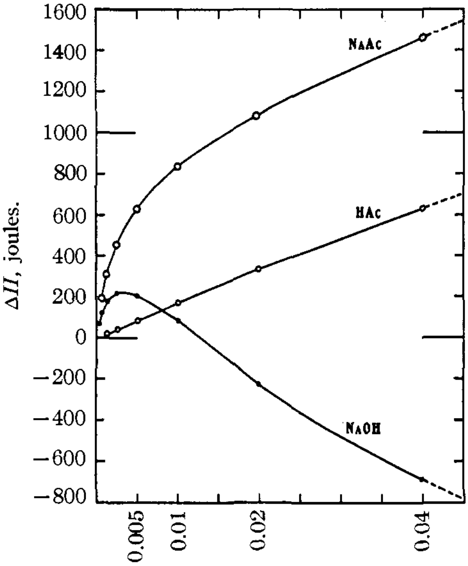
Moles of water/mole of NaAc		ΔH_{16}		$\Delta H_{20°}$		$\frac{\Delta H_{20} - \Delta H_{16}}{4}$	
Factor	Product	Joules	20° Cal.	Joules	20° Cal.	Mayers	Cal./Deg.
25	51	−277.9	− 66.4	− 382.9	− 91.6	−26.3	− 6.3
25	101	−450.8	−107.7	− 623.3	−149.1	−43	−10.4
25	201	−616	−147.2	− 831	−198.6	−54	−12.9
25	401	−766	−183.1	−1007	−241	−60	−14.5
25	801	−894	−213	−1156	−276	−65	−15.7
25	1601	−991	−238	−1275	−312	−71	−17.0
25	∞	[−1152]	[−276]	[−1464]	[−351]	[−78]	[−19]

The heats of dilution in Tables V, VI and VII are plotted in Fig. 2 in such a way as to be most directly comparable.

Since at zero concentration all heats of dilution must approach zero, the curves are drawn from a common origin. The concentration is plotted in moles of solute per mole of water as abscissa, while as ordinate is plotted the heat *absorbed* in going *from* zero concentration *to* that represented by the abscissa of the point.

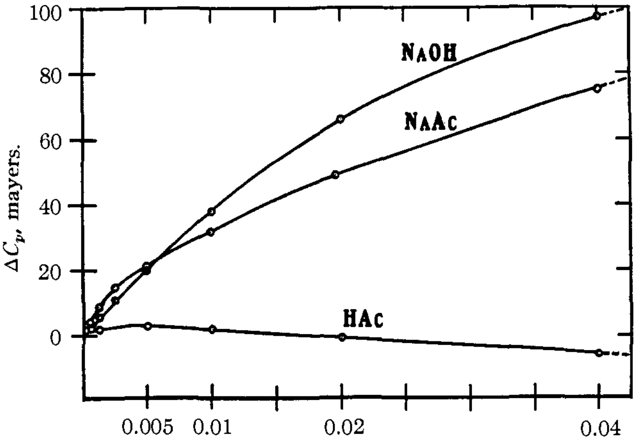
It is interesting to see that in every case at the lowest concentration heat is given out by further dilution. Lange and Messner[18] in their recent study of extremely dilute solutions have found this to be a general rule.

The temperature coefficients of the heats of dilution, which represent the change of heat capacity with change of concentration, were plotted in Fig. 3. Here also the curves are drawn from a common origin, to be more directly comparable. The abscissas again represent concentration and the ordinates the *gain* in heat capacity, per mole of solute, in going *from* zero concentration *to* that repre-



Concentration, moles of substance per mole of water.

Fig. 2.—Heats of dilution.



Concentration, moles of substance per mole of water.

Fig. 3.—Change of heat capacity (in mayers).

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[18] Lange and Messner, *Naturwissenschaften*, **15**, 521 (1927).

sented by the abscissa. The curves for sodium hydroxide and sodium acetate are regular and similar. That of acetic acid is more interesting. In the more concentrated range its slope is opposite to that of the others, but at a concentration of about $HC_2H_3O_2 \cdot 600H_2O$ it changes sign and then behaves normally.

All the solutions of acids, bases and salts studied by Richards and Rowe[19] (including sodium hydroxide) showed a diminution in heat capacity on dilution. This is seen to be true also of sodium acetate and dilute acetic acid solutions. Concentrated acetic acid solutions, however, when diluted show an increase in heat capacity.

The heats of dilution given in Tables V–VII can be used to calculate the change with concentration of the heat of neutralization of sodium hydroxide and acetic acid, by the familiar addition of thermochemical equations.[20]

Knowing the heat of neutralization at any single concentration, the whole course of the curve is fixed. The best value available in the literature is $NaOH \cdot 200H_2O + HC_2H_3O_2 \cdot 200H_2O = NaC_2H_3O_2 \cdot 401H_2O + 13.48$ Cal.[21] Our dilution data show that the heat of neutralization at infinite dilution is 0.04 cal. greater than this, or 13.52 cal. This result is not far below the extrapolated value of 13.62 found for the neutralization of strong acids. It seems safe to conclude that the heat evolved by the reaction $H^+ + OH^- = H_2O$ is not very far from 13.6 cal. The weakest link in this chain is the heat of neutralization of acetic acid at ordinary concentrations, which will be taken up in a paper by Dr. B. J. Mair and one of us.

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

This paper presents new data on the specific heats and heats of dilution at 16 and 20° of sodium acetate, sodium hydroxide and acetic acid. These data are necessary in order to compute the heats of neutralization involved

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[19] Richards and Rowe, THIS JOURNAL, **43**, 788 ff. (1921).

[20] *Cf.* Richards and Rowe, *ibid.*, **44**, 700 (1922).

[21] Thomsen found the heat of neutralization of hydrochloric acid at about 18° to be 13.74 Cal. and that of acetic acid to be 0.34 Cal. less, a difference of 2.5%. The factors in both of these reactions contain $200H_2O$. Richards and Rowe found 57.75 kilojoules for the heat of neutralization of hydrochloric acid at 20° (making a small correction for the error in analysis of the sodium hydroxide used by them). Subtracting 2.5% from this gives 56.3 kilojoules or 13.47 Cal. as the heat of neutralization of acetic acid reduced to the same standard. Mathews and Germann [*J. Phys. Chem.*, **15**, 75 (1911)] find that the heat of neutralization at 18° of 0.25 N $HC_2H_3O_2$ and NaOH is 2.3% less than that of HCl at the same concentration. This would give a value of 56.4 kj., or 13.49 Cal., at 20°, on our standard. The average of these is 13.48 Cal.

at various concentrations. The apparatus has been improved and all temperature measurements made by a platinum resistance thermometer. A careful study of the possible errors has been made and suitable corrections applied for them.

It has been found that although all the other heats of neutralization studied in this way *decrease* as the concentration of the reagents is diminished, that for acetic acid (which is distinctly less than those of stronger acids) *increases* as the solutions become more dilute. Apparently, however, they tend toward the same value at infinite dilution, about 13.6 Cal. (or 56.8 kilojoules), which would appear to be the most probable value for the heat of the reaction $H^+ + OH^- = H_2O$. A more exact evaluation will be found in a later paper of this series.

WILMINGTON, DELAWARE

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

HEATS OF DILUTION AND HEAT CAPACITIES OF HYDROCHLORIC ACID SOLUTIONS[1]

BY T. W. RICHARDS, B. J. MAIR AND L. P. HALL

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Introduction

Since the publication of preliminary data of the specific heats and heats of dilution of hydrochloric acid solutions by Richards and Rowe,[2] more accurate methods for the determination of these data have been developed in this Laboratory.[3] With the aid of these new methods and apparatus the specific heats of hydrochloric acid solutions at various concentrations have been obtained directly and also indirectly from the heats of dilution at 16 and 20°.[4]

Specific Heats of Hydrochloric Acid Solutions

The specific heats of hydrochloric acid solutions at three concentrations were determined in a manner identical with that previously described.[5] A variable but small error may have been caused by the action of the hydrochloric acid on the gold-plated heating coil, particularly at the soldered connections. At first a celluloid cement was used to coat these sections. In spite of this precaution the acid solution was able to attack the solder

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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 authors.

[2] Richards and Rowe, THIS JOURNAL, **42**, 1621 (1920).

[3] (a) Richards and Gucker, *ibid.*, **47**, 1876 (1925); (b) **51**, 712 (1929).

[4] The relationship between the temperature coefficient of the heat of dilution and the heat capacity of the factors and products $(\Delta H' - \Delta H)/(T' - T) = \Delta C_p$ generally known as Kirchhoff's Law was used for this purpose (ref. 2).

[5] Richards and Hall, THIS JOURNAL, **51**, 707 (1929).