

which elevations were in the order of the transport numbers of the cations concerned. If it is assumed that the change in junction potential produced by sodium sulfate is small, one may infer that about $\frac{2}{3}$ of the change produced by sulfuric acid is due to solution-junction potential and the other third to a real increase in the single electrode potential of zinc, due presumably to the depression of the electrolytic dissociation of zinc sulfate.

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THE HEATS OF NEUTRALIZATION OF POTASSIUM, SODIUM AND LITHIUM HYDROXIDES WITH HYDROCHLORIC, HYDROBROMIC, HYDRIODIC AND NITRIC ACIDS, AT VARIOUS DILUTIONS

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The quantity of heat developed by the neutralization of acids with bases has been the subject of numerous investigations. Hess,¹ Graham,² Andrews,³ Favre and Silbermann,⁴ Favre,⁵ Thomsen,⁶ Berthelot,⁷ v. Steinwehr,⁸ Wörmann,⁹ Rümelin,¹⁰ Mathews and Germann¹¹ and Muller¹² (among others) have made measurements of this kind, using many different methods and varying the conditions widely. The fact observed by the earlier experimenters that with strong acids and bases the heat liberated is almost (but not quite) independent of the base or acid used, found explanation when the theory of electrolytic dissociation was developed by Arrhenius.¹³ As every chemist knows, the action is now considered as being essentially that between hydrogen and hydroxyl ions alone, the other ions remaining almost if not quite undisturbed in the process. The experimental results coincided approximately with this theory, but the data available at the time when this investigation was begun were

¹ Hess, *Pogg. Ann.*, **50**, 385 (1840); **53**, 499 (1841); **57**, 569 (1842).

² Graham, *Ann. chim. phys.*, [3] **13**, 188 (1845).

³ Andrews, *Pogg. Ann.*, **54**, 208 (1841); **143**, 101 (1871).

⁴ Favre and Silbermann, *Ann. chim. phys.*, [3] **37**, 494 (1853).

⁵ Favre, *Compt. rend.*, **73**, 772 (1871).

⁶ Thomsen, "Thermochemische Untersuchungen," Barth, vol. I, 1882.

⁷ Berthelot, "Thermochimie," Ganthier, vols. I and II, 1897.

⁸ v. Steinwehr, *Inaug. Diss.*, Göttingen, 1900.

⁹ Wörmann, *Ann. Physik*, [4] **18**, 775 (1905).

¹⁰ Rümelin, *Inaug. Diss.*, Göttingen, 1905.

¹¹ Mathews and Germann, *J. Phys. Chem.*, **15**, 73 (1911).

¹² Muller, *Bull. soc. chim.*, [4] **23**, 8 (1918).

¹³ S. Arrhenius, *Z. physik. Chem.*, **1**, 631 (1887).

not adequate to determine whether the deviations between them were due to differences in the heats of dissociation of the remaining undissociated fractions of the several greatly ionized substances, or whether the differences were due merely to experimental inaccuracies. The thermal behavior of weak acids and bases is indubitably complicated by heats of dissociation.

In seeking an answer to the question, our first step was to determine with accuracy many heats of dilution of strong acids and alkalies, and their salts. The results were published in *THIS JOURNAL* in 1920 and 1921.¹⁴ Of course these heats of dilution (as will be exemplified later) fix the change of heat of neutralization with change of concentration. They were found to be so great, even at considerable dilution, as to influence the heats of neutralization to an important degree. This having been accomplished, the next step was to determine accurately, under precisely similar conditions, many heats of neutralization at one definite concentration, in order to provide a basis for the calculation of accurate values at all other concentrations, and especially to extrapolate the results to infinite dilution, when the heats of dilution would be zero (the idiosyncrasies of the individual salts having supposedly been eliminated) and the result should indicate the true heat of dissociation of water. The results of this part of the work follow. The research, which formed a part of the comprehensive thermochemical study of electrolytes,¹⁵ was begun in 1907, and was continued, with occasional interruptions, for 7 years, the last experimental work recorded in the present paper having been done in June, 1914. Publication has been delayed by the war, and other preoccupations which postponed the time-consuming correlation and recalculation of the copious experimental material.

With the help of the adiabatic calorimeter¹⁶ which has been used in this laboratory since 1905, we hoped to attain greater accuracy than had yet been possible. Serious possibilities of error in the earlier methods were soon discovered. The most important of these errors were found to be: first, defects in the methods of mixing the solutions, involving irregular cooling effects; and second, the presence of carbonate in the alkalies. The outcome leads to a considerably higher estimate of the heat of neutralization of the strong acids and bases than was formerly believed to exist. There is reason to hope that this conclusion is trustworthy, since the various checks and cross-verifications to which the work has been submitted have been satisfactory: the mass of data forms a reasonably

¹⁴ Richards and Rowe, *THIS JOURNAL*, **42**, 1621 (1920); **43**, 770 (1921).

¹⁵ Richards and Rowe, *Proc. Am. Acad.*, **43**, 473 (1908); *Z. physik. Chem.*, **64**, 187 (1908). Richards, Rowe and Burgess, *THIS JOURNAL*, **32**, 1176 (1910). Richards and Rowe, *Proc. Am. Acad.*, **49**, 173 (1913); *Z. physik. Chem.*, **84**, 585 (1913); *THIS JOURNAL*, **42**, 1621 (1920); **43**, 770 (1921).

¹⁶ Richards, Henderson and Forbes, *Proc. Am. Acad.*, **41**, 1 (1905).

consistent whole. Furthermore, the suspicion that the old results were too low has been confirmed in a welcome manner as regards sodium chloride by an interesting result of F. G. Keyes¹⁷ and his assistants, attained by a radically different method without knowledge of the quantitative outcome of our work and entirely independent of it.¹⁸

Because our work dealt with many substances at various temperatures and widely varying concentrations, a variety of interesting conclusions may be drawn from it which were not within reach before. These conclusions are explained in the latter part of this paper.

Apparatus.—The adiabatic calorimeter used in this research has been already described in full detail, having been employed for the heats of dilution of salt solutions with equal volumes of water.¹⁹ It is pictured in the diagram on p. 1623, of *THIS JOURNAL*, vol. 42 (1920).

In brief, it consisted of an inner platinum can (a) of 0.7-liter capacity to contain the alkali, and an outer platinum can of double the capacity, A, to contain the acid in the annular space between the two cans. The inner can was provided with small stoppered baffled holes (g,g) below, and larger stoppered holes (k,k, and C) above and below; these holes could be opened one by one to effect gradual mixing. The stirrers (one in each can) were reciprocating: one rose when the other fell. Thus they exerted a backwards and forwards pumping effect on the liquid, through the holes in the inner can. Since one rose as the other fell, there was little or no tendency to draw in air from the outside, or to expel it. The stirring correction was negligible—and the precision of adjustment was proved by the perfect constancy of temperature before and after the reaction.

The whole was enclosed (with an intervening air space) in a water-tight burnished nickel-plated copper receptacle ("submarine") which was immersed in the outer bath. This outer bath was warmed during a determination at exactly the same rate as the calorimeter, the equality of temperature being established with the help of thermometers both in the inner can of the calorimeter and the annular space, as well as in the outside bath. It was shown that the mixing of acid and alkali progressed with great regularity. No difference of more than 0.03° between the liquid in the innermost can and that in the annular space between a and A ever appeared during the 10 minutes needed for complete neutralization. Hence it was possible to obtain very satisfactory adiabatic conditions; the great difficulty of irregular mixing had been overcome.

The apparatus was arranged in this form primarily in order that the two solutions should have exactly the same temperature at the moment of mixing. Many trials had convinced us of the difficulty of introducing a so-

¹⁷ Keyes, Gillespie and Mitsukuri, *THIS JOURNAL*, **44**, 707 (1922).

¹⁸ Professor Keyes has kindly communicated to me orally the result of his most recent work, which essentially confirms our conclusion that the old values for heats of neutralization were much too low. For a description of the method as applied to dilution, see J. B. Dickson, *Thesis*, Mass. Inst. Technology, Boston, 1917. His value for sodium chloride is even somewhat higher than ours.

¹⁹ Richards and Rowe, *THIS JOURNAL*, **42**, 1622, 1625 (1920).

lution from outside the calorimeter without causing uncertainty as to the exact temperature of this added solution at that moment. Accordingly the two solutions were placed in concentric cans, and thus attained precisely uniform temperature before mixing. The form of apparatus prevented the mixing from being very rapid. This was not a disadvantage, since it enabled the adjustment of the adiabatic conditions to be made with much greater accuracy. Mathematically (according to the usual exponential expression, which, however, probably does not hold here with exactness), the increase of accuracy in this adjustment must be proportional to the increase in time, or the outcome will suffer. This condition was probably more than fulfilled.

The complete mixing of liquids is not always as prompt as it seems. The accurate quantitative analyst knows that he must shake his volumetric solutions very thoroughly in order to attain homogeneity. Thermal homogeneity is perhaps easier to attain than homogeneity of material, since thermal conduction assists in its attainment. In the present case, however, the equable distribution of the *substances* present is necessary, especially if they are present exactly in equivalent proportions. Our custom of al-

ways using a slight excess of alkali was a distinct help in this respect, since our neutralization was complete when the mixing process still lacked 0.5% of completeness. Some of the earlier experimenters on heat of neutralization doubtless lost sight of this danger; in their work the rise of temperature which ought to have been caused by the evolution of the last few calories was masked by the cooling effect, of which usually very inadequate account was taken. The adiabatic method affords the best method of detecting and avoiding this cause of error; it eliminates the cooling effect, and enables the slow conclusion of the mixing process to be followed thermometrically. The accurate study of

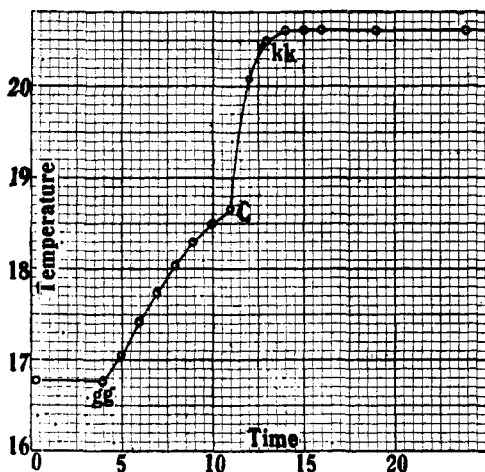


Fig. 1.--The course of a typical experiment. Temperatures are ordinates; times (in minutes), abscissas. After 4 minutes' test of constancy of temperature, the small orifices *g,g* were opened; after 7 minutes more, the central plug *C* was opened; 2 minutes later the side valves *k,k* were opened. The temperature remained exactly constant indefinitely after two minutes' further mixing. The correction for heat developed by stirring was negligibly small

slow reactions is indeed the most important province of the method.

Some experimenters have found difficulty in keeping the outside bath at the same temperature as the calorimeter proper when using an adiabatic calorimeter of this type, but our own experience has been that this is easily accomplished unless the reaction is so rapid as to make the estimation of temperature exchange with the surroundings uncertain according to any method of experimentation. In the present case, as already stated, the rise of temperature was so gradual that there was no difficulty whatever in maintaining the outside bath within a few hundredths of a degree of the temperature of the calorimeter at all times. The most serious possible constant error with any method seems to be from the cooling effect caused by evaporation through the tubes communicating with the outside air. This is much diminished and in most cases rendered harmless by plugging these outlets with cotton wool throughout the experiment; with our apparatus the arrangement of the stirrers almost eliminated it.

The thermometers were standardized with great care.²⁰ Of course the specific heats of the various solutions were necessary in order to make possible the calculation of the results; their determination has already been described in full in earlier papers, the final results for the specific heats having been given in our paper of 1921.

The Preparation of Materials.—The importance of purity of materials was very soon discovered. The heat of neutralization of a carbonate is far less than that of an hydroxide. If the acid is in equivalent quantity, or in excess, of course, both carbonate and hydroxide are neutralized. Accordingly, we used always a slight excess of alkali and soon found that with ordinary caustic solutions, the greater the excess used the greater was the observed heat of neutralization. This was traced to carbonate. When a sufficiently liberal excess of alkali was used to eliminate the influence of carbonate—in other words to leave that substance undecomposed in solution—the results were concordant and ceased to indi-

²⁰ At the time of experimentation the thermochemical thermometers were standardized in an exceedingly thorough and scrupulous manner by comparison with the Paris standards, as represented by our two thermometers Baudin 15200 and 15276. Recently, these two latter thermometers have been repeatedly compared with the platinum standard by O. C. Bridgeman and one of us, (using a Leeds and Northrup platinum thermometer standardized by the U. S. Bureau of Standards) as well as very kindly by Professor H. N. Davis and V. Yngve (using the very accurate platinum thermometers of the Jefferson Physical Laboratory of Harvard University). The two entirely independent series of results with the platinum thermometers essentially agreed. The algebraic sum of the original correction referred to the Baudin thermometers and the supercorrection of the Baudin referred to the platinum standard was applied in each case. Hence, all the results given in this paper refer to the present standard of temperature as indicated by the contemporary platinum thermometer. For the short intervals used in the previous papers on heat of dilution, the Baudin thermometers were essentially correct according to this standard.

cate a larger figure with yet further excess of alkali. Thomsen used an excess of acid. Berthelot expresses his results in terms of alkali, a fact which suggests that he used an excess of acid, although his description apparently implies that exactly equivalent amounts were used. In either case, carbonate would affect the neutralization values. More recent workers may have used more precaution, but this point is not always made entirely clear; at any rate it is not emphasized. Keyes,¹⁷ in his very recent work, quite independently has come to the same conclusion as that to which we came in 1909. There can be no doubt as to the deleterious effect of carbonate in most of the earlier work.

While it was possible to eliminate the effect of carbonate by the use of an adequate excess of alkali, this practice, if carried to an extreme, would cause uncertainty in the calculation of the final value, because of the effect of the excess on the heat capacity of the solution. For that reason, in our work each alkali was carefully freed from carbonate, as indicated below.

In the cases of sodium and potassium very pure imported solid hydroxide was dissolved in a quantity of pure freshly distilled water somewhat less than that needed for the desired concentration. Having been titrated for its carbonate content, this solution was treated with slightly more than the calculated amount of a hot saturated solution of barium hydroxide. After thorough mixing the solution was allowed to stand until the precipitated barium carbonate had completely settled. The clear supernatant liquid was then siphoned into a clean paraffin-lined bottle.²¹ Several portions of this liquid were then drawn off, weighed, neutralized with pure hydrochloric acid and determined as to their barium content, gravimetrically through precipitation as sulfate. The exact amount of very pure sulfuric acid necessary to precipitate the barium present was added to the solution in the paraffin-lined bottle; and after thorough shaking and a sufficient lapse of time, fully protected from the air of the room, the liquid was again siphoned into another paraffin-lined bottle, titrated, diluted to the exact strength with water free from carbon dioxide, and finally analyzed with great care to determine its exact composition. It was protected by a safety tube containing caustic alkali.

The analysis was conducted with great care by means of weight burets, using

²¹ These bottles were of 8- to 20-liter capacity and after having been thoroughly cleaned and dried, were heated to about 80°, when about 0.7 liter of specially purified, melted paraffin was poured into each. With the glass stopper inserted, the bottle was slowly inverted and rotated so that concentric layers of the paraffin formed on the inner surface of the glass walls as the substance solidified. When the neck and shoulders of the bottle were thoroughly coated, the bottle, still constantly rotated, was brought to a horizontal position and the walls in turn were covered. Finally the bottle was restored to its normal position and the remaining paraffin allowed to solidify slowly at the bottom. The glass stopper was next withdrawn and the the paraffin coating across the neck excised with a sharp knife, and the edges of the still warm and plastic paraffin smoothed. The inside of the neck was painted with hot liquid paraffin and when this had cooled the glass stopper, heated to the melting point of the wax, was again inserted and rapidly rotated. The stopper was again withdrawn and the whole allowed to cool. Bottles prepared in this way have been used for over two years without the development of any break in the lining.

methyl red²² as an indicator. The standard was hydrochloric acid, which was prepared in several solutions from time to time and analyzed gravimetrically by precipitation of the chlorine of silver chloride. The acid solutions were analyzed and used soon after preparation, since in time alkali dissolved from even the best glass diminishes slightly the hydrogen-ion concentration without affecting the chloride contents. The titer of the sodium hydroxide solution was proved to remain essentially constant even after having been in a paraffin bottle for over 7 months. The weight burets were of the familiar Ripper type.

Further details concerning the preparation of potassium and sodium hydroxides and of hydrochloric and nitric acids (which last had both been carefully redistilled with the usual precautions) are perhaps unnecessary, but the lithium hydroxide and the two other halogen acids need more detailed discussion. Because no lithium hydroxide of sufficiently pure quality was available in commerce, a quantity was prepared from a special sample of lithium chloride made for this research by the General Chemical Company, Baker and Adamson Works. This contained, according to factory analysis, less than 0.1% of the chlorides of sodium and potassium. Our own analysis (following the procedure recommended by Gooch²³ gave 0.0074 g. of the mixed chlorides in an 8g. sample—an excellent confirmation of the factory analysis. A kilogram of this salt was placed in a very large platinum dish and a small excess of a calculated amount of very pure sulfuric acid added. The mass was heated gradually and the excess of sulfuric acid slowly distilled, while the residue was occasionally stirred with a platinum spatula. The sulfate, found to be practically free from chloride, was weighed and dissolved in a minimum amount of water. A nearly saturated and carefully analyzed solution of very pure barium hydroxide was added in slight excess of the calculated amount to the lithium solution. After the large mass of barium sulfate had subsided, the clear supernatant liquid was siphoned, with the usual precautions against carbon dioxide, into a paraffin-lined bottle, and the excess of barium determined gravimetrically as sulfate. The calculated amount of sulfuric acid was then added to the main solution; and the clear liquid, after the separation of the resulting barium sulfate, was transferred (out of contact with the air of the room) to its final container, analyzed, properly diluted with freshly distilled water free from carbon dioxide, and finally analyzed once more to make certain that the true concentration had been attained. This solution, like the other alkaline solutions, was of course saturated with a trace of barium sulfate and paraffin, but each was harmless as regards our processes.

Hydrobromic acid was prepared by fractional distillation of a sufficiently pure specimen of the substance, likewise manufactured especially for this research. It contained no hydriodic acid and less than 0.1% of hydrochloric acid, which could have had no essential effect on the heat of neutralization, so that the preparation of a purer sample was considered to be unnecessary. Like all the other acids, it was suitably diluted and carefully analyzed by comparison with a known sodium hydroxide solution, standardized as described above.

Hydriodic acid offered difficulties absent in the case of other acids. The substance is unstable: iodine is set free by dissolved oxygen especially in the presence of light, and excess of alkali may thus form hypo-iodites of the several bases. These difficulties were not easy to overcome. Our initial material was concentrated acid especially prepared for this research by the manufacturers already mentioned. The factory analysis showed the amount of hydrochloric acid to be less than 0.03% while hydrobromic acid was absent. The solution contained a small amount of free iodine which imparted a yellow

²² At the time of our earlier titrations, methyl red was not easy to obtain. We are indebted to Professor H. H. Willard for his kindness in furnishing the substance.

²³ Gooch, *Proc. Am. Acad.*, **22**, 177 (1886).

color to the liquid. To this acid was added rather more pure distilled water than would dilute it to the constant boiling mixture and the resulting solution was fractionally distilled in the dark, using a quartz condenser and rejecting the initial portion of the distillate. The pure acid thus obtained was again fractionated under similar conditions and the final yellow distillate set aside for the work. Inasmuch as the oxygen dissolved in the diluent water is the factor determining the decomposition of the acid, water nearly free from this gas was prepared by bubbling very pure hydrogen through it for many hours. Weighed portions of the very pure conc. hydriodic acid were added to the water and, after a thorough shaking, more hydrogen was bubbled through the solution in the dark for another 2 hours. In drawing a sample, this first portion was always rejected together with enough of the unchanged solution to wash the tube thoroughly. The bottles, still kept in a dark cupboard, were connected through a suitable system of glass tubes and stopcocks with the delivery tube of the purifiers of the automatic hydrogen generator, and the withdrawal of acid samples was procured by the admission of the gas under pressure to the acid container. As is shown by the subsequent analyses, these precautions were quite adequate to protect the solutions from serious further decomposition. The small amount of free iodine originally present and still remaining was titrated by sodium thiosulfate, following the analytical procedure recommended by Treadwell.

In carrying out the initial analyses of the hydriodic acid solutions, the following routine was adopted. One of the weight burets was filled with the standard alkali while the other, carefully protected from the sunlight, contained the acid. A portion of acid was run into an Erlenmeyer flask in which had been placed about 0.1 liter of oxygen-free water. Inasmuch as the hydriodic acid was sufficiently concentrated to decompose somewhat the sodium thiosulfate solution, the major portion of the acid was neutralized. Neutral starch paste was added, and then exactly enough of the neutral thiosulfate solution to discharge the blue color of the iodine compound. The acid titration was completed in the usual manner, using methyl red. Preliminary controls showed that the hydrolysis of the sodium tetrathionate did not appreciably affect the end-point of the indicator. In all, three different samples of hydriodic acid were prepared and carefully analyzed.

The fact that the acid contained a little free iodine and that there was the possibility of further decomposition during a calorimetric experiment introduced several factors of uncertainty into the heat measurements. That the acid might decompose during a determination and thus lower the hydrogen-ion concentration was recognized and a procedure designed, as has already been stated, to eliminate error from this source. It was evident, however, that a simple iodine titration at the end of an experiment would not give the true iodine content of the reaction mixture, since some of the iodine would be attacked by the alkali always in excess. For this reason, the following method of analysis was adopted. At the end of a calorimetric determination the entire reaction-mixture was transferred to a large Erlenmeyer flask, starch paste added and thiosulfate solution run in until the blue color was discharged. This titration gave the free iodine remaining in the solution. The liquid was then slightly acidified with standard hydrochloric acid and the blue color again discharged by the addition of more thiosulfate. This gave the amount of iodine bound by the secondary reaction; and the sum of the two titrations gave the total iodine in the portion of acid used. From this, the total amount of free hydriodic acid which had actually been neutralized was readily computed.

The possible effect of the free iodine, however, did not cease here. The extraneous *thermal* effects from the decomposition of the acid during the actual calorimetric measurement and from the secondary hypo-iodite reaction had also to be considered. Fortunately, each of these effects was found to be negligible. By parallel experiments it was

found that only 2 mg. of iodine was set free during the 10 minutes needed for the thermo-chemical work, a quantity too small to affect the outcome appreciably.

The solutions used in the calorimetric work were all very close to a composition represented by the general formulas $\text{MOH} \cdot 100 \text{H}_2\text{O}$ and $\text{HX} \cdot 100 \text{H}_2\text{O}$, almost always within $0.2 \text{H}_2\text{O}$. The specific heats of these solutions were, therefore, within the limit of measurement, identical with those given in our previous paper²⁴ for $100 \text{H}_2\text{O}$ solutions. In making the calculations of the output of heat on a gram-molecular basis, however, the exact concentration of the acid solution, which was always used as a standard of reference, was taken into account, as will be seen in the sequel.

The following tables are typical of the grade of accuracy attained in these titrations, all of which were performed with weight burets.

TABLE I
ACCURACY ATTAINED IN TITRATIONS
Standardization of HCl reference solution

HCl ref. sol. G.	AgCl G.	HCl %
97.9121	9.4323	2.4507
101.9680	9.8233	2.4508
Standardization of $\text{NaOH} \cdot 100 \text{H}_2\text{O}$ calorimetric solution		
HCl ref. sol. G.	NaOH cal. sol. G.	Mols H_2O in NaOH sol.
45.31	56.19	100.205
48.09	59.60	100.183
50.01	62.01	100.190
52.78	65.43	100.168
		Average 100.187

Successive tests of the $\text{HCl} \cdot 100 \text{H}_2\text{O}$ calorimetric solution by comparison with another alkali solution, again using the reference solution as a standard, gave successive values for its molal content of water as follows: 100.060; 100.060; 100.058; 100.077; in mean 100.063. Hence this solution had the formula $\text{HCl} \cdot 100.06 \text{H}_2\text{O}$.

None of these weights was corrected to the vacuum standard, nor were the atmospheric conditions during weighing taken into account, unless these were very extreme, since the possible effects of both these corrections, especially the latter, were beyond the order of accuracy of the calorimetric part of the work. The vacuum correction, if applied, would diminish each final result by only about one part in 14,000 or about 1 calorie, since solid silver chloride was the standard of reference.

The Calorimetric Determinations

With the apparatus and solutions prepared as described, careful calorimetric determinations were made of the heats of neutralization of each of the 4 acids with each of the 3 alkalies, giving 12 varieties of neutrali-

²⁴ Richards and Rowe, *THIS JOURNAL*, 43, 781, 782 (1921).

zation in all. Moreover, each process was conducted over two ranges of temperature, one finishing somewhat above and one somewhat below the temperature of 20.00° , in order to eliminate as much as possible unavoidable errors in the calibration of the thermometers. In a case like this where the heat capacities of the *factors* are used for the calculation of the result, the latter corresponds to an isothermal reaction conducted at the *final* temperature.²⁵ Each pair of results, therefore, was reduced to the value at exactly 20.00° by interpolation from the two values, one obtained above and one below the point desired. Another method of reducing all the results to 20.00° would have been to apply the temperature coefficients as determined in the previous paper to the results for the heat of neutralization at the two temperatures and take the average of the resulting figures. This method yields essentially the same result as the method adopted. The results at the higher and lower temperatures themselves could have been used for the calculation of the temperature coefficient of the reaction, but this seemed to us a questionable practice, since the temperature change (which rarely exceeded 1.5°) was not large enough to give accurate values. The outcome (which averaged about -51 cal. per degree) would represent a small difference between large quantities. Therefore the individual temperature coefficients calculated from these results could hardly be as accurate as the values (averaging also about -51 cal.) calculated from the change of heat capacity in a previous paper.²⁶ The exact agreement of the average values is, however, strong confirmation of the accuracy of the combined corrections which had been applied to the thermometer scale.

The details of a single experiment, taken at random, may be given to elucidate the description (Table II).

The value thus obtained, namely, 13,853 calories (18°) represents the heat of the reaction $\text{HCl.100 H}_2\text{O} + \text{NaOH.100 H}_2\text{O} = \text{NaCl.201 H}_2\text{O}$ at 20.61° . In order to make sure that the neutralization was complete and that there was an excess of ionized hydroxyl, the residual solution was titrated with acid. 1.08 cc. was needed to neutralize it, using phenolphthalein; and 0.40 cc. more was needed to attain the neutral point with methyl orange. Evidently, therefore, an ample, but not too great excess of sodium hydroxide had been present.

Table III contains the summarized results of all the 12 different neutralizations, each at two different temperatures. For the most part the conditions were essentially the same as those described for the detailed experiment. In three of the earlier determinations, (Nos. 8, 9, 10), 2 thermometers were present in the calorimeter in order to make sure of equable distribution of the increasing temperature. Hence in these

²⁵ Richards, *THIS JOURNAL*, **25**, 209 (1903).

²⁶ Richards and Rowe, *ibid.*, **43**, 795 (1921).

TABLE II
THE NEUTRALIZATION OF NaOH.100 H₂O BY HCl.100 H₂O
Series A, No. 4, Feb. 5, 1911 (Serial No. 11 in table below)

Heat capacity of the calorimetric system

	G.	Sp. heat	Heat capacity cal./1°
Platinum (cans, stirrers, wires, valves).....	455.29	0.0324	14.75
Rubber (valves).....	2.65	0.481	1.27
Thermometer II (portion immersed).....	2.48
Beeswax.....	0.23	0.62	0.14
Total heat capacity of apparatus (C')			18.64
HCl.100.06 H ₂ O.....	610.29	0.9634	587.95
NaOH.100.19 H ₂ O.....	615.31	0.9669	594.93
Total heat capacity			1201.52

Temperature change

Initial temperature (T_1) corrected.....	16.784°
Final temperature (T_2) corrected.....	20.612°
Difference ($T_2 - T_1$).....	3.828°
Corr. for stem temperature (24.0°).....	-0.002
$T_2 - T_1$	3.826°

Heat evolved (Q) = 1201.52 × 3.826° = 4596.9 cal.

610.29 g. HCl.100.06 H₂O solution = 0.33183 mol HCl

Therefore heat per mol acid = $U = \frac{4596.9}{0.33183} = 13,853$ cal.

determinations the heat capacity of the apparatus was 20.13 units, instead of 18.64 units, which was the value in Serial Nos. 11 and 12. In all the other determinations the calorimeter was somewhat strengthened with extra platinum, but the second thermometer, having been found unnecessary, was omitted. In these cases (all except 8, 9, 10, 11, 12) the heat capacity of the apparatus was 18.98 units. The specific heats of the 7 solutions containing (per 100 mols of water) one mol each of KOH,²⁷ NaOH, LiOH, HCl, HBr, HI and HNO₃ had been found in earlier parts of the research, and were accordingly taken as 0.9567; 0.9669; 0.9813; 0.9634; 0.9433; 0.9213 and 0.9583, respectively.²⁸ As above, the 18° calorie is the heat unit indicated in the comprehensive table of data, since 18° was the mean temperature in both the specific heat and neutralization determinations. These values are afterwards expressed in terms of 20.00° calories and also of kilojoules. The atomic weights used are the current international values: H = 1.008; O = 16.00; K = 39.10; Na = 23.00; Li = 6.94; Cl = 35.46; Br = 79.92; I = 126.92; N = 14.008.

²⁷ Attention is called to an unfortunate error in the specific heat of KOH.100 H₂O in our previous paper (Ref. 24, p. 782). The molecular weight was wrongly taken as 1859.7 instead of 1857.7. Accordingly the specific heat was given as 0.9556 instead of the true value 0.9567. Compare *Proc. Am. Acad.*, 49 198 (1913).

²⁸ Ref. 15; see our papers, p. 198 (1913); p. 1632 (1920) and pp. 781, 782 (1921).

TABLE III
HEATS OF NEUTRALIZATION (U) OF FOUR ACIDS BY THREE BASES

Each given at three temperatures in 18° calories

HYDROCHLORIC ACID						
Expt.	Weight of HCl sol. + 100.15 H ₂ O	Weight of KOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	U_{T°	U_{20°
1	610.20	618.64	20.68	3.864	13,972	
2	610.25	618.68	20.61	3.865	13,976	
3	610.24	619.72	20.61	3.862	13,973	
Heat of neut. HCl.100 H ₂ O + KOH.100 H ₂ O at 20.63°					13,974	
4	610.34	619.62	19.47	3.876	14,026	
5	610.25	619.65	19.55	3.879	14,038	
6	610.28	619.69	19.41	3.877	14,031	
7	610.26	619.62	19.58	3.879	14,037	
Heat of neut. HCl.100 H ₂ O + KOH.100 H ₂ O at 19.50°					14,033	
Heat of neut. HCl.100 H ₂ O + KOH.100 H ₂ O at 20.00°						14,007
Expt.	Weight of HCl sol. + 100.06 H ₂ O	Weight of NaOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	U_{T°	U_{20°
8	610.26	615.24	20.63	3.824	13,863	
9	610.24	615.29	20.61	3.822	13,855	
10	610.16	615.26	20.68	3.821	13,848	
11	610.29	615.31	20.61	3.826	13,853	
12	610.27	615.31	20.57	3.828	13,860	
Heat of neut. HCl.100 H ₂ O + NaOH.100 H ₂ O at 20.62°					13,856	
13	610.22	615.42	19.50	3.841	13,912	
14	610.24	615.44	19.55	3.841	13,912	
15	610.26	615.42	19.42	3.843	13,918	
16	610.24	615.42	19.56	3.844	13,915	
Heat of neut. HCl.100 H ₂ O + NaOH.100 H ₂ O at 19.50°					13,914	
Heat of neut. HCl.100 H ₂ O + NaOH.100 H ₂ O at 20.00°						13,888
Expt.	Weight of HCl + 100.00 H ₂ O	Weight of LiOH sol.	Final tempera- ture ° C.	$T_2^\circ - T_1^\circ$ corrected ° C.	U_{T°	U_{20°
17	610.30	609.37	20.71	3.843	13,946	
18	610.28	609.37	20.75	3.844	13,949	
19	610.27	609.37	20.68	3.844	13,949	
Heat of neut. HCl.100 H ₂ O + LiOH.100 H ₂ O at 20.71°					13,948	
20	610.27	609.42	19.34	3.863	14,018	
21	610.29	609.39	19.33	3.864	14,022	
22	610.29	609.39	19.37	3.863	14,019	
Heat of neut. HCl.100 H ₂ O + LiOH.100 H ₂ O at 19.35°					14,020	
Heat of neut. HCl.100 H ₂ O + LiOH.100 H ₂ O at 20.00°						13,985

HYDROBROMIC ACID

Expt.	Weight of HBr + 100.20 H ₂ O	Weight of KOH sol.	Final tempera- ture °C.	$T_2^\circ - T_1^\circ$ corrected °C.	U_T°	U_{20}°
23	630.20	624.78	20.67	3.847	13,945	
24	630.20	624.78	20.73	3.848	13,949	
25	630.20	624.78	20.72	3.841	13,924	
26	630.20	624.78	20.74	3.846	13,942	
Heat of neut. HBr.100 H ₂ O + KOH.100 H ₂ O, at 20.72°					13,940	
27	630.20	624.68	19.39	3.867	14,016	
28	630.20	624.78	20.35	3.868	14,021	
29	630.20	624.78	20.38	3.866	14,015	
30	630.20	624.78	20.38	3.866	14,015	
Heat of neut. HBr.100 H ₂ O + KOH.100 H ₂ O at 19.38°					14,017	
Heat of neut. HBr.100 H ₂ O + KOH.100 H ₂ O at 20.00°						13,981
Expt.	Weight of HBr + 100.20 H ₂ O	Weight of NaOH sol.	Final tempera- ture °C.	$T_2^\circ - T_1^\circ$ corrected °C.	U_T°	U_{20}°
31	630.20	618.35	20.66	3.810	13,813	
32	630.20	618.28	20.66	3.810	13,812	
33	630.20	618.35	20.64	3.807	13,802	
34	630.20	618.35	20.72	3.806	13,800	
Heat of neut. HBr.100 H ₂ O + NaOH.100 H ₂ O at 20.67°					13,807	
35	630.20	618.31	19.33	3.823	13,860	
36	630.20	618.28	19.34	3.826	13,871	
37	630.20	618.33	19.38	3.824	13,863	
38	630.20	618.33	19.36	3.825	13,867	
Heat of neut. HBr.100 H ₂ O + NaOH.100 H ₂ O at 19.35°					13,865	
Heat of neut. HBr.100 H ₂ O + NaOH.100 H ₂ O at 20.00°						13,836
Expt.	Weight of HBr + 100.24 H ₂ O	Weight of LiOH sol.	Final tempera- ture °C.	$T_2^\circ - T_1^\circ$ corrected °C.	U_T°	U_{20}°
39	630.27	612.38	20.74	3.835	13,974	
40	630.28	612.39	20.70	3.833	13,967	
41	630.27	612.40	20.71	3.833	13,967	
42	630.27	612.27	20.67	3.833	13,967	
Heat of neut. HBr.100 H ₂ O + LiOH.100 H ₂ O at 20.71°					13,969	
43	630.28	612.40	19.36	3.849	14,026	
44	630.29	612.39	19.38	3.851	14,033	
45	630.28	612.39	19.40	3.852	14,036	
46	630.29	612.38	19.38	3.851	14,033	
Heat of neut. HBr.100 H ₂ O + LiOH.100 H ₂ O at 19.38°					14,032	
Heat of neut. HBr.100 H ₂ O + LiOH.100 H ₂ O at 20.00°						14,002

HYDRIODIC ACID^a

Expt.	Weight of HI sol.	Weight of KOH sol.	Final temperature °C.	$T_2^\circ - T_1^\circ$ corrected °C.	U_T°	U_{20}°
47	640.30	627.39	20.49	3.821	13,886	

48	640.27	622.37	19.31	3.827	13,945	
49	640.32	637.41	19.30	3.776	13,935	
Heat of neut. KOH.100 H ₂ O + HI.100 H ₂ O at 19.30°					13,940	
Heat of neut. KOH.100 H ₂ O + HI.100 H ₂ O at 20.00°						13,908
Expt.	Weight of HI sol.	Weight of NaOH sol.	Final temperature °C.	T ₂ ° - T ₁ ° corrected °C.	U _T °	U ₂₀ °
50	640.32	619.42	20.66	3.788	13,742	
51	640.29	619.42	20.69	3.787	13,738	
Heat of neut. NaOH.100 H ₂ O + HI.100 H ₂ O at 20.67°					13,740	
52	640.29	619.41	19.35	3.810	13,806	
53	640.31	619.38	19.31	3.810	13,812	
54	640.27	619.42	19.35	3.809	13,801	
Heat of neut. NaOH.100 H ₂ O + HI.100 H ₂ O at 19.34°					13,806	
Heat of neut. NaOH.100 H ₂ O + HI.100 H ₂ O at 20.00°						13,773
Expt.	Weight of HI sol.	Weight of LiOH sol.	Final temperature °C.	T ₂ ° - T ₁ ° corrected °C.	U _T °	U ₂₀ °
55	640.30	607.40	20.72	3.834	13,884	
56	640.30	607.37	20.70	3.827	13,880	
Heat of neut. LiOH.100 H ₂ O + HI.100 H ₂ O at 20.71°					13,882	
57	640.30	607.40	19.44	3.844	13,941	
58	640.30	607.37	19.45	3.846	13,949	
59	640.30	607.37	19.45	3.845	13,946	
Heat of neut. LiOH.100 H ₂ O + HI.100 H ₂ O at 19.45°					13,945	
Heat of neut. LiOH.100 H ₂ O + HI.100 H ₂ O at 20.00°						13,918

^a In each of these individual determinations the amount of hydriodic acid actually neutralized was carefully determined in the way already described. The individual amounts of HI in determinations Nos. 47 to 59 inclusive were, respectively, 42.563, 42.283; 42.250; 42.583; 42.582; 42.634; 42.613; 42.634; 42.565; 42.568; 42.570; 42.568 and 42.565 g. The full details of these laborious determinations would take too much space here, but the several quantities must be used in the calculation of *U*.

NITRIC ACID

Expt.	Weight of HNO ₃ + 100.19 H ₂ O	Weight of KOH sol.	Final temperature °C.	T ₂ ° - T ₁ ° corrected °C.	U _T °	U ₂₀ °
60	620.24	620.65	20.62	3.862	14,040	
61	620.27	620.62	20.66	3.863	14,043	
62	620.25	620.63	20.61	3.862	14,038	
Heat of neut. KOH.100 H ₂ O + HNO ₃ .100 H ₂ O at 20.63°					14,040	
63	620.24	620.17	19.47	3.885	14,119	
64	620.24	620.65	19.49	3.876	14,091	
65	620.24	620.64	19.49	3.880	14,106	
66	620.24	620.62	19.50	3.880	14,106	
67	620.27	620.64	19.57	3.882	14,112	
68	620.26	620.64	19.55	3.884	14,120	
Heat of neut. KOH.100 H ₂ O + HNO ₃ .100 H ₂ O at 19.52°					14,109	
Heat of neut. KOH.100 H ₂ O + HNO ₃ .100 H ₂ O at 20.00°						14,079

Expt.	Weight of HNO ₃ + H ₂ O	Weight of NaOH sol.	Final temperature °C.	T ₂ ° - T ₁ ° corrected °C.	U _T °	U ₂₀ °
69	620.25	614.62	20.64	3.795	13,800	
70	620.25	614.62	20.55	3.796	13,803	
71	620.27	614.65	20.48	3.798	13,810	
72	615.24	614.67	20.55	3.778	13,795	
Heat of neut. NaOH .100 H ₂ O + HNO ₂ .100 H ₂ O at 20.55°					13,802	
73	620.26	614.58	19.29	3.810	13,855	
74	620.18	614.69	19.43	3.809	13,853	
75	620.27	614.68	19.33	3.813	13,866	
76	620.24	614.62	19.38	3.811	13,858	
77	620.27	614.62	19.32	3.815	13,873	
78	620.25	614.67	19.37	3.812	13,862	
79	620.25	614.67	19.47	3.813	13,865	
Heat of neut. of NaOH .100 H ₂ O + HNO ₃ .100 H ₂ O at 19.37°					13,862	
Heat of neut. of NaOH .100 H ₂ O + HNO ₃ .100 H ₂ O at 20.00°						13,830
Expt.	Weight of HNO ₃ + H ₂ O	Weight of LiOH sol.	Final temperature °C.	T ₂ ° - T ₁ ° corrected °C.	U _T °	U ₂₀ °
80	620.27	610.37	20.68	3.786	13,823	
81	620.27	610.35	20.66	3.786	13,823	
82	620.29	610.40	20.72	3.787	13,826	
83	620.32 ^a	611.85	20.68	3.785	13,824	
84	620.32 ^a	611.82	20.68	3.785	13,824	
Heat of neut. LiOH .100 H ₂ O + HNO ₃ .100 H ₂ O at 20.690°					13,824	
85	620.27	610.37	19.31	3.804	13,887	
86	620.29	610.37	19.29	3.805	13,891	
87	620.29	610.39	19.29	3.805	13,891	
88	620.29 ^a	615.37	19.33	3.797	13,891	
89	620.30 ^a	611.82	19.33	3.804	13,893	
Heat of neut. LiOH .100 H ₂ O + HNO ₃ .100 H ₂ O at 19.30°					13,890	
Heat of neut. LiOH .100 H ₂ O + HNO ₃ .100 H ₂ O at 20.00°						13,856

^a These four determinations were made subsequently to the others with entirely new solutions. The new nitric acid solution was of the composition HNO₃ .100.09 H₂O, a circumstance which must be taken into account in calculating these four determinations.

After the conclusion of these systematic determinations, which took many months, a single confirmatory calorimetric determination was made with each pair of solutions (excepting those pairs including potassium hydroxide, of which all our pure material had been exhausted). In some cases fresh solutions were prepared and analyzed; in others new analyses were made of solutions used before. The confirmation was on the whole very good, the maximum deviation of a single determination from the appropriate average given above being less than 0.07%, and the mean deviation being only 0.04%. These check determinations were made at various temperatures in the neighborhood of 20.00°; of course, the

temperature coefficient of the reaction was duly reckoned into this calculation. The satisfactory agreement of these "control" determinations tends to show that no serious accidental error could have entered into the work. Even if some unsuspected *constant* error should have been present, it must have affected all the results alike, and hence be without effect on the comparison of the several values.

This being the case, it is a matter of great interest to compare the results with one another, and of still greater interest to compare them with values of heats of neutralization at other concentrations. First, the values may be tabulated as follows (each augmented by 0.05% in order to convert it to terms of the 20.00° calorie, and also reduced to kilojoules) in parallel columns (1 cal. (20.00°) = 0.004180 kj.).

TABLE IV
VALUES OF U_{20° OF NEUTRALIZATION YIELDING MX.201 H₂O
In 20° calories and kilojoules

	KOH		NaOH		LiOH	
	Cal.	Kj.	Cal.	Kj.	Cal.	Kj.
HCl.....	14,014	58.58	13,895	58.08	13,993	58.49
HBr.....	13,988	58.47	13,843	57.86	14,009	58.56
HI.....	13,915	58.16	13,780	57.60	13,925	58.21
HNO ₃	14.086	58.87	13,837	57.83	13,863	57.94

The values thus arranged show some systematic tendency: in particular, those for potassium salts are always greater than those for sodium salts, and those for bromides always greater than those for iodides. Nevertheless in other cases they exhibit distinct irregularity.

For the sake of completeness the temperature coefficients of six of these heats of neutralization are given below, having been calculated from the heat capacities of factors and products in our previous paper (p. 795). The necessary data for the other six have not yet been determined, but will be studied in the near future.

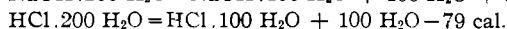
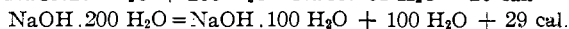
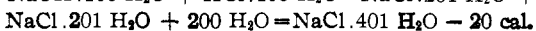
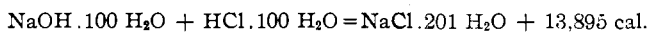
TABLE V
TEMPERATURE COEFFICIENTS OF HEATS OF NEUTRALIZATION
In calories and kilojoules per 1°

	G. calorie units		Kilojoule units	
	HCl.100 H ₂ O	HNO ₃ .100 H ₂ O	HCl.100 H ₂ O	HNO ₃ .100 H ₂ O
LiOH (100 H ₂ O).....	-55.4	-53.6	-0.232	-0.224
NaOH (100 H ₂ O).....	-52.7	-50.5	-0.220	-0.211
KOH (100 H ₂ O).....	-48.4	-45.1	-0.202	-0.189
Av.....	-52.1	-49.7	-0.218	-0.209

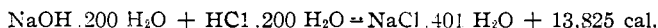
Most properties of solutions tend toward greater regularity with increasing dilution. Therefore, it is desirable to discover the change in heat of neutralization with increasing volume; this was indeed one of the chief objects of the research. The calorimetric work of others was not suffi-

ciently precise to form the basis of any certain conclusions with regard to the question. Our data, however, furnish exactly the best means of securing the desired values. For example, the heat of the reaction $\text{NaOH} \cdot 200 \text{ H}_2\text{O} + \text{HCl} \cdot 200 \text{ H}_2\text{O} = \text{NaCl} \cdot 401 \text{ H}_2\text{O}$ may be obtained from the data concerning more concentrated solutions by simply taking account of the heats of dilution of factors and products, without performing anew the actual experimental calorimetric neutralization of the dilute solutions. The needed heats of dilution are implied in the figures recorded in our next previous publication.²⁹ Each value needed for this particular case may be obtained very simply by subtraction of two figures there given; *e. g.*, in the case of sodium hydroxide, the value -127 given for the reaction $\text{NaOH} \cdot 10 \text{ H}_2\text{O} + 90 \text{ H}_2\text{O}$ is subtracted from the value -156 given for the reaction $\text{NaOH} \cdot 10 \text{ H}_2\text{O} + 190 \text{ H}_2\text{O}$.³⁰ The difference (-29 cal.) is the heat of dilution of $\text{NaOH} \cdot 100 \text{ H}_2\text{O}$ to $\text{NaOH} \cdot 200 \text{ H}_2\text{O}$.

Applying the values thus calculated to the case in hand (transposing the dilution equations of the factors) we obtain the following typical thermochemical calculation, which gives the desired heat of neutralization in the more dilute solution.



Therefore

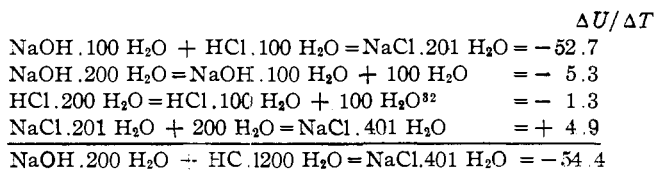


This result was satisfactorily confirmed by a series of direct neutralization experiments with the above named dilute solutions, carrying out calorimetrically the reaction $\text{NaOH} \cdot 200 \text{ H}_2\text{O} + \text{HCl} \cdot 200 \text{ H}_2\text{O} = \text{NaCl} \cdot 401 \text{ H}_2\text{O}$. These experiments were made, indeed, before the determination of the heat of dilution of the salt solution had made the above calculation possible. Ten determinations of this kind were made; the final temperatures (varying from 17.44° to 20.65°) averaged 18.89° , and the average rise of temperature was about 1.9° . Naturally the agreement between

²⁹ Ref. 24, pp. 779, 780. It should be noted that the heat of dilution of $\text{NaCl} \cdot 201 \text{ H}_2\text{O}$ to $\text{NaCl} \cdot 401 \text{ H}_2\text{O}$ is 0.3 cal. different from that of $\text{NaCl} \cdot 200 \text{ H}_2\text{O}$ to $\text{NaCl} \cdot 400 \text{ H}_2\text{O}$, as found from the curves giving heats of dilution at various concentrations. Even with double these concentrations the added molecule of water also makes less than 1 cal. difference. Only in the case of potassium nitrate is the correction important (4 cal.) with this concentration. On diluting salt solutions containing as little as 50 H_2O the extra molecule has a more important effect, amounting to the following quantities: KCl , 3 cal.; KNO_3 , 13 cal.; NaCl , 6 cal.; NaNO_2 , 8 cal.; LiCl , 3 cal.; LiNO_3 , 0.6 cal. All these corrections are applied in the table following. The sign of each correction is obvious; in each case it *diminishes* the thermal effect.

³⁰ These values are more trustworthy than those from $\text{NaOH} \cdot 5.77 \text{ H}_2\text{O}$, since these latter were the first dilution experiments carried out, and were less satisfactory in many ways than the later experiments.

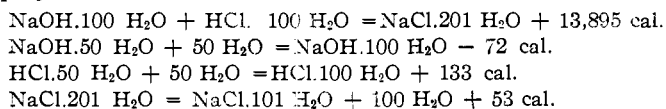
the successive results was less satisfactory than with the more concentrated solutions; the values ranged between 0.15% above to 0.15% below the mean, after correcting each value to the same temperature, and the "probable error" of the average result (13,879 cal. 18°) was about 3 cal. This evolution of heat corresponds to the isothermal reaction at 18.89°; and we need that at 20.00°. The temperature coefficient of the reaction may be found as usual from the difference of the heat capacities of factors and products on dilution³¹ as follows (the signs in the second and third equations below being changed, because they apply in the reverse direction).



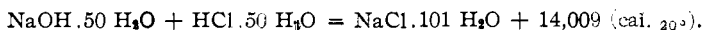
The decimals of these figures can hardly be certain, but the outcome is exact enough to show that the temperature coefficient of the dilute neutralization is not far from -54.4 cal./°C. The value 13,879 cal. at 18.89° then becomes 13,819 cal._{18°} when corrected to 20.00°, or 13,826 cal._{20°}.

The agreement of this result, 13,826, with that calculated in the more satisfactory way from the data for more concentrated solutions, with the help of dilution-heats, namely, 13,825, must be partly accidental, since it is much within the limit of error for the quantities concerned. Evidently the "control" thus afforded as to the data for all of the properties involved is entirely satisfactory.

The method of calculation from dilution-heats, being far more convenient and probably more exact than the direct determination in very dilute solutions, was used in calculating also the heats of neutralization of the five other processes for which data were available. Not only the values for the more dilute solutions were thus obtained; the values of the heats of neutralization for more concentrated solutions were calculated in a similar fashion. For example, to compute the heats of the reaction $\text{HCl.50 H}_2\text{O} + \text{NaOH.50 H}_2\text{O} = \text{NaCl.101 H}_2\text{O}$ the following equations are employed.



Therefore



³¹ Ref. 24, pp. 779, 780, 795.

³² Taken from the curve in our paper of 1920 on p. 1634.

In the same way the reaction $\text{NaOH} \cdot 25 \text{H}_2\text{O} + \text{HCl} \cdot 25 \text{H}_2\text{O}$ was found to give 14,227 cal.

For the stage of dilution involving factors containing 400 mols of water, it was needful to obtain the corresponding values of heats of dilution of the products (to 0.0695 *N*, containing 801 H_2O) by slight extrapolation from the experimental results. This was done on a large scale with great care; curves were drawn like those in the next previous paper, using calories instead of kilojoules.³³ Thus the heats of dilution of the several salt solutions from 201 to 801 mols of water were found to be as follows: KCl , -26; KNO_3 , -218; NaCl , -31; NaNO_3 , -112; LiCl , +62; LiNO_3 , +43 cal. These values were combined as before with the appropriate values found directly for the alkalis and acids (diluted from 100 to 400 mols of water) to calculate the heats of neutralization of these very dilute solutions. The experimental errors are greatly magnified in the calculation, therefore the results are necessarily less trustworthy than those with greater concentrations; but at least they present the best information now available concerning the questions chiefly at issue.

The results thus found are recorded in the following double table which records all the values first in 20° calories and again in kilojoules.

HEATS OF NEUTRALIZATION AT VARIOUS CONCENTRATIONS
In 20° calories (temperature 20°)

Mols H_2O In factors = In products = Reaction						Extra- polated (Parabolic)
	25 + 25	50 + 50	100 + 100	200 + 200	400 + 400	801 Infinite
$\text{KOH} + \text{HCl}$	14,569	14,209	14,014	13,905	13,819	13,695
$\text{KOH} + \text{HNO}_3$	14,724	14,325	14,086	13,934	13,834	13,700
$\text{NaOH} + \text{HCl}$	14,228	14,009	13,895	13,825	13,761	13,660
$\text{NaOH} + \text{HNO}_3$	14,012	13,892	13,837	13,790	13,756	13,705
$\text{LiOH} + \text{HCl}$	14,433	14,149	13,993	13,889	13,803	13,685
$\text{LiOH} + \text{HNO}_3$	13,986	13,905	13,863	13,825	13,788	13,715
					Average	13,693
	In kilojoules (temperature 20°) (1 kilojoule = 4,180 calories (20°))					
$\text{KOH} + \text{HCl}$	60.90	59.39	58.58	58.12	57.76	57.25
$\text{KOH} + \text{HNO}_3$	61.55	59.88	58.88	58.24	57.83	57.27
$\text{NaOH} + \text{HCl}$	59.47	58.56	58.08	57.79	57.52	57.10
$\text{NaOH} + \text{HNO}_3$	58.57	58.07	57.84	57.64	57.50	57.29
$\text{LiOH} + \text{HCl}$	60.33	59.14	58.49	58.06	57.70	57.20
$\text{LiOH} + \text{HNO}_3$	58.46	58.12	57.95	57.79	57.63	57.33
					Average	57.24

All the figures (excepting the last column) in the upper half of this

³³ See Ref. 24, p. 786.

table were plotted with care. Smooth curves were then drawn by means of a device similar in principle to the curve ruler of Lord Berkeley.³⁴ The result, of which the more important part is depicted in Fig. 2, is striking. The curves, which are nearly straight lines with concentrated solutions, converge with increasing dilution, apparently tending almost toward a

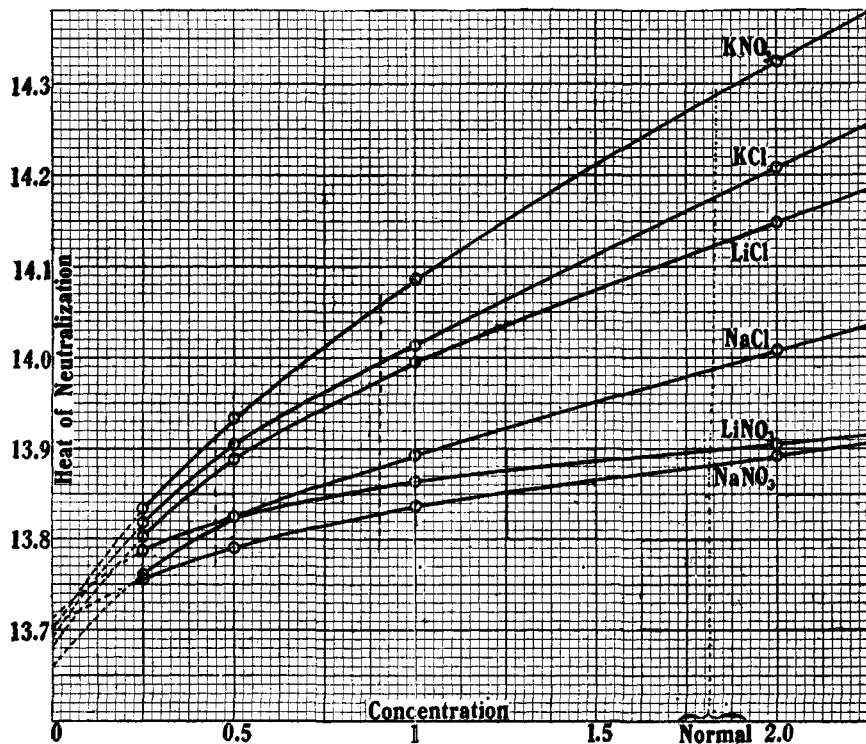


Fig. 2.—Heats of neutralization (at 20°) of all concentrations up to 50 H₂O per mol of acid or alkali, for 3 bases and 2 acids. Kilogram calories are plotted as ordinates; concentrations in mols acid or alkali per 100 H₂O of initial solutions are plotted as abscissas. *N*, 0.5*N* and 0.25*N* solutions are approximately indicated by broken vertical lines. The extrapolation is parabolic, based upon the left hand known portions of the curves as drawn with a flexible ruler under suitable unequal stresses.

single point. This point should give the heat of the reaction $H^+ + OH^- = H_2O$. Accordingly, the extrapolation of these curves is a matter of interest. Trial showed that the ruler had given their left hand branches a near-parabolic shape, although the right hand extremities are almost linear. Accordingly, at first parabolic equations were used for extrapolating to infinite dilution in order to obtain a maximum value (see below). For example, the parabola corresponding to potassium nitrate

³⁴ Lord Berkeley, *Phil. Mag.*, 24, 664 (1912); Richards and Sameshima; *THIS JOURNAL*, 42, 51 (1920).

had its focus at the point (outside the diagram) $x = 0.348$ and $y = 13.446$ with the parameter 0.87 cal. This fits all four known points on the diagram. Similar equations with decreasing parameters were found for the other curves, and with their help all the curves were extrapolated to infinite dilution. The values thus found are recorded in the last column of the foregoing table. The average, 13.69 Cal., may be supposed to be a maximum value for the heat of ionization of water, since the order of the curves can hardly be less than quadratic.

The nearly linear character of the right hand ends of the curves suggests the hyperbola; and this conic section also was tested. An hyperbola in which $C = 1.065$, and the latus rectum = 0.65, with focus at point $x = 0.325$ and $y = 13.54$ corresponds well with all the points in the potassium nitrate curve, even with the heat of neutralization of the most concentrated solution. This hyperbola cuts the y axis at the point 13.67—somewhat below the point given by the parabola. The nearest hyperbolas to the other curves also cut the y axis at lower points than the parabolas, but the agreement of these calculated curves with observed points, as well as the agreement between the resulting extrapolated values, is not much better than in the case of the parabolas.

According to either method the extrapolated values are not very concordant, the extremes differing by nearly 0.4%. This difference is

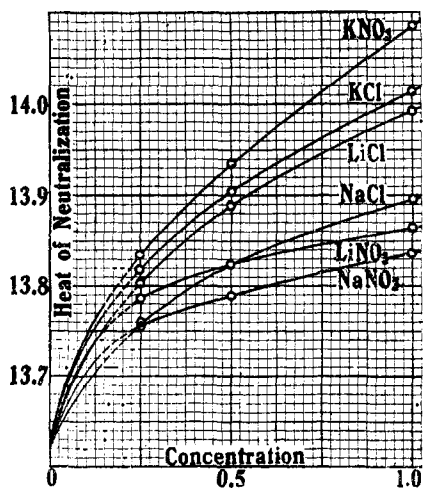


Fig. 3.—Heats of neutralization. Extrapolated, assuming exact convergence, to a compromise point.

not larger than many other thermochemical discrepancies, but it is worthy of consideration, since although many data are involved in each number, even the sum of possibly accumulated experimental inaccuracies could hardly explain the difference between the values for sodium chloride and lithium nitrate. Extrapolation of curves which, like these, are the result of the superposition of many individually undetermined tendencies, is an uncertain procedure. Probably the assumption of parabolic curvature is unwarranted; it certainly does not apply to the left hand branches of the curves. For other alternatives (including the logarithmic, and equations of higher powers) space is lacking. An entirely different mode of attacking the problem is to assume that the curves must come together at infinite dilution, and find a point

which seems to accomplish their convergence smoothly. Such a point could hardly correspond to more than 13,620 calories (on account of the shape of the sodium chloride curve) and might correspond to less. A small diagram (Fig. 3) repeats the neighboring known portions of the curves, and depicts this alternative assumption. On the whole this treatment of the results seems more reasonable than the other. When thus extrapolated, the curves show qualitative likeness to the well-known curves recording electrolytic conductivity. That heats of dilution (upon which these curves depend) give a verdict not very different from that of conductivity has been already pointed out.³⁵

The final answer to the interesting questions thus raised must await further experimental investigation, involving also other salts, and yet greater dilution. This will be undertaken here in the near future.

The diagram (Fig. 2) is a convenient table of reference; it possesses no greater probable error than the results themselves. The heat of neutralization for any dilution of acid and alkali less than 1.25 *N* may obviously be read off directly from the graph, provided that the acid and alkali both have the same concentration. If their concentration is different, the appropriate heats of dilution must be duly entered in the reckoning. For convenience, normal, half normal, and quarter normal concentrations are marked approximately on the diagram.³⁶

The previous published results of others, insofar as they may be compared with these, are usually much lower.³⁷ The most detailed of the earlier work seems to have been done by Wörmann, but his outcome differs from ours in many respects. There are really no results available in the literature which satisfactorily cover the ground of the present ones. Very few experimenters have given data suitable for even a rough extrapolation to infinite dilution.

³⁵ Ref. 24, p. 793.

³⁶ Normal solutions of potassium and sodium hydroxides, and hydrochloric and nitric acids (at 18°) have respectively the formulas KOH.55.1 H₂O; NaOH.55.6 H₂O; HCl.54.4 H₂O; HNO₃.53.8 H₂O, calculated from the well-known densities of these solutions. That is to say, for each 100 mols of water there are present 1.815, 1.799, 1.838 and 1.859 mols of these substances, respectively. The average concentrations, thus given, of each neutralizing pair of these solutions fix the course of the slightly irregular nearly vertical dotted line in Fig. 2 which indicates closely the heat of neutralization of normal solutions. (Of course, to be absolutely exact, heats of dilution should be considered in fixing the points; but the solutions are so nearly equally hydrated that this precaution would be supererogatory with the present data.) Half normal and quarter normal loci are also noted. In a similar way, the heats of dilution of normal solutions can easily be found from the appropriate curves given in the previous paper. (Ref. 24, p. 786.)

³⁷ The following table giving values for NaOH + HCl will serve as an example of the comparison; the first column of figures gives the heat of neutralization as recorded by the observers; the second column, the average final temperature of the determination; the

The greater values with greater concentrations are, of course, dependent upon the varying heats of dilution of the several factors and products. These are specific properties of the individual compounds. In such a case as potassium nitrate, the effect of the salt is very great. The interesting specific curves of the several substances recorded in this paper tempt yet further discussion; they are bound to assist in the final interpretation of the nature of electrolytic solutions. For the present, however, this discussion may be postponed. Evidently the new results do not especially favor the recent theory that strong electrolytes are wholly dissociated in moderately concentrated solutions. As already stated, one of us hopes to continue the experimental investigation of the problem, with other substances and greater dilutions.

In conclusion, the authors take pleasure in expressing their indebted-
last column, each heat of neutralization reduced to 20.00° by the temperature coefficient found by the observer in question.

Observer	U	T_2	U_{20°	Concentration
Richards and Rowe.....	13895	20.00	13895	HCl ₂ .100 H ₂ O, etc.
Thomsen	13627	24.60	13814	HCl ₂ .100 H ₂ O, etc.
	14247	10.14		
[“Thermochemische Untersuchungen,” I, pp. 63, 64 (1882)]				
Berthelot.....	13690	?	13690 (?)	
v. Steinwehr.....	14085	11.80	13630 (?)	Very dilute solution
Wörmann.....	13731	19.86	13723	0.5 <i>N</i>
	13739	18.45	13658	0.25 <i>N</i>
	13703	17.08	13551	0.1 <i>N</i>
Rümelin.....	14100	11.40	13630 (?)	Very dilute solution
Richards and Rowe.....	13880	20.00	13880	0.5 <i>N</i>

Thomsen's first results were obtained in a roundabout way involving the neutralization of sulfuric acid and precipitation of barium sulfate. His later results are better in every respect, but his temperature coefficient is too low, for some unexplained reason. Wörmann's results are the most complete and systematic. He seems to have missed the effect of concentration with moderately dilute solutions, because he calculated his results for the mean temperature and not for the final temperature of the reaction, apparently using the heat capacities of the factors in his calculation. His temperature coefficients average nearly the same as ours, given in the previous paper. His results for potassium salts were much higher than those for sodium salts, although still lower than ours when correction is made to the same temperature. Probably his potassium hydroxide was purer than his sodium hydroxide. The work of J. A. Muller [*Bull. soc. chim.*, [4] 23, 8 (1918)], on potassium chloride and sulfate is very briefly stated. He extrapolated to infinite dilution but his method of extrapolation is not wholly clear. If the heat of dilution of the acids needs to be applied, that of the salt solutions also should be considered. As usual, heed is not given to the fact that when the heat capacities of the factors are used, the result corresponds to the final temperature. Muller's results, as stated, are therefore not comparable with ours. The interesting result of A. A. Noyes, Y. Kato and R. B. Sosman [THIS JOURNAL, 32, 159 (1910)], 13956 at 20°, was calculated rather indirectly from the hydrolysis of ammonium acetate. It agrees much better with our result than with earlier ones and is perhaps as near as could be expected under the circumstances.

ness to the Carnegie Institution of Washington, which through generous subsidy alone made possible the execution of this costly research.

Summary

The results of this investigation may be summarized as follows.

1. The most serious errors in work of this kind were shown to be irregularity of mixing and presence of carbonate in the hydroxides, besides, of course, inadequate avoidance of loss of heat by cooling.

2. Solutions of uniform molal concentration (+ 100 H₂O) of nitric and the three halogen acids and of three alkaline hydroxides have been mutually neutralized calorimetrically in all possible pairs over two ranges of temperatures not far apart, and the results interpolated exactly to 20°. The values ranged from 13,750 to 14,085, sodium hydroxide giving the lowest values among the bases, and hydriodic acid among the acids.

3. Check determinations based upon different analyses and performed independently at various temperatures showed complete agreement with the values originally obtained.

4. With the help of the heats of dilution of factors and products, previously determined, the heats of neutralization at other concentrations have been determined, and these have been extrapolated in two ways through a short range to infinite dilution.

5. The heat of formation of water from its ions at 20° is found by this short extrapolation to be probably not over 13.69 Cal._{20°} or 57.22 kilojoules, and possibly not under 13.62 Cal. or 56.93 kilojoules.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 142]

A CONTINUOUS-FLOW CALORIMETER, AND THE DETERMINATION OF THE HEAT OF NEUTRALIZATION OF A SOLUTION OF HYDROCHLORIC ACID BY ONE OF SODIUM HYDROXIDE

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The continuous-flow principle of calorimetry, which was developed by Callendar and Barnes¹ for measuring the specific heat of water, and applied by Swann² and by Scheel and Heuse³ for specific heats of gases, offers certain advantages over the more usual calorimetry for heats of neutralization, dilution, etc. Among these advantages are equal adaptability to any temperatures at which thermostats can be successfully

¹ Callendar and Barnes, *Trans. Roy. Soc. (London)*, **199A**, 55-263 (1902).

² Swann, *Proc. Roy. Soc. (London)*, **82A**, 147-149 (1909); *Phil. Trans. Roy. Soc.*, **210A**, 199-238 (1910).

³ Scheel and Heuse, *Ann. Physik*, [4] **37**, 79-95 (1912).