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 ($+ 100\ H_2O$) 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.

CAMBRIDGE 38, MASSACHUSETTS

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

BY FREDERICK G. KEYES, LOUIS J. GILLESPIE AND SHINROKU MITSUKURI

The continuous-flow principle of calorimetry, which was developed by Callendar and Barnes[1] for measuring the specific heat of water, and applied by Swann[2] and by Scheel and Heuse[3] 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).

operated, and promise of higher precision. It requires separate determination of the specific heat of the reaction product.

At the suggestion of F. G. Keyes, Dickson[4] made experiments with a continuous-flow calorimeter, studying the heat of neutralization of hydrochloric acid and sodium hydroxide. His result for the approximately 0.05 weight-formal sodium chloride solution produced at 25° was about 2% lower than the corresponding interpolated value of Wörmann,[5] and was too low because of a defect in the calorimeter. With improvements in various details of the apparatus used by him, we have been able to trace the defect, and largely to eliminate it.

The continuous-flow method has been used by F. R. Pratt for heats of dilution.[6] In many details, the apparatus is quite unlike ours, and does not require review here.

Principle of the Method and General Apparatus

The two liquids which are to react are led down from reservoirs through coils of silver tubes[7] immersed in an upper constant-temperature bath controlled to about 0.1°, then through silver coils immersed in a lower, precision thermostat controlled to about 0.001°, and finally into the mixing calorimeter, which is immersed in the precision thermostat. The mixed liquid passes out of the calorimeter through a narrow tube which permits the mixture to be collected and weighed at suitable time intervals.

In order that equivalent quantities of the two liquids shall mix in a given time, the rates of their flow are adjusted, first with stopcocks and finally with screws which lift or lower the two large bottles used as reservoirs. To preserve equality of flow, each bottle is sealed with a rubber stopper and wax, through which pass both the tube to the calorimeter and also a tube which admits air at a low level. By this "Mariotte bottle" arrangement the hydrostatic head is kept constant during the emptying of the bottles.

One platinum thermometer is immersed in the oil of the precision thermostat and another in the mixed liquid within the vacuum-jacketed space of the calorimeter. The difference in temperature of the two thermometers is a measure of the heating of the mixture by the reaction taking place in the calorimeter, provided that the two liquids have attained the temperature of the thermostat before entering the calorimeter, and that the difference of temperature is corrected for any discrepancy between the two thermometers and for any heat effect due to loss of kinetic energy. From the differences of temperature, measured successively

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[4] Dickson, *Thesis* for doctorate, Massachusetts Institute of Technology, June, **1917**.

[5] Wörmann, *Ann. Physik*, [4] **18**, 775–795 (1905).

[6] Pratt, *J. Franklin Inst.*, **185**, 663–695 (1918).

[7] The first pair of silver tubes contained 3 meters each of thin-walled tubing about 2 mm. inside diameter, the second pair contained 2.1 meters each of the same.

at different measured rates of flow, the heat loss can be eliminated, as in the flow method for specific heats. Two rates of flow are mathematically sufficient, but more are observed for precision and also for control of the method and apparatus.

Calorimeter

The calorimeter is shown in Fig. 1.

The silver tubes are silver-soldered to platinum tubes, which are fused to the glass tubes A of the calorimeter. The two liquids enter the tubes at A, and are squirted from two concentric nozzles at B through an air-space to the bottom of the inverted test-tube C. The mixture travels down the inside wall of the test-tube and up through the narrow space around it to a single nozzle D, whence it emerges to impinge upon a second inverted test-tube E, to travel around the test-tube, then around the platinum thermometer F, finally emerging through the tube G, which connects through a horizontal tube to an upright capillary outlet tube used for controlling in part the rate of flow.

The entire calorimeter, with its metal standard which carries the silver tubes, is immersed in the oil of the precision thermostat to the level shown by the dotted horizontal line in the figure. The reacting liquids are exposed in all directions to the temperature of the thermostat, except in the small area in the vertical direction, which is occupied by the reaction mixture itself flowing upwards. The only doubtful heat loss is that up along the platinum thermometer, and this is located to take advantage of the motion of the mixture. The reacting fluids and the active portion of the thermometer are enclosed in the vacuum jacket J. The jacket walls were not silvered.

The heat loss[8] at the different rates of flow of the present work varied from 6.9 to 2.2% of the heat liberated. From the disposition of the apparatus it is clear, however, that the loss should be regular and capable of calculation, and the straight line graph discussed below gives a test of the reliability of the calculation.

In the construction of the calorimeter, the thin, diaphragm-like portion, I, was introduced to provide elasticity against breakage during the cooling. The vacuum jacket was exhausted, while being baked at about 300°, by a mercury diffusion pump backed by an efficient oil-pump, for about 6 hours. Assuming Newton's law of cooling, the heat loss was found to be about 1 calorie per minute and per degree of temperature difference.

We found, working with a calorimeter almost identical with that used by Dickson, that the theoretical straight line graph discussed below was not realized, after substantial improvements in various
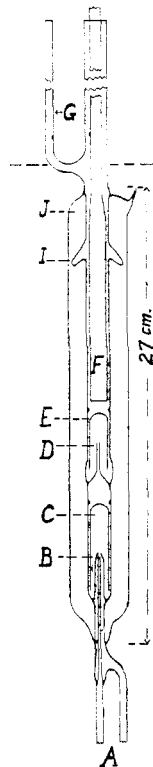

Fig. 1.—Continuous-flow calorimeter.

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[8] The heat loss was evaluated during the determination of the heat of neutralization.

details of the general apparatus. The maximal temperature difference for a given fixed rate of flow was not reached when the effluent was neutral, but when it was distinctly acid (due to the fact that a small quantity of acid fluid succeeded in escaping the action of the baffles), and the temperature difference varied when the apparatus was not disturbed. When the apparatus was set up so that the flow could be watched by the aid of a sensitive, 2-colored indicator (bromothymol-sulfonephthalein), which was added to the alkali, the difficulties could be traced, the most important defect being that a variable mixture of liquid was delivered to the baffle plates.

The same optical test was applied to the new calorimeter shown in Fig. 1, and only faint and momentary fluctuations of color could be seen in the tube above E, and these only when the rates of flow were very exactly adjusted to neutrality. The fluctuations were limited to small localities in the liquid. When the new calorimeter was tested in a calorimetric experiment the constancy of temperature was much better and the temperature difference was maximal for a neutral effluent.

Course of the Determinations

The resistance to flow was not the same for the two liquids, owing to unsymmetry in the apparatus, and for each rate of flow, secured by changing the capillary outlet tube, the equality of flow had to be reëstablished by adjustment of stopcocks and of the height of the reservoirs. In 5 or 10 minutes, conditions were constant enough to permit the thermometer readings. These were taken every minute alternately for the bath and the mixture for 5 or 10 minutes, and the mean for each thermometer for the period of constancy. Both thermometers showed fluctuations of $0.001°$ and occasionally $0.002°$, during the period of "constancy."

The time of flow, in minutes per gram of effluent, was determined by collection of the effluent in a tared Erlenmeyer flask during a time of about 5 minutes, measured with a stop watch.

An indirect test was applied to study the efficiency of the silver tubes in bringing to the same temperature the enclosed flowing liquid and the bath.[9] For the main experiment the upper bath was adjusted to equality of the lower bath temperature to about $0.1°$, by means of a $0.1°$ mercury thermometer checked by the platinum thermometer. In the control experiments it was found that the upper bath could be varied several tenths of a degree without influencing the temperatures of the two platinum thermometers, and when the upper bath temperature was varied enough to change perceptibly the temperature of the reacting mixture, the temperature of the lower bath itself was changed in equal degree.

[9] A similar test was applied by Pratt (Ref. 6), who also placed his (mercury) thermometers in similar positions and referred results to the scale of a single thermometer.

In order to measure the heat produced by friction in the apparatus, pure water was passed through it, at 0.053 and at 0.028 minutes per gram of total effluent, whereupon the two platinum thermometers showed a difference of 0.039°. This being greater than the total fall of liquid (about 2 meters) could have produced, the two thermometers were carefully compared by immersion in the same (precision) oil-bath, and it was found that this difference was identical within 0.001° with the discrepancy between the thermometers at the temperature of the test. The discrepancy was studied over the range of temperature at which the lower bath was kept during the main experiment, and the correction (0.0386° to 0.0389°) was applied to the thermometer in the bath so that the final results were virtually secured with one thermometer (No. 2).

Thermometry

The manganin coils of our thermometer bridge were not kept at constant temperature, and the fixed points were not as reproducible as sometimes reported by other workers.[10] Nevertheless, errors in thermometer standardization should have affected our final result by less than 0.1%, since this result is based on temperature differences, and its dependence upon the absolute temperature is relatively small. The ice-points were obtained in the usual way, and also by a technique which showed that the discrepancy between the two thermometers was in no way due to our manipulation. The steam and naphthalene points were obtained in series of measurements which gave best straight lines intersecting the 760 mm. abscissas. The normal boiling point of naphthalene was taken as 218.04°. The various constants were, for thermometers No. 1 and 2, respectively: R_0, 25.3543 and 25.3343; R_{100}, 35.2305 and 35.2028; R_{218} 46.5210 and 46.4768; fundamental coefficient, 0.00389528 and 0.00389531; and δ value, 1.4452 and 1.4755. So far as the final results are concerned, the constants of No. 1 do not matter, because of the mode of referring all temperatures to the scale of No. 2. The δ value for No. 2, although the higher of the two, is still rather low, but there is no ground for supposing this to be significant, since a calculation shows that an assumed variation in δ, even of 0.05 (or in the form of the correction equation equivalent to such a variation) would affect the temperature differences by about 0.0001°, or only 0.01% in the final result.

The thermometers were Leeds and Northrup instruments of the Bureau of Standards pattern.[11] The bridge was a modified Leeds and Northrup calorimetric bridge, in which the contact resistance at the slide wire affected equally the two bridge arms.

[10] Assuming a temperature coefficient for manganin of 2.10^{-5} ohms per ohm and per degree, a difference of 1° in the coils affects their resistance so as to show apparent variations in really fixed points of 0.005° at 0°, and of 0.009° at 218°.

[11] No. 1 had undergone repairs which may have introduced strains.

It reads directly to 0.00025 ohms, corresponding to about 0.0025°, and the galvanometer sensitivity permits subdivisions to be estimated on the bridge which correspond to 0.001°.

In measuring the temperatures during the flow experiments, the resistance of the coils was always the same, 25.5 ohms, the slide wire being used for the differences between the two thermometers and for the changes of temperature.

Solutions Used for the Experiments

A good grade of sodium hydroxide purified by alcohol was used. It contained about 0.84 mol-per cent. of sodium carbonate, determined by volumetric titration. In the flow experiments, the end-point was about 10^{-7}, the indicator being bromothymol-sulfonephthalein, so that about 0.42 mol-per cent. of the alkalinity "neutralized" was due to carbonate.

All other titrations were done with weight-burets. The alkali solution was titrated against hydrochloric acid prepared from constant-boiling acid according to Hulett and Bonner,[12] against hydrochloric acid standardized gravimetrically with silver chloride, and against recrystallized potassium hydrogen phthalate. The mean result was that 1 g. of sodium hydroxide solution used for the experiments contained 0.00021111 mols of sodium hydroxide, and neutralized 0.99200 g. of the hydrochloric acid used for the experiments: therefore each gram of sodium chloride solution formed during the neutralization contained 0.00010598 mols of sodium chloride. This figure is the quotient of 0.00021111 divided by (1 + 0.992).

The sodium chloride solution formed was thus approximately 0.1 N.

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TABLE I

THE EXPERIMENTAL DATA

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No.	Time of flow Minutes per gram	Bath temperature °C.	Mixture temperature °C.	Difference of temperature °C.	Reciprocal of difference
1	0.0670	32.3296	33.6550	1.3254	0.75449
2	0.0511	32.3105	33.6530	1.3425	0.74488
3	0.0416	32.3277	33.6892	1.3615	0.73448
4	0.0369	32.2934	33.6589	1.3655	0.73233
5	0.0311	32.2899	33.6631	1.3732	0.72823
6	0.0298	32.3075	33.6781	1.3706	0.72961
7	0.0255	32.3085	33.6892	1.3807	0.72427
8	0.0246	32.3085	33.6912	1.3827	0.72322
9	0.0228	32.2915	33.6791	1.3876	0.72067
10	0.0220	32.2975	33.6801	1.3826	0.72327

Calculation of the Results

The data are presented in Table I. The temperatures are in degrees Centigrade, obtained from the properties of Thermometer No. 2, as stated above.

During the flow experiment, let Q calories per gram of mixture be generated constantly. If we assume Newton's law of cooling to be exact over the small range of temperatures, each gram of mixture will lose, for every degree of temperature difference, qt calories, where t is the time of flow in minutes per gram and q is the loss of heat from the cooling

[12] Hulett and Bonner, THIS JOURNAL, **31**, 390–393 (1909).

space (between the mixing tip and the thermometer) per minute and per degree of temperature difference.[13]   The temperature difference controlling the loss of heat varies from D_0, the difference between the temperature immediately developed upon mixing and the temperature of the surrounding bath, to D, the measured temperature difference at the thermometer, and is then the mean of these values, $(D_0 + D)/2$.   The heat lost by every gram is therefore $qt(D_0 + D)/2$, leaving the quantity, $Q - qt(D_0 + D)/2$ calories per gram available for raising the temperature; and if it requires k calories per gram to raise the temperature $1°$, k being the specific heat of the salt solution, we shall have

$$D = -q/k \cdot t(D_0 + D)/2 + Q/k \tag{1}$$

When t is zero, the heat loss, $qt(D_0 + D)/2$, is also zero, so that the corresponding value of D is D_0, the initial temperature difference before any cooling has occurred.   Equation 1 can be solved conveniently as follows. The term $(D_0 + D)/2$ is approximately equal to D_0, or to D, leading to the two approximate equations,

$$D = -(D_0 q/k) \cdot t + Q/k \tag{2}$$
$$\text{and } D = -Dt \cdot q/k + Q/k \text{ or } 1/D = -t \cdot q/Q + k/Q \tag{3}$$

In either case, when $t = 0$, $D = D_0 = Q/k$.   Either equation can be used to obtain a first approximation.   With the present data, Equation 2 gives 1.415 for D_0, Equation 3 gives 1.417, whereas either of these values, used in Equation 1, leads to an exact value, 1.4160, by the method of least squares.   All three equations can be represented by a straight line, by plotting for Equations 1, 2 and 3, respectively, the variables: D, $t(D_0 + D)/2$; D, t; and $1/D$, t.

Fig. 2 shows how Equation 3 represents the data.   The line cuts the axis where $t = 0$ at $1/D = 0.706$, corresponding to $D_0 = 1.417$. The data are equally well represented by the other two Equations, 1 and 2. The scale of heat loss in Fig. 2 shows, for a given time of flow, the calculated heat loss as percentage of the total heat liberated.   This scale shows also the effect on the final result of uncertainty in the extrapolation to zero time of flow.   Thus, let us suppose that the limiting value of $1/D$ may be 0.709 instead of 0.706.   Then the point corresponding to 0.709 on the scale of heat loss is 0.4%, which signifies that the heat of neutralization would be this percentage, 0.4%, lower than the value we actually find.

[13] Our t is the time for 1 gram to enter the Erlenmeyer weighing flask, and hence the time to leave the mixing tips.   Then tG is the time to fill the cooling space of capacity G grams, i. e., the time a gram is in the cooling space, on the average.   Since the total liquid occupying this space cools q calories per minute and per degree temperature difference, the corresponding cooling for 1 g. is q/G, per minute and per degree temperature difference.   Therefore $tG \cdot q/G = qt$, is the heat lost by the gram, per degree temperature difference.

From Richards and Rowe's[14] figures for the loss of heat capacity on diluting sodium chloride solutions we obtain, by extrapolation, $k = 0.9913$. The two end values in their curve for sodium chloride are possibly irregular, according to them; we assumed, however, the curvature necessary to make both end values exact, but the effect upon k of any error in this assumption is slight, since the molecular heat capacity of our sodium chloride solution is over 9000.

From the exact value, 1.4160, for Q/k, we find therefore $Q = 1.4037$ calories per gram mixture. Dividing by the concentration of the solution, 0.00010598 mol. of sodium chloride per gram, we find the heat of neutralization to be 13,245 calories per mol. The method of least squares indicates the "probable error" to be slightly below 0.1% of this value.

The slope of the line in Fig. 2 gives $q/k = 1.04$, or $q = 1.03$, the probable error being about 2% of this value.

The above result for the heat of neutralization needs to be corrected finally for the presence of carbonate in the hydrate. Through an oversight, the hydrate solution itself was not used for the carbonate determination. The solution was, however, carefully protected from atmospheric carbon dioxide by a tube of soda-lime. From data in Landolt-Börnstein, "Tabellen," 4th edition, it is calculated that the neutralization of Na_2CO_3 to the stage of $NaHCO_3$ would produce at $18°$ only 4,600 calories per mol. of hydrochloric acid used, instead of 13,700. The value found above points, therefore, to a still larger value for the heat of neutralization of carbonate-free sodium hydroxide, which is found finally to be 13,280 calories per mol. This value refers to the isothermal heat of neutralization at $32.3°$, the mean initial temperature, since the heat capacity of the products was used in the calculation.[15]
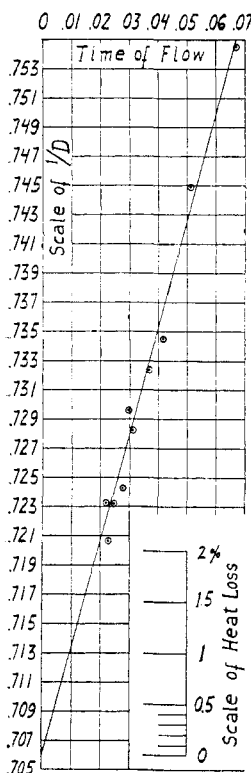

Fig. 2.—The reciprocal rise of temperature as a linear function of the time of flow.

Discussion

Since our data give only one point of temperature and concentration, only limited comparison is possible with the data of previous workers. Wörmann[5] determined the heat of neutralization of the 4 combinations between sodium hydroxide, potassium hydroxide, hydrochloric acid, and nitric acid, at $0°$, $6°$, $18°$, and $32°$, and his lines are shown in Fig. 3. These are the best straight lines found by him for the mean values at concentrations from 0.25 to 0.1 N (normality referring to salt solution formed).
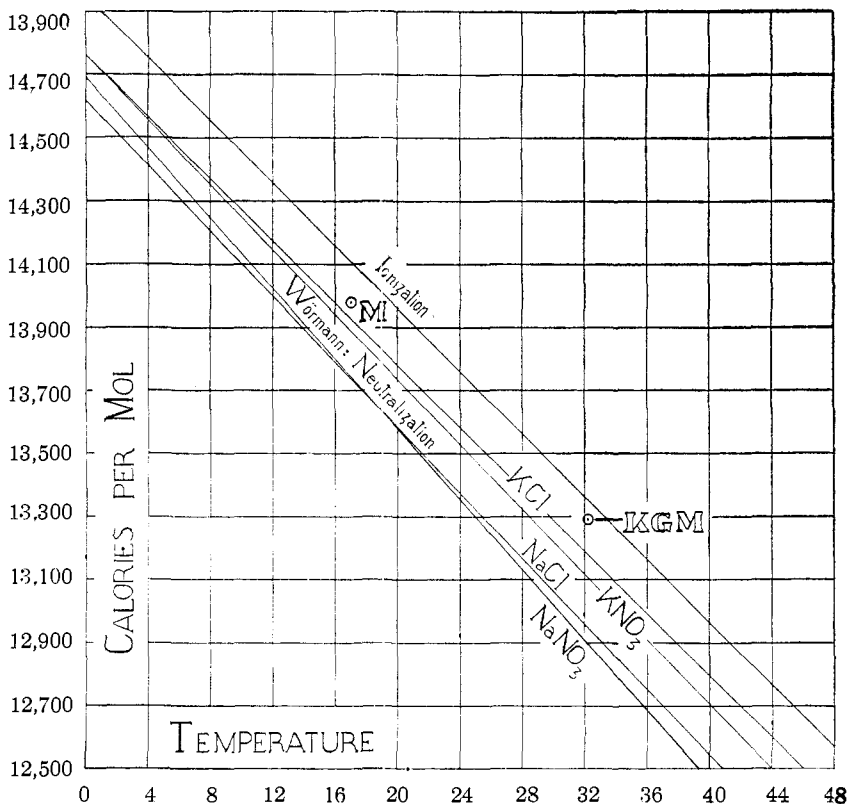

Fig. 3.—Comparison of some heats of neutralization with the heat of ionization calculated by Noyes, Kato and Sosman.

The values for the potassium salts are higher by about 1% than those for sodium. Another line shown in Fig. 3 for comparison is that for the heat of ionization of water, calculated by Noyes, Kato, and Sosman.[16] Our point is shown by the mark KGM. Another point, M, is one obtained by Muller[17] for the heat of neutralization at infinite dilution, obtained

[16] Noyes, Kato and Sosman, THIS JOURNAL, **32,** 159–178 (1910).

[17] Muller, *Bull. soc. chim.,* [4] **23,** 8–13 (1918).

by measuring heats of dilution and of neutralization, this point being the mean for the neutralization of potassium hydroxide with sulfuric acid and with hydrochloric acid.

The agreement of the heat of ionization line with Wörmann's lines has been considered good.[16]   Muller's point agrees still better with the ionization line.   Our point deviates from it, being smaller, by about 0.5%. The disagreement between our point and Wörmann's line for sodium chloride is, however, outside the accidental errors of both pieces of work, being 2.6%.   Differences of concentration cannot explain the discrepancy, as our solution was about $0.1\ N$, and gives a higher heat than his averages over the interval 0.25 to $0.1\ N$, whereas Wörmann found at $0°$ a higher value for sodium chloride in $0.5\ N$ solution than in the more dilute solutions.

We are continuing the work.   In the meantime, we wish to point out that Wörmann mentions no correction for carbonate in the alkali solutions, and gives no analysis for carbonate.   The presence of about 5.2 mol-per cent. of sodium carbonate in the sodium hydroxide solution would be required to bring the corrected value into agreement with our point and the slope of Richards and Rowe, which is nearly that of the ionization curve.   We should hardly expect agreement between the heats of neutralization and of ionization at concentrations where potassium hydroxide is given different values than sodium hydroxide.   If, however, a 2.6% correction is justified in the case of sodium hydroxide, a smaller one for potassium hydroxide would suffice to bring the alkalies into better agreement.

Summary

A continuous-flow calorimeter has been so developed that measurement of the rise of temperature for 10 rates of flow leads to a value of the heat of neutralization, the "probable error" of which is calculated by least squares to be less than 0.1% of the heat itself.   Obvious improvements are expected to increase the precision.

For the heat of neutralization resulting in the formation of NaCl.521 H_2O (about $0.107\ N$ sodium chloride) at $32.3°$, we find 13,280 calories per mol.   Use was made of the specific-heat data of Richards and Rowe, so that the unit is the $18°$ calorie (equivalent to 4.18 joules).

We should expect our value to be correct within about 0.3%.   It is, however, 2.6% higher than the corresponding point on the curve of Wörmann for the same neutralization.   This may be due to the absence in his work of a correction for carbonate in the alkali used.

Our point is about 0.5% lower than the corresponding point on the line given by Noyes, Kato and Sosman for the heat of ionization.   In our opinion, the 1% difference in the heat, reported by Wörmann, when potassium

hydroxide is substituted for sodium hydroxide in the neutralization, is questionable, because of the lack of a carbonate correction.

This work has been done, and is being continued, with the aid of a grant from the Rumford Fund of the American Academy of Sciences.

CAMBRIDGE 39, MASSACHUSETTS

THE ABNORMALITY OF STRONG ELECTROLYTES AND THE IONIZATION THEORY OF GHOSH[1]

BY JAMES KENDALL

Many attempts have been made during the past 30 years to account for the failure of the Ostwald dilution law $\mu_v^2/\mu_\infty \cdot (\mu_\infty - \mu_v) \cdot v = k$ to reproduce the ionization of strong electrolytes. It has been suggested, for example, that the degree of ionization is not correctly represented by the conductivity ratio μ_v/μ_∞, that the ionization equilibrium is not correctly represented by the equation $RX \rightleftharpoons R^+ + X^-$, or that the law of mass action is not applicable to the equilibrium between ions and undissociated molecules. The only alternative theory that has been received with any great degree of favor, however, is one recently developed by Ghosh,[2] which rejects the fundamental assumptions of Arrhenius entirely. It is the purpose of the present article to give a critical analysis of the arguments advanced by Ghosh and others in support of this theory.

The Postulates of Ghosh.—The theory, as applied to a uni-univalent salt RX in solution, is based upon the following postulates: (1) the electrolyte is completely dissociated at all dilutions into oppositely charged radicals R^+ and X^-; (2) the arrangement of these charged particles in the solution is analogous to the marshaling of atoms in a simple cubic crystal lattice; (3) the oppositely charged radicals of a salt-molecule RX form a completely saturated electrical doublet, and the work necessary to separate them is the electrical work done in moving them from their fixed mean distance in the solution to an infinite distance apart; (4) a radical is free to conduct the current only if its kinetic energy is greater than half the work required to separate it from its partner; (5) the distribution of velocities among the particles is according to Maxwell's law.

For salts of other valence types, and for acids and bases, other postulates are made, which will be referred to later. The essential point in the theory of Ghosh is that strong electrolytes are wholly dissociated in solution, partly into *free* and partly into *bound* ions, only the former being capable of conducting the current. The ratio μ_v/μ_∞ consequently ex-

[2] Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918); **117**, 823, 1390 (1920).